Table 2. *Selected geometric parameters* (Å, °)

K(1)—O(15)	2.800 (3)	C(23)—C(24)	1.399 (4)
K(1)—O(9)	2.839 (3)	C(24)—C(25)	1.400 (4)
K(1)—O(35)	2.852 (3)	C(24)—N(34)	1.408 (4)
K(1)—O(18)	2.873 (3)	C(25)—C(26)	1.356 (4)
K(1)—O(3)	2.878 (3)	C(26)—N(37)	1.433 (4)
K(1)—O(6)	2.887 (3)	C(27)—Cl(30)	1.771 (3)
K(1)—O(12)	2.931 (4)	C(27)—Cl(29)	1.772 (3)
K(1)—O(39^i)	3.038 (3)	C(27)—Cl(28)	1.785 (3)
K(1)—O(36)	3.098 (3)	N(31)—O(32)	1.231 (4)
K(1)—N(34)	3.359 (3)	N(31)—O(33)	1.236 (4)
C(21)—C(26)	1.503 (4)	N(34)—O(36)	1.241 (4)
C(21)—C(22)	1.504 (4)	N(34)—O(35)	1.246 (4)
C(21)—C(27)	1.553 (5)	N(37)—O(38)	1.217 (4)
C(22)—C(23)	1.351 (4)	N(37)—O(39)	1.239 (4)
C(22)—N(31)	1.432 (4)		
O(15)—K(1)—O(35)	76.52 (10)	O(18)—K(1)—O(36)	138.03 (8)
O(9)—K(1)—O(35)	97.14 (10)	O(3)—K(1)—O(36)	111.44 (9)
O(35)—K(1)—O(18)	109.63 (9)	O(6)—K(1)—O(36)	87.32 (8)
O(35)—K(1)—O(3)	130.79 (9)	O(12)—K(1)—O(36)	99.20 (11)
O(15)—K(1)—O(6)	151.55 (9)	C(26)—C(21)—C(22)	107.8 (2)
O(35)—K(1)—O(6)	129.81 (9)	C(26)—C(21)—C(27)	112.1 (3)
O(35)—K(1)—O(12)	84.29 (10)	C(22)—C(21)—C(27)	110.9 (3)
O(3)—K(1)—O(12)	144.33 (10)	C(22)—C(23)—C(24)	119.9 (3)
O(15)—K(1)—O(39^i)	94.74 (10)	C(23)—C(24)—C(25)	119.6 (3)
O(9)—K(1)—O(39^i)	137.93 (9)	C(26)—C(25)—C(24)	119.9 (3)
O(35)—K(1)—O(39^i)	61.34 (9)	C(25)—C(26)—C(21)	122.7 (3)
O(18)—K(1)—O(39^i)	70.89 (8)	C(21)—C(27)—Cl(30)	110.5 (2)
O(3)—K(1)—O(39^i)	70.14 (8)	C(21)—C(27)—Cl(29)	112.3 (2)
O(6)—K(1)—O(39^i)	107.25 (8)	C(21)—C(27)—Cl(28)	110.1 (2)
O(12)—K(1)—O(39^i)	141.63 (10)	O(32)—N(31)—O(33)	121.6 (3)
O(15)—K(1)—O(36)	118.29 (10)	O(36)—N(34)—O(35)	121.4 (3)
O(9)—K(1)—O(36)	72.52 (9)	O(38)—N(37)—O(39)	122.8 (3)
O(35)—K(1)—O(36)	42.51 (8)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection, cell refinement and data reduction: *CAD*-4 *Software* (Enraf–Nonius, 1989). The structure was solved using the direct methods routine *TREF* in *SHELXS*86 (Sheldrick, 1990), which located the K^+ ion, most of the 18-crown-6 molecule and part of the anion, and gave three unexpected strong peaks which were eventually interpreted as the Cl atoms of the CCl_3 group. Routine least-squares refinement and difference syntheses carried out using *SHELX*76 (Sheldrick, 1976), with *SHELXL* (Sheldrick, 1994) used for the last cycles, completed the structure. Molecular graphics were prepared using *PLUTON*92 (Spek, 1992).

We wish to thank Professor R. Foster and Dr J. A. Chudek (Dundee University) for suggesting the problem, providing a sample of (II) and valuable discussions of the results, and Drs C. K. Prout and D. J. Watkin, Oxford University, for the opportunity to use the diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Nitrato-κO)(triphenylphosphine-κP){3,6,9-trithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene-$\kappa^3 S^{3,6,9}$}mercury(II) Nitrate Hydrate Hemiethanol Solvate

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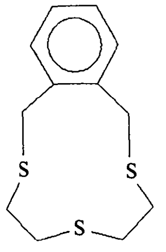
Abstract

In the title compound, $[Hg(NO_3)(C_{12}H_{16}S_3)(C_{18}H_{15}P)][NO_3].H_2O.0.5C_2H_6O$, the coordination sphere of the Hg^{2+} ion is a distorted trigonal bipyramid defined by the three S atoms of the trithiamacrocycle, the P atom of the triphenylphosphine group and an O atom of one nitrate group.

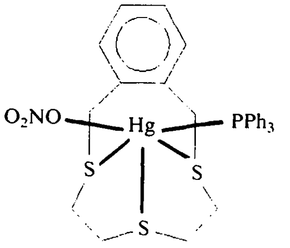
Comment

Among crown thioethers, 1,4,7-trithianonane (9S3) is unique in the unusual electronic and redox behaviour of its complexes (Blake & Scröder, 1990). By extension, interest has been aroused in the coordinating capabilities of related trithiamacrocycles, especially

3,6,9-trithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (oS3) (deGroot, Hannan & Loeb, 1991), which exhibits similar conformational trends as 9S3 (Lockhart, Mousley, Stuart Hill, Tomkinson, Teixidor, Almajano, Escriche, Casabó, Sillanpää & Kivekäs, 1992). There is a potential use for these trithiamacrocycles as sensors for thiophilic metal ions. Experimental evidence has confirmed that these ligands are excellent sensors for silver(I)-selective membrane electrodes, since they show little response towards Hg^{2+} ions, which constitute the most severe interference in silver(I) detection (Casabó, Mestres, Escriche, Teixidor & Perez-Jimenez, 1991). Thus, we have aimed at synthesizing and structurally characterizing Hg^{II} complexes of the oS3 ligand similar to those encountered in the membranes. Here we describe the structure of such a complex, (I).



oS3



(I)

The asymmetric unit of the stucture consists of the complex unit $[Hg(oS3)(PPh_3)(NO_3)]^+$, one half of a nitrate ion at the twofold axis, one half of a disordered nitrate ion occupying two positions in the vicinity of the twofold axis, one disordered crystal water molecule occuping two positions in the vicinity of the twofold axis and one half of a disordered ethanol molecule situated across a centre of inversion. Fig. 1 shows a perspective view of the $[Hg(oS3)(PPh_3)(NO_3)]^+$ cation and the atomic numbering scheme adopted. The coordination sphere of the Hg^{2+} ion is defined by the three S atoms of the oS3 trithiamacrocycle, the P atom of the triphenylphosphine group and an O atom of the coordinated nitrate group. The bonds to Hg are non-equivalent, varying from 2.412 (3) to 2.877 (12) Å [the greatest value representing the Hg—O(31) distance and indicating that the nitrate ion is only weakly coordinated to the metal]. The coordination sphere of Hg^{2+} may be described as a strongly distorted trigonal bipyramid, with the atoms O(31) and S(3) occupying the elongated axial positions and the atoms S(1), S(2) and P the equatorial positions. In addition, the Hg^{2+} ion deviates −0.196 (1) Å from the plane defined by atoms S(1), S(2) and P, revealing a slight tendency towards square-pyramidal stereochemistry. It is interesting to note that bond angles defined by the Hg^{2+} ion and the equatorial coordinating atoms are quite different. The S(1)—Hg—P bond angle is close to the ideal value for trigonal bipyramidal stereochemistry (120°), while angles S(2)—Hg—P and S(2)—Hg—S(1) both differ significantly from this ideal value, evidently as a result of the steric interactions between the bulky triphenylphosphine group and the benzo moiety of oS3.

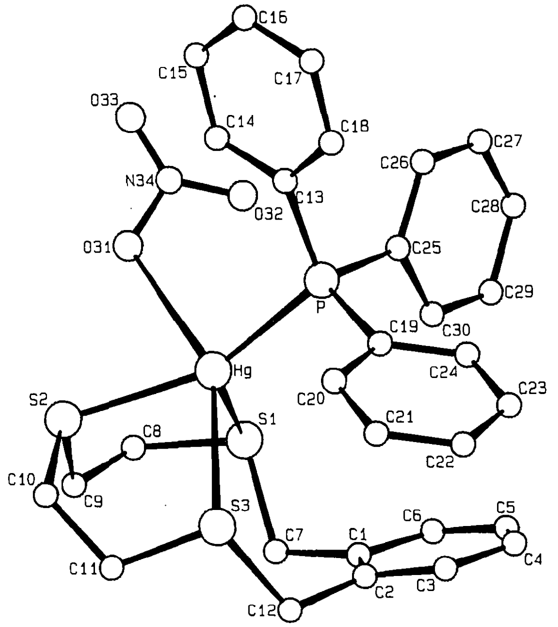


Fig. 1. View of the $[Hg(oS3)(PPh_3)(NO_3)]^+$ complex unit showing labelling of the non-H atoms.

The S atoms of oS3 are in an overall *endo*-dentate conformation. This is in agreement with the known structural data for this ligand (deGroot & Loeb, 1990) and confirms its coordinating capability as a facial tridentate ligand.

Experimental

The ligand oS3 was synthesized by a previously reported procedure (deGroot, Hannan & Loeb, 1991). The Hg^{II} complex was prepared by adding a solution of oS3 (0.05 g, 0.2 mmol) in ethanol/CH_2Cl_2 (10:1, 5 ml) to a solution of $Hg(NO_3)_2.H_2O$ (0.07 g, 0.2 mmol) and triphenylphosphine (0.05 g, 0.2 mmol) in ethanol (5 ml). The mixture was refluxed for 1 h and allowed to stand for 24 h at 268 K. The colourless prismatic crystals that precipitated were filtered off and vacuum dried. Yield 23%. Crystals of the title compound were obtained directly from the synthesis.

Crystal data

$[Hg(NO_3)(C_{12}H_{16}S_3)(C_{18}H_{15}P)][NO_3].H_2O.0.5C_2H_6O$
$M_r = 884.4$
Monoclinic
$C2/c$
$a = 30.198\ (8)$ Å
$b = 15.642\ (5)$ Å
$c = 18.147\ (5)$ Å
$\beta = 122.60\ (3)°$
$V = 7221\ (4)$ Å^3
$Z = 8$
$D_x = 1.627$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.8–18.3°$
$\mu = 4.52$ mm^{-1}
$T = 296$ K
Plate
$0.18 \times 0.12 \times 0.10$ mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.81$, $T_{\max} = 1.00$
12 563 measured reflections
6365 independent reflections
3587 observed reflections $[F > 3\sigma(F)]$
$R_{\rm int} = 0.0631$

$\theta_{\max} = 25°$
$h = -35 \rightarrow 29$
$k = -18 \rightarrow 18$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 150 reflections intensity variation: −36% (linear correction applied)

Refinement

Refinement on F
$R = 0.057$
$wR = 0.052$
$S = 1.80$
3587 reflections
371 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.23$
$\Delta\rho_{\max} = 1.3$ e Å^{-3}
$\Delta\rho_{\min} = -1.1$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *Xtal*3.0 (Hall & Stewart, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Hg	0.58058 (2)	0.32684 (3)	0.65893 (3)	0.0538 (3)
S(1)	0.6060 (1)	0.3099 (2)	0.5390 (2)	0.061 (2)
S(2)	0.4987 (1)	0.3962 (2)	0.5367 (2)	0.060 (2)
S(3)	0.5130 (1)	0.1854 (2)	0.6053 (2)	0.072 (2)
P	0.6475 (1)	0.2995 (2)	0.8101 (2)	0.046 (2)
C(1)	0.6098 (6)	0.1360 (9)	0.5529 (8)	0.080 (9)
C(2)	0.5879 (6)	0.0892 (8)	0.5902 (9)	0.08 (1)
C(3)	0.6205 (7)	0.0312 (9)	0.657 (1)	0.12 (1)
C(4)	0.6708 (8)	0.020 (1)	0.683 (1)	0.16 (1)
C(5)	0.6892 (7)	0.062 (1)	0.644 (1)	0.13 (1)
C(6)	0.6620 (6)	0.121 (1)	0.580 (1)	0.10 (1)
C(7)	0.5815 (5)	0.2070 (8)	0.4865 (8)	0.074 (9)
C(8)	0.5570 (5)	0.3848 (9)	0.4614 (8)	0.071 (8)
C(9)	0.5030 (5)	0.3750 (9)	0.4427 (7)	0.066 (7)
C(10)	0.4479 (5)	0.326 (1)	0.5251 (8)	0.082 (8)
C(11)	0.4537 (5)	0.230 (1)	0.5132 (8)	0.091 (9)
C(12)	0.5306 (7)	0.0965 (8)	0.557 (1)	0.10 (1)
C(13)	0.6511 (4)	0.3744 (7)	0.8875 (7)	0.047 (7)
C(14)	0.6396 (5)	0.4584 (8)	0.8640 (8)	0.073 (9)
C(15)	0.6500 (6)	0.5191 (8)	0.9283 (9)	0.08 (1)
C(16)	0.6719 (5)	0.4939 (8)	1.0146 (8)	0.070 (9)
C(17)	0.6822 (5)	0.4097 (7)	1.0377 (8)	0.061 (8)
C(18)	0.6715 (5)	0.3502 (7)	0.9734 (7)	0.054 (7)
C(19)	0.6387 (4)	0.1937 (7)	0.8410 (7)	0.047 (6)
C(20)	0.5911 (5)	0.1752 (7)	0.8294 (7)	0.056 (7)
C(21)	0.5820 (5)	0.0929 (9)	0.8479 (8)	0.071 (9)
C(22)	0.6210 (5)	0.0323 (8)	0.8799 (8)	0.076 (9)
C(23)	0.6691 (5)	0.0520 (8)	0.8936 (9)	0.076 (9)
C(24)	0.6774 (5)	0.1323 (8)	0.8738 (8)	0.061 (7)
C(25)	0.7115 (4)	0.3003 (7)	0.8224 (7)	0.045 (6)
C(26)	0.7534 (4)	0.3482 (7)	0.8865 (7)	0.050 (7)
C(27)	0.8006 (4)	0.3469 (7)	0.8927 (8)	0.059 (7)
C(28)	0.8066 (5)	0.2982 (8)	0.8368 (9)	0.069 (8)
C(29)	0.7657 (5)	0.2491 (9)	0.7744 (9)	0.074 (9)
C(30)	0.7180 (5)	0.2512 (8)	0.7655 (8)	0.063 (8)
O(31)	0.6023 (4)	0.5016 (7)	0.6393 (7)	0.121 (4)
O(32)	0.6808 (5)	0.4759 (8)	0.7096 (8)	0.160 (5)
O(33)	0.6520 (5)	0.6005 (9)	0.7087 (9)	0.166 (5)
N(34)	0.6484 (5)	0.5293 (8)	0.6908 (8)	0.111 (5)
O(35)	1/2	0.332 (1)	3/4	0.119 (5)
O(36)	0.5087 (4)	0.4510 (7)	0.7035 (7)	0.123 (4)
N(37)	1/2	0.408 (1)	3/4	0.093 (6)
O(38)†‡	0.5546 (7)	−0.156 (1)	0.673 (1)	0.067 (5)
O(39)†‡	0.5000 (7)	−0.061 (1)	0.661 (1)	0.128 (8)
O(40)†‡	0.5354 (8)	−0.147 (1)	0.771 (1)	0.18 (1)
N(41)†‡	0.5300 (4)	−0.1213 (7)	0.7017 (7)	0.067 (6)
O(42*W*)†	0.5188 (7)	0.636 (1)	0.755 (1)	0.093 (7)
O(43*W*)†	0.5962 (8)	0.697 (1)	0.774 (1)	0.112 (7)
C(44)†§	0.789 (2)	0.321 (2)	0.592 (3)	0.15 (2)
C(45)†	0.790 (2)	0.252 (4)	0.561 (3)	0.23 (2)
C(46)†§	0.747 (2)	0.209 (2)	0.476 (3)	0.15 (2)

† Occupancy factor 0.5.
‡ Disordered NO_3^- refined as a rigid group with N—O = 1.24 Å.
§ O atom of ethanol solvate could not be distinguished.

Table 2. *Selected geometric parameters* (Å, °)

Hg—S(1)	2.683 (5)	P—C(19)	1.81 (1)
Hg—S(2)	2.511 (3)	P—C(25)	1.82 (1)
Hg—S(3)	2.806 (4)	C(1)—C(2)	1.38 (3)
Hg—P	2.412 (3)	C(1)—C(6)	1.39 (2)
Hg—O(31)	2.877 (12)	C(1)—C(7)	1.52 (2)
S(1)—C(7)	1.81 (1)	C(2)—C(3)	1.40 (2)
S(1)—C(8)	1.82 (1)	C(2)—C(12)	1.50 (3)
S(2)—C(9)	1.81 (2)	C(3)—C(4)	1.33 (3)
S(2)—C(10)	1.80 (2)	C(4)—C(5)	1.29 (3)
S(3)—C(11)	1.81 (1)	C(5)—C(6)	1.35 (2)
S(3)—C(12)	1.87 (2)	C(8)—C(9)	1.48 (2)
P—C(13)	1.79 (1)	C(10)—C(11)	1.54 (2)
S(1)—Hg—S(2)	84.4 (1)	C(2)—C(3)—C(4)	122 (2)
S(1)—Hg—S(3)	96.6 (1)	Hg—S(1)—C(8)	95.5 (6)
S(1)—Hg—P	118.3 (1)	C(7)—S(1)—C(8)	103.5 (5)
S(1)—Hg—O(31)	79.0 (3)	Hg—S(2)—C(9)	102.5 (4)
S(2)—Hg—S(3)	81.3 (1)	Hg—S(2)—C(10)	102.2 (4)
S(2)—Hg—P	154.7 (1)	C(9)—S(2)—C(10)	105.5 (7)
S(2)—Hg—O(31)	70.2 (2)	Hg—S(3)—C(11)	101.0 (5)
S(3)—Hg—P	105.2 (1)	Hg—S(3)—C(12)	114.2 (6)
S(3)—Hg—O(31)	151.4 (2)	C(11)—S(3)—C(12)	104.1 (7)
P—Hg—O(31)	101.6 (2)	Hg—P—C(13)	115.9 (3)
Hg—S(1)—C(7)	107.4 (6)	Hg—P—C(19)	109.9 (3)
Hg—P—C(25)	108.8 (4)	C(3)—C(4)—C(5)	119 (2)
C(13)—P—C(19)	108.2 (6)	C(4)—C(5)—C(6)	125 (2)
C(13)—P—C(25)	106.7 (6)	C(1)—C(6)—C(5)	118 (2)
C(19)—P—C(25)	106.9 (6)	S(1)—C(7)—C(1)	109.7 (8)
C(2)—C(1)—C(6)	119 (1)	S(1)—C(8)—C(9)	117 (1)
C(2)—C(1)—C(7)	124 (1)	S(2)—C(9)—C(8)	113.2 (8)
C(6)—C(1)—C(7)	117 (2)	S(2)—C(10)—C(11)	117 (1)
C(1)—C(2)—C(3)	118 (2)	S(3)—C(11)—C(10)	112.1 (8)
C(1)—C(2)—C(12)	121 (1)	S(3)—C(12)—C(2)	115.3 (9)
C(3)—C(2)—C(12)	121 (2)		
C(8)—S(1)—C(7)—C(1)	−165 (1)	C(2)—C(1)—C(7)—S(1)	104 (1)
C(7)—S(1)—C(8)—C(9)	62 (1)	C(6)—C(1)—C(7)—S(1)	−72 (2)
C(10)—S(2)—C(9)—C(8)	−147 (1)	C(1)—C(2)—C(3)—C(4)	−1 (2)
C(9)—S(2)—C(10)—C(11)	54 (1)	C(12)—C(2)—C(3)—C(4)	176 (2)
C(12)—S(3)—C(11)—C(10)	−150 (1)	C(1)—C(2)—C(12)—S(3)	−86 (2)

C(11)—S(3)—C(12)—C(2)	138 (1)	C(3)—C(2)—C(12)—S(3)	98 (1)
C(6)—C(1)—C(2)—C(3)	3 (2)	C(2)—C(3)—C(4)—C(5)	−2 (3)
C(6)—C(1)—C(2)—C(12)	−174 (1)	C(3)—C(4)—C(5)—C(6)	4 (3)
C(7)—C(1)—C(2)—C(3)	−174 (1)	C(4)—C(5)—C(6)—C(1)	−2 (3)
C(7)—C(1)—C(2)—C(12)	9 (2)	S(1)—C(8)—C(9)—S(2)	65 (1)
C(2)—C(1)—C(6)—C(5)	−1 (2)	S(2)—C(10)—C(11)—S(3)	61 (1)
C(7)—C(1)—C(6)—C(5)	176 (1)		

Cell refinement, data collection and data reduction: Rigaku AFC-5*S* software. Program used to solve the structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine the structure: *XTAL*3.0 (Hall & Stewart, 1990). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Programs used to prepare material for the publication: *Xtal*3.0 *BONDLA* and *ATABLE*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AB1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzyl(bromo)diphenyllead

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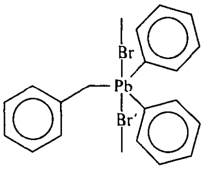
Abstract

The coordination polyhedron around Pb in the title compound, $[PbBr(C_6H_5)_2(C_7H_7)]$, is a slightly distorted trigonal bipyramid, the trigonal plane being formed by the C(Pb) atoms of the three organic ligands. The axial positions are occupied by Br atoms [Pb(1)—Br(1) 2.985 (2), Pb(1)—Br(1*a*) 2.885 (2) Å], each Br atom bridging neighbouring molecules to form infinite Br(1*a*)—Pb(1)—Br(1)—Pb(1*b*) chains [Br(1*a*)—Pb(1)—Br(1) 173.610 (15), Pb(1)—Br(1)—Pb(1*b*) 122.73 (5)°], *i.e.* *catena*-poly-[(benzyldiphenyllead)-μ-bromo].

Comment

The structures of three triorganolead halides are known to have been investigated by diffraction methods. In all cases, the Pb atom proved to be pentacoordinated: in Ph_3PbX (X = Cl, Br) intermolecular X—Pb coordination generates one-dimensional chains *via* unsymmetrical X—Pb—X links (Preut & Huber, 1977), while in $[PbI(C_7H_7)(C_9H_{12}N)(C_7H_7O)]$ (van der Kooi, den Brinker & de Kok, 1985), a compound with three different R groups attached to the Pb atom, pentacoordination is attained by intramolecular N—Pb coordination. Pentacoordination of Pb and formation of infinite chains by way of halogen bridging was also inferred from vibrational studies for trimethyllead halides (Clark, Davies & Puddephatt, 1968) and for triphenyllead halides (Clark, Davies & Puddephatt, 1969). We report here the solid-state structure of a triorganolead compound, (I), with two types of R group on Pb.



(I)

The coordination polyhedron around Pb can be described as a slightly distorted trigonal bipyramid, with C(1), C(21) and C(31) in the equatorial plane and two Br atoms in the axial positions. The structure is similar to that of $[PbBr(C_6H_5)_3]$ (Preut & Huber, 1977); however, some noteworthy differences exist. The distances Pb(1)—Br(1) and Pb(1)—Br(1*a*) are more similar to each other in the title compound [2.985 (2) and 2.885 (2) Å, respectively], than in $[PbBr(C_6H_5)_3]$ [2.852 (1) and 3.106 (1) Å, respectively]. Hence, the difference between the Pb(1)—Br(1) and Pb(1)—Br(1*a*) distances of 0.100 Å in the title compound is less marked than in $[PbBr(C_6H_5)_3]$ (0.254 Å), and this corresponds to a distinctly shorter distance of Pb from the plane defined by C(1), C(21) and C(31) in the title compound {0.052 (5) Å, compared to 0.127 (10) Å in $[PbBr(C_6H_5)_3]$ (Preut & Huber, 1977)}. In this respect, the distortion of the trigonal bipyramid is smaller than in $[PbBr(C_6H_5)_3]$;