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Structure of Trisodium D-2-Phosphoglycerate Hexahydrate

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Abstract. $3Na^+.C_3H_4O_7P^{3-}.6H_2O$, $M_r = 360\cdot1$, orthorhombic, $P2_12_12$, $a = 34\cdot82\ (2)$, $b = 6\cdot334\ (4)$, $c = 6\cdot146\ (3)$ Å, $V = 1355\cdot5$ Å^3, $Z = 4$, $D_m = 1\cdot74$, $D_x = 1\cdot76$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu = 3\cdot4$ mm^{-1}, $F(000) = 744$, $T = 289\ (1)$ K, final $R = 0\cdot032$ for 2500 data including both hkl and $\bar{h}\bar{k}\bar{l}$ reflexions. The length of the phosphate ester bond is 1·625 (2) Å. One of the phosphate O atoms, which is nearly *trans* to C(2), forms (as acceptor) four hydrogen bonds with four different water molecules and is therefore formally pentacoordinated. The crystal structure is stabilized by the three-dimensional hydrogen-bonding network.

Introduction. D-2-Phosphoglyceric acid is the glycolytic intermediate between D-3-phosphoglyceric acid and phosphoenolpyruvic acid (Ballou & Fischer, 1954). Of these three compounds, the crystal structure of D-2-phosphoglyceric acid is not known. Therefore, the structure of this acid as the trisodium salt has been determined. This study is a continuation of our earlier studies on the crystal structures of β-glycerophosphates (Lis & Starynowicz, 1983) and sugar phosphates (Lis, 1985).

Experimental. Crystals of trisodium D-3-phosphoglycerate hexahydrate were obtained by slow concentration of an aqueous solution, containing a small amount of methanol, of the commercially available compound (Boehringer). The compound crystallized mostly as plates elongated along **b**, with **a** perpendicular to the plate. D_m by flotation in 1,2-dibromoethane/CCl_4. Preliminary examination by rotation and Weissenberg photographs. A specimen 0·05 × 0·25 × 0·17 mm was cut from a large crystal. Syntex $P2_1$ diffractometer, Cu $K\alpha$ radiation for lattice parameters (15 reflexions in range $22 < 2\theta < 35°$) and intensity measurements; ω–2θ scan technique, 2583 reflexions measured below $\theta = 73°$; h 0→42, k 0→7, l 0→7; most of Friedel pairs measured; after every 50 reflexions two standards measured, variation 5%; most calculations performed on a Nova 1200 computer with locally modified *XTL/XTLE* programs (Syntex, 1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), real and imaginary components of anomalous dispersion included for all non-H atoms; structure solved by direct methods; H atoms from difference synthesis; refinement based on F values; Na, P, O, C anisotropic, H isotropic; 2500 reflexions with $I > 1\cdot96\ \sigma(I)$, $w = 1/\sigma^2(F_o)$ gave $R = 0\cdot032$ and $wR = 0\cdot039$ (the refinement of the parameters for the inverted structure gave $R = 0\cdot039$ and $wR = 0\cdot047$); max. Δ/σ 0·15 (the 020 reflexion suffered from strong extinction and was omitted from the calculations). An absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) applied on isotropically refined data; min. and max. absorption correction 0·911 and 1·159. Residual electron density in final difference Fourier map within −0·20 and 0·24 e Å^{-3}.

The final atomic parameters are given in Table 1.*

Discussion. The crystals of the title compound are composed of sodium cations, D-2-phosphoglycerate trianions and water of hydration. The principal bond lengths, bond angles and torsion angles are summarized in Table 2. The molecular configuration and the atom-numbering scheme of the anion are illustrated in Fig. 1.

In the glycerate residue of the anion all C—O and C—C bond lengths are normal. The carboxyl group is oriented perpendicular to the C-atom chain. O(3) is antiperiplanar to C(1). The conformation of the glycerate part of the anion is thus different from that found in calcium DL-glycerate dihydrate (Taga, Ohashi & Osaki, 1978), cadmium D-3-phosphoglycerate trihydrate (Mostad & Rosenqvist, 1971) and disodium D-3-phosphoglycerate (Fewster & Fenn, 1982), where the α-hydroxy O atom lies approximately in the plane of the carboxyl group.

The orientation of the phosphate group relative to the C-atom chain is essentially the same as that found in the second modification of disodium β-glycerophosphate $5\cdot5\,H_2O$ (Lis & Starynowicz, 1983). Also, neither the phosphate ester bond, the P—O bond lengths, the O—P—O bond angles, nor the C—O—P—O

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* Lists of structure amplitudes, anisotropic thermal parameters and Na—O distances and O—Na—O angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42370 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates and isotropic thermal parameters with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq} or B(Å^2)
P	0·09171 (2)	0·7753 (1)	0·3469 (1)	1·43 (3)
Na(1)	0·25286 (4)	0·3584 (2)	0·5602 (3)	3·42 (9)
Na(2)	0·11525 (3)	0·2168 (2)	0·0272 (2)	2·52 (8)
Na(3)	0·47373 (3)	0·7109 (2)	0·2431 (2)	2·17 (7)
O(0)	0·21541 (6)	0·5629 (4)	0·3190 (5)	3·22 (17)
O(1)	0·17313 (6)	0·3298 (4)	0·1939 (4)	2·69 (15)
O(2)	0·11832 (5)	0·6416 (3)	0·1788 (3)	1·86 (11)
O(3)	0·14618 (6)	0·9108 (4)	−0·1627 (4)	2·27 (14)
O(4)	0·10049 (5)	0·6988 (4)	0·5760 (3)	2·07 (12)
O(5)	0·05166 (5)	0·7120 (4)	0·2748 (3)	1·81 (11)
O(6)	0·10026 (6)	1·0062 (3)	0·3176 (4)	2·33 (13)
W(1)	0·04002 (6)	0·8521 (4)	−0·1458 (4)	2·40 (14)
W(2)	0·09399 (6)	0·2774 (4)	0·6677 (4)	2·62 (15)
W(3)	0·19888 (7)	0·1116 (5)	0·5690 (5)	3·28 (18)
W(4)	0·04715 (7)	0·3076 (5)	0·1039 (4)	2·66 (16)
W(5)	0·23913 (8)	0·0760 (6)	0·1321 (6)	4·54 (23)
W(6)	0·0	1·0	0·4474 (6)	3·40 (27)
W(7)	0·0	0·5	0·5561 (5)	2·11 (20)
C(1)	0·18377 (7)	0·5148 (5)	0·2339 (5)	1·99 (18)
C(2)	0·15800 (7)	0·6966 (5)	0·1590 (5)	1·68 (16)
C(3)	0·16727 (8)	0·7365 (6)	−0·0790 (5)	2·22 (19)
H(3)	0·1303 (11)	0·876 (7)	−0·244 (8)	4·4 (10)
H(*W*1)	0·0439 (12)	0·797 (7)	−0·017 (7)	4·0 (10)
H(*W*11)	0·0561 (10)	0·776 (7)	−0·227 (7)	3·6 (9)
H(*W*2)	0·0979 (11)	0·382 (7)	0·625 (7)	2·6 (9)
H(*W*21)	0·0983 (11)	0·196 (7)	0·555 (8)	3·9 (9)
H(*W*3)	0·1813 (16)	0·073 (10)	0·656 (10)	8·4 (18)
H(*W*31)	0·1843 (15)	0·175 (9)	0·476 (9)	7·0 (15)
H(*W*4)	0·0478 (12)	0·405 (8)	0·165 (8)	3·4 (10)
H(*W*41)	0·0495 (13)	0·232 (8)	0·204 (8)	4·9 (12)
H(*W*5)	0·2158 (13)	0·202 (8)	0·133 (8)	6·3 (12)
H(*W*51)	0·2449 (22)	0·086 (11)	−0·017 (13)	11·2 (23)
H(*W*6)	0·0121 (10)	0·934 (7)	0·366 (6)	2·7 (8)
H(*W*7)	0·0146 (12)	0·546 (8)	0·472 (8)	5·1 (12)
H(2)	0·1652 (8)	0·821 (5)	0·230 (5)	1·6 (6)
H(31)	0·1954 (10)	0·760 (7)	−0·088 (6)	3·3 (8)
H(32)	0·1623 (9)	0·607 (6)	0·168 (6)	2·3 (7)

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

P–O(2)	1·625 (2)	P–O(4)	1·520 (2)
P–O(5)	1·517 (2)	P–O(6)	1·503 (2)
C(1)–O(0)	1·257 (3)	C(1)–O(1)	1·254 (3)
C(1)–C(2)	1·530 (4)	C(2)–C(3)	1·520 (4)
C(2)–O(2)	1·430 (3)	C(3)–O(3)	1·422 (4)
O(2)–P–O(4)	108·0 (2)	O(2)–P–O(5)	101·6 (2)
O(2)–P–O(6)	108·5 (2)	O(4)–P–O(5)	111·8 (2)
O(4)–P–O(6)	112·4 (2)	O(5)–P–O(6)	113·8 (2)
P–O(2)–C(2)	118·6 (2)	O(0)–C(1)–O(1)	124·5 (3)
O(0)–C(1)–C(2)	117·2 (3)	O(1)–C(1)–C(2)	118·1 (3)
O(2)–C(2)–C(1)	111·0 (3)	O(2)–C(2)–C(3)	109·1 (3)
C(1)–C(2)–C(3)	106·9 (3)	C(2)–C(3)–O(3)	111·6 (3)
C(2)–O(2)–P–O(4)	77·2 (3)	C(2)–O(2)–P–O(5)	165·1 (3)
C(2)–O(2)–P–O(6)	44·9 (4)	P–O(2)–C(2)–C(1)	116·3 (5)
P–O(2)–C(2)–C(3)	−126·1 (5)	O(2)–C(2)–C(3)–O(3)	62·9 (5)
O(2)–C(2)–C(1)–O(0)	148·3 (4)	O(2)–C(2)–C(1)–O(1)	36·2 (4)
O(0)–C(1)–C(2)–C(3)	92·8 (4)	O(1)–C(1)–C(2)–C(3)	−82·7 (4)
O(3)–C(3)–C(2)–C(1)	177·0 (5)	H(3)–O(3)–C(3)–C(2)	−109 (4)

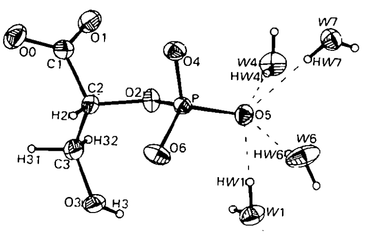

Fig. 1. The molecular configuration and the atom-numbering scheme for the D-2-phosphoglycerate trianion. Dashed lines show the hydrogen bonds formed by O(5).

torsion angles differ significantly. Therefore it is not surprising that O(5) as acceptor forms, in both crystals, hydrogen bonds with four independent water molecules. (Hydrogen-bonding parameters in the title crystal are given in Table 3.) Thus O(5) is formally pentacoordinated. The four H atoms form the base of a slightly distorted tetragonal pyramid around O(5) (see Fig. 1). It is of special interest if a similar type of hydrogen bonding occurs in other phosphate esters – for example in nucleotides and nucleic acids. O(2) is not involved in hydrogen bonds and the two remaining phosphate O atoms, O(4) and O(6), form three and two hydrogen bonds, respectively.

The packing arrangement is shown in Fig. 2. There are three kinds of Na$^+$ ions in the structure. Na(3) is coordinated by six water molecules at distances of 2·335 (3)–2·498 (3) Å, forming a distorted octahedron. Na(2) is surrounded by two water molecules, phosphate O(6), hydroxyl O(3) and carboxyl O(1) at distances of 2·289 (2)–2·505 (2) Å; the sixth position at a distance of 2·850 (3) Å is occupied by O(2). Na(1) is five-coordinated in the form of a somewhat distorted tetragonal pyramid by three water molecules and two carboxyl O atoms at distances of 2·297 (3)–2·454 (3) Å. The crystal structure is stabilized by the three-dimensional hydrogen-bonding network (Table 3). All O-bonded H atoms are utilized in hydrogen bonds. Each water molecule is coordinated to two Na$^+$ ions and acts as donor in two hydrogen bonds.

Table 3. *Geometry of the hydrogen bonds* (*distances in* Å, *angles in* °)

O–H···O	O···O	O–H	H···O	∠O–H···O
O(3)–H(3)···O(4^{i})	2·629 (3)	0·78 (5)	1·89 (5)	159 (5)
W(1)–H(*W*1)···O(5)	2·762 (3)	0·88 (5)	1·89 (5)	173 (4)
W(1)–H(*W*11)···O(4^{i})	2·881 (3)	0·89 (4)	2·02 (4)	161 (4)
W(2)–H(*W*2)···O(4)	2·738 (3)	0·73 (4)	2·03 (5)	165 (5)
W(2)–H(*W*21)···O(6^{ii})	2·762 (3)	0·88 (5)	1·89 (5)	172 (4)
W(3)–H(*W*3)···O(3^{iii})	2·776 (3)	0·85 (6)	1·95 (6)	165 (6)
W(3)–H(*W*31)···O(1)	2·834 (4)	0·87 (6)	2·03 (6)	155 (5)
W(4)–H(*W*4)···O(5)	2·773 (3)	0·72 (5)	2·06 (5)	168 (5)
W(4)–H(*W*41)···O(6^{ii})	2·965 (3)	0·78 (5)	2·38 (5)	133 (5)
W(5)–H(*W*5)···O(1)	2·830 (4)	1·14 (5)	1·73 (5)	160 (4)
W(5)–H(*W*51)···O(0^{iv})	3·194 (4)	0·94 (9)	2·32 (9)	155 (7)
W(6)–H(*W*6)···O(5)	2·773 (2)	0·77 (4)	2·05 (4)	156 (4)
W(7)–H(*W*7)···O(5)	2·833 (3)	0·78 (5)	2·06 (5)	171 (5)

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

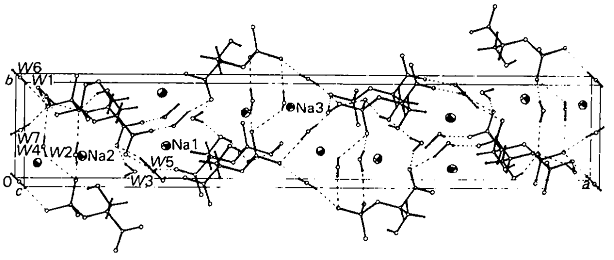

Fig. 2. The packing arrangement. Dashed lines show hydrogen bonds.

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Structure of *catena*-Poly[(1,3-thiazolidine-2-thionecadmium)-μ-chloro-μ_3-chloro]

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Abstract. $[CdCl_2(C_3H_5NS_2)]_n$, $M_r = 302\cdot5$, monoclinic, $P2_1/c$, $a = 3\cdot933\,(1)$, $b = 22\cdot418\,(5)$, $c = 9\cdot934\,(2)$ Å, $\beta = 112\cdot81\,(4)°$, $V = 807\cdot4$ Å^3, $Z = 4$, $D_m = 2\cdot47\,(2)$, $D_x = 2\cdot49$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu = 3\cdot74$ mm^{-1}, $F(000) = 576$, room temperature, final $R = 0\cdot049$ for 1214 observed reflections. The structure is polymeric, with octahedrally coordinated Cd linked into infinite chains by double Cl bridges, which are further condensed in pairs by Cl bridges. The S-bonded 1,3-thiazolidine-2-thione ligand completes the coordination sphere about Cd with a Cd—S distance of $2\cdot605\,(2)$ Å. There is an intramolecular hydrogen bond between the N atom and equatorial Cl [N···Cl $3\cdot343\,(8)$ Å and N—H···Cl 158°].

Introduction. The thiazolidine-2-thione (ttz) ligand is a potentially ambidentate ligand with either the exocyclic S or heterocyclic N atom available for coordination (Raper, Oughtred & Nowell, 1983). As part of our programme of structure determinations of metal complexes of ttz, the results for tetrakis(1,3-thiazolidine-2-thione)palladium(II) dichloride–1,3-thiazolidine-2-thione (1:2) have been published (Kubiak & Głowiak, 1982).

Spectroscopic and magnetic-susceptibility studies of the interaction of Cd^{II} with ttz (Preti & Tosi, 1976) have suggested that the Cd(ttz)$_2$ complex is tetrahedral and has a polymeric structure with the ligands linked to the metal ion through the S and N atoms.

In an attempt to obtain crystallographic evidence of the coordination sites, we have prepared the CdCl$_2$(ttz) complex in the low pH region and undertaken its X-ray analysis.

Experimental. Clear, colourless crystals from cadmium(II) chloride and ttz at room temperature (293 K), dimensions $0\cdot15 \times 0\cdot09 \times 0\cdot10$ mm; D_m by flotation in bromoform–benzene; monoclinic from Weissenberg photographs, $P2_1/c$; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 1432 independent reflections; variable $\theta/2\theta$ scan, scan rate $2\cdot0$–$29\cdot3°$ min^{-1} (depending on intensity), $2\theta_{\max} = 60°$; two standards measured every 30 reflections, no significant change; corrections for Lorentz and polarization, not for absorption; 1214 with $F > 8\sigma(F)$ used for structure determination, index range $h\,0\rightarrow4$, $k\,0\rightarrow26$, $l\,-11\rightarrow10$; 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); heavy-atom method, full-matrix least squares (on F); non-H atoms refined with anisotropic and H atoms with fixed positional and isotropic thermal parameters, 82 variables; $(\Delta/\sigma)_{\max} = 0\cdot10$; $\Delta\rho_{\max} = \pm0\cdot40$ e Å^{-3}; $R = 0\cdot049$, $wR = 0\cdot051$, $S = 5\cdot72$, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1* and interatomic distances and angles in Table 2. A view of the coordination polyhedron about the Cd^{II} ion, ligand stereochemistry and the atom-numbering scheme are presented in Fig. 1. Fig. 2 shows the polymeric structure viewed along **b**.

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* Lists of structure amplitudes, anisotropic thermal parameters, calculated H-atom parameters, torsion angles and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42325 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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