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Structure of Phosphoglycolate (PG) in Different Ionization States. Structure of Phosphoglycolic Acid (H_3PG) and its Salts: KH_2PG, NaH_2PG, $K_3H_3(PG)_2$, $Na_2HPG.0.5H_2O$, $Na_5H(PG)_2.4H_2O$ and $Na_3PG.4H_2O$

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Abstract. Crystalline phosphoglycolic acid and its sodium and potassium salts in different ionization states have been prepared and analyzed by X-ray diffraction. Phosphoglycolic acid, $C_2H_5O_6P$ (I), $M_r = 156.03$, monoclinic, $P2_1/c$, $a = 14.860$ (5), $b = 4.850$ (2), $c = 8.221$ (4) Å, $\beta = 105.58$ (4)°, $V = 570.7$ (5) Å^3, $Z = 4$, $D_x = 1.816$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 4.3$ cm^{-1}, $F(000) = 320$, $T = 295$ (2) K, final $R = 0.0254$ for 1152 observed reflections. Potassium phosphoglycolate, $K^+.C_2H_4O_6P^-$ (II), $M_r = 194.12$, monoclinic, $P2_1$, $a = 10.570$ (6), $b = 4.588$ (3), $c = 7.935$ (4) Å, $\beta = 126.92$ (4)°, $V = 307.6$ (4) Å^3, $Z = 2$, $D_m = 2.07$, $D_x = 2.095$ (3) g cm^{-3}, μ(Mo $K\alpha$) = 10.8 cm^{-1}, $F(000) = 196$, $T = 300$ (2) K, final $R = 0.026$ for 1818 observed (hkl and $\bar{h}\bar{k}\bar{l}$) reflections. Sodium phosphoglycolate, $Na^+.C_2H_4O_6P^-$ (III), $M_r = 178.01$, monoclinic, $P2/n$, $a = 9.782$ (6), $b = 5.366$ (3), $c = 11.175$ (9) Å, $\beta = 91.39$ (6)°, $V = 586.4$ (7) Å^3, $Z = 4$, $D_m = 1.98$, $D_x = 2.016$ (3) g cm^{-3}, μ(Mo $K\alpha$) = 4.9 cm^{-1}, $F(000) = 360$, $T = 301$ (2) K, final $R = 0.031$ for 1051 observed reflections. Tripotassium bis(phosphoglycolate), $3K^+.(C_2H_3O_6P\cdots H\cdots C_2H_3O_6P)^{3-}$ (IV), $M_r = 426.34$, triclinic, $P\bar{1}$, $a = 8.643$ (6), $b = 9.013$ (7), $c = 9.907$ (7) Å, $\alpha = 113.97$ (6), $\beta = 95.41$ (6), $\gamma = 95.01$ (6)°, $V = 695.3$ (9) Å^3, $Z = 2$, $D_m = 2.03$, $D_x = 2.036$ (4) g cm^{-3}, μ(Mo $K\alpha$) = 12.6 cm^{-1}, $F(000) = 428$, $T = 296$ (2) K, final $R = 0.034$ for 2112 observed reflections. Disodium phosphoglycolate hemihydrate, $2Na^+.(C_2H_3O_6P)^{2-}.0.5H_2O$ (V), $M_r = 209.00$, orthorhombic, $P2_12_12$, $a = 10.520$ (6), $b = 13.442$ (6), $c = 8.996$ (5) Å, $V = 1272.1$ (12) Å^3, $Z = 8$, $D_m = 2.13$, $D_x = 2.182$ (3) g cm^{-3}, μ(Mo $K\alpha$) = 5.4 cm^{-1}, $F(000) = 840$, $T = 299$ (3) K, final $R = 0.0303$ for 2409 observed (hkl and $\bar{h}\bar{k}\bar{l}$) reflections. Pentasodium bis(phosphoglycolate) tetrahydrate, $5Na^+.(C_2H_2O_6P\cdots H\cdots C_2H_2O_6P)^{5-}.4H_2O$ (VI), $M_r = 494.04$, monoclinic, $C2/c$, $a = 6.960$ (4), $b = 17.793$ (12), $c = 13.151$ (9) Å, $\beta = 96.88$ (5)°, $V = 1617$ (2) Å^3, $Z = 4$, $D_m = 1.98$, $D_x = 2.029$ (3) g cm^{-3}, μ(Mo $K\alpha$) = 4.7 cm^{-1}, $F(000) = 1000$, $T = 301$ (2) K, final $R = 0.0281$ for 1189 observed reflections. Trisodium phosphoglycolate tetrahydrate, $3Na^+.(C_2H_2O_6P)^{3-}.4H_2O$ (VII), $M_r = 294.04$, orthorhombic, $Pbcn$, $a = 10.617$ (9), $b = 6.977$ (8), $c = 27.65$ (2) Å, $V = 2048$ (4) Å^3, $Z = 8$, $D_x = 1.907$ (4) g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 41.2$ cm^{-1}, $F(000) = 1200$, $T = 295$ (2) K, final $R = 0.030$ for 1567 non-zero reflections. Trisodium phosphoglycolate tetrahydrate, $3Na^+.(C_2H_2O_6P)^{3-}.4H_2O$ (VIII), $M_r = 294.04$, monoclinic, $P2_1/n$, $a = 6.243$ (6), $b = 26.08$ (2), $c = 6.763$ (7) Å, $\beta = 115.29$ (9)°, $V = 995.6$ (18) Å^3, $Z = 4$, $D_m = 1.98$, $D_x = 1.962$ (4) g cm^{-3}, μ(Cu $K\alpha$) = 42.4 cm^{-1}, $F(000) = 600$, $T = 296$ (2) K, final $R = 0.0264$ for 1467 non-zero reflections. The orientation of the phosphate group relative to the glycolate moiety is different in each compound and suggests conformational flexibility around the C—O(ester) bond in water solutions. There is a tendency for the ester O atom to lie in the plane of the acetate group. The P—O(ester) bond length changes slowly and irregularly with the protonation level, from 1.566 (2) Å in H_3PG (I) to 1.635 (2) Å in the trianion (VIII).

Introduction. This investigation was undertaken as part of the structural study of biologically significant organic phosphate esters in different ionization states. One of the simplest of the naturally occurring organic phosphate esters is phosphoglycolate (PG). For example, PG is a competitive inhibitor of enolase and the crystal structure of the inhibitory complex yeast enolase–Zn^{2+}–PG was recently determined by X-ray methods (Lebioda, Stec, Brewer & Tykarska, 1991). Formally, PG may exist in four different forms: tribasic acid, monoanion, dianion and trianion. All these forms are characterized in the crystalline state in this paper which attempts to assess the influence of pH and chemical environment on PG geometry through an examination of the molecular structure of the PG moiety at different levels of protonation and in different crystals. Only one comparable system has previously been characterized at all protonation levels, namely phosphoenolpyruvate (PEP) (Weichsel & Lis, 1991).

Experimental. Commercially available (Sigma) tri-(monocyclohexylammonium) phosphoglycolate tri-

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Table 1. *Summary of data collection and structure refinement*; Cu *Kα X-rays were used for* (VII) *and* (VIII) *and* Mo *Kα for all other structures*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Crystal size (mm): length	0.06	0.1	0.2	0.5	0.4	0.55	0.08	0.12
breadth	0.2	0.5	0.5	0.25	0.25	0.02	0.09	0.03
height	0.1	0.2	0.07	0.25	0.1	0.12	0.04	0.04
Instrument	Kuma KM4	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$	Kuma KM4	Kuma KM4	Kuma KM4
Lattice parameters (°)	$13 < 2\theta < 28$	$21 < 2\theta < 30$	$15 < 2\theta < 28$	$19 < 2\theta < 28$	$19 < 2\theta < 25$	$18 < 2\theta < 26$	$15 < 2\theta < 29$	$16 < 2\theta < 34$
Number of reflections	25	15	15	15	15	15	25	25
$\theta_{\max}$ (°)	30	30	30	26	30	26	80	70
Scan ranges: h	−20 to 5	−16 to 14	−13 to 5	−10 to 10	−14 to 0	−9 to 9	−13 to 13	−7 to 0
k	−6 to 6	−6 to 6	−7 to 7	−11 to 11	−17 to 17	0 to 24	−8 to 0	−31 to 31
l	−11 to 11	−11 to 11	−15 to 15	−12 to 12	−12 to 12	−18 to 18	−35 to 35	−8 to 8
Measured reflections	4557	3678	2901	6431	9500	4608	9100	5498
Data with $I > 3\sigma(I)$	2760	3532	1713	4402	5722	2154	5074	3906
Unique observed reflections	1152	1818	1051	2112	2409	1189	1567	1467
R_{merge} (after *DIFABS*)	0.0145	0.0170	0.0175	0.0219	0.0234	0.0161	0.0375	0.0249
Absorption corrections								
Min.	0.940	0.906	0.920	0.960	0.897	0.921	0.873	0.937
Max.	1.036	1.151	1.046	1.040	1.043	1.044	1.240	1.147
R	0.0254	0.0258	0.0305	0.0341	0.0303	0.0281	0.0298	0.0264
wR	0.0251	0.0339	0.0310	0.0378	0.0288	0.0292	0.0333	0.0317
Refined parameters	102	107	109	220	241	148	186	185
$(\Delta/\sigma)_{\max}$ in last cycle	0.05	0.14	0.04	0.06	0.12	0.12	0.07	0.09
$\Delta\rho$ (e Å^{-3})	−0.19; 0.26	−0.68; 0.74	−0.36; 0.33	−0.47; 0.55	−0.55; 0.42	−0.29; 0.27	−0.40; 0.35	−0.33; 0.50

hydrate was passed over Dowex 50W(H^+) resin, and slightly hygroscopic crystals of phosphoglycolic acid were grown by slow concentration of the eluate. A small specimen was cut from a large many-faced crystal and mounted in a capillary. All other crystalline compounds were obtained by slow concentration of aqueous solutions of phosphoglycolic acid and KOH or NaOH in approximate stoichiometric ratios. All these crystals were coated with lacquer. $Na_3(PG).4H_2O$ was first isolated as orthorhombic crystals (VII). After recrystallization, the second, monoclinic, modification (VIII) was obtained. The densities of the crystals were measured by flotation in $CCl_4/C_2H_4Br_2$ mixture. Preliminary examinations were by oscillation and Weissenberg photographs. Syntex $P2_1$ or Kuma KM4 diffractometers with graphite monochromator were used for lattice parameters and intensity measurements; ω–2θ scan technique. The experimental details are summarized in Table 1.* Two standards were monitored after each group of 50 reflections in each crystal; maximum variation ∓3% except in the case of (VI). [Its standard reflections decreased in intensity by approximately 60% over the period of data collection; some other reflections, which were remeasured from time to time, showed that the decomposition was isotropic. The data for (VI) were therefore rescaled using the intensities of the standards.] Atomic scattering factors for P, O, C, H, Na^+ and K^+ were from *International Tables for X-ray Crystallography* (1974, Vol, IV); anomalous dispersion was included for all non-H atoms. All structures were solved by direct methods and refined on F by *SHELX*76 (Sheldrick, 1976). The H atoms were found from difference syntheses. [In the case of (VII), the H atoms from disordered water molecules, O(10) and O(11), were not determined.] Final refinement was performed using anisotropic thermal parameters (isotropic for H atoms); $w = 1/\sigma^2(F_o)$ {in the case of (II) an isotropic extinction correction of the form $1 - xF_c^2/\sin\theta$ was applied [refinement of x gave the value $40\,(3) \times 10^{-7}$] and the weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ was applied (the g parameter refined to 0.0025)}. In the case of the noncentrosymmetric crystals, the refinement of the inverted structure gave $R = 0.0299$ and $wR = 0.0421$ for (II) and 0.0307 and 0.0291 for (V). In each case, absorption corrections were made following the *DIFABS* procedure (Walker & Stuart, 1983). The final atom parameters are given in Tables 2–9.

Discussion. Principal bond distances, bond angles and torsion angles in the phosphoglycolate residues are summarized in Table 10. The hydrogen-bond distances and angles are listed in Table 11. The same atom-numbering scheme has been used for each PG residue.

Structure (I). The molecular structure and numbering scheme are illustrated in Fig. 1. The unprotonated O(3) atom of the dihydrogenphosphate group is *trans* to the C(2) atom. A similar situation has been observed in most structures of monoesterified phosphates where two phosphate O atoms are protonated (Weichsel, Lis & Kuczek, 1989). The crystal packing and hydrogen-bonding schemes are shown in Fig. 2. The carboxyl groups are involved in hydrogen bonding in the usual way, *i.e.* carboxyl to carboxyl. The unprotonated O(3)

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* Lists of structure factors and anisotropic thermal parameters for all eight crystals have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55721 (115 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1010]

Table 2. *Final atom parameters for phosphoglycolic acid* (I)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
P	0.13711 (3)	0.01170 (8)	0.23702 (5)	0.0199 (1)
O(1)	0.07090 (9)	0.2200 (3)	0.12256 (16)	0.0306 (3)
O(2)	0.21645 (9)	0.1699 (3)	0.36767 (14)	0.0287 (3)
O(3)	0.09102 (9)	−0.1694 (3)	0.33619 (14)	0.0298 (3)
O(4)	0.18906 (10)	−0.1376 (3)	0.12376 (16)	0.0295 (3)
O(5)	0.38701 (11)	−0.0515 (3)	0.47729 (19)	0.0470 (4)
O(6)	0.45088 (12)	0.2764 (4)	0.35354 (26)	0.0644 (6)
C(1)	0.38096 (14)	0.1560 (4)	0.39240 (23)	0.0320 (5)
C(2)	0.29087 (14)	0.3079 (4)	0.32291 (26)	0.0317 (5)
H(2)	0.2816 (16)	0.330 (5)	0.208 (3)	0.052 (7)
H(21)	0.2994 (17)	0.492 (4)	0.369 (3)	0.055 (7)
H(1)	0.0179 (17)	0.275 (5)	0.155 (3)	0.063 (8)
H(4)	0.1576 (18)	−0.199 (5)	0.040 (4)	0.074 (10)
H(6)	0.5033 (23)	0.198 (6)	0.408 (4)	0.116 (13)

Table 3. *Final atom parameters for potassium phosphoglycolate* (II)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
K	0.47073 (3)	0.75	0.18643 (5)	0.0239 (1)
P	0.74102 (3)	0.29981 (10)	0.60953 (5)	0.0137 (1)
O(1)	0.68238 (13)	0.18604 (31)	0.39582 (17)	0.0230 (3)
O(2)	0.91952 (11)	0.40645 (26)	0.73718 (18)	0.0222 (3)
O(3)	0.65135 (13)	0.55629 (24)	0.60475 (19)	0.0208 (3)
O(4)	0.74372 (13)	0.05581 (24)	0.74780 (18)	0.0202 (3)
O(5)	1.13116 (14)	0.56054 (34)	0.68923 (22)	0.0310 (3)
O(6)	1.30297 (13)	0.21768 (33)	0.90401 (19)	0.0282 (3)
C(1)	1.17195 (15)	0.32950 (34)	0.80536 (20)	0.0181 (3)
C(2)	1.04349 (14)	0.20211 (36)	0.81244 (21)	0.0193 (3)
H(2)	1.076 (4)	0.182 (8)	0.950 (5)	0.044 (8)
H(21)	1.014 (3)	0.037 (6)	0.737 (4)	0.013 (5)
H(4)	0.708 (4)	−0.149 (8)	0.687 (5)	0.034 (7)
H(5)	1.232 (5)	0.591 (17)	0.682 (9)	0.127 (17)

Table 4. *Final atom parameters for sodium phosphoglycolate* (III)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
P	0.17314 (8)	0.31252 (13)	0.05803 (6)	0.0143 (2)
O(1)	0.31824 (19)	0.2346 (4)	0.04171 (16)	0.0192 (5)
O(2)	0.11955 (18)	0.1403 (4)	0.16448 (15)	0.0192 (5)
O(3)	0.15090 (19)	0.5791 (4)	0.09094 (15)	0.0196 (5)
O(4)	0.08974 (23)	0.2367 (4)	−0.05588 (17)	0.0228 (5)
O(5)	0.02374 (19)	−0.1821 (4)	0.33067 (16)	0.0221 (5)
O(6)	−0.12722 (22)	0.1047 (4)	0.38903 (18)	0.0282 (5)
C(1)	−0.0336 (3)	0.0179 (5)	0.31771 (23)	0.0187 (6)
C(2)	−0.0071 (3)	0.1989 (6)	0.21822 (23)	0.0185 (6)
Na(1)	0.5	0.5	0.0	0.0329 (5)
Na(2)	0.25	0.8017 (3)	0.25	0.0199 (4)
H(2)	−0.007 (3)	0.365 (6)	0.248 (3)	0.021 (8)
H(21)	−0.082 (4)	0.173 (6)	0.157 (3)	0.033 (9)
H(4)	0.002 (4)	0.295 (7)	−0.061 (3)	0.050 (12)
H(6)	−0.138 (4)	−0.001 (7)	0.443 (4)	0.065 (14)

atom in the phosphate group accepts two H atoms, whereas the remaining OH groups act as donors only, forming a network (Table 11).

Structure (II). The crystals are composed of potassium cations and phosphoglycolate monoanions. Contrary to other PG moieties, the carboxylic hydroxyl group is in a *syn* orientation to the ester

Table 5. *Final atom parameters for tripotassium bis(phosphoglycolate)* (IV)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
K(1)	0.16876 (11)	0.18216 (9)	0.95228 (8)	0.0341 (7)
K(2)	0.67537 (12)	0.55877 (10)	0.31234 (9)	0.0423 (8)
K(3)	0.05	0.0	0.5	0.0341 (9)
K(4)	0.0	0.0	0.5	0.0308 (9)
P(*A*)	0.22188 (12)	0.11771 (11)	0.27518 (9)	0.0231 (7)
P(*B*)	0.25864 (12)	0.79463 (11)	0.64340 (9)	0.0239 (7)
O(1*A*)	0.06809 (29)	0.08760 (29)	0.17984 (26)	0.0319 (16)
O(2*A*)	0.28639 (32)	−0.05232 (28)	0.24304 (25)	0.0339 (19)
O(3*A*)	0.22730 (32)	0.19255 (29)	0.43908 (25)	0.0339 (19)
O(4*A*)	0.34030 (33)	0.21293 (30)	0.21762 (27)	0.0310 (18)
O(5*A*)	0.45327 (33)	−0.28627 (28)	0.23308 (26)	0.0350 (19)
O(6*A*)	0.43556 (42)	−0.39040 (33)	−0.01270 (27)	0.0582 (25)
O(1*B*)	0.39440 (30)	0.70062 (29)	0.62282 (26)	0.0339 (17)
O(2*B*)	0.16749 (34)	0.75292 (29)	0.48172 (25)	0.0397 (19)
O(3*B*)	0.28634 (33)	0.97495 (28)	0.71600 (28)	0.0393 (19)
O(4*B*)	0.14474 (34)	0.72131 (31)	0.72111 (29)	0.0343 (19)
O(5*B*)	−0.03905 (33)	0.69620 (30)	0.24340 (25)	0.0349 (23)
O(6*B*)	0.07260 (34)	0.48491 (29)	0.10530 (25)	0.0411 (25)
C(1*A*)	0.4096 (5)	−0.2855 (5)	0.1136 (4)	0.0317 (30)
C(2*A*)	0.3175 (7)	−0.1577 (6)	0.0995 (5)	0.0389 (25)
C(1*B*)	0.0519 (5)	0.5971 (5)	0.2298 (4)	0.0272 (30)
C(2*B*)	0.1514 (7)	0.5950 (5)	0.3621 (4)	0.0307 (11)
H(2*A*)	0.226 (6)	−0.215 (6)	0.029 (5)	0.062 (15)
H(21*A*)	0.382 (6)	−0.105 (6)	0.048 (5)	0.065 (15)
H(4*A*)	0.442 (8)	0.238 (8)	0.276 (7)	0.126 (25)
H(6*A*)	0.5	−0.5	0.0	0.096 (25)
H(2*B*)	0.250 (5)	0.569 (5)	0.339 (4)	0.034 (12)
H(21*B*)	0.104 (5)	0.524 (5)	0.391 (4)	0.038 (12)
H(4*B*)	0.071 (6)	0.790 (6)	0.759 (5)	0.062 (16)
H(6*B*)	0.0	0.5	0.0	0.160 (38)

Table 6. *Final atom parameters for disodium phosphoglycolate hemihydrate* (V)

$U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
Na(1)	0.60024 (15)	0.24661 (10)	0.59949 (15)	0.0257 (4)
Na(2)	0.22691 (13)	0.37428 (11)	0.77215 (15)	0.0236 (4)
Na(3)	0.84764 (13)	0.12210 (11)	0.83234 (14)	0.0212 (4)
Na(4)	0.0	0.5	0.36508 (23)	0.0290 (6)
Na(5)	0.5	0.5	0.56606 (23)	0.0239 (5)
P(*A*)	0.90133 (9)	0.35362 (7)	−0.33139 (9)	0.0153 (2)
P(*B*)	0.67809 (9)	0.39205 (7)	0.29199 (9)	0.0155 (2)
O(1*A*)	0.98043 (24)	0.36992 (20)	−0.46553 (24)	0.0226 (7)
O(2*A*)	1.00067 (22)	0.36088 (19)	−0.19515 (24)	0.0217 (7)
O(3*A*)	0.82564 (23)	0.25928 (16)	−0.31893 (25)	0.0197 (6)
O(4*A*)	0.80853 (25)	0.44324 (18)	−0.30120 (29)	0.0222 (6)
O(5*A*)	1.16555 (24)	0.36245 (23)	0.02837 (26)	0.0298 (8)
O(6*A*)	1.01277 (24)	0.35284 (19)	0.20139 (25)	0.0237 (6)
O(1*B*)	0.59725 (24)	0.37135 (19)	0.42232 (23)	0.0224 (6)
O(2*B*)	0.58071 (21)	0.38789 (19)	0.15284 (24)	0.0198 (6)
O(3*B*)	0.74960 (24)	0.48781 (17)	0.28866 (27)	0.0229 (6)
O(4*B*)	0.77248 (25)	0.30305 (18)	0.25936 (28)	0.0197 (6)
O(5*B*)	0.41841 (23)	0.38435 (20)	−0.07946 (26)	0.0218 (6)
O(6*B*)	0.57540 (22)	0.39349 (19)	−0.24441 (24)	0.0186 (6)
O(7)	0.80866 (29)	0.10930 (26)	0.46647 (29)	0.0278 (7)
C(1*A*)	1.05314 (31)	0.35895 (26)	0.06783 (37)	0.0148 (8)
C(2*A*)	0.94976 (37)	0.36195 (36)	−0.04707 (39)	0.0220 (10)
C(1*B*)	0.53259 (32)	0.38894 (26)	−0.11337 (38)	0.0166 (8)
C(2*B*)	0.63357 (34)	0.38774 (36)	0.00650 (36)	0.0162 (8)
H(2*A*)	0.903 (4)	0.305 (3)	−0.031 (4)	0.021 (11)
H(21*A*)	0.905 (6)	0.427 (4)	−0.031 (6)	0.075 (18)
H(4*A*)	0.722 (6)	0.432 (4)	−0.280 (7)	0.101 (24)
H(2*B*)	0.675 (4)	0.328 (3)	−0.008 (4)	0.004 (9)
H(21*B*)	0.678 (4)	0.442 (3)	−0.007 (4)	0.021 (11)
H(4*B*)	0.857 (5)	0.301 (4)	0.237 (5)	0.053 (16)
H(71)	0.790 (6)	0.054 (5)	0.525 (6)	0.099 (23)
H(72)	0.818 (5)	0.160 (4)	0.506 (4)	0.025 (13)

Table 7. *Final atom parameters for pentasodium bis(phosphoglycolate) tetrahydrate* (VI)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
Na(1)	0.31283 (17)	0.51828 (7)	0.39723 (8)	0.0242 (3)
Na(2)	0.10890 (20)	0.34746 (8)	0.35440 (10)	0.0373 (4)
Na(3)	0.0	0.16941 (9)	0.75	0.0224 (4)
P	0.21294 (11)	0.47520 (4)	0.14919 (5)	0.0138 (2)
O(1)	0.2252 (3)	0.41038 (10)	0.22155 (14)	0.0206 (5)
O(2)	0.2424 (4)	0.54637 (10)	0.22455 (13)	0.0237 (6)
O(3)	0.3636 (3)	0.47839 (12)	0.07639 (13)	0.0193 (5)
O(4)	0.0083 (3)	0.48116 (12)	0.08966 (13)	0.0212 (5)
O(5)	0.2631 (4)	0.64832 (13)	0.36959 (16)	0.0350 (6)
O(6)	0.2636 (4)	0.74363 (12)	0.26090 (21)	0.0467 (8)
O(7)	0.0731 (5)	0.15446 (16)	0.57300 (19)	0.0338 (7)
O(8)	−0.0623 (4)	0.28897 (15)	0.47000 (19)	0.0323 (6)
C(1)	0.2570 (5)	0.67536 (17)	0.28202 (25)	0.0270 (8)
C(2)	0.2391 (6)	0.62213 (16)	0.19005 (22)	0.0221 (8)
H(2)	0.361 (5)	0.6347 (18)	0.155 (3)	0.034 (10)
H(21)	0.117 (5)	0.6324 (17)	0.151 (3)	0.024 (9)
H(4)	0.0	0.5	0.0	0.096 (23)
H(7)	0.042 (7)	0.1834 (24)	0.537 (4)	0.064 (17)
H(71)	−0.012 (7)	0.1185 (24)	0.565 (3)	0.057 (14)
H(8)	−0.130 (6)	0.3066 (22)	0.511 (3)	0.049 (14)
H(81)	−0.129 (7)	0.271 (3)	0.418 (4)	0.072 (17)

Table 8. *Final atom parameters for trisodium phosphoglycolate tetrahydrate* (*orthorhombic modification*) (VII)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
Na(1)	0.21601 (10)	0.44759 (15)	0.42324 (4)	0.0274 (3)
Na(2)	0.78591 (12)	0.64113 (15)	0.74592 (4)	0.0346 (3)
Na(3)	0.50434 (10)	0.74522 (14)	0.49309 (4)	0.0266 (3)
P	0.50189 (6)	0.71324 (8)	0.62178 (2)	0.0172 (2)
O(1)	0.63536 (16)	0.7615 (3)	0.60690 (6)	0.0218 (4)
O(2)	0.43456 (17)	0.6495 (3)	0.57137 (6)	0.0250 (5)
O(3)	0.43063 (19)	0.8825 (3)	0.64158 (7)	0.0277 (5)
O(4)	0.49521 (18)	0.5368 (3)	0.65424 (6)	0.0232 (4)
O(5)	0.34746 (18)	0.5116 (3)	0.48975 (7)	0.0309 (5)
O(6)	0.14895 (17)	0.5102 (3)	0.51267 (7)	0.0272 (5)
O(7)	0.27499 (23)	0.3921 (4)	0.69787 (7)	0.0328 (6)
O(8)	0.52478 (19)	0.2068 (4)	0.59457 (8)	0.0309 (5)
O(9)	0.27390 (23)	0.6055 (4)	0.31232 (7)	0.0322 (5)
O(10)†	0.5022 (6)	0.0478 (6)	0.76638 (15)	0.0401 (10)
O(11)†	0.4616 (4)	0.6671 (6)	0.75133 (21)	0.0401 (10)
C(1)	0.26356 (22)	0.5373 (4)	0.52029 (9)	0.0186 (5)
C(2)	0.30354 (25)	0.6039 (4)	0.57095 (9)	0.0231 (6)
H(2)	0.279 (4)	0.491 (5)	0.5938 (14)	0.046 (11)
H(21)	0.250 (4)	0.728 (5)	0.5785 (13)	0.041 (10)
H(7)	0.330 (5)	0.432 (6)	0.6825 (15)	0.053 (13)
H(71)	0.205 (5)	0.386 (6)	0.6779 (17)	0.076 (15)
H(8)	0.517 (4)	0.293 (6)	0.6123 (14)	0.041 (11)
H(81)	0.493 (4)	0.114 (5)	0.6112 (13)	0.035 (10)
H(9)	0.225 (6)	0.670 (8)	0.3385 (21)	0.116 (21)
H(91)	0.347 (5)	0.576 (6)	0.3223 (16)	0.065 (14)

† Occupancy factor = 0.5.

Table 9. *Final atom parameters for trisodium phosphoglycolate tetrahydrate* (*monoclinic modification*) (VIII)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
Na(1)	0.19931 (19)	0.02417 (4)	0.41176 (17)	0.0251 (3)
Na(2)	0.21971 (19)	0.15443 (4)	0.23495 (17)	0.0253 (3)
Na(3)	0.25854 (20)	0.24865 (5)	0.79434 (17)	0.0303 (3)
P	0.56226 (11)	0.12996 (2)	0.04147 (10)	0.0149 (2)
O(1)	0.6127 (3)	0.13056 (7)	0.2801 (3)	0.0214 (4)
O(2)	0.7735 (4)	0.16628 (7)	0.0369 (3)	0.0225 (4)
O(3)	0.3311 (4)	0.15370 (7)	−0.1082 (3)	0.0236 (5)
O(4)	0.6015 (4)	0.07750 (6)	−0.0379 (3)	0.0209 (4)
O(5)	0.6895 (4)	0.26551 (7)	−0.0820 (3)	0.0231 (4)
O(6)	0.8258 (4)	0.25502 (7)	−0.3336 (3)	0.0238 (5)
O(7)	0.2286 (4)	0.00745 (8)	0.7707 (4)	0.0263 (5)
O(8)	0.0850 (4)	0.06534 (8)	0.0734 (4)	0.0284 (5)
O(9)	0.6077 (4)	0.05462 (7)	0.5628 (4)	0.0262 (5)
O(10)	0.1066 (4)	0.10982 (8)	0.4912 (4)	0.0241 (5)
C(1)	0.7610 (5)	0.23834 (9)	−0.1949 (4)	0.0160 (5)
C(2)	0.7648 (6)	0.18076 (10)	−0.1702 (5)	0.0222 (6)
H(2)	0.896 (7)	0.1673 (14)	−0.197 (6)	0.051 (11)
H(21)	0.620 (6)	0.1715 (12)	−0.286 (5)	0.031 (9)
H(7)	0.340 (9)	0.0331 (19)	0.829 (8)	0.097 (18)
H(71)	0.278 (6)	−0.0193 (14)	0.844 (6)	0.038 (10)
H(8)	0.109 (7)	0.0532 (14)	−0.017 (6)	0.042 (11)
H(81)	−0.075 (7)	0.0715 (14)	0.027 (6)	0.047 (11)
H(9)	0.615 (7)	0.0820 (15)	0.478 (6)	0.053 (11)
H(91)	0.594 (7)	0.0674 (13)	0.653 (6)	0.034 (11)
H(10)	0.167 (7)	0.1215 (14)	0.610 (6)	0.038 (11)
H(01)	−0.034 (8)	0.1152 (16)	0.436 (7)	0.068 (15)

O(2) atom (Fig. 3). The packing of the crystal is depicted in Fig. 4. The O(4) atoms (as donors) form infinite chains with O(3^{i}) atoms parallel to **b** (Table 11). Anions related by the 2_1 screw axes are linked to each other, resulting in helical O(5)—H(5)···O(1^{ii}) hydrogen bonding which extends along **b**. The K^+ ion is octacoordinate, participating in K—O distances of 2.70 (1)–3.16 (1) Å to three carbonyl and five phosphate O atoms (Table 12). Each K^+ ion is coordinated to six independent phosphoglycolate anions.

Structure (III). The crystals are composed of phosphoglycolate monoanions (Fig. 5) and two crystallographically independent Na^+ cations. The Na(1) atoms occupy centers of symmetry and Na(2) atoms are situated on twofold axes. Both are hexacoordinated (Table 12) by phosphate and carboxyl O atoms forming distorted octahedra. The crystal packing and hydrogen-bonding schemes are shown in Fig. 6. The phosphate tetrahedra are linked by a double hydrogen bridge on two sides of a symmetry center, forming a dimer. The carboxylic hydroxyl group (as donor) forms a hydrogen bond with a phosphate O atom from another anion, thus producing a polymeric structure.

Structure (IV). The asymmetric unit comprises two crystallographically independent phosphoglycolate residues (*A* and *B*), each of which have a formal negative charge of − 1.5, the carboxyl group bearing a charge of −0.5. In both anions, the acidic H atoms are attached to the phosphate groups and are shared between pairs of centrosymmetrically related O atoms of carboxyl groups [Figs. 7(*a*) and 7(*b*)]. The symmetrically related pairs of O atoms are thereby involved in very short hydrogen bonds of 2.438 (5) Å (in *A*) and 2.455 (4) Å (in *B*). [Short hydrogen bonds involving carboxylic O atoms have been previously observed, *e.g.* in sodium hydrogen acetate (Speakman & Mills, 1961).] Furthermore, the phosphate groups of anions *A* and *B* are linked by the

Table 10. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for phosphoglycolate moieties*

	(I)	(II)	(III)	(IV*A*)	(IV*B*)	(V*A*)	(V*B*)	(VI)	(VII)	(VIII)
P—O(1)	1.542 (2)	1.506 (2)	1.495 (2)	1.491 (3)	1.488 (3)	1.482 (2)	1.475 (2)	1.491 (2)	1.513 (2)	1.507 (2)
P—O(2)	1.566 (2)	1.590 (2)	1.604 (2)	1.596 (3)	1.596 (3)	1.614 (2)	1.619 (2)	1.606 (2)	1.628 (2)	1.635 (2)
P—O(3)	1.485 (2)	1.497 (2)	1.494 (2)	1.478 (3)	1.472 (3)	1.502 (2)	1.491 (3)	1.503 (2)	1.506 (2)	1.497 (2)
P—O(4)	1.541 (2)	1.556 (2)	1.550 (2)	1.570 (3)	1.563 (3)	1.574 (3)	1.582 (3)	1.544 (2)	1.525 (2)	1.527 (2)
O(2)—C(2)	1.423 (2)	1.419 (2)	1.425 (3)	1.420 (5)	1.419 (5)	1.436 (4)	1.429 (4)	1.422 (3)	1.427 (3)	1.430 (3)
C(2)—C(1)	1.500 (4)	1.510 (3)	1.504 (4)	1.500 (7)	1.506 (5)	1.501 (5)	1.514 (5)	1.529 (4)	1.536 (4)	1.510 (4)
C(1)—O(5)	1.214 (3)	1.297 (2)	1.218 (3)	1.211 (4)	1.216 (5)	1.236 (4)	1.241 (4)	1.244 (4)	1.240 (3)	1.256 (3)
C(1)—O(6)	1.304 (4)	1.221 (2)	1.314 (3)	1.280 (4)	1.279 (5)	1.277 (4)	1.263 (4)	1.248 (4)	1.249 (3)	1.248 (3)
O(1)—P—O(2)	109.7 (1)	110.6 (1)	104.9 (2)	109.7 (2)	107.6 (2)	104.2 (2)	104.1 (2)	102.9 (2)	103.8 (2)	102.3 (2)
O(1)—P—O(3)	114.2 (1)	114.7 (1)	116.2 (2)	118.6 (2)	119.7 (2)	118.9 (2)	118.0 (2)	116.4 (2)	113.3 (2)	114.8 (2)
O(1)—P—O(4)	106.3 (1)	111.4 (1)	108.0 (2)	106.0 (2)	106.3 (2)	112.1 (2)	111.5 (2)	110.8 (3)	112.5 (2)	113.2 (2)
O(2)—P—O(3)	106.6 (1)	105.4 (1)	108.5 (2)	103.2 (2)	104.2 (2)	109.7 (2)	109.5 (2)	108.4 (2)	107.7 (2)	107.4 (2)
O(2)—P—O(4)	103.8 (1)	105.1 (1)	106.4 (2)	105.1 (2)	106.1 (2)	103.0 (2)	103.2 (2)	107.5 (2)	105.2 (2)	105.1 (2)
O(3)—P—O(4)	115.7 (1)	109.1 (1)	112.1 (2)	113.6 (2)	112.2 (2)	107.7 (2)	109.4 (2)	110.2 (2)	113.3 (2)	112.7 (2)
P—O(2)—C(2)	123.1 (2)	120.5 (2)	119.2 (2)	122.5 (3)	122.7 (3)	117.6 (3)	117.8 (3)	123.7 (2)	119.7 (2)	118.6 (2)
O(2)—C(2)—C(1)	110.3 (2)	110.6 (2)	109.7 (3)	109.1 (4)	108.5 (4)	111.6 (4)	112.5 (3)	109.8 (3)	110.1 (2)	111.3 (3)
C(2)—C(1)—O(5)	123.1 (2)	114.9 (2)	124.7 (3)	122.4 (4)	122.1 (4)	119.6 (4)	120.2 (4)	118.9 (3)	117.8 (3)	119.1 (3)
C(2)—C(1)—O(6)	112.0 (2)	120.8 (2)	110.8 (3)	112.7 (4)	113.2 (4)	114.1 (3)	114.5 (3)	115.4 (3)	118.0 (3)	115.8 (3)
O(5)—C(1)—O(6)	124.8 (2)	124.3 (2)	124.5 (3)	125.0 (4)	124.7 (4)	126.2 (4)	125.2 (4)	125.7 (4)	124.2 (3)	125.1 (3)
O(1)—P—O(2)—C(2)	−72.4 (3)	−69.5 (7)	168.1 (3)	59.8 (5)	36.1 (8)	171.5 (5)	−169.2 (4)	−179.0 (3)	−176.3 (7)	−171.3 (5)
O(3)—P—O(2)—C(2)	163.4 (3)	166.0 (7)	43.2 (3)	−173.0 (5)	164.1 (7)	−60.1 (5)	63.7 (4)	57.1 (5)	−55.9 (9)	−50.0 (6)
O(4)—P—O(2)—C(2)	40.8 (3)	50.8 (7)	−77.6 (3)	−53.7 (5)	−77.3 (7)	54.4 (5)	−52.7 (4)	−62.0 (4)	65.2 (8)	70.2 (6)
P—O(2)—C(2)—C(1)	−109.4 (4)	145.7 (7)	−178.2 (3)	167.3 (6)	176.9 (7)	174.5 (4)	−177.1 (4)	175.9 (3)	−176.8 (7)	121.7 (8)
O(2)—C(2)—C(1)—O(5)	−1.4 (5)	−16.0 (9)	−17.3 (4)	−3.3 (7)	−22.9 (8)	4.6 (5)	−4.0 (5)	−3.0 (4)	7.9 (7)	−22.9 (7)
O(2)—C(2)—C(1)—O(6)	179.9 (4)	163.8 (10)	162.7 (4)	176.8 (7)	157.6 (6)	−175.4 (5)	176.9 (5)	177.2 (3)	−173.0 (7)	158.8 (7)

Table 11. *Probable hydrogen bonds*

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Phosphoglycolic acid (I)				
O(1)—H(1)$\cdots$O(3$^{\rm i}$)	2.575 (3)	0.93 (3)	1.66 (3)	165 (3)
O(4)—H(4)$\cdots$O(3$^{\rm ii}$)	2.596 (3)	0.78 (3)	1.81 (3)	175 (3)
O(6)—H(6)$\cdots$O(5$^{\rm iii}$)	2.670 (3)	0.87 (4)	1.80 (4)	178 (4)

Symmetry code: (i) $-x$, $0.5+y$, $0.5-z$; (ii) x, $-0.5-y$, z—0.5; (iii) $1-x$, $-y$, $1-z$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Potassium phosphoglycolate (II)				
O(4)—H(4)$\cdots$O(3$^{\rm i}$)	2.482 (3)	1.02 (4)	1.46 (4)	177 (4)
O(5)—H(5)$\cdots$O(1$^{\rm ii}$)	2.504 (3)	1.11 (8)	1.43 (7)	159 (7)

Symmetry code: (i) x, $y-1$, z, (ii) $2-x$, $0.5+y$, $1-z$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Sodium phosphoglycolate (III)				
O(4)—H(4)$\cdots$O(3$^{\rm i}$)	2.574 (4)	0.91 (4)	1.67 (4)	170 (4)
O(6)—H(6)$\cdots$O(1$^{\rm ii}$)	2.560 (4)	0.84 (4)	1.73 (4)	171 (4)

Symmetry code: (i) $-x$, $1-y$, $-z$, (ii) $x-0.5$, $-y$, $0.5+z$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Tripotassium bis(phosphoglycolate) (IV)				
O(4A)—H(4A)$\cdots$O(1$B^{\rm i}$)	2.523 (4)	0.96 (7)	1.57 (7)	174 (7)
O(4B)—H(4B)$\cdots$O(1$A^{\rm ii}$)	2.614 (4)	0.93 (5)	1.69 (5)	177 (5)
O(6A)$\cdots$H(6A)$\cdots$O(6$A^{\rm iii}$)	2.438 (5)	1.22 (1)	1.22 (1)	180
O(6B)$\cdots$H(6B)$\cdots$O(6$B^{\rm iv}$)	2.455 (4)	1.23 (1)	1.23 (1)	180

Symmetry code: (i) $1-x$, $1-y$, $1-z$; (ii) $-x$, $1-y$, $1-z$; (iii) $1-x$, $-1-y$, $-z$; (iv) $-x$, $1-y$, $-z$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Disodium phosphoglycolate hemihydrate (V)				
O(4A)—H(4A)$\cdots$O(6B)	2.593 (3)	0.94 (6)	1.66 (6)	171 (6)
O(4B)—H(4B)$\cdots$O(6A)	2.666 (4)	0.92 (5)	1.81 (5)	156 (5)
O(7)—H(71)$\cdots$O(3B$^{\rm i}$)	2.810 (4)	0.93 (6)	1.95 (6)	153 (6)
O(7)—H(72)$\cdots$O(3A$^{\rm ii}$)	2.797 (4)	0.77 (5)	2.07 (4)	158 (5)

Symmetry code: (i) $1.5-x$, $y-0.5$, $1-z$; (ii) x, y, $z+1$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Pentasodium bis(phosphoglycolate) tetrahydrate (VI)				
O(4)$\cdots$H(4)$\cdots$O(4$^{\rm i}$)	2.441 (3)	1.22 (1)	1.22 (1)	180
O(7)—H(7)$\cdots$O(8)	2.854 (4)	0.72 (5)	2.16 (5)	162 (5)
O(7)—H(71)$\cdots$O(3$^{\rm ii}$)	2.781 (4)	0.87 (5)	1.94 (5)	161 (4)
O(8)—H(8)$\cdots$O(5$^{\rm iii}$)	2.891 (3)	0.82 (5)	2.07 (4)	172 (4)
O(8)—H(81)$\cdots$O(6$^{\rm iv}$)	2.980 (4)	0.84 (5)	2.17 (5)	162 (5)
O(8)—H(81)$\cdots$O(5$^{\rm iv}$)	3.016 (3)	0.84 (5)	2.37 (6)	134 (4)

Symmetry code: (i) $-x$, $1-y$, $-z$; (ii) $x-0.5$, $0.5-y$, $z+0.5$; (iii) $-x$, $1-y$, $1-z$; (iv) $x-0.5$, $y-0.5$, z.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Trisodium phosphoglycolate tetrahydrate (orthorhombic modification) (VII)				
O(7)—H(7)$\cdots$O(4)	2.818 (3)	0.77 (5)	2.06 (5)	169 (5)
O(7)—H(71)$\cdots$O(3$^{\rm i}$)	2.682 (3)	0.93 (5)	1.75 (5)	178 (5)
O(8)—H(8)$\cdots$O(4)	2.850 (3)	0.78 (4)	2.07 (4)	175 (4)
O(8)—H(81)$\cdots$O(3$^{\rm ii}$)	2.794 (3)	0.86 (4)	1.94 (4)	172 (4)
O(9)—H(9)$\cdots$O(1$^{\rm iii}$)	2.831 (3)	1.00 (6)	1.85 (6)	168 (5)
O(9)—H(91)$\cdots$O(4$^{\rm iv}$)	2.802 (3)	0.85 (5)	1.96 (5)	170 (5)

Symmetry code: (i) $0.5-x$, $y-0.5$, z; (ii) x, $y-1$, z; (iii) $x-0.5$, $1.5-y$, $1-z$; (iv) $1-x$, $1-y$, $1-z$.

D—H$\cdots A$	$D\cdots A$ (Å)	D—H (Å)	H$\cdots A$ (Å)	D—H$\cdots A$(°)
Trisodium phosphoglycolate tetrahydrate (monoclinic modification) (VIII)				
O(7)—H(7)$\cdots$O(4$^{\rm i}$)	2.803 (3)	0.92 (5)	1.89 (6)	171 (5)
O(7)—H(71)$\cdots$O(4$^{\rm ii}$)	2.768 (3)	0.83 (4)	1.94 (4)	175 (4)
O(8)—H(8)$\cdots$O(7$^{\rm iii}$)	2.973 (3)	0.76 (4)	2.22 (4)	168 (4)
O(8)—H(81)$\cdots$O(4$^{\rm iv}$)	2.799 (3)	0.92 (5)	1.88 (5)	172 (4)
O(9)—H(9)$\cdots$O(1)	2.762 (3)	0.93 (4)	1.84 (4)	173 (4)
O(9)—H(91)$\cdots$O(4$^{\rm i}$)	2.782 (3)	0.73 (4)	2.09 (4)	159 (4)
O(10)—H(10)$\cdots$O(3$^{\rm i}$)	2.715 (3)	0.79 (4)	1.93 (4)	175 (4)
O(10)—H(01)$\cdots$O(1$^{\rm iv}$)	2.842 (3)	0.81 (6)	2.04 (6)	176 (5)

Symmetry code: (i) x, y, $z+1$; (ii) $1-x$, $-y$, $1-z$; (iii) x, y, $z-1$; (iv) $x-1$, y, z.

phosphate hydroxyl groups to form a polymeric structure (Fig. 8). In the crystal there are four crystallographically independent K^+ cations; two lie in general positions and the remaining two occupy centers of symmetry. All coordinate to phosphate and carboxyl O atoms (Table 12).

Structure (V). The asymmetric unit comprises two crystallographically independent phosphoglycolate dianions (*A* and *B*), five crystallographically independent sodium cations (three in general positions and two on twofold axes) and one water molecule of hydration. The *A* and *B* anions are related by a pseudo-inversion center at $x \simeq 0.79$, $y \simeq 0.373$, $z \simeq -0.02$. The acidic H atoms in both anions are attached to the phosphate groups [Figs. 9(*a*) and 9(*b*)]. The hydroxyl group of anion *A* forms a hydrogen bond with the carboxylate group of anion *B* and the hydroxyl group of anion *B* forms a hydrogen bond with the carboxylate group of anion *A*. Thus,

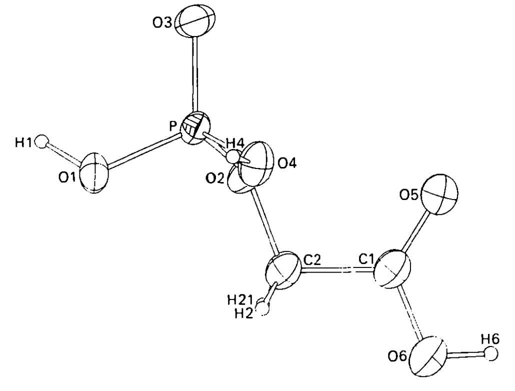


Fig. 1. The molecular structure of phosphoglycolic acid (I).

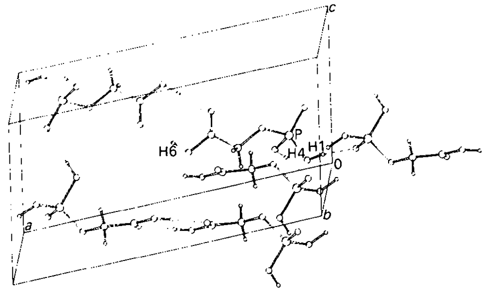


Fig. 2. Molecular packing in the crystal of phosphoglycolic acid. Dashed lines show hydrogen bonds.

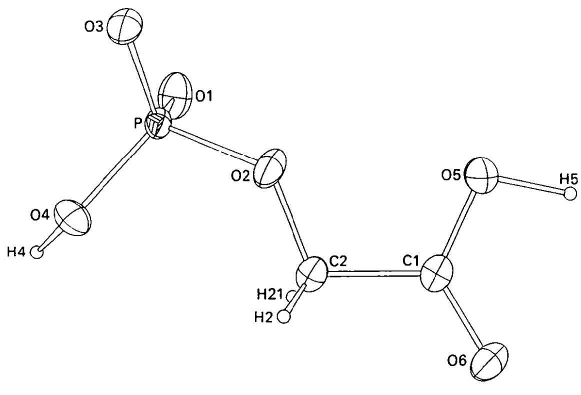


Fig. 3. The molecular structure of the phosphoglycolate monoanion in the potassium salt.

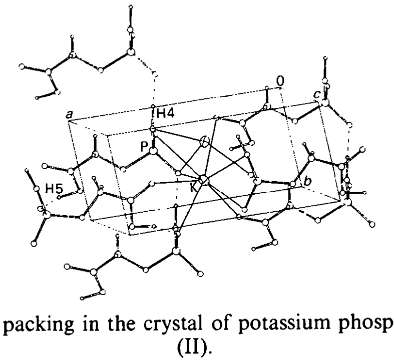


Fig. 4. The packing in the crystal of potassium phosphoglycolate (II).

Table 12. *Metal coordination distances* (Å)

Potassium phosphoglycolate (II)

K—O(1)	3.161 (2)	K—O(1^{i})	2.702 (2)
K—O(3)	2.800 (2)	K—O(3^{ii})	2.992 (2)
K—O(4^{ii})	2.761 (2)	K—O(6^{iii})	3.059 (2)
K—O(6^{iv})	2.828 (2)	K—O(6^{v})	2.884 (2)

Symmetry code: (i) x, $1 + y$, z; (ii) $1 - x$, $0.5 + y$, $1 - z$; (iii) $x - 1$, y, $z - 1$; (iv) $x - 1$, $1 + y$, $z - 1$; (v) $2 - x$, $0.5 + y$, $1 - z$.

Sodium phosphoglycolate (III)

Na(1)—O(1)	2.334 (2)	Na(2)—O(2^{iii})	2.405 (2)
Na(1)—O(5^{i})	2.563 (2)	Na(2)—O(3)	2.333 (2)
Na(1)—O(6^{ii})	2.741 (2)	Na(2)—O(5^{iii})	2.412 (2)

Symmetry code: (i) $0.5 - x$, $1 + y$, $0.5 - z$; (ii) $0.5 - x$, y, $0.5 - z$; (iii) x, $1 + y$, z.

Tripotassium bis(phosphoglycolate) (IV)

K(1)—O($1A^{\mathrm{i}}$)	2.893 (3)	K(1)—O($1A^{\mathrm{ii}}$)	2.802 (3)
K(1)—O($4A^{\mathrm{i}}$)	2.790 (3)	K(1)—O($3B^{\mathrm{iii}}$)	2.689 (3)
K(1)—O($5B^{\mathrm{iv}}$)	2.783 (3)	K(1)—O($6B^{\mathrm{i}}$)	2.776 (3)
K(2)—O($3A^{\mathrm{v}}$)	2.567 (3)	K(2)—O($5A^{\mathrm{vi}}$)	2.707 (3)
K(2)—O($6A^{\mathrm{vii}}$)	2.753 (3)	K(2)—O($1B^{\mathrm{v}}$)	2.700 (3)
K(2)—O($4B^{\mathrm{v}}$)	3.000 (3)	K(2)—O($5B^{\mathrm{viii}}$)	2.927 (3)
K(3)—O($3A$)	3.198 (3)	K(3)—O($2A$)	2.845 (2)
K(3)—O($5A$)	2.808 (2)	K(3)—O($3B^{\mathrm{v}}$)	3.018 (3)
K(3)—O($2B^{\mathrm{v}}$)	3.422 (3)	K(3)—O($1B^{\mathrm{v}}$)	3.470 (3)
K(4)—O($3A$)	2.778 (3)	K(4)—O($3B^{\mathrm{iv}}$)	3.200 (3)
K(4)—O($2B^{\mathrm{iv}}$)	2.715 (3)	K(4)—O($5B^{\mathrm{iv}}$)	2.845 (2)

Symmetry code: (i) x, y, $1 + z$; (ii) $-x$, $-y$, $1 - z$; (iii) x, $y - 1$, z; (iv) $-x$, $1 - y$, $1 - z$; (v) $1 - x$, $1 - y$, $1 - z$; (vi) x, $y + 1$, z; (vii) $1 - x$, $-y$, $-z$; (viii) $1 + x$, y, z.

Disodium phosphoglycolate hemihydrate (V)

Na(1)—O($1A^{\mathrm{i}}$)	2.344 (3)	Na(1)—O($3A^{\mathrm{ii}}$)	2.488 (3)
Na(1)—O($6A^{\mathrm{iii}}$)	2.417 (3)	Na(1)—O($1B$)	2.314 (3)
Na(1)—O($6B^{\mathrm{ii}}$)	2.437 (3)	Na(2)—O($2A^{\mathrm{iv}}$)	2.405 (3)
Na(2)—O($4A^{\mathrm{v}}$)	2.567 (3)	Na(2)—O($5A^{\mathrm{iv}}$)	2.399 (3)
Na(2)—O($4B^{\mathrm{iii}}$)	2.448 (3)	Na(2)—O($5B^{\mathrm{ii}}$)	2.421 (3)
Na(2)—O(7^{iii})	2.323 (3)	Na(3)—O($3A^{\mathrm{ii}}$)	2.303 (3)
Na(3)—O($5A^{\mathrm{iii}}$)	2.298 (3)	Na(3)—O($2B^{\mathrm{vi}}$)	2.459 (3)
Na(3)—O($3B^{\mathrm{vii}}$)	2.343 (3)	Na(3)—O($5B^{\mathrm{vi}}$)	2.346 (3)
Na(4)—O($1A^{\mathrm{iv,v}}$)	2.328 (3)	Na(4)—O($6A^{\mathrm{viii,ix}}$)	2.470 (3)
Na(4)—O($3B^{\mathrm{viii,ix}}$)	2.727 (3)	Na(5)—O($1B^{\mathrm{ix}}$)	2.389 (3)
Na(5)—O($6B^{\mathrm{ii,v}}$)	2.363 (3)	Na(5)—O($7^{\mathrm{iii,x}}$)	2.509 (3)

Symmetry code: (i) $x - 0.5$, $0.5 - y$, $-z$; (ii) x, y, $1 + z$; (iii) $x - 0.5$, $0.5 - y$, $1 - z$; (iv) $x - 1$, y, $1 + z$; (v) $1 - x$, $1 - y$, $1 + z$; (vi) $0.5 + x$, $0.5 - y$, $1 - z$; (vii) $1.5 - x$, $y - 0.5$, $1 - z$; (viii) $x - 1$, y, z; (ix) $1 - x$, $1 - y$, z; (x) $1.5 - x$, $0.5 + y$, $1 - z$.

Pentasodium bis(phosphoglycolate) tetrahydrate (VI)

Na(1)—O(2)	2.320 (2)	Na(1)—O(3^{i})	2.347 (2)
Na(1)—O(3^{ii})	2.341 (2)	Na(1)—O(4^{iii})	2.357 (2)
Na(1)—O(5)	2.361 (3)	Na(2)—O(1)	2.302 (2)
Na(2)—O(1^{iii})	2.665 (2)	Na(2)—O(4^{iii})	2.648 (3)
Na(2)—O(6^{iv})	2.612 (3)	Na(2)—O(7^{v})	2.303 (3)
Na(2)—O(8)	2.291 (3)	Na(3)—O($1^{\mathrm{v,vi}}$)	2.375 (2)
Na(3)—O($6^{\mathrm{ii,vii}}$)	2.391 (3)	Na(3)—O(7^{viii})	2.456 (3)

Symmetry code: (i) $1 - x$, y, $0.5 - z$; (ii) x, $1 - y$, $0.5 + z$; (iii) $-x$, y, $0.5 - z$; (iv) $0.5 - x$, $y - 0.5$, $0.5 - z$; (v) $0.5 - x$, $0.5 - y$, $1 - z$; (vi) $x - 0.5$, $0.5 - y$, $0.5 + z$; (vii) $-x$, $1 - y$, $1 - z$; (viii) $-x$, y, $1.5 - z$.

Trisodium phosphoglycolate tetrahydrate (orthorhombic modification) (VII)

Na(1)—O(1^{i})	2.305 (2)	Na(1)—O(1^{ii})	2.355 (2)
Na(1)—O(5)	2.351 (2)	Na(1)—O(6)	2.610 (2)
Na(1)—O(8^{iii})	2.350 (2)	Na(2)—O(7^{iv})	2.419 (2)
Na(2)—O(7^{v})	2.344 (2)	Na(2)—O(9^{i})	2.441 (2)
Na(2)—O(9^{vi})	2.394 (2)	Na(2)—O(10^{vii})	2.409 (5)
Na(2)—O(10^{v})	2.411 (5)	Na(2)—O(11^{iv})	2.636 (4)
Na(3)—O(2)	2.383 (2)	Na(3)—O(5)	2.332 (2)

Table 12 (*cont.*)

Na(3)—O(5^{i})	2.431 (2)	Na(3)—O(6^{viii})	2.522 (2)
Na(3)—O(6^{vi})	2.301 (2)	Na(3)—O(8^{i})	2.466 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 0.5, 1.5 - y, 1 - z$; (iii) $x - 0.5, 0.5 - y, 1 - z$; (iv) $1 - x, y, 1.5 - z$; (v) $0.5 + x, 0.5 + y, 1.5 - z$; (vi) $x + 0.5, 1.5 - y, 1 - z$; (vii) $1.5 - x, 0.5 + y, z$; (viii) $0.5 - x, 0.5 + y, z$.

Trisodium phosphoglycolate tetrahydrate (monoclinic modification) (VIII)

Na(1)—O(7)	2.396 (2)	Na(1)—O(7^{i})	2.554 (3)
Na(1)—O(8)	2.346 (2)	Na(1)—O(9)	2.439 (3)
Na(1)—O(9^{ii})	2.351 (2)	Na(1)—O(10)	2.425 (2)
Na(2)—O(1)	2.421 (2)	Na(2)—O(2^{iii})	2.542 (2)
Na(2)—O(3)	2.692 (2)	Na(2)—O(5^{iv})	2.475 (2)
Na(2)—O(6^{iv})	2.548 (2)	Na(2)—O(8)	2.552 (2)
Na(2)—O(10)	2.429 (3)	Na(3)—O(2^{iv})	2.846 (2)
Na(3)—O(3^{v})	2.553 (2)	Na(3)—O(5^{v})	2.492 (3)
Na(3)—O(5^{iv})	2.421 (2)	Na(3)—O(6^{vi})	2.465 (3)
Na(3)—O(6^{vii})	2.369 (2)		

Symmetry code: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x - 1, y, z$; (iv) $x - 0.5, 0.5 - y, 0.5 + z$; (v) $x, y, z + 1$; (vi) $x - 1, y, z + 1$; (vii) $x - 0.5, 0.5 - y, 1.5 + z$.

cyclic dimers are formed (Fig. 10). The O(7) water molecule forms two hydrogen bonds (as donor) with phosphate O atoms from anions *A* and *B* (Table 11) and coordinates to two sodium cations (Table 12). Two Na^+ cations [Na(1) and Na(3)] are pentacoordinate and the remaining three are hexacoordinate, forming bonds with phosphate, carboxylate and water O atoms.

Structure (VI). In the crystal, the phosphate groups of two PG residues related by a center of symmetry are joined by a short hydrogen bond with an O···O distance of 2.441 (3) Å. The resulting bis(glycolate) pentaanion is shown in Fig. 11. The packing of the crystal is shown in Fig. 12. The O(7) water molecule (as donor) forms hydrogen bonds with the O(8) water molecule and the O(3^{ii}) phosphate atom. The O(8) water molecule (as donor) forms hydrogen bonds with carboxylate O atoms of adjacent anions (Table 11). In such a way, an extensive net is generated. Of the three crystallographically distinct sodium cations, two are in general positions and one [Na(3)] is situated on a twofold axis. Na(2) and Na(3) are hexacoordinate and Na(1) is pentacoordinate, forming bonds with phosphate, carboxylate and water O atoms (Table 12).

Structure (VII). The crystals are composed of phosphoglycolate trianions (Fig. 13), Na^+ cations and water molecules of hydration. The water molecules [O(10) and O(11)] are disordered around twofold axes. There are three crystallographically independent Na^+ ions in the structure. The nature of their interaction with the surroundings is different. Na(1) has five nearest neighbors. Two are contributed by the phosphate O atoms of two different PG^{3-} ions, two are part of the same carboxylate group, and the fifth is a water O atom. Na(2) is

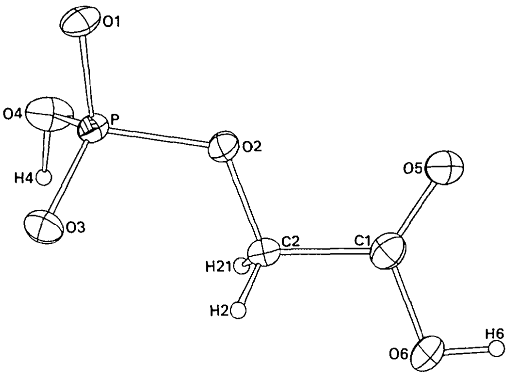


Fig. 5. The molecular structure of the phosphoglycolate monoanion in the sodium salt (III).

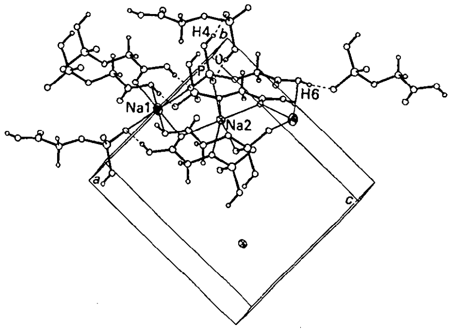
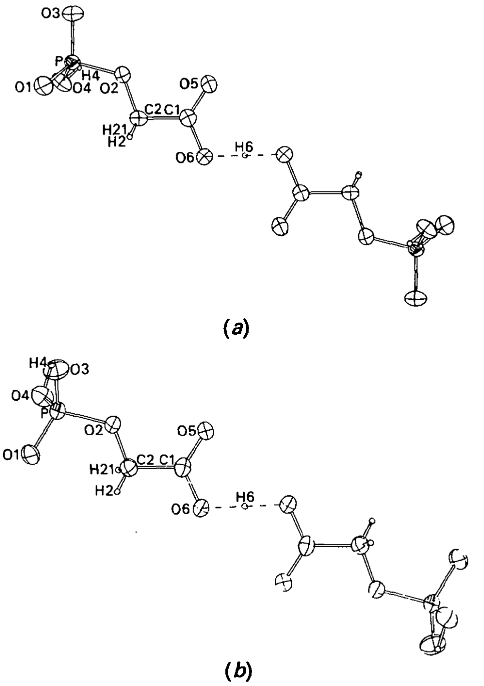


Fig. 6. The packing in the crystal of sodium phosphoglycolate (III).



(*a*)

(*b*)

Fig. 7. The molecular structure of the two crystallographically independent (*A* and *B*) bis(phosphoglycolate) trianions (IV).

coordinated only to water molecules. Four coordination places are utilized by O(7^{iv}), O(7^{v}), O(9^{i}) and O(9^{vi}). Three more are taken up by O(10^{vii}), O(10^{v}) and O(11^{v}), which have occupation factors of 0.5. The average coordination number of this cation is therefore 5.5. Na(3) is hexacoordinate (one phosphate, one water molecule and four carboxylate O atoms). All water H atoms that have been located are utilized in hydrogen bonds with phosphate O atoms (Fig. 14, Table 11).

Structure (VIII). The crystals are composed of phosphoglycolate trianions (Fig. 15), three crystallographically independent Na$^+$ cations and four

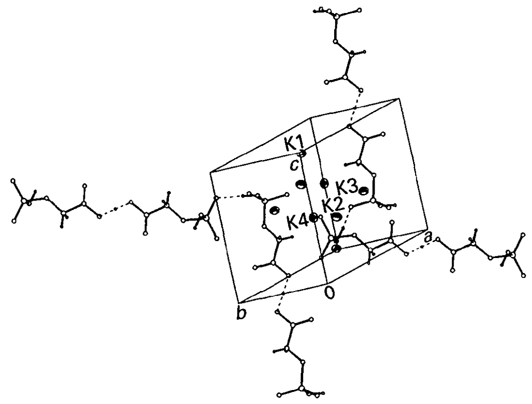
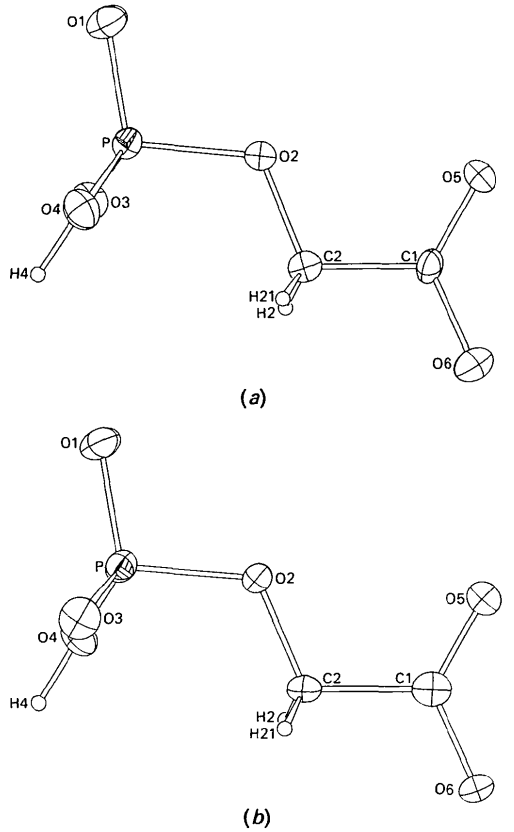


Fig. 8. The packing in the crystal of tripotassium bis(phosphoglycolate) (IV).



(*a*)

(*b*)

Fig. 9. The molecular structure of the two crystallographically independent (*A* and *B*) phosphoglycolate dianions (V).

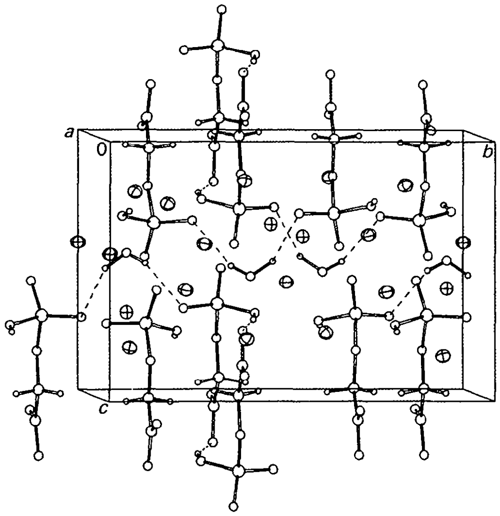


Fig. 10. The packing in the crystal of disodium phosphoglycolate hemihydrate (V).

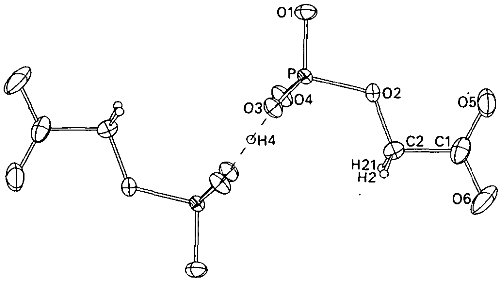


Fig. 11. The structure of the bis(phosphoglycolate) pentaanion (VI).

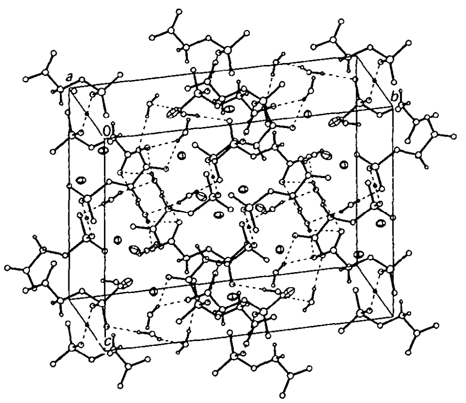


Fig. 12. The packing in the crystal of pentasodium bis(phosphoglycolate) tetrahydrate (VI).

independent water molecules. The Na(1) ion coordinates to six water molecules only. Na(2) is heptacoordinate (three phosphate, two carboxylate and two water O atoms). Na(3) is hexacoordinate (two phosphate and four carboxylate O atoms). All water H atoms are involved in hydrogen bonds to phosphate with the exception of O(8)—H(8)···O(7^{iii}). The O(4) atom accepts four H atoms and thus is formally pentacoordinate (Table 12). This situation is sometimes observed in organic phosphate crystals (Weichsel & Lis, 1990).

In this work, the molecular structures of phosphoglycolates at all levels of protonation have been described. The crystallization of the PG residue in different ionization states from water solutions suggests that it is stable over a large range of pH. This is in contrast with phosphoenolpyruvate (PEP), some forms of which hydrolyze easily and therefore require special conditions to be isolated in the crystalline state (Weichsel & Lis, 1991). The tendency of highly ionized phosphates groups to form hydrated crystals is typical behavior for both organic and inorganic salts. On going from phosphoglycolic acid to the triionized anion, it is apparent that the first proton to dissociate comes from the phosphate group, that the second H atom to dissociate is lost from the carboxylic group and that the third dissociation involves the second (less-acidic) H atom from the phosphate group. [In the ternary complex enolase–Zn^{2+}–PG, phosphoglycolate is bound to the Zn^{2+} ion through the carboxylic group in a monodentate fashion (Lebioda, Stec, Brewer & Tykarska, 1991). It may therefore be concluded that PG in this complex probably exists as the dianion. This is in accordance with the solution pH during crystal preparation.] The isolation of the $(C_2H_3O_6P\cdots H\cdots C_2H_3O_6P)^{3-}$ and $(C_2H_2O_6P\cdots H\cdots C_2H_2O_6P)^{5-}$ bisanions indicates that such moieties may also be formed in concentrated water soutions at appropriate pH ranges. It is already known that in the case of glycolic acid the bisglycolate residues are readily prepared (Golič & Speakman, 1965).

The main points of interest in the PG structure are the description of the phosphate-group orientation with respect to the acetate group, the phosphate-group deviation from tetrahedral shape and the phosphate ester bond length [P—O(2)].

The configuration of the C—COO atoms of each PG moiety is quite closely planar. There is also an evident tendency for the ester O(2) atom to lie in this

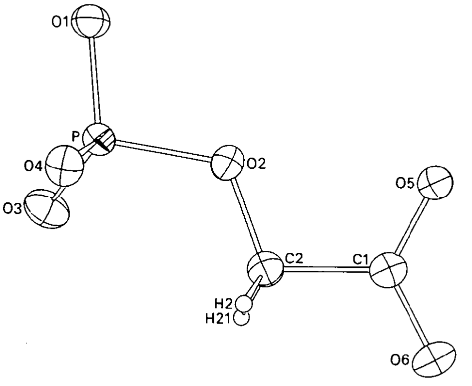


Fig. 13. The structure of the phosphoglycolate trianion in the orthorhombic modification of trisodium phosphoglycolate tetrahydrate (VII).

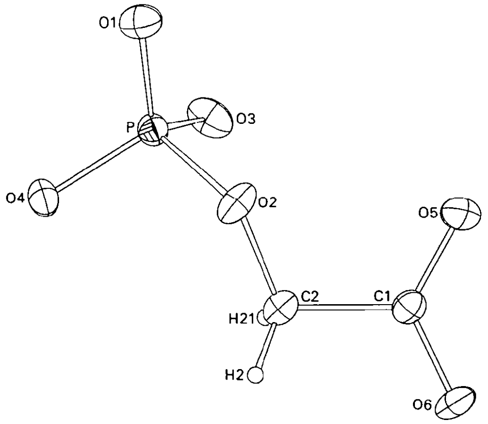


Fig. 15. The structure of the phosphoglycolate trianion in the monoclinic modification of trisodium phosphoglycolate tetrahydrate (VIII).

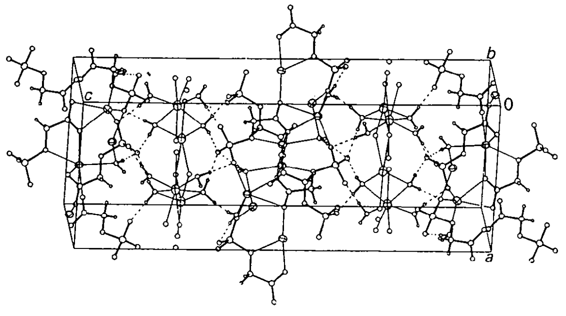


Fig. 14. The packing of the orthorhombic modification of trisodium phosphoglycolate tetrahydrate (VII).

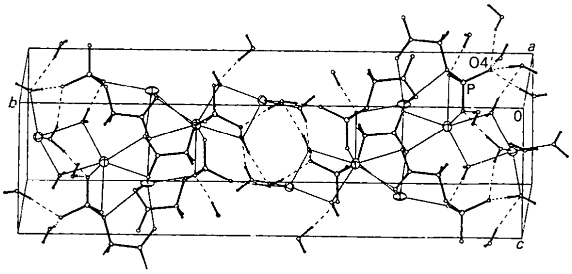


Fig. 16. The packing of the monoclinic modification of trisodium phosphoglycolate tetrahydrate (VIII).

plane, as indicated by the O(2)—C(2)—C(1)—O(5) and O(2)—C(2)—C(1)—O(6) conformation angles (Table 10). The maximum displacements of the O(2) atom from this plane are observed in molecule *B* of (IV) [0.51 (1) Å] and in (VIII) [0.49 (1) Å]. Similar trends have been noted in other structures containing the glycolate moiety (Lis, 1980, and references therein). The orientation of the phosphate group relative to the acetate moiety may be described by torsion angles P—O(2)—C(2)—C(1) and O—P—O(2)—C(2) (Table 10). The values of these angles suggest considerable conformational flexibility around the P—O(2) and O(2)—C(2) bonds. It is interesting to note that the carboxylic OH group is *trans* to the O ester atom in (I), (III) and (IV) but *syn* in (II). Both these structural variations were also observed in PEP salts (Lis, 1992).

Bond lengths, bond angles and torsion angles of the ten PG residues described in this work are collected in Table 10. In two crystals, two PG moieties occur in the asymmetric unit. Among the bonds only P—O(2) is partially correlated with the degree of ionization of PG. This bond varies from 1.566 (2) Å in H_3PG (I) to 1.635 (2) Å in the trianion (VIII). However, the values of this bond for the ionized forms with charges 1, 1.5, 2 and 2.5 do not correlate strictly with the degree of ionization of PG. This is in contrast with PEP (Weichsel & Lis, 1991). To facilitate comparison with other phosphate monoester structures, the statistical analysis of the geometry of the singly and doubly ionized phosphate groups in phosphate monoesters was performed (Starynowicz, 1986; Starynowicz, Lis & Weichsel, 1986). Mean values of 1.593 and 1.624 Å were found for P—O(ester) bond lengths in singly and doubly ionized phosphate groups, respectively. In a few examples of non-ionized phosphate groups in non-aromatic phosphate monoesters, the P—O(ester) bond length ranges from 1.567 (4) Å (Srikrishnan, Friday & Parthasarathy, 1979) to 1.594 (3) Å (Weichsel, Lis & Kuczek, 1991); thus, this bond in H_3PG (I) [1.566 (2) Å] is amongst the shortest.

The other bond lengths and angles in the structures are normal within experimental error and do not merit comment. The hydrogen bonds and sodium or potassium coordination are probably the most inportant factors which affect the shape of the system.

Note added in proof. Three new PG structures: $Zn(H_2PG)_2.2H_2O$, $Ca(H_2PG)_2.2H_2O$ and $K_3PG.$-$2H_2O$ were recently determined by the author.

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Structure of 1,2-Diphenylcarbaborane, 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$

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Abstract. 1,2-Diphenyl-1,2-dicarba-*closo*-dodecaborane(12), $C_{14}H_{20}B_{10}$, $M_r = 296.41$, monoclinic, $P2_1/c$, $a = 10.832\,(4)$, $b = 24.890\,(13)$, $c = 13.9243\,(21)$ Å, $\beta = 111.881\,(21)°$, $V = 3483.6$ Å^3, $Z = 8$, $D_x = 1.130$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.051$ mm^{-1}, $F(000) = 1232$, $T = 291\,(1)$ K, $R =$

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