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Structure of Lead(II) D-Gluconate, Pb[$C_6H_{11}O_7$]$_2$

By T. Lis

Institute of Chemistry, The University, 50-383 *Wrocław, Poland*

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Abstract. $M_r = 597{\cdot}5$, trigonal, $P3_221$, $a = 5{\cdot}498$ (5), $c = 47{\cdot}28$ (5) Å, $V = 1238$ Å^3, $Z = 3$, $D_x = 2{\cdot}40$, $D_m = 2{\cdot}40$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}2$ mm^{-1}, $F(000) = 864$, $T = 293$ K. Final $R = 0{\cdot}037$ for 838 non-zero reflexions. The Pb atom lies on the twofold axis and is surrounded by six O atoms from four gluconate ligands; each Pb atom is chelated by the α-hydroxyl O atom at 2·48 (2) Å and a carboxylate O atom at 2·43 (2) Å forming a five-membered ring. The second carboxylate O atom (from another gluconate anion) is bonded at 2·71 (2) Å. Thus the carboxylate groups bridge two Pb atoms forming two-dimensional nets parallel to (001). The gluconate ligands have the zig-zag, nearly planar carbon-chain conformation with their long molecular axis approximately parallel to **c**.

Introduction. This work is a continuation of investigations into the crystal structures of metal gluconate salts. The compounds of Pb^{II} in acidic and basic solutions have been investigated by some authors who found that in water the Pb^{2+} ions may coordinate with different numbers of gluconate ligands and with different numbers of O atoms from carboxylate or hydroxyl groups forming mono- or polynuclear complexes (Pecsok & Juvet, 1956; Sawyer & Brannan, 1966; Coccioli & Vicedomini, 1978). Preliminary X-ray data for lead(II) D-gluconate were given by Pepinsky (1942), but no attempt has been made to determine the full crystal structure.

Experimental. Title compound prepared by heating an equimolar ratio of $PbCO_3$ and δ-gluconolactone in water until all $PbCO_3$ dissolved. After slow evaporation of water (at room temperature) platy trigonal crystals appeared. Analysis: calculated for $C_{12}H_{22}O_{14}Pb$: C 24·1, H 3·7, Pb 34·7%; found C 24·1, H 3·6, Pb 34·7%. Weissenberg and oscillation photographs showed crystals to be trigonal. Extinctions for 00*l* reflexions if $l \neq 3n$. For a few investigated crystals the *c* axis was similar to that reported by Pepinsky (1942) but *a* was, however, half Pepinsky's value. It may be suggested that the crystal investigated by Pepinsky was twinned. An almost hexagonal platy crystal, approximately 0·2 × 0·2 × 0·07 mm selected. D_m measured pycnometrically in 1,2-dibromoethane/CH_2Br_2. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω-scan technique. 15 reflexions in range $15 \leq 2\theta \leq 30°$ used for measuring lattice parameters. 1685 reflexions measured up to $2\theta = 65°$, range of *hkl*: $-6 \leq h \leq 6$, $-3 \leq k \leq 2$, $-48 \leq l \leq 49$ ($|h| > |k|$). Two standards, variation ±1·5%. Empirical absorption corrections from φ-scan data. Pb atoms found from Patterson map, which also showed $P3_121$ (or $P3_221$) space group; all other non-H atoms from difference syntheses and correct enantiomer believed to have $P3_221$ space group; C-bonded H atoms included in calculated positions at 1·0 Å and fixed. Least-squares refinement on *F* (Pb, C, O anisotropic, H isotropic) led to final $R = 0{\cdot}037$, $R_w = 0{\cdot}031$, $S = 1{\cdot}812$ for 838

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non-zero reflexions [$I > 3{\cdot}0\sigma(I)$]; $w = 1/\sigma^2(F_o)$. Max. $\Delta/\sigma = 0{\cdot}01$. On final difference map five highest peaks ($1{\cdot}1$–$0{\cdot}8$ e Å^{-3}) around Pb; all other peaks smaller than $0{\cdot}7$ e Å^{-3}, O-bonded H atoms not located unequivocally and therefore not included in calculations. All calculations performed with programs supplied by Syntex (1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion included for Pb, O and C atoms.

Table 1. *Final atom coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	$B_{\rm eq}$(Å^2)
Pb	0·5968 (2)	0	$\frac{2}{3}$	2·55 (7)
O(0)	0·650 (3)	0·441 (3)	0·6499 (3)	3·2 (10)
O(1)	0·555 (4)	0·690 (3)	0·6203 (3)	8·5 (17)
O(2)	0·215 (3)	−0·038 (3)	0·6358 (3)	3·2 (10)
O(3)	0·597 (3)	0·141 (3)	0·5881 (3)	4·3 (12)
O(4)	0·074 (3)	−0·361 (3)	0·5882 (2)	4·0 (11)
O(5)	0·220 (4)	0·112 (3)	0·5268 (3)	7·4 (16)
O(6)	−0·293 (3)	−0·406 (4)	0·5260 (3)	8·2 (19)
C(1)	0·514 (3)	0·475 (5)	0·6300 (4)	3·9 (18)
C(2)	0·270 (5)	0·191 (4)	0·6177 (4)	4·5 (19)
C(3)	0·348 (4)	0·154 (4)	0·5878 (3)	3·9 (18)
C(4)	0·120 (5)	−0·113 (4)	0·5732 (3)	4·9 (18)
C(5)	0·201 (5)	−0·117 (5)	0·5426 (4)	6·4 (24)
C(6)	−0·023 (6)	−0·384 (5)	0·5275 (4)	7·3 (25)

Table 2. *Bond lengths* (Å) *and bond and torsion angles* (°)

Pb—O(0)	2·43 (2)	Pb—O(1$^{\rm i}$)	2·71 (2)
Pb—O(2)	2·48 (2)		
C(1)—O(0)	1·27 (3)	C(1)—O(1)	1·18 (3)
C(2)—O(2)	1·42 (2)	C(3)—O(3)	1·41 (3)
C(4)—O(4)	1·44 (3)	C(5)—O(5)	1·42 (3)
C(6)—O(6)	1·43 (4)	C(1)—C(2)	1·57 (3)
C(2)—C(3)	1·52 (3)	C(3)—C(4)	1·54 (3)
C(4)—C(5)	1·52 (3)	C(5)—C(6)	1·54 (4)
O(0)—Pb—O(0$^{\rm ii}$)	135·5 (4)	O(1$^{\rm i}$)—Pb—O(1$^{\rm iii}$)	153·5 (5)
O(2)—Pb—O(2$^{\rm ii}$)	72·9 (4)	O(0)—Pb—O(1$^{\rm i}$)	107·1 (5)
O(0)—Pb—O(1$^{\rm iii}$)	83·2 (4)	O(0)—Pb—O(2)	64·2 (4)
O(0)—Pb—O(2$^{\rm ii}$)	80·0 (4)	O(1$^{\rm i}$)—Pb—O(2)	70·7 (5)
O(1$^{\rm i}$)—Pb—O(2$^{\rm ii}$)	134·4 (5)	Pb—O(0)—C(1)	127·0 (11)
Pb—O(1$^{\rm i}$)—C(1$^{\rm i}$)	103·4 (13)	Pb—O(2)—C(2)	119·0 (11)
O(0)—C(1)—O(1)	126·8 (19)	O(0)—C(1)—C(2)	113·6 (16)
O(1)—C(1)—C(2)	119·6 (18)	C(1)—C(2)—C(3)	108·7 (16)
C(1)—C(2)—O(2)	110·6 (15)	C(3)—C(2)—O(2)	112·9 (15)
C(2)—C(3)—C(4)	113·4 (16)	C(2)—C(3)—O(3)	110·3 (15)
C(4)—C(3)—O(3)	107·9 (15)	C(3)—C(4)—C(5)	109·7 (17)
C(3)—C(4)—O(4)	110·6 (16)	C(5)—C(4)—O(4)	111·8 (17)
C(4)—C(5)—C(6)	110·7 (19)	C(4)—C(5)—O(5)	112·3 (18)
C(6)—C(5)—O(5)	105·9 (19)	C(5)—C(6)—O(6)	113·8 (20)
O(0)—C(1)—C(2)—O(2)	13 (3)	O(1)—C(1)—C(2)—O(2)	−167 (3)
C(1)—C(2)—C(3)—C(4)	−178 (3)	C(2)—C(3)—C(4)—C(5)	174 (3)
C(3)—C(4)—C(5)—C(6)	179 (3)	C(4)—C(5)—C(6)—O(6)	63 (3)
O(2)—C(2)—C(3)—C(4)	59 (3)	O(2)—C(2)—C(3)—O(3)	−62 (3)

Symmetry code: (i) $x, y-1, z$; (ii) $x-y, -y, \frac{4}{3}-z$; (iii) $1+x-y, 1-y, \frac{4}{3}-z$.

Discussion. The final atomic parameters are listed in Table 1, the bond lengths and bond and torsion angles in Table 2.* The view of the gluconate ligand on the (100) plane, its chelation to the Pb atom and the atom-numbering scheme are shown in Fig. 1. The extended-chain C atoms [C(1) to C(6)] lie, within 0·06 Å, in one plane. The conformation is essentially the same as that in potassium D-gluconate (Littleton, 1953) and in sodium D-gluconate (Lis, 1984) and differs only in the O(6) rotation from that in potassium D-gluconate monohydrate (Jeffrey & Fasiska, 1972). [In D-gluconic acid monohydrate (Lis, 1983) and in other D-gluconate salts the gluconate moieties have different bent-chain conformations.] The α-hydroxy O atom approximates to the plane of the carboxylate group (Table 2) similar to most α-hydroxy carboxylate compounds. All interatomic distances and angles are acceptable although the standard deviations for the gluconate ligand are larger than those in other gluconate crystals.

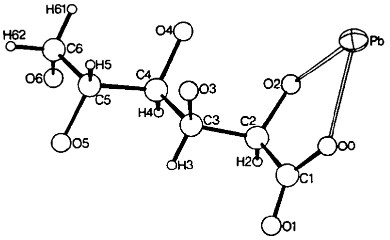

Fig. 1. The D-gluconate ligand chelated to the Pb atom.

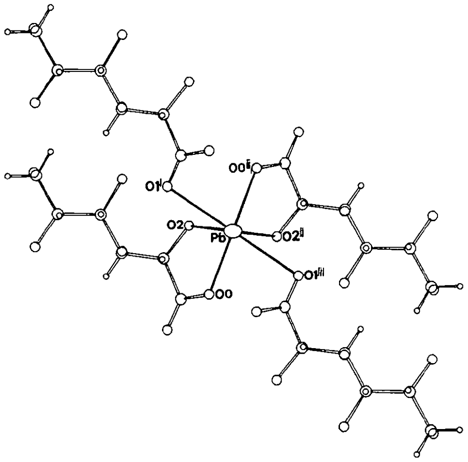

Fig. 2. Projection along the twofold axis of the six-coordinated polyhedron around Pb.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38968 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Pb atom is situated on a twofold crystallographic axis parallel to **a** and coordinates six O atoms. The projection along the twofold axis of the six-coordinated polyhedron around Pb is shown in Fig. 2. The geometry around the metal atom can be described as a very distorted octahedron, not particularly close to either of the common regular sixfold coordination polyhedra. [Sixfold coordination for Pb^{2+} has been reported for example in the structure of lead ethanediylidenetetrathiotetraacetate dihydrate (Houttemane, Boivin & Thomas, 1981).]

The metal atoms are chelated by an α-hydroxyl [O(2)] atom [at 2·48 (2) Å] and one carboxylate [O(0)] atom [at 2·43 (2) Å] forming five-membered rings. The second carboxylate [O(1)] atom [at 2·71 (2) Å] is bonded from another gluconate ligand. Each gluconate ion is tridentate and each carboxylate group links two Pb atoms forming two-dimensional nets parallel to the (001) plane. The gluconate ligands are situated with their long molecular axis along the [001] direction and probably connected by hydrogen bonds. Although O-bonded H atoms were not located the O···O interatomic distances suggest the existence of hydrogen bonds. Most of them link the ligands in the (001) plane and the structure is rather loose in the [001] direction which results in perfect cleavage parallel to (001).

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Structure of Sodium D-Gluconate, Na[$C_6H_{11}O_7$]

BY T. LIS

Institute of Chemistry, The University, 50-383 *Wrocław, Poland*

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Abstract. $M_r = 218{\cdot}1$, monoclinic, $P2_1$, $a = 8{\cdot}560$ (6), $b = 8{\cdot}694$ (6), $c = 5{\cdot}654$ (3) Å, $\beta = 104{\cdot}59$ (4)°, $V = 407{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}22$ mm^{-1}, $F(000) = 228$, $T = 300$ (2) K, final $R = 0{\cdot}027$ and $R_w = 0{\cdot}033$ for 1119 non-zero reflexions. The gluconate anion has nearly planar zig-zag carbon-chain conformation with one intramolecular H bond. The α-hydroxy O atom lies almost in the plane of the carboxylate group. The Na ion is surrounded by six O atoms forming a distorted octahedron with Na···O distances between 2·340 (2) and 2·540 (2) Å.

Introduction. This investigation is a continuation of the studies of the structure of the D-gluconate ion. Preliminary X-ray data for sodium D-gluconate have been given by Littleton (1953) but no attempt was made to solve the full structure.

Experimental. Crystals grown from aqueous solution by slow evaporation at room temperature; specimen 0·35 × 0·45 × 0·45 mm cut from a large crystal; Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator [unit-cell parameters similar to those reported by Littleton (1953): $a = 8{\cdot}28$, $b = 8{\cdot}71$, $c = 5{\cdot}22$ Å, $\beta = 104{\cdot}7°$]; 2θ–ω scan; after each group of 50 reflexions intensities of 2 standard reflexions measured, no significant change; 1229 independent intensities, $2\theta_{\max} = 60°$, h 0–11, k 0–12, $l \pm 7$; no corrections for absorption and extinction; all calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); anomalous dispersion included for Na and O atoms; structure solved by direct methods; H atoms from difference synthesis; refinement (Na, O, C anisotropic, H isotropic) gave $R = 0{\cdot}027$ and

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