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Bis[4-(dimethylamino)pyridinium] 3.75-bromido-0.25-chloridodiphenylplumbate(IV)

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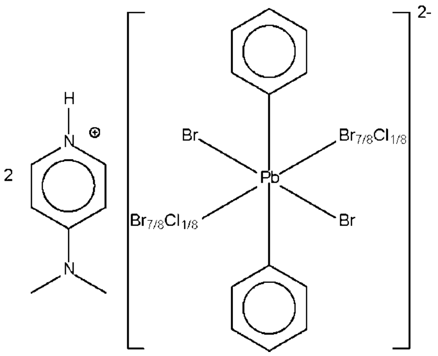
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.022; wR factor = 0.048; data-to-parameter ratio = 20.0.

The Pb^{IV} atom of the plumbate dianion in the title compound, $(C_7H_{11}N)_2[Pb(Br_{3.75}Cl_{0.25})(C_6H_5)_2]$, lies on a centre of inversion in a tetragonally compressed octahedral geometry. One of the attached Br atoms is disordered with respect to a Cl atom in a 7:1 ratio. The disordered halogen atom is an N—H···(Br/Cl) hydrogen-bond acceptor for the cation.

Related literature

For the structure of the isostructural compound bis(4-dimethylaminopyridinium) tetrabromidodiphenylplumbate(IV), see: Lo & Ng (2008).



Experimental

Crystal data

$(C_7H_{11}N)_2[Pb(Br_{3.75}Cl_{0.25})(C_6H_5)_2]$
M_r = 916.27
Monoclinic, $P2_1/n$
a = 9.5010 (2) Å
b = 13.8916 (3) Å
c = 10.9851 (2) Å
β = 92.996 (1)°
V = 1447.88 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 11.05 mm^{-1}
T = 100 (2) K
0.12 × 0.11 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.351, T_{max} = 0.405 (expected range = 0.287–0.331)
10028 measured reflections
3327 independent reflections
2909 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.048
S = 1.02
3327 reflections
166 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Selected bond lengths (Å).

X = Br, Cl.

Pb1—C1	2.184 (3)	Pb1—Br2	2.8885 (3)
Pb1—X1	2.8523 (3)		

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

X = Br, Cl.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···X1	0.87 (1)	2.49 (2)	3.260 (3)	148 (4)

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

We thank the University of Malaya for funding this study (grant No. FS339/2008A) for the purchase of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2863).

References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
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supplementary materials

Acta Cryst. (2009). E**65**, m13   [**doi:10.1107/S1600536808040312**]

Bis[4-(dimethylamino)pyridinium] 3.75-bromido-0.25-chloridodiphenylplumbate(IV)

K. M. Lo and S. W. Ng

Experimental

Diphenyllead dichloride (1.3 g, 3 mmol) and 4-dimethylaminopyridine hydrobromide perbromide (1.1 g, 3 mmol) were heated in chloroform (100 ml) for an hour. The filtered solution when allowed to evaporate yielded large colorless crystals of (I).

Refinement

The carbon-bound H-atoms were placed in calculated positions (C—H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2 to 1.5U_{eq}(C). The ammonium H atom was located in a difference Fourier map, and was refined with a distance constraint of N—H = 0.88 (1) Å; its U_{iso} value was refined.

The two independent halogen atoms were initially refined as full-occupancy Br atoms; however, the difference Fourier map had a deep hole near one of the two. When this atom was allowed to refine as a mixture of bromine and chlorine, the refinement converged, and it gave the Br:Cl ratio as 0.88:0.12. The ratio was subsequently fixed as 0.875:0.125. Attempts to model the Br and Cl atoms on separate sites were not successful.

The published $(C_7H_{11}N)_2[PbBr_4(C_6H_5)_2]$ structure (Lo & Ng, 2008) does not contain any chlorine as the compound was synthesized by the cleavage of tetraphenyllead by 4-aminomethylpyridine hydrobromide perbromide.

Figures

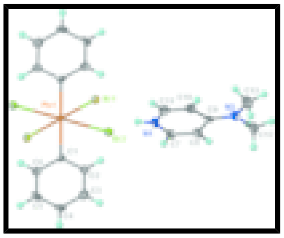

Fig. 1. View of the molecular structure of (I) at the 70% probability level. H atoms are drawn as spheres of arbitrary radius. Unlabelled atoms in the anion are generated by the symmetry operation (1 - *x*, 1 - *y*, 1 - *z*).

Bis[4-(dimethylamino)pyridinium] 3.75-bromido-0.25-chloridodiphenylplumbate(IV)

Crystal data

$(C_7H_{11}N)_2[PbBr_{3.75}(C_6H_5)_2Cl_{0.25}]$	F_{000} = 867
M_r = 916.27	D_x = 2.102 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 4255 reflections

a = 9.5010 (2) Å

b = 13.8916 (3) Å

c = 10.9851 (2) Å

β = 92.996 (1)°

V = 1447.88 (5) Å^3

Z = 2

θ = 2.4–28.4°

μ = 11.05 mm^{-1}

T = 100 (2) K

Faceted block, colourless

0.12 × 0.11 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 100(2) K

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

T_{min} = 0.351, T_{max} = 0.405

10028 measured reflections

3327 independent reflections

2909 reflections with $I > 2\sigma(I)$

R_{int} = 0.028

θ_{max} = 27.5°

θ_{min} = 2.4°

$h = -12 \rightarrow 12$

$k = -15 \rightarrow 18$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.022

$wR(F^2)$ = 0.048

S = 1.02

3327 reflections

166 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0227P)^2 + 0.2619P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}}$ = 0.77 e Å^{-3}

$\Delta\rho_{\text{min}}$ = −0.52 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Pb1	0.5000	0.5000	0.5000	0.01182 (5)	
Br1	0.55819 (4)	0.61268 (2)	0.29147 (3)	0.01476 (8)	0.875

Br2	0.76221 (3)	0.40251 (2)	0.46037 (3)	0.01660 (8)	
Cl1	0.55819 (4)	0.61268 (2)	0.29147 (3)	0.01476 (8)	0.125
N1	0.8894 (3)	0.5871 (2)	0.2345 (3)	0.0224 (7)	
H1	0.815 (3)	0.582 (3)	0.277 (3)	0.042 (13)*	
N2	1.1998 (3)	0.59111 (19)	−0.0113 (2)	0.0173 (6)	
C1	0.6143 (3)	0.6021 (2)	0.6197 (3)	0.0138 (6)	
C2	0.7445 (3)	0.6367 (2)	0.5890 (3)	0.0152 (7)	
H2	0.7856	0.6156	0.5167	0.018*	
C3	0.8144 (4)	0.7030 (2)	0.6660 (3)	0.0198 (7)	
H3	0.9040	0.7271	0.6465	0.024*	
C4	0.7533 (4)	0.7336 (2)	0.7709 (3)	0.0191 (7)	
H4	0.8009	0.7790	0.8229	0.023*	
C5	0.6228 (4)	0.6982 (2)	0.8003 (3)	0.0204 (7)	
H5	0.5814	0.7194	0.8724	0.024*	
C6	0.5527 (4)	0.6321 (2)	0.7248 (3)	0.0163 (7)	
H6	0.4635	0.6076	0.7448	0.020*	
C7	1.0060 (4)	0.5338 (3)	0.2555 (3)	0.0208 (7)	
H7	1.0141	0.4941	0.3260	0.025*	
C8	1.1124 (4)	0.5356 (2)	0.1781 (3)	0.0189 (7)	
H8	1.1945	0.4980	0.1953	0.023*	
C9	1.1019 (3)	0.5933 (2)	0.0715 (3)	0.0146 (7)	
C10	0.9798 (4)	0.6523 (2)	0.0576 (3)	0.0189 (7)	
H10	0.9701	0.6959	−0.0089	0.023*	
C11	0.8778 (4)	0.6469 (2)	0.1382 (3)	0.0220 (8)	
H11	0.7962	0.6860	0.1267	0.026*	
C12	1.3282 (4)	0.5343 (3)	0.0091 (3)	0.0225 (7)	
H12A	1.3034	0.4683	0.0313	0.034*	
H12B	1.3872	0.5632	0.0752	0.034*	
H12C	1.3803	0.5332	−0.0656	0.034*	
C13	1.1938 (4)	0.6535 (3)	−0.1175 (3)	0.0267 (8)	
H13A	1.0952	0.6658	−0.1434	0.040*	
H13B	1.2414	0.6222	−0.1840	0.040*	
H13C	1.2409	0.7146	−0.0970	0.040*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.01154 (9)	0.01443 (9)	0.00939 (8)	−0.00187 (6)	−0.00034 (6)	−0.00126 (6)
Br1	0.01359 (18)	0.01750 (17)	0.01320 (16)	0.00047 (13)	0.00073 (13)	0.00243 (12)
Br2	0.01506 (17)	0.02009 (17)	0.01462 (16)	0.00203 (12)	0.00038 (12)	−0.00043 (12)
Cl1	0.01359 (18)	0.01750 (17)	0.01320 (16)	0.00047 (13)	0.00073 (13)	0.00243 (12)
N1	0.0161 (17)	0.0309 (17)	0.0206 (16)	−0.0016 (13)	0.0056 (12)	−0.0050 (13)
N2	0.0201 (16)	0.0158 (14)	0.0162 (14)	0.0043 (11)	0.0029 (11)	0.0024 (11)
C1	0.0133 (17)	0.0130 (16)	0.0146 (16)	−0.0008 (12)	−0.0031 (12)	0.0003 (12)
C2	0.0157 (17)	0.0171 (16)	0.0127 (16)	0.0016 (13)	−0.0020 (12)	0.0004 (12)
C3	0.0186 (19)	0.0201 (18)	0.0204 (18)	−0.0036 (14)	−0.0008 (14)	0.0032 (13)
C4	0.024 (2)	0.0171 (18)	0.0156 (17)	−0.0024 (14)	−0.0081 (14)	−0.0015 (13)
C5	0.029 (2)	0.0191 (18)	0.0133 (16)	−0.0003 (14)	−0.0015 (14)	−0.0027 (13)

C6	0.0147 (18)	0.0197 (17)	0.0143 (16)	0.0007 (13)	−0.0017 (13)	0.0031 (13)
C7	0.022 (2)	0.0252 (18)	0.0149 (17)	−0.0029 (15)	0.0004 (14)	−0.0010 (14)
C8	0.0188 (18)	0.0211 (17)	0.0170 (17)	0.0021 (14)	0.0014 (13)	−0.0004 (13)
C9	0.0158 (17)	0.0164 (16)	0.0113 (15)	−0.0013 (12)	−0.0011 (12)	−0.0051 (12)
C10	0.0213 (19)	0.0171 (17)	0.0183 (18)	0.0024 (14)	−0.0009 (14)	−0.0008 (13)
C11	0.0188 (19)	0.0229 (19)	0.0242 (19)	0.0047 (14)	−0.0015 (14)	−0.0052 (14)
C12	0.0190 (19)	0.0306 (19)	0.0180 (18)	0.0059 (15)	0.0027 (14)	0.0008 (15)
C13	0.032 (2)	0.028 (2)	0.0203 (19)	0.0065 (16)	0.0057 (16)	0.0057 (15)

Geometric parameters (Å, °)

Pb1—C1^{i}	2.184 (3)	C4—C5	1.388 (5)
Pb1—C1	2.184 (3)	C4—H4	0.9500
Pb1—Br1	2.8523 (3)	C5—C6	1.385 (4)
Pb1—Cl1^{i}	2.8523 (3)	C5—H5	0.9500
Pb1—Br1^{i}	2.8523 (3)	C6—H6	0.9500
Pb1—Br2	2.8885 (3)	C7—C8	1.355 (4)
Pb1—Br2^{i}	2.8885 (3)	C7—H7	0.9500
N1—C7	1.342 (5)	C8—C9	1.419 (4)
N1—C11	1.345 (5)	C8—H8	0.9500
N1—H1	0.87 (1)	C9—C10	1.421 (4)
N2—C9	1.335 (4)	C10—C11	1.348 (5)
N2—C13	1.452 (4)	C10—H10	0.9500
N2—C12	1.461 (4)	C11—H11	0.9500
C1—C6	1.385 (4)	C12—H12A	0.9800
C1—C2	1.385 (4)	C12—H12B	0.9800
C2—C3	1.395 (4)	C12—H12C	0.9800
C2—H2	0.9500	C13—H13A	0.9800
C3—C4	1.383 (4)	C13—H13B	0.9800
C3—H3	0.9500	C13—H13C	0.9800
C1^{i}—Pb1—C1	180.00 (12)	C3—C4—C5	120.2 (3)
C1^{i}—Pb1—Br1	89.09 (8)	C3—C4—H4	119.9
C1—Pb1—Br1	90.91 (8)	C5—C4—H4	119.9
C1^{i}—Pb1—Cl1^{i}	90.91 (8)	C6—C5—C4	120.2 (3)
C1—Pb1—Cl1^{i}	89.09 (8)	C6—C5—H5	119.9
Br1—Pb1—Cl1^{i}	180.0	C4—C5—H5	119.9
C1^{i}—Pb1—Br1^{i}	90.91 (8)	C5—C6—C1	119.2 (3)
C1—Pb1—Br1^{i}	89.09 (8)	C5—C6—H6	120.4
Br1—Pb1—Br1^{i}	180.0	C1—C6—H6	120.4
Cl1^{i}—Pb1—Br1^{i}	0.000 (17)	N1—C7—C8	121.2 (3)
C1^{i}—Pb1—Br2	90.60 (8)	N1—C7—H7	119.4
C1—Pb1—Br2	89.40 (8)	C8—C7—H7	119.4
Br1—Pb1—Br2	86.065 (9)	C7—C8—C9	120.4 (3)
Cl1^{i}—Pb1—Br2	93.935 (9)	C7—C8—H8	119.8
Br1^{i}—Pb1—Br2	93.935 (9)	C9—C8—H8	119.8

C1^{i}—Pb1—Br2^{i}	89.40 (8)	N2—C9—C8	121.9 (3)
C1—Pb1—Br2^{i}	90.60 (8)	N2—C9—C10	122.3 (3)
Br1—Pb1—Br2^{i}	93.935 (9)	C8—C9—C10	115.9 (3)
Cl1^{i}—Pb1—Br2^{i}	86.065 (9)	C11—C10—C9	120.5 (3)
Br1^{i}—Pb1—Br2^{i}	86.065 (9)	C11—C10—H10	119.7
Br2—Pb1—Br2^{i}	180.0	C9—C10—H10	119.7
C7—N1—C11	120.6 (3)	N1—C11—C10	121.2 (3)
C7—N1—H1	124 (3)	N1—C11—H11	119.4
C11—N1—H1	116 (3)	C10—C11—H11	119.4
C9—N2—C13	122.3 (3)	N2—C12—H12A	109.5
C9—N2—C12	120.9 (3)	N2—C12—H12B	109.5
C13—N2—C12	116.3 (3)	H12A—C12—H12B	109.5
C6—C1—C2	121.3 (3)	N2—C12—H12C	109.5
C6—C1—Pb1	118.6 (2)	H12A—C12—H12C	109.5
C2—C1—Pb1	120.1 (2)	H12B—C12—H12C	109.5
C1—C2—C3	119.0 (3)	N2—C13—H13A	109.5
C1—C2—H2	120.5	N2—C13—H13B	109.5
C3—C2—H2	120.5	H13A—C13—H13B	109.5
C4—C3—C2	120.1 (3)	N2—C13—H13C	109.5
C4—C3—H3	120.0	H13A—C13—H13C	109.5
C2—C3—H3	120.0	H13B—C13—H13C	109.5
Br1—Pb1—C1—C6	133.5 (2)	C4—C5—C6—C1	−0.2 (5)
Cl1^{i}—Pb1—C1—C6	−46.5 (2)	C2—C1—C6—C5	0.2 (5)
Br1^{i}—Pb1—C1—C6	−46.5 (2)	Pb1—C1—C6—C5	−178.8 (2)
Br2—Pb1—C1—C6	−140.4 (2)	C11—N1—C7—C8	−2.8 (5)
Br2^{i}—Pb1—C1—C6	39.6 (2)	N1—C7—C8—C9	−0.8 (5)
Br1—Pb1—C1—C2	−45.5 (2)	C13—N2—C9—C8	−176.7 (3)
Cl1^{i}—Pb1—C1—C2	134.5 (2)	C12—N2—C9—C8	−4.9 (5)
Br1^{i}—Pb1—C1—C2	134.5 (2)	C13—N2—C9—C10	4.3 (5)
Br2—Pb1—C1—C2	40.6 (2)	C12—N2—C9—C10	176.2 (3)
Br2^{i}—Pb1—C1—C2	−139.4 (2)	C7—C8—C9—N2	−174.7 (3)
C6—C1—C2—C3	0.0 (5)	C7—C8—C9—C10	4.3 (5)
Pb1—C1—C2—C3	179.0 (2)	N2—C9—C10—C11	174.6 (3)
C1—C2—C3—C4	−0.3 (5)	C8—C9—C10—C11	−4.4 (5)
C2—C3—C4—C5	0.3 (5)	C7—N1—C11—C10	2.6 (5)
C3—C4—C5—C6	−0.1 (5)	C9—C10—C11—N1	1.1 (5)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1	0.87 (1)	2.49 (2)	3.260 (3)	148 (4)

Fig. 1