

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 Pb²⁺ has been reported for example in the structure of lead ethanediyliidenetetrathiotetraacetate 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).

The author thanks Dr M. Jaskólski for diffractometer measurements and Mr J. Okrucinski for assistance.

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Acta Cryst. (1984). **C40**, 376–378

Structure of Sodium D-Gluconate, Na[C₆H₁₁O₇]

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(Received 20 September 1983; accepted 24 November 1983)

Abstract. $M_r = 218.1$, monoclinic, $P2_1$, $a = 8.560$ (6), $b = 8.694$ (6), $c = 5.654$ (3) Å, $\beta = 104.59$ (4)°, $V = 407.2$ Å³, $Z = 2$, $D_x = 1.78$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.22$ mm⁻¹, $F(000) = 228$, $T = 300$ (2) K, final $R = 0.027$ and $R_w = 0.033$ 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): $a = 8.28$, $b = 8.71$, $c = 5.22$ Å, $\beta = 104.7^\circ$]; 2θ - ω scan; after each group of 50 reflexions intensities of 2 standard reflexions measured, no significant change; 1229 independent intensities, $2\theta_{\max} = 60^\circ$, h 0–11, k 0–12, l ± 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 $R = 0.027$ and

$R_w = 0.033$ for 1119 reflexions with $I > 2\sigma(I)$; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F_o)$; during the last cycle of refinement, $\Delta/\sigma < 0.1$; max. $\Delta\rho$ excursion on final difference synthesis ($0.23 \text{ e } \text{\AA}^{-3}$) near Na; other $\Delta\rho$ excursions $< 0.2 \text{ e } \text{\AA}^{-3}$ confined to the molecular bonds; the highest of them were on the C—C bonds.*

Discussion. Final atomic parameters are listed in Table 1, interatomic distances and bond and torsion angles and hydrogen-bonding data in Table 2. Fig. 1 is an ORTEP diagram (Johnson, 1976) of one gluconate anion and also gives the atom numbering scheme. The C—O and C—C bond distances and the C—C—C and C—C—O bond angles are in the range found in other D-gluconate crystals. The gluconate anion has a nearly planar zig-zag carbon-chain configuration. The conformation is essentially the same as that found in the K salt (Littleton, 1953) and in the Pb^{II} salt (Lis, 1984) and differs only in the O(6) rotation from that in the monoclinic modification of the K salt monohydrate (Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974). [The extended planar conformation was also found in *N*-(2-chloroethyl)-D-gluconamide (Sindt & Mackay, 1977).] Similar to the monoclinic modification of the K salt monohydrate there is an intramolecular H bond between O(4) (as donor) and O(2). However, the O...O distance of $2.80 \text{ (1) } \text{\AA}$ is longer than that found by Panagiotopoulos *et al.* (1974), $2.61 \text{ (1) } \text{\AA}$. The bent-chain conformation has been found in D-gluconic acid monohydrate (Lis, 1983) and in other salts of this acid.

The packing of the crystal is shown in Fig. 2. In the structure there are four intermolecular (and one intramolecular) H bonds. The O(6) atoms (as donors) form with O(3) atoms infinite chains parallel to *c*. The O(5) (as donors) form very weak H bonds with O(0) giving infinite chains along *a*. The carboxylate oxygens O(0) and O(1) from one gluconate ion accept hydrogens H(3) and H(2) of another anion; these pairs of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39049 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

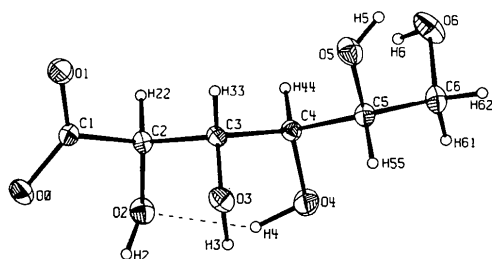


Fig. 1. ORTEP plot of D-gluconate ion (Johnson, 1976). The thermal ellipsoids are at 50% probability.

hydrogen-bonded gluconate ions are related to each other by a twofold screw axis, resulting in a helical hydrogen-bonding scheme which extends along *b*.

Table 1. The final atom coordinates and isotropic thermal parameters

For non-H atoms $B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq} or $B(\text{\AA}^2)$
Na	0.7144 (2)	0.7 (fixed)	0.7586 (2)	1.64 (5)
O(0)	0.4051 (3)	0.3466 (3)	0.9824 (4)	2.31 (11)
O(1)	0.6081 (2)	0.4998 (3)	0.9505 (4)	1.89 (10)
O(2)	0.4654 (2)	0.1433 (3)	0.6555 (3)	1.40 (9)
O(3)	0.7610 (2)	0.1251 (3)	1.0644 (3)	1.42 (9)
O(4)	0.7303 (2)	-0.0286 (3)	0.6000 (3)	1.66 (10)
O(5)	1.0834 (2)	0.2045 (3)	0.8589 (3)	1.64 (9)
O(6)	1.0708 (2)	0.0970 (3)	0.3767 (3)	2.10 (11)
C(1)	0.5254 (3)	0.3788 (3)	0.9033 (4)	1.21 (12)
C(2)	0.5782 (3)	0.2653 (3)	0.7307 (4)	1.08 (11)
C(3)	0.7506 (3)	0.2076 (3)	0.8430 (4)	1.04 (10)
C(4)	0.8161 (3)	0.1135 (3)	0.6606 (4)	1.04 (11)
C(5)	0.9943 (3)	0.0702 (3)	0.7618 (4)	1.21 (11)
C(6)	1.0633 (3)	-0.0060 (3)	0.5696 (4)	1.54 (13)
H(22)	0.577 (3)	0.326 (3)	0.574 (5)	0.4 (5)
H(33)	0.820 (3)	0.291 (4)	0.888 (5)	0.9 (5)
H(44)	0.805 (3)	0.173 (3)	0.511 (5)	0.4 (5)
H(55)	1.001 (4)	-0.001 (4)	0.907 (5)	1.1 (5)
H(61)	1.011 (5)	-0.091 (5)	0.519 (7)	2.4 (7)
H(62)	1.171 (4)	-0.039 (4)	0.632 (5)	1.5 (5)
H(2)	0.439 (5)	0.108 (5)	0.803 (7)	3.3 (8)
H(3)	0.699 (4)	0.039 (5)	1.019 (6)	2.9 (8)
H(4)	0.622 (6)	-0.011 (7)	0.617 (9)	6.2 (12)
H(5)	1.151 (5)	0.221 (5)	0.792 (7)	3.8 (9)
H(6)	0.971 (4)	0.102 (4)	0.281 (6)	1.6 (6)

Table 2. Bond distances (\AA) and bond and torsion angles ($^\circ$) and H-bonding data

(a) In the gluconate ion

C(1)—O(0)	1.253 (3)	C(1)—O(1)	1.259 (3)
C(1)—C(2)	1.534 (3)	C(2)—O(2)	1.425 (3)
C(2)—C(3)	1.536 (3)	C(3)—O(3)	1.426 (3)
C(3)—C(4)	1.529 (3)	C(4)—O(4)	1.434 (3)
C(4)—C(5)	1.536 (3)	C(5)—O(5)	1.427 (3)
C(5)—C(6)	1.514 (3)	C(6)—O(6)	1.425 (3)
O(0)—C(1)—O(1)	125.4 (3)	O(0)—C(1)—C(2)	119.0 (2)
O(1)—C(1)—C(2)	115.6 (2)	C(1)—C(2)—C(3)	110.7 (2)
C(1)—C(2)—O(2)	112.5 (2)	C(3)—C(2)—O(2)	112.8 (2)
C(2)—C(3)—C(4)	111.9 (2)	C(2)—C(3)—O(3)	111.6 (2)
C(4)—C(3)—O(3)	111.8 (2)	C(3)—C(4)—C(5)	112.2 (2)
C(3)—C(4)—O(4)	111.7 (2)	C(5)—C(4)—O(4)	106.2 (2)
C(4)—C(5)—C(6)	111.7 (2)	C(4)—C(5)—O(5)	109.1 (2)
C(6)—C(5)—O(5)	111.5 (2)	C(5)—C(6)—O(6)	112.1 (2)
O(0)—C(1)—C(2)—O(2)	8.1 (5)	O(1)—C(1)—C(2)—O(2)	-170.9 (5)
C(1)—C(2)—C(3)—C(4)	-171.5 (5)	C(2)—C(3)—C(4)—C(5)	173.8 (4)
C(3)—C(4)—C(5)—C(6)	-173.1 (6)	C(4)—C(5)—C(6)—O(6)	66.3 (6)
O(2)—C(2)—C(3)—C(4)	61.5 (5)	O(2)—C(2)—C(3)—O(3)	-64.6 (5)
C(3)—C(4)—O(4)—H(4)	29 (3)	C(5)—C(4)—O(4)—H(4)	151 (3)

(b) In the distorted octahedron surrounding sodium

Na—O(0 ^a)	2.360 (2)	Na—O(1)	2.352 (2)
Na—O(2 ^b)	2.506 (2)	Na—O(4 ⁱⁱⁱ)	2.540 (2)
Na—O(5 ^{iv})	2.406 (2)	Na—O(6 ^v)	2.340 (2)

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

H-bond distances (\AA) and angles ($^\circ$)

O—H...O	O...O	O—H	H...O	$\angle \text{O—H...O}$
O(2)—H(2)...O(1 ^{vi})	2.760 (2)	0.97 (4)	1.81 (4)	167 (4)
O(3)—H(3)...O(0 ⁱⁱ)	2.786 (3)	0.92 (4)	1.89 (4)	164 (4)
O(4)—H(4)...O(2)	2.799 (2)	0.97 (5)	1.95 (5)	145 (5)
O(5)—H(5)...O(0 ⁱⁱⁱ)	2.937 (3)	0.78 (4)	2.43 (4)	124 (4)
O(6)—H(6)...O(3 ^{viii})	2.802 (2)	0.89 (3)	1.91 (3)	176 (3)

Symmetry code: (vi) $1-x, y-\frac{1}{2}, 2-z$; (vii) $1+x, y, z$; (viii) $x, y, z-1$

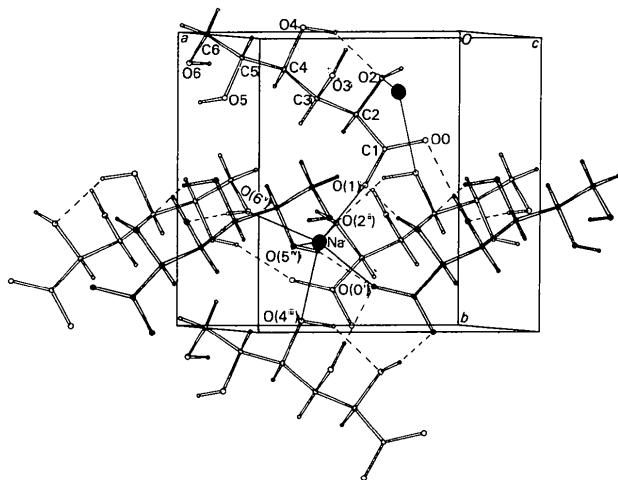


Fig. 2. Molecular packing and H-bonding scheme in the crystal structure of sodium D-gluconate. Roman numerals are the same as in Table 2(b).

The Na^+ ion is coordinated to six O atoms belonging to six different gluconate anions. O(3) does not participate in the Na coordination. The polyhedron of the six O atoms is a distorted octahedron with the $\text{Na}\cdots\text{O}$ distances ranging from 2.340 (2) to 2.540 (2) Å.

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Acta Cryst. (1984). **C40**, 378–381

Structure of Tetraphenylphosphonium Dioxo[4-(1,3-thiazol-2-ylazo)resorcinolato]vanadate(V) Monohydrate, $[\text{P}(\text{C}_6\text{H}_5)_4][\text{VO}_2(\text{C}_9\text{H}_5\text{N}_3\text{O}_2\text{S})]\cdot\text{H}_2\text{O}$

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(Received 25 July 1983; accepted 7 November 1983)

Abstract. $M_r = 659.57$, triclinic, $P\bar{1}$, $a = 11.363$ (3), $b = 14.932$ (5), $c = 9.273$ (3) Å, $\alpha = 96.30$ (2), $\beta = 107.10$ (3), $\gamma = 91.65$ (1)°, $V = 1491.7$ (8) Å³, $Z = 2$, $D_m = 1.46$, $D_x = 1.468$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 4.355$ mm⁻¹, $F(000) = 680$, $T = 293$ K, final $R = 0.036$ for 4328 observed reflections. The 4-(1,3-thiazol-2-ylazo)resorcinolato anion (tar) acts as a terdentate ligand complexing V through the phenolic O atom, the azo N adjacent to the resorcinol ring, and the thiazolyl N atom, thus forming two five-membered chelate rings. Two oxo O atoms complete the pentagonal V coordination sphere with an O–V–O angle of 109.1 (1)° and V–O bond lengths of 1.613 (2) and 1.622 (3) Å. A resonance effect through the azo group is evident from the lengthened azo N–N bond of 1.343 (3) Å and shortened neighbouring N–C bonds of 1.318 (4) and 1.355 (4) Å.

Introduction. The thiazolylazophenols belong to a relatively large group of heterocyclic azo dyes with a wide range of applications. Heterocyclic *o*-hydroxy compounds have been used in analytical chemistry as spectrophotometric and extraction-spectrophotometric reagents for metal ions in aqueous and organic solutions and also as metallochromic indicators. As thiazolylazophenols are prepared more easily than the analogous pyridylazophenols, a large number of derivatives have been prepared and investigated for analytical purposes, but few have found extensive practical analytical application (Hovind, 1975).

4-(1,3-Thiazol-2-ylazo)resorcinol (H_2tar) is the most frequently used spectrophotometric reagent of the thiazolylazophenol class of azo dyes. It appears to be similar in character to the reagent 4-(2-pyridylazo)resorcinol (H_2par). Differences and similarities between