

Fig. 1. A molecule of *trans*-PdCl₂(PPh₃)₂. The phenyl-ring C atoms are numbered sequentially C(*i*1)–C(*i*6) (*i* = 1, 2, 3). For clarity only one atom in each ring is numbered. C(*i*1) is bonded to P.

Table 3. Bond lengths (Å) in *trans*-dichlorobis(phosphine)palladium complexes

L in <i>trans</i> -PdCl ₂ L ₂	Pd–Cl	Pd–P	Reference
PPh ₃	2.290 (1)	2.337 (1)	This work
(Bu ^t) ₂ P(CH ₂) ₂ CHMe(CH ₂) ₂ P(Bu ^t) ₂	2.291 (5)	2.388 (6)	(1)
	2.305 (6)	2.380 (6)	
	2.302 (5)	2.372 (6)	
	2.305 (6)	2.374 (6)	
Ph ₂ PCH=CClCF ₃	2.291 (1)	2.322 (1)	(2)
PMe ₂ (<i>neo</i> -menthyl)	2.304 (5)	2.344 (4)	(3)
	2.297 (5)	2.361 (5)	
PMe ₂ (menthyl)	2.296 (9)	2.310 (5)	(3)
	2.267 (9)		
(Bu ^t) ₂ P(CH ₂) ₂ P(Bu ^t) ₂	2.316 (5)	2.379 (4)	(4)
	2.287 (5)	2.376 (4)	
	2.302 (4)	2.370 (4)	
	2.326 (4)	2.378 (4)	
Ph ₂ PCH ₂ C ₁₈ H ₁₀ CH ₂ PPh ₂	2.311 (2)	2.326	(5)
	2.293 (2)	2.322	

References: (1) Al-Salem, McDonald, Markham, Norton & Shaw (1980); (2) Taylor, Jacobson & Carty (1975); (3) Kan, Miki, Kai, Yasuoka & Kasai (1978); (4) McDonald (1979); (5) Bachechi, Zambonelli & Venanzi (1977).

The small distortion of the Cl–Pd–P angle from 90° [to 92.0(1)°] is undoubtedly a consequence of intramolecular crowding effects. Thus, the phenyl-ring C atom (C11) comes close to eclipsing the Cl atom

[torsion angle Cl–Pd–P–C(11) 16.0(2)°] and Pd–P–C(11) [118.1(1)°] is considerably larger than the other Pd–P–C angles [110.7 and 112.1(1)°]. As is commonly found in PPh₃ complexes, the C–P–C angles are all less than tetrahedral [104.0–106.3(1)°]. The orientations adopted by the phenyl rings C(21)–C(26) and C(31)–C(36) are such that an *ortho* proton on each ring is directed towards the Pd atom but the distances [Pd···H(22) 2.92, Pd···H(36) 3.22 Å] are too great for any significant interaction. The remaining dimensions [mean P–C 1.816(1), C–C 1.384(4) Å] are normal and in accord with accepted values.

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Structure of Bis[hydroxolead(II)] 5,5'-Azotetrazolediide

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Abstract. 2[PbOH]⁺.C₂N₁₀²⁻, triclinic, *P* $\bar{1}$, *a* = 4.3604(4), *b* = 7.4214(6), *c* = 7.5016(9) Å, α = 101.31(1), β = 96.97(2), γ = 109.19(1)°, *V* = 220.24 Å³, *M_r* = 612.484, *Z* = 1, *D_c* = 4.62 Mg m⁻³.

Mo *K*α radiation, λ = 0.71069 Å, μ (Mo *K*α) = 38.53 mm⁻¹. Final *R* = 0.055 for 959 unique reflections. In the [Pb(OH)]⁺ complex ion each lead atom is coordinated to three oxygen atoms, and each oxygen atom to three lead atoms, thus forming an infinite ladder-like chain. The azotetrazolediide anion adopts a *trans* conformation about the N=N bond.

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Introduction. Remarkably little is known about the chemical nature of many important explosives. The title compound, otherwise monobasic lead azotetrazole (phase D), was patented for use in detonators many years ago (Rathsburg, 1926) and has considerable potential as a stab-sensitive material (Chaudhri, 1976). The structure was determined as part of a programme of research into primary explosives. Clear yellow chunky crystals of a suitable size were prepared by gel growth techniques (Henisch, 1970); lead acetate solution was allowed to diffuse into a gel of sodium silicate, sodium azotetrazole pentahydrate and acetic acid (pH ~7.5). The crystals were removed from the growth medium after four months.

Preliminary Weissenberg photographs indicated that the crystals were suffering radiation damage. Thus one crystal, selected optically, was used for determination of accurate parameters and to find appropriate reflections to serve as standards and orienting planes. Parameters were refined by least-squares fit to the reflecting positions of nineteen high-angle reflections ($2\theta > 50^\circ$). A fresh crystal of approximate dimensions $0.1 \times 0.06 \times 0.06$ mm was used for data collection. Measurements were obtained using a Hilger and Watts Y290 four-circle diffractometer with niobium-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and ω - 2θ scans, the scan width varying with $\tan \theta$. Scanning rate was 1.5 s per $0.04^\circ \theta$ ($1.6^\circ \text{ min}^{-1}$), with background measured on both sides of the peak for $7\frac{1}{2}$ s. A complete set of unique reflections was measured up to $2\theta = 50^\circ$; from 50 to 60° only those reflections with $I/\sigma(I) > 3$ were collected.

1078 reflections were collected of which 941 were considered observed [$I/\sigma(I) > 3$]. In total the crystal was irradiated for about 36 h, after which time the standard reflections showed no significant drop in intensity.

The data were corrected for Lorentz and polarization effects and also for absorption using the method of Alcock (1970).

The position of the Pb atom was readily determined by the heavy-atom method. Electron density maps

phased from this indicated the positions of all other non-hydrogen atoms. Parameters were refined by least squares, with anisotropic temperature factors applied to all atoms in the final cycles. The hydroxyl H was not clearly visible in the final difference map. The weighting scheme was based on $w = 1.0/(A + DF_{\text{obs}} + EF_{\text{obs}}^2)$, which was adjusted to make the average $w\Delta^2$ independent of F_{obs} ($A = 19.85$; $D = -0.3972$; $E = 0.0039$). The final R value for 959 reflections (including 18 unobserved reflections with $F_c > F_o$) is 0.055 ($R_w = 0.066$).

Atomic scattering factors and anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974). Final atom parameters are given in Table 1.*

Discussion. The atomic scheme of the azotetrazolide anion is illustrated in Fig. 1, together with the interatomic distances and angles. It is centrosymmetric, the centre of symmetry at $\frac{1}{2}, 0, 0$ being at the midpoint of the central N=N bond. The geometry of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36941 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

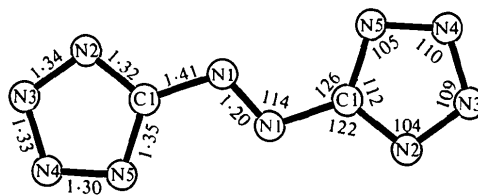


Fig. 1. Atomic numbering in the anion, with bond lengths (Å) and angles ($^\circ$). E.s.d.'s range from 0.02 to 0.03 Å and from 1.5 to 2.1° .

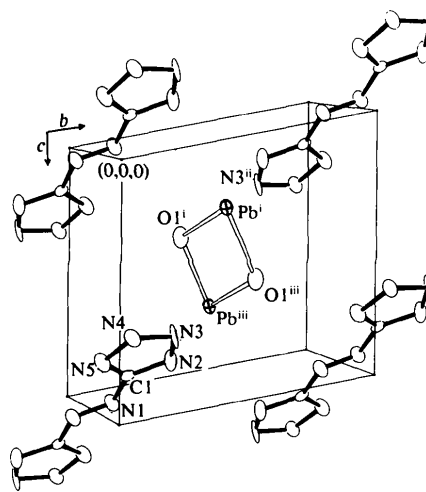


Fig. 2. The packing arrangement within a unit cell viewed along a . The thermal ellipsoids enclose 50% probability (Johnson, 1965). Symmetry code as in Table 2.

Table 1. Positional parameters with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

	x	y	z	U_{eq}^*
C(1)	0.269 (4)	0.090 (3)	0.858 (3)	1.5
N(1)	0.522 (4)	0.081 (3)	0.990 (3)	2.0
N(2)	0.259 (5)	0.259 (3)	0.831 (3)	2.7
N(3)	-0.020 (5)	0.206 (2)	0.704 (3)	2.6
N(4)	-0.167 (5)	0.011 (3)	0.659 (3)	2.8
N(5)	0.006 (4)	-0.066 (3)	0.753 (3)	2.4
O(1)	0.334 (4)	0.616 (2)	0.591 (3)	2.3
Pb	0.1653 (2)	0.4499 (1)	0.2761 (1)	1.6

* U_{eq} ($\text{Å}^2 \times 10^2$) = $\frac{1}{3}(U_{11} + U_{22} + U_{33})$.

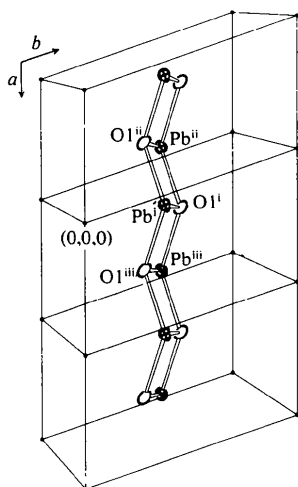


Fig. 3. Pb—O ladder-like chain parallel to *a*. Thermal ellipsoids enclose 50% probability (Johnson, 1965). Symmetry code as in Table 2.

Table 2. Selected interatomic distances (Å) and angles (°) involving the Pb—OH cation

E.s.d.'s are in parentheses.

Pb ⁱ —O(1) ⁱ	2.34 (2)	O(1) ⁱ ...O(1) ⁱⁱ	2.85 (2)
Pb ⁱ —O(1) ⁱⁱ	2.45 (2)	O(1) ⁱ ...O(1) ⁱⁱⁱ	2.85 (2)
Pb ⁱ —O(1) ⁱⁱⁱ	2.52 (2)	O(1) ⁱ ...N(4) ^v	2.92 (2)
Pb ⁱ —N(5) ^{iv}	2.65 (2)		
Pb ⁱ —N(3) ⁱⁱ	2.81 (2)		
O(1) ⁱ —Pb ⁱ —O(1) ⁱⁱ	73.0 (5)	O(1) ⁱⁱⁱ —Pb ⁱ —N(3) ⁱⁱ	133.4 (6)
O(1) ⁱ —Pb ⁱ —O(1) ⁱⁱⁱ	71.6 (6)	N(5) ^{iv} —Pb ⁱ —N(3) ⁱⁱ	152.6 (6)
O(1) ⁱⁱ —Pb ⁱ —O(1) ⁱⁱⁱ	122.5 (6)	Pb ⁱ —O(1) ⁱ —Pb ⁱⁱ	107.0 (5)
O(1) ⁱ —Pb ⁱ —N(5) ^{iv}	108.7 (6)	Pb ⁱ —O(1) ⁱ —Pb ⁱⁱⁱ	108.4 (7)
O(1) ⁱ —Pb ⁱ —N(3) ⁱⁱ	75.6 (6)	Pb ⁱⁱ —O(1) ⁱ —Pb ⁱⁱⁱ	122.5 (8)
O(1) ⁱⁱ —Pb ⁱ —N(5) ^{iv}	79.2 (6)	Pb ⁱ —O(1) ⁱ ...N(4) ^v	113.2 (8)
O(1) ⁱⁱ —Pb ⁱ —N(3) ⁱⁱ	76.3 (6)	Pb ⁱⁱ —O(1) ⁱ ...N(4) ^v	122.8 (8)
O(1) ⁱⁱⁱ —Pb ⁱ —N(5) ^{iv}	71.2 (5)	Pb ⁱⁱⁱ —O(1) ⁱ ...N(4) ^v	81.1 (8)

Symmetry code

(i)	<i>x, y, z</i>	(iv)	$-x, -y, 1 - z$
(ii)	$-x, 1 - y, 1 - z$	(v)	$1 + x, 1 + y, z$
(iii)	$1 - x, 1 - y, 1 - z$		

the tetrazole ring is similar to that found in sodium tetrazolide monohydrate (Palenik, 1963) and in the two reported polymorphs of tetrazene and in tetrazene hydrobromide (Duke, 1971). The exocyclic C—N bond [1.41 (3) Å] falls within the range found in comparable systems; though the N=N bond [1.20 (3) Å] is rather short for a double bond, which normally lies in the range 1.23 to 1.27 Å (*Molecular Structures and Dimensions*, 1972). However, this may not be signifi-

cant owing to the high standard deviations. The tetrazole rings are flat [maximum deviation from planarity is 0.002 (2) Å], but not completely coplanar, one being rotated by about 4° with respect to the other.

The packing arrangement within a unit cell is shown in Fig. 2 and important distances and angles are given in Table 2. Each Pb atom is weakly coordinated to two azotetrazolide anions: one *via* N(5) [2.65 (2) Å] and the other *via* N(3) [2.81 (2) Å]. Fig. 3 shows the lead—oxygen coordination. Each Pb atom is closely linked to three O atoms and each O to three Pb atoms, resulting in an infinite ladder-like chain of PbOH ions along *a*. The Pb—O distances range from 2.34 (2) to 2.52 (2) Å [*cf.* 2.34 to 2.55 Å expected from addition of ionic radii (Shannon, 1976)].

Thus the lead is five-coordinate, adopting a very distorted square-pyramidal geometry. The Pb—O—Pb angles are 107.0 (5), 108.4 (7) and 122.5 (8)°. The hydrogen is probably weakly hydrogen bonded to N(4) [O(1)···N(4) is 2.92 (2) Å], thus giving approximate tetrahedral geometry about the O atom, somewhat distorted by the angle of 122.5 (6)° between the steps of the ladder.

All calculations were performed on the IBM 360/195 at the Rutherford Computer Laboratory, using the XRAY 74 system (Stewart, 1974).

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