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The Structure of the Lead Salt of 2,4,6-Trinitro-1,3-benzenediol Monohydrate (α Polymorph), $\alpha\text{-Pb}^{2+}.\text{C}_6\text{HN}_3\text{O}_8^{2-}.\text{H}_2\text{O}$

By Melanie A. Pierce-Butler

Propellants, Explosives and Rocket Motor Establishment (PERME), Waltham Abbey, Essex EN9 1BP, England

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Abstract. $M_r = 468{\cdot}29$, monoclinic, $P2_1/a$, $a = 10{\cdot}0299\,(20)$, $b = 12{\cdot}5418\,(9)$, $c = 8{\cdot}0331\,(6)$ Å, $\beta = 92{\cdot}782\,(14)°$, $U = 1009{\cdot}3$ Å^3, $Z = 4$, $D_x = 3{\cdot}083$ Mg m^{-3}, $F(000) = 856$, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) $= 16{\cdot}91$ mm^{-1}, room temperature. Final $R = 0{\cdot}032$ for 2399 reflections, $R_w = 0{\cdot}030$. The benzene ring shows distortion, internal angles ranging from 112·9 (5) to 126·1 (6)° and C—C bond lengths from 1·377 (9) to 1·462 (9) Å. The C—O bond lengths are 1·301 (8) and 1·242 (8) Å. The Pb atoms are seven coordinate and are paired *via* oxygen bridges. The water molecule is coordinated to the metal and is also hydrogen-bonded to the anion.

Introduction. The title compound (henceforth α-lead styphnate) is a widely used primary explosive. Crystallographic data were first detailed by Miles (1931) and a preliminary structural investigation was carried out by Reed (1959). An R factor of 0·146 was reported and consequently the accuracy of determination of the light atoms was poor. This reinvestigation is part of a programme of research into the structural properties of primary explosives. The structure of the β polymorph of lead styphnate has already been reported (Pierce-Butler, 1982*b*) and it was interesting to compare the two different forms.

Experimental. α-Lead styphnate prepared from freshly made magnesium styphnate (pH~4·2) and lead acetate; crystal approximately 0·08 × 0·06 × 0·06 mm, Hilger & Watts Y290 four-circle automatic diffractometer, Nb- filtered Mo $K\alpha$ radiation, θ–2θ scans, scan rate 0·004°s^{-1}, scan ranges varied from 0·6° (low θ) to 0·8° (high θ), backgrounds measured on both sides of the peak for half the peak scan time; $2\theta_{\text{max.}} = 56°$ [reflections with $I/\sigma(I) > 2$ considered observed]. At higher angles (to $2\theta = 70°$) reflections prescanned; only those showing $I/\sigma(I) > 3$ measured. Every measurement repeated at least once and the intensities averaged. Of 2835 unique reflections 2362 considered observed, index range h 0–15, k 0–20, l −12–12; three standard reflections monitored at intervals of 50 showed ~7% deterioration of the crystal by the end of data collection. Appropriate scale factors applied and intensities corrected for Lorentz–polarization and for absorption using the method of Alcock (1970) (transmission factors ranged from 0·57 to 0·66). Accurate cell parameters obtained by least-squares fit to the reflecting angles of 14 reflections ($2\theta > 60°$). Heavy-atom method, least squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic temperature factors applied to all non-hydrogen atoms in final cycles; non-aqueous H discernible in difference map and included in the refinement with fixed isotropic thermal parameter (0·025 Å^2). $w = 1{\cdot}0/(A + DF_o + EF_o^2)$ adjusted to make the average $w\Delta^2$ independent of F_o ($A = 18{\cdot}165$, $D = -0{\cdot}307$, $E = 0{\cdot}0016$). Final $R = 0{\cdot}032$ for 2399 reflections (including 37 unobserved with $F_c > F_o$), $R_w = 0{\cdot}030$; $(\Delta/\sigma)_{\text{max}}$ in final least-squares cycle $= 0{\cdot}24$, final $\Delta\rho$ excursions within +1 and −2 e Å^{-3}. Atomic scattering factors (metal atoms assumed ionic) and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974); all calculations performed at the Rutherford and Appleton Computer Laboratory using the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The geometry of the carbon skeleton in substituted benzene derivatives is well known to be affected by electronic properties of the substituents (Pierce-Butler, 1982*a*; Domenicano & Murray-Rust, 1979; Domenicano, Vaciago & Coulson, 1975; Katritzky & Topsom, 1970). Electron-withdrawing substituents such as $-\text{NO}_2$ tend to increase the internal angle at the *ipso* carbon and shorten the adjacent C—C bonds. The opposite effect occurs for electron-releasing groups. In the presence of conjugation the bond to the substituent tends to be shorter, the adjacent C—C bonds longer and the angle at the *ipso* carbon smaller than in the absence of conjugation, regardless of the electronegativity of the substituent. These effects have been found to be much larger in anions such as styphnate (Pierce-Butler, 1982*b*) and picrate (Maartmann-Moe, 1969; Palenik, 1972) than in purely organic compounds.

Table 1. *Positional parameters* ($\times 10^4$; *for* H $\times 10^3$) *and equivalent isotropic thermal parameters* (Å^2 $\times$ 100) *with e.s.d.'s in parentheses*

$$U_{eq}=\tfrac{1}{3}(U_{11}+U_{22}+U_{33}).$$

	x	y	z	U_{eq}
Pb	815·6 (3)	581·5 (1)	2207·5 (3)	2·18 (1)
C(1)	1671 (7)	1305 (5)	8439 (8)	2·0 (4)
C(2)	2560 (7)	825 (5)	7291 (9)	2·3 (3)
C(3)	3410 (7)	1425 (6)	6362 (9)	2·5 (3)
C(4)	3477 (7)	2516 (5)	6545 (9)	2·4 (3)
C(5)	2706 (7)	3096 (5)	7712 (8)	2·2 (3)
C(6)	1772 (7)	2418 (5)	8569 (8)	2·1 (3)
O(1)	797 (5)	751 (4)	9215 (6)	2·5 (2)
O(2)	2790 (6)	4059 (4)	8059 (7)	3·5 (3)
O(3)	3308 (7)	1041 (6)	2048 (10)	5·8 (4)
N(1)	880 (6)	2977 (4)	9626 (7)	2·5 (3)
O(11)	572 (7)	2574 (5)	10946 (7)	4·4 (3)
O(12)	418 (6)	3844 (4)	9189 (8)	3·7 (3)
N(2)	4376 (6)	3055 (5)	5506 (7)	2·6 (3)
O(21)	4522 (6)	4036 (4)	5571 (7)	3·6 (3)
O(22)	5021 (7)	2532 (5)	4522 (8)	4·9 (4)
N(3)	2657 (7)	−319 (5)	7074 (9)	3·2 (3)
O(31)	3510 (7)	−671 (5)	6211 (12)	8·3 (5)
O(32)	1908 (6)	−925 (4)	7813 (8)	3·6 (3)
H(1)	403 (11)	110 (9)	563 (14)	

Table 2. *Metal–oxygen bond distances* (Å) *with e.s.d.'s in parentheses*

Pb—O(3)	2·575 (7)	Pb—O(32^{ii})	2·765 (6)
Pb—O(11^{i})	2·704 (6)	Pb—O(2^{iii})	2·383 (5)
Pb—O(1^{i})	2·412 (5)	Pb—O(21^{iii})	2·668 (5)
Pb—O(1^{ii})	2·556 (5)		

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

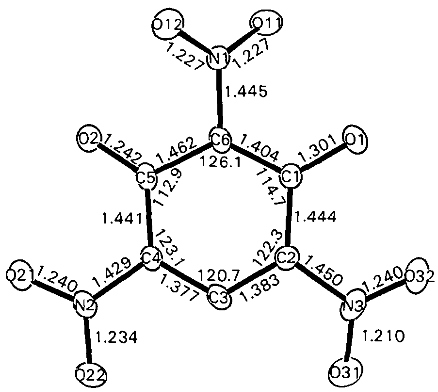

Fig. 1. Perspective view of the styphnate ion, showing the atom-numbering scheme, bond lengths (Å) and selected angles (°). E.s.d.'s range from 0·008 to 0·011 Å and from 0·6 to 0·7°. C(3)—H is 1·0 (1) Å. Thermal ellipsoids enclose 50% probability (Johnson, 1976).

Atomic parameters are given in Table 1.* Fig. 1 illustrates the anion and shows the atomic numbering, bond lengths and selected angles.

The C—C bond lengths vary from 1·377 (9) to 1·462 (9) Å and follow the predicted pattern. The average C—C bond length of 1·418 Å is similar to that found for the β polymorph and larger than that found for styphnic acid (1·388 Å) (Pierce-Butler, 1982*a*). This is consistent with substantial delocalization of charge from the O atoms around the ring; the ring does not depart significantly from planarity [$\Delta_{\max} = 0{\cdot}03$ (2) Å].

The $-NO_2$ group with the greatest angle of rotation from the ring plane [N(1)O(11)O(12), at 36·8 (9)°] is attached to the ring at C(6), the position of the largest internal ring angle [126·1 (6)°] possibly indicating reduced conjugation. The remaining nitro groups have much smaller rotation angles [6·4° at C(2) and 2·3° at C(4)] and the corresponding internal ring angles are 122·3 (6) and 123·1 (6)°.

The C—O bonds are different, C—O(1) being 1·301 (8) Å and C—O(2) being 1·242 (8) Å. A typical C—O single-bond length is 1·36 Å (*Molecular Structures and Dimensions,* 1972); that found in the parent acid is 1·326 Å (Pierce-Butler, 1982*a*) and that in the β polymorph of lead styphnate is 1·29 Å (Pierce-Butler, 1982*b*). The internal ring angles at C(1) and C(5) are also different at 114·7 (6) and 112·9 (6)° respectively, the smaller angle corresponding to the shorter C—O bond length. This is consistent with increased delocalization of the ionic charge onto the ring. This oxygen, O(2), is coordinated to one Pb atom, whereas O(1), with the longer C—O bond, is involved in coordination to two Pb atoms. Presumably there is thus less electron density available for interaction with the ring.

Pb—O distances are listed in Table 2. Pb is seven coordinate and paired *via* two O bridges [O(1) from two anions]. Du (1982) calculated the geometry about Pb from Reed's (1959) data but could not include the aqueous O atom as no coordinates were given. This is well within the coordination sphere of the lead [2·575 (7) Å]. Fig. 2 illustrates the lead coordination. A notable feature is the 'hole' in the coordination sphere opposite the symmetry centre. O(21) and O(22)($x-\frac{1}{2}$, $\frac{1}{2}-y$, z) are situated in this region at 3·091 (6) and 3·136 (6) Å from the lead. Du has included these two O atoms when discussing the lead coordination, although he comments on the inhomogeneity of the set of Pb—O distances. Excluding these O atoms from the coordination shell the average Pb—O distance is 2·580 Å [*cf.* 2·63 Å expected for seven-coordinate lead from

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* Lists of structure factors and anisotropic thermal parameters and Fig. 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38898 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

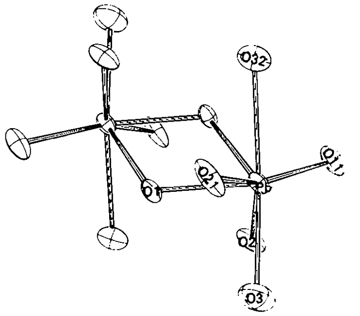

Fig. 2. A Pb_2 pair, together with coordination shells of oxygen atoms. Thermal ellipsoids enclose 50% probability (Johnson, 1976).

addition of ionic radii (Shannon, 1976)]. Many of the Pb—O distances are short, indicating some degree of covalency. They are similar to those found in the *β* form of lead styphnate.

Fig. 3* shows the packing arrangement within a unit cell. The styphnate ions lie in approximately parallel planes linked by Pb atoms. The water of crystallization [O(3)] is coordinated to the metal and is also H-bonded to the anion [O(3)···O(2) is 2·718 (9) Å].

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* This figure has been deposited, see deposition footnote.

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Structure of Tribromobis(pyridine)thallium(III), $TlBr_3(C_5H_5N)_2$

By S. E. Jeffs, R. W. H. Small and I. J. Worrall

Department of Chemistry, The University, Lancaster, England

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Abstract. $M_r = 602{\cdot}3$, monoclinic, $P2_1$, $a = 8{\cdot}991$ (5), $b = 21{\cdot}59$ (2), $c = 8{\cdot}393$ (5) Å, $\beta = 117{\cdot}8$ (1)°, $V = 1441{\cdot}2$ Å^3, $Z = 4$, $D_x = 2{\cdot}77$, $D_m = 2{\cdot}68$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7106$ Å, $\mu = 18{\cdot}9$ mm^{-1}, $F(000) = 1080$, room temperature. Final $R = 0{\cdot}073$ for 2184 unique observed reflections. The unit cell contains two crystallographically independent distorted trigonal-bipyramidal molecules which have similar geometrical parameters within the limits of experimental error. The two molecules differ in respect to the orientation of the pyridine ligands which occupy axial positions. A weak interaction between the two independent molecules accounts for the large distortions observed in the Br—Tl—Br equatorial bond angles (113·0–131·1°).

Introduction. Complexes of the Group III halides of stoichiometry $MX_3.2L$ are known for all the metallic elements of the group and whilst many of these have trigonal-bipyramidal geometry around the metal, *e.g.* $AlCl_3$.2(dioxane) (Boardman, Small & Worrall, 1983), $AlCl_3.2NH(CH_3)_2$ (Lobovski, Korobov & Semenko, 1978), $InCl_3.2PPh_3$ (Veidis & Palenik, 1969), $TlBr_3.2Ph_3PO$ (Jeffs, Small & Worrall, 1984*b*), there are exceptions, *e.g.* $GaCl_3.2C_5H_5N$ (Sinclair, Small & Worrall, 1981) which is ionic, *i.e.* $[GaCl_2Py_4]^+.GaCl_4^-$. TlX_3.2(pyridine) complexes may also be exceptional since on the basis of spectroscopic data it has been proposed that these are either halogen-bridged dimers or polymers containing six-coordinate thallium (Walton, 1968). In this paper we report the crystal structure of $TlBr_3$.2(pyridine).

Experimental. Title compound prepared by adding stoichiometric amount of pyridine to an acetonitrile

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