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A lead–halide ladder complex: *catena*-poly[bis(2,3-dimethylquinoxalinium) [[di-μ_2-bromido-bis[dibromoplumbate(II)]]-di-μ_2-bromido]]

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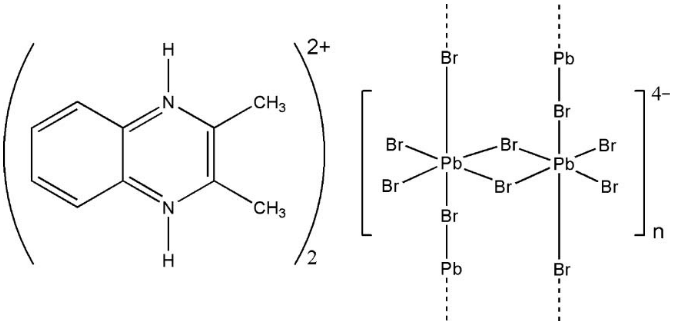
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.019 Å; R factor = 0.054; wR factor = 0.123; data-to-parameter ratio = 17.5.

In the title compound, $\{(C_{10}H_{12}N_2)_2[Pb_2Br_8]\}_n$, the asymmetric unit consists of half a cation and one-quarter of a doubly-bridged dinuclear anionic unit. The planar cations lies on a twofold axis that runs lengthwise through both rings. The Pb and one Br atoms are located on twofold axes, whereas the second Br atom is located on a mirror plane and the third lies on a general position. The polymeric anion forms an infinite ladder structure running along the c axis with rungs consisting of Pb and bridging Br atoms, with two octahedra sharing edges as the rungs of the ladder and sharing vertices as the rails. There are N—H···Br hydrogen-bonding interactions, *ca* 3.21 Å, linking the PbBr ladders to the cations.

Related literature

For related literature, see: Billing & Lemerrer (2005); Chakravarthy & Guloy (1997); Cui *et al.* (2000); Klapotke *et al.* (1999); Lacroix *et al.* (1994); Reynolds *et al.* (2003); Willett & Twamley (2001).



Experimental

Crystal data

$(C_{10}H_{12}N_2)_2[Pb_2Br_8]$
M_r = 1374.04
Monoclinic, $C2/m$
a = 9.4180 (19) Å
b = 28.141 (6) Å
c = 6.0290 (12) Å
β = 101.83 (3)°
V = 1563.9 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 20.99 mm^{-1}
T = 295 K
0.20 × 0.15 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: numerical (*SHAPE* Tracing Software; Rigaku, 2000)
T_{min} = 0.102, T_{max} = 0.228
7780 measured reflections
1419 independent reflections
875 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.123
S = 0.73
1419 reflections
81 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.30 e Å^{-3}
$\Delta\rho_{min}$ = −1.46 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···Br1	0.86	2.35	3.206 (10)	171
C1—H1C···Br2	0.96	3.06	3.752 (14)	130

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2167).

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supplementary materials

Acta Cryst. (2007). E**63**, m1569 [**doi:10.1107/S1600536807021186**]

A lead-halide ladder complex: *catena*-poly[bis(2,3-dimethylquinoxalinium) [[di-μ_2-bromido-bis[dibromoplumbate(II)]]-di-μ_2-bromido]]

B. F. Ali, **R. Al-Far** and **S. Haddad**

Comment

Research in the field of organic inorganic hybrid compounds is of great interest. This is because of the their special magnetic, electronic and optoelectronic properties (Cui *et al.*, 2000; Lacroix *et al.*,1994; Chakravarthy & Guloy, 1997). Haloplumbates, have demonstrated a structural diversity in lead-halide based organic inorganic hybrids (Billing & Lemerrer, 2005) in particular, in terms of the nets formed by the inorganic components, which show many distinct topologies. Examples are layers of corner sharing octahedra, linear chains of face sharing octahedra as well as a number of mixed intermediates (Billing & Lemerrer, 2005). In the crystal structure of the title complex, (I). The use of 2,3-dimethylquinoxaline (henceforth dmqxH_2) and its protonation were expected to create many important centers of interaction with the bromo-lead anion, *e.g.* NH···Br, CH···Br and possibly Br···aryl and aryl···aryl interactions.

In the title compound, (I), $\{C_{10}H_{12}Br_4N_2Pb\}_n$, the asymmetric unit consists of half of the repeated extended structure of both cation and anion. The planar cations $[C_{10}H_{12}N_2]^{2+}$ with both nitrogen atoms protonated, lies on a 2-fold axis that runs lengthwise between the two halves (Fig. 1). The dinuclear unit $[Pb_2Br_{10}]^{6-}$ consists of two distorted octahedra bridged by Br_3 and its symmetry related Br_3^i [Symmetry code: (iii) $-x + 1$, $-y$, $-z + 1$). These dinuclear units are further interconnected through bridging Br_2 to form a polymeric chain structure developping parallel to the *c* axis (Fig. 2). This anion chain demonstrates a novel structural arrangement in metal halide extended anion networking.

The Pb—Br distances are similar, 3.0242 (6)–3.0448 (16) Å and fall within the range of Pb—Br distances reported previously for compounds containing lead-bromides (Reynolds *et al.*, 2003; Cui *et al.*, 2000; Klapotke *et al.*, 1999). The bond angles for linear Br—Pb—Br are in the range 170.87 (9)– 174.84 (4)°, while those for perpendicular Br—Pb—Br are in the range 83.85 (5)–94.95 (6)°. In the dmqxH_2 cation, the bond distances and angles are the same as those reported previously, within experimental error (Willett & Twamley, 2001).

The extra supramolecularity in the structure is represented by H-bonding (Table 1) leading to a layer arrangement in *ac* plane.

Experimental

A solution of $PbCl_2$ (1.0 mmol), in absolute ethanol (10 ml), was added to a stirred hot solution of 2,3-dimethylquinoxaline (1 mmol) in absolute ethanol (10 ml) containing 60% HBr (3 ml) and liquid Br_2 (2 ml). After heating to reflux for *ca* 3 h, the mixture was filtered and the filtrate allowed to stand undisturbed at room temperature. Complex (**I**) crystallized out over 2 days as red blocks. Crystals were filtered off, washed with diethyl ether and dried under vacuum.

Refinement

All H atoms were initially located in a difference Fourier map and were subsequently refined using a riding model, with C—H distances of 0.96 Å and $U_{iso}(H) = 1.5_{eq}(C)$ for methyl H atoms; C—H = 0.96 Å and $U_{iso}(H) = 1.2_{eq}(C)$ for aromatic H atoms, and N—H = 0.86 Å and $U_{iso}(H) = 1.2_{eq}(N)$.

Figures

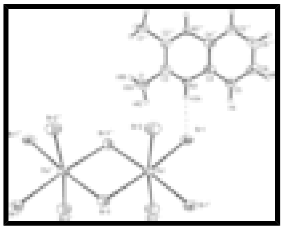

Fig. 1. Displacement ellpisoid (30%) plot of (I), showing the atom-numbering scheme. The complete coordination about Pb1 and cation have been included. [Symmetry codes: (i) 1 − *x*, −*y*, 1 − *z*; (ii) *x*, *y*, 1 + *z*; (iii) 1 − *x*, − *y*, 1 − *z*; (iv) *x*, 1 − *y*, *z*; (v) 1 − *x*, 1 − *y*, 1 − *z*; (vi) 2 − *x*, *y*, −*z*].

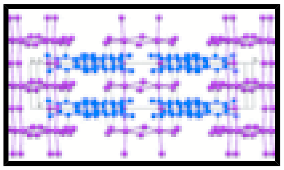

Fig. 2. View of unit cell approximately down *a* axis showing H-bonding between Br1 and N3.

catena-poly[bis(2,3-dimethylquinoxalinium) [[di-μ2-bromido-bis[dibromoplumbate(II)]]-di-μ2-bromido]]

Crystal data

$(C_{10}H_{12}N_2)_2[Pb_2Br_8]$

$M_r = 1374.04$

Monoclinic, *C*2/*m*

Hall symbol: -C 2y

$a = 9.4180\ (19)$ Å

$b = 28.141\ (6)$ Å

$c = 6.0290\ (12)$ Å

$\beta = 101.83\ (3)°$

$V = 1563.9\ (6)$ Å^3

$Z = 2$

$F_{000} = 1232$

$D_x = 2.918$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 3034 reflections

$\theta = 1.5–27.9°$

$\mu = 20.99$ mm^{-1}

$T = 295$ K

Block, red

0.20 × 0.15 × 0.10 mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 14.6306 pixels mm^{-1}

$T = 295(2)$ K

dtintegrate.ref scans

1419 independent reflections

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

$R_{int} = 0.092$

$\theta_{max} = 25.2°$

$\theta_{min} = 3.1°$

$h = -11 \rightarrow 11$

Absorption correction: numerical (SHAPE Tracing Software; Rigaku, 2000)

$T_{\min} = 0.102$, $T_{\max} = 0.228$

7780 measured reflections

$k = -33 \rightarrow 33$

$l = -7 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.123$

$S = 0.73$

1419 reflections

81 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0005P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.30$ e Å^{-3}

$\Delta\rho_{\min} = -1.46$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Pb1	0.5000	0.57831 (3)	0.5000	0.0288 (3)
Br1	0.73667 (15)	0.65358 (6)	0.5497 (2)	0.0386 (5)
Br2	0.5000	0.58691 (8)	0.0000	0.0475 (7)
Br3	0.2733 (2)	0.5000	0.4132 (4)	0.0358 (6)
C1	0.9022 (16)	0.5680 (5)	0.167 (3)	0.038 (4)
H1A	0.9785	0.5551	0.2817	0.057*
H1B	0.8762	0.5455	0.0461	0.057*
H1C	0.8192	0.5746	0.2316	0.057*
C2	0.9527 (13)	0.6126 (5)	0.078 (2)	0.027 (3)
C4	0.9533 (12)	0.6952 (5)	0.076 (2)	0.027 (3)
C5	0.9127 (14)	0.7363 (5)	0.169 (2)	0.034 (4)
H5	0.8598	0.7362	0.2829	0.040*
C6	0.9558 (15)	0.7782 (6)	0.080 (2)	0.045 (4)
H6	0.9249	0.8071	0.1283	0.054*

N3	0.9122 (11)	0.6516 (4)	0.1469 (17)	0.022 (2)
H3A	0.8561	0.6510	0.2429	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0225 (4)	0.0360 (6)	0.0290 (5)	0.000	0.0080 (3)	0.000
Br1	0.0285 (8)	0.0535 (12)	0.0373 (9)	−0.0104 (7)	0.0145 (7)	−0.0096 (7)
Br2	0.0521 (15)	0.0652 (18)	0.0253 (13)	0.000	0.0083 (11)	0.000
Br3	0.0244 (11)	0.0332 (14)	0.0494 (14)	0.000	0.0066 (9)	0.000
C1	0.042 (9)	0.042 (10)	0.036 (9)	0.002 (8)	0.021 (8)	0.004 (8)
C2	0.023 (7)	0.033 (9)	0.024 (8)	−0.001 (7)	0.001 (6)	0.001 (7)
C4	0.015 (6)	0.040 (10)	0.024 (8)	0.003 (7)	0.003 (5)	0.002 (7)
C5	0.037 (8)	0.036 (10)	0.032 (9)	−0.002 (8)	0.016 (7)	−0.003 (8)
C6	0.045 (10)	0.055 (12)	0.037 (10)	0.011 (8)	0.013 (7)	−0.012 (8)
N3	0.023 (6)	0.018 (7)	0.025 (6)	0.000 (5)	0.010 (5)	−0.003 (5)

Geometric parameters (Å, °)

Pb1—Br2	3.0242 (6)	C4—C5	1.372 (18)
Pb1—Br3	3.0380 (14)	C4—N3	1.381 (16)
Pb1—Br1	3.0448 (16)	C4—C4^{i}	1.40 (2)
C1—C2	1.481 (18)	C5—C6	1.389 (19)
C1—H1A	0.9600	C5—H5	0.9300
C1—H1B	0.9600	C6—C6^{i}	1.40 (3)
C1—H1C	0.9600	C6—H6	0.9300
C2—N3	1.262 (15)	N3—H3A	0.8600
C2—C2^{i}	1.42 (2)		
Br2^{ii}—Pb1—Br2	170.81 (9)	H1B—C1—H1C	109.5
Br2^{ii}—Pb1—Br3	94.95 (6)	N3—C2—C2^{i}	119.4 (8)
Br2—Pb1—Br3	91.71 (6)	N3—C2—C1	118.4 (12)
Br3—Pb1—Br3^{iii}	87.00 (6)	C2^{i}—C2—C1	122.2 (8)
Br2^{ii}—Pb1—Br1	89.76 (5)	C5—C4—N3	120.4 (12)
Br2—Pb1—Br1	83.85 (5)	N3—C4—C4^{i}	117.2 (7)
Br3—Pb1—Br1	174.84 (4)	C4—C5—C6	115.6 (13)
Br3^{iii}—Pb1—Br1	90.76 (4)	C4—C5—H5	122.2
Br1—Pb1—Br1^{iv}	91.84 (6)	C6—C5—H5	122.2
Pb1—Br3—Pb1^{iii}	93.00 (6)	C5—C6—C6^{i}	121.9 (8)
C2—C1—H1A	109.5	C5—C6—H6	119.1
C2—C1—H1B	109.5	C2—N3—C4	123.3 (12)
H1A—C1—H1B	109.5	C2—N3—H3A	118.3
C2—C1—H1C	109.5	C4—N3—H3A	118.3
H1A—C1—H1C	109.5		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···Br1	0.86	2.35	3.206 (10)	171
C1—H1C···Br2	0.96	3.06	3.752 (14)	130

Fig. 1

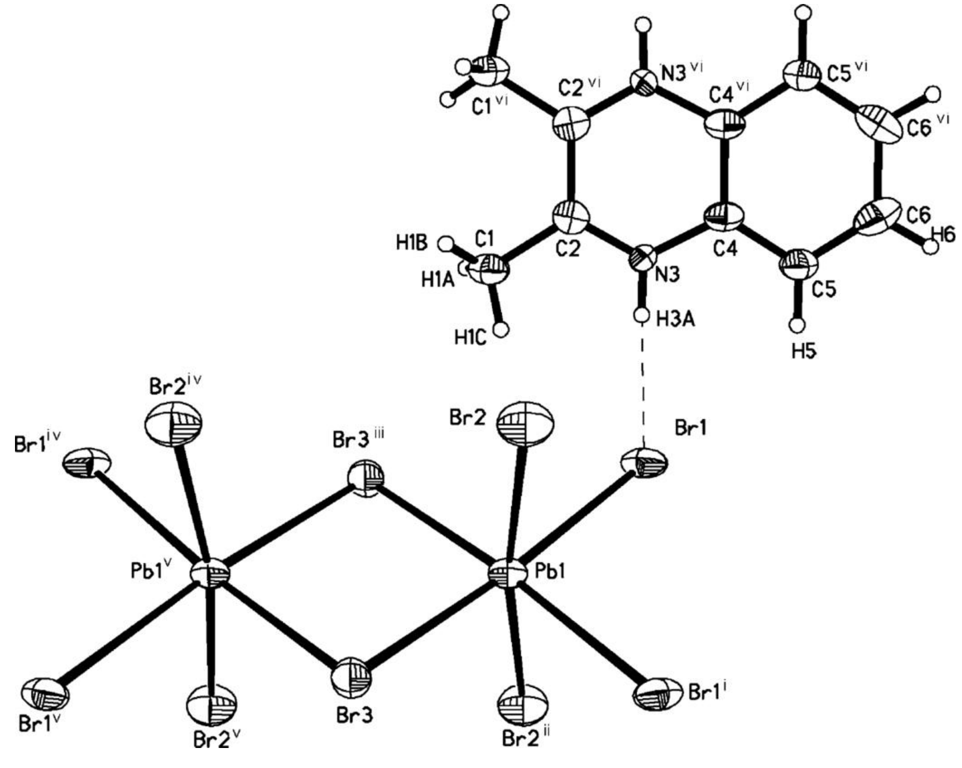
C1vi
C2vi
N3vi
C4vi
C5vi
C6vi
H1B
C1
H1A
H1C
C2
N3
H3A
C4
C5
H5
C6
H6
Br2iv
Br1iv
Br3iii
Br2
Br1
Pb1v
Pb1
Br1v
Br2v
Br3
Br2ii
Br1i

Fig. 2