$wR = 0.053$
$S = 1.62$
1517 reflections
269 parameters
All H-atom parameters
  refined

$\Delta\rho_{max} = 0.2$ e Å^{-3}
$\Delta\rho_{min} = -0.2$ e Å^{-3}
Atomic scattering factors
from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
O1	0.6586 (3)	0.2952 (2)	0.3367 (2)	0.0497 (8)
O2	0.6043 (3)	0.1472 (2)	0.4290 (2)	0.0583 (9)
O3	0.4789 (4)	0.3309 (3)	0.7122 (2)	0.0712 (11)
C2	0.6585 (4)	0.2470 (3)	0.4147 (2)	0.0420 (10)
C2a	0.7332 (4)	0.3381 (3)	0.4746 (2)	0.0361 (10)
C3	0.6665 (4)	0.3319 (3)	0.5611 (2)	0.0359 (9)
C4	0.5500 (4)	0.4108 (3)	0.5787 (2)	0.0355 (9)
C5	0.4930 (4)	0.4950 (3)	0.5132 (2)	0.0374 (10)
C6	0.4989 (4)	0.6041 (3)	0.3736 (2)	0.0452 (11)
C7	0.5128 (5)	0.5364 (4)	0.2894 (2)	0.0541 (13)
C8	0.6739 (5)	0.4943 (4)	0.2690 (3)	0.0585 (14)
C8a	0.7420 (4)	0.4137 (3)	0.3364 (2)	0.0460 (11)
C8b	0.7247 (4)	0.4617 (3)	0.4272 (2)	0.0374 (9)
C8c	0.5669 (4)	0.5204 (3)	0.4418 (2)	0.0365 (9)
C9	0.8592 (5)	0.5467 (4)	0.4524 (3)	0.0555 (14)
C10	0.7327 (6)	0.2355 (5)	0.6177 (3)	0.057 (2)
C11	0.4745 (4)	0.4167 (3)	0.6630 (2)	0.0437 (10)
C12	0.3961 (7)	0.5347 (5)	0.6877 (3)	0.067 (2)
C13	0.3280 (5)	0.6333 (4)	0.3892 (3)	0.0573 (15)
C14	0.5833 (7)	0.7295 (4)	0.3693 (4)	0.066 (2)

Table 2. *Selected geometric parameters* (Å, °)

C2—O1	1.347 (4)	C8c—C5	1.334 (5)
C8a—O1	1.468 (4)	C7—C6	1.533 (5)
C2—O2	1.196 (4)	C8c—C6	1.530 (5)
C11—O3	1.214 (4)	C13—C6	1.532 (6)
C2a—C2	1.516 (5)	C14—C6	1.540 (6)
C3—C2a	1.495 (4)	C8—C7	1.501 (6)
C8b—C2a	1.535 (4)	C8a—C8	1.503 (6)
C4—C3	1.348 (4)	C8b—C8a	1.545 (5)
C10—C3	1.492 (6)	C8c—C8b	1.522 (4)
C5—C4	1.469 (4)	C9—C8b	1.535 (5)
C11—C4	1.495 (5)	C12—C11	1.496 (6)
C2—O1—C8a	109.9 (3)	C14—C6—C7	110.0 (3)
C2a—C2—O1	109.3 (3)	C8—C7—C6	114.0 (3)
C2a—C2—O2	129.1 (3)	C8a—C8—C7	112.6 (3)
O1—C2—O2	121.6 (3)	C8b—C8a—O1	104.0 (3)
C3—C2a—C8b	118.3 (3)	C8b—C8a—C8	115.9 (3)
C3—C2a—C2	112.8 (3)	O1—C8a—C8	108.3 (3)
C8b—C2a—C2	103.5 (3)	C8c—C8b—C9	113.0 (3)
C4—C3—C10	127.0 (3)	C8c—C8b—C2a	109.2 (3)
C4—C3—C2a	116.9 (3)	C8c—C8b—C8a	111.7 (3)
C10—C3—C2a	116.1 (3)	C9—C8b—C2a	110.8 (3)
C5—C4—C11	117.7 (3)	C9—C8b—C8a	111.9 (3)
C5—C4—C3	119.6 (3)	C2a—C8b—C8a	99.5 (2)
C11—C4—C3	122.7 (3)	C5—C8c—C6	122.9 (3)
C8c—C5—C4	124.9 (3)	C5—C8c—C8b	118.3 (3)
C7—C6—C8c	108.1 (3)	C6—C8c—C8b	118.8 (3)
C7—C6—C13	108.4 (3)	C12—C11—O3	119.6 (3)
C8c—C6—C13	112.2 (3)	C12—C11—C4	118.1 (3)
C8c—C6—C14	111.6 (3)	O3—C11—C4	122.3 (3)
C13—C6—C14	106.5 (3)		

The ω-scan width was symmetrical over 1.2% about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and -1.0 in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min^{-1} (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV).

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Tripotassium Phosphoglycolate Dihydrate and Tris(cyclohexylammonium) Phosphoglycolate Trihydrate

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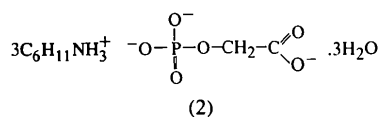
Abstract

The structures of the potassium and cyclohexylammonium salts of the phosphoglycolate trianion, $3K^+.C_2H_2O_6P^{3-}.2H_2O$ and $3C_6H_{14}N^+.C_2H_2O_6P^{3-}.3H_2O$, respectively, have been determined by X-ray analysis. The respective ester P—O bond lengths are 1.642 (2) and 1.628 (3) Å.

Comment

This work is part of a systematic study of the structures of phosphoglycolate (PG) residues in different ionization states and different chemical environments (Lis, 1993, 1994). The potassium salt and some other phosphoglycolate and phosphoenolpyruvate crystals are now the subject of investigations aimed at finding the experimental electron density in organic phosphate esters. The structures of the title salts (1) and (2) are reported here.

$$3K^+ \quad {}^-O{-}\overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{P}}{-}O{-}CH_2{-}C\overset{\diagup O}{\diagdown_{O^-}} \quad .2H_2O$$

(1)

$$3C_6H_{11}NH_3^+ \quad {}^-O{-}\overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{P}}{-}O{-}CH_2{-}C\overset{\diagup O}{\diagdown_{O^-}} \quad .3H_2O$$

(2)
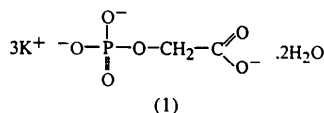
Crystals of the potassium salt (1) are composed of phosphoglycolate trianions (Fig. 1), K$^+$ cations and water molecules of hydration. There are three crystallographically independent K$^+$ ions in the structure. K1 and K2 are octacoordinate and K3 is hexacoordinate. All of them form irregular polyhedra (Fig. 2). K1 is bound to four symmetry related PG^{3-} anions and to three water molecules. K2 coordinates four PG^{3-} anions and two water molecules. The K3 octahedron is formed by the O atoms of one water molecule and four PG^{3-} anions; three of these PG^{3-} anions are attached to K3 by one O atom while the fourth is bidentate, the chelating atoms being O3 and O4. Thus, the O atoms of the single crystallographically independent PG^{3-} anion are bonded to the K$^+$ ions either twice (O2, O3 and O5), three times (O1 and O6) or four times (O4). Consequently, the PG^{3-} anion as a whole coordinates or bridges eleven K$^+$ ions forming a very close-packed structure. Furthermore, all water H atoms are involved in hydrogen bonds (Table 3). A very stable three-dimensional network is thereby formed. Note that the O7 water molecule forms (as a donor) two hydrogen bonds and is coordinated to four K$^+$ ions so that it is formally hexacoordinate.

The crystals of the cyclohexylammonium salt (2) are built up of phosphoglycolate trianions (Fig. 3), three crystallographically independent cyclohexylammonium cations and water molecules of hydration. All independent cyclohexyl rings adopt chair conformations. The crystal packing is very characteristic (Fig. 4). There is an extensive three-dimensional hydrogen-bond network in which all N- and O-bonded H atoms (Table 6) are involved. As a consequence, a columnar structure parallel to the c axis is formed in which all hydrophobic parts of the cyclohexylammonium cations are close to one another.

The molecular shapes of the phosphoglycolate trianions in both crystals (Figs. 1 and 3) are similar to those observed in other crystals of PG. The C—COO$^-$ group
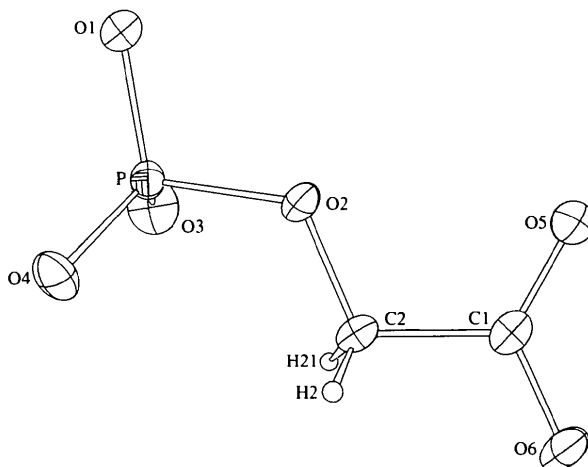

Fig. 1. The molecular structure of the phosphoglycolate trianion in tripotassium phosphoglycolate dihydrate (1). Displacement ellipsoids are shown at the 50% probability level.
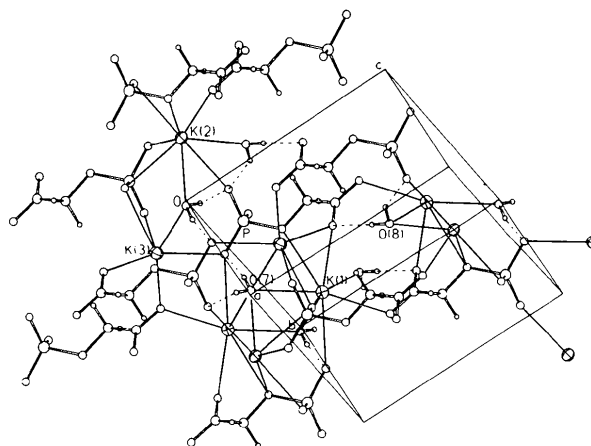

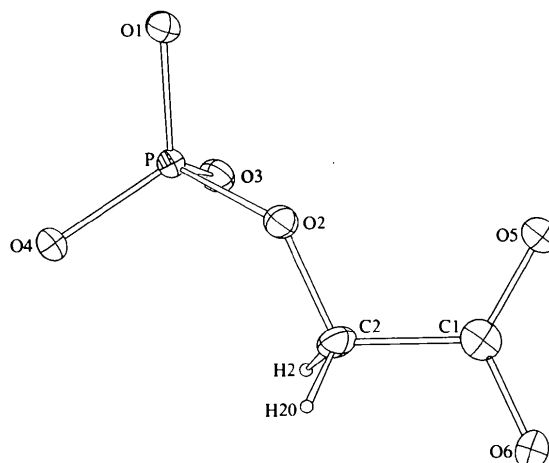Fig. 2. The packing arrangement in the crystal of tripotassium phosphoglycolate dihydrate (1).

Fig. 3. The molecular structure of the phosphoglycolate trianion in tris(cyclohexylammonium) phosphoglycolate trihydrate (2). Displacement ellipsoids are shown at the 50% probability level.
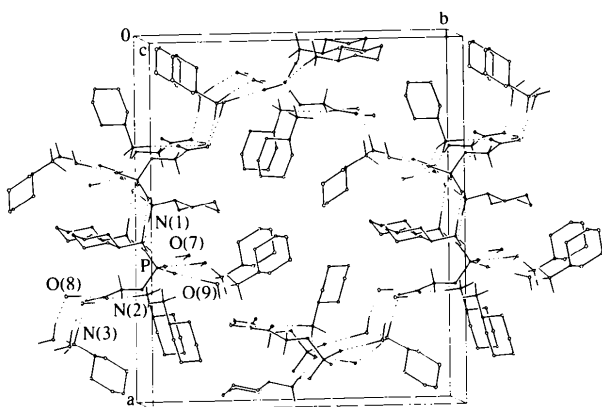
Fig. 4. The packing arrangement in the crystal of tris(cyclohexyl-ammonium) phosphoglycolate trihydrate (2).

of each PG trianion is planar. There is also a tendency for the ester O2 atom to lie in this plane. Differences are visible in the orientation of the phosphate groups relative to the acetoxy moieties, as may be seen from the P—O2—C2—C1 and O—P—O2—C2 torsion angles (Tables 2 and 5). The ester P—O bond lengths are 1.642 (2) and 1.628 (3) Å in compounds (1) and (2), respectively. The value in (1) is the longest among all known PG structures and is even longer than the corresponding bond in triammonium phosphoenolpyruvate (Weichsel & Lis, 1994). It may be concluded that this is the effect of the previously described coordination to the K^+ ions.

Experimental

Colourless crystals of the potassium salt (1) were grown by slow concentration of an aqueous solution containing a 1:3 molar ratio of phosphoglycolic acid (Lis, 1993) and KOH. The density D_m of the crystal of (1) was measured by flotation in $C_2H_4Br_2/CCl_4$. Commercially available tris(cyclohexylammonium) phosphoglycolate (2) (Sigma) was recrystallized from water (a second monoclinic form was obtained from methanol).

Compound (1)

Crystal data

$3K^+.C_2H_2O_6P^{3-}.2H_2O$
$M_r = 306.34$
Triclinic
$P\bar{1}$
$a = 7.296 (4)$ Å
$b = 7.451 (3)$ Å
$c = 9.333 (4)$ Å
$\alpha = 87.77 (5)°$
$\beta = 79.45 (5)°$
$\gamma = 82.03 (4)°$
$V = 493.9 (4)$ Å^3
$Z = 2$
$D_x = 2.060 (3)$ Mg m^{-3}
$D_m = 2.02$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 11–16°$
$\mu = 1.558$ mm^{-1}
$T = 296 (2)$ K
Large thick plate
$0.2 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Syntex $P2_1$ four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
3002 measured reflections
2902 independent reflections
2450 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.015$
$\theta_{max} = 30°$
$h = -10 \rightarrow 0$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 12$
2 standard reflections monitored every 50 reflections
intensity decay: 6%

Refinement

Refinement on F^2
$R(F) = 0.0263$
$wR(F^2) = 0.0665$
$S = 1.082$
2367 reflections
151 parameters
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.11P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.12$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

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

	x	y	z	U_{eq}
P	0.12694 (5)	0.19370 (5)	0.13494 (4)	0.01533 (9)
O1	0.2440 (2)	0.2249 (2)	-0.01413 (13)	0.0236 (3)
O2	0.2468 (2)	0.2756 (2)	0.24396 (12)	0.0233 (3)
O3	0.1222 (2)	-0.0044 (2)	0.17585 (15)	0.0267 (3)
O4	-0.0650 (2)	0.3043 (2)	0.15613 (14)	0.0237 (3)
O5	0.4910 (2)	0.2564 (2)	0.43164 (14)	0.0294 (3)
O6	0.2583 (2)	0.2818 (2)	0.62475 (13)	0.0278 (3)
O7	0.6034 (2)	0.2470 (2)	0.01221 (15)	0.0272 (3)
O8	0.7278 (3)	0.2696 (3)	0.63435 (19)	0.0403 (4)
C2	0.1716 (3)	0.2703 (3)	0.3963 (2)	0.0266 (4)
C1	0.3210 (3)	0.2703 (3)	0.4904 (2)	0.0191 (3)
K1	0.58545 (5)	0.50068 (5)	0.20978 (4)	0.02332 (9)
K2	0.05386 (5)	-0.35918 (5)	0.16374 (4)	0.02282 (9)
K3	0.29230 (6)	-0.03470 (5)	-0.22480 (4)	0.02740 (10)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

P—O1	1.521 (2)	O2—C2	1.428 (2)
P—O2	1.642 (2)	C1—C2	1.520 (2)
P—O3	1.513 (2)	C1—O5	1.253 (2)
P—O4	1.507 (2)	C1—O6	1.256 (2)
O1—P—O2	101.9 (1)	C2—O2—P	116.6 (2)
O1—P—O3	113.8 (1)	O2—C2—C1	112.7 (2)
O1—P—O4	112.6 (1)	O5—C1—C2	119.6 (2)
O2—P—O3	106.8 (1)	O6—C1—C2	114.6 (2)
O2—P—O4	107.2 (1)	O5—C1—O6	125.7 (2)
O3—P—O4	113.4 (1)		
O4—P—O2—C2	60.4 (2)	P—O2—C2—C1	155.5 (2)
O3—P—O2—C2	-61.5 (2)	O2—C2—C1—O5	-7.1 (3)
O1—P—O2—C2	178.9 (2)	O2—C2—C1—O6	174.0 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °) *for* (1)

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7···O3^i	0.92 (4)	1.87 (4)	2.776 (2)	169 (4)
O7—H71···O1	0.83 (3)	1.83 (4)	2.653 (2)	174 (3)
O8—H8···O5	0.86 (3)	1.94 (4)	2.799 (2)	172 (3)
O8—H81···O3^{ii}	0.92 (3)	2.04 (3)	2.842 (2)	145 (3)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, -y, 1 - z$.

Compound (2)

Crystal data (at 299 K in square brackets)
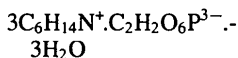
$3C_6H_{14}N^+.C_2H_2O_6P^{3-}.$
$3H_2O$
$M_r = 507.60$
Orthorhombic
$Pna2_1$
$a = 22.512\,(9)$ [23.64 (3)] Å
$b = 19.613\,(9)$ [19.49 (2)] Å
$c = 6.201\,(3)$ [6.222 (7)] Å
$V = 2737.9\,(21)$
$\quad$ [2867 (6)] Å^3
$Z = 4$
$D_x = 1.231\,(2)$
$\quad$ [1.176 (3)] Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 40 [25] reflections
$\theta = 10\text{--}15$ [9–15]°
$\mu = 0.149$ mm^{-1}
$T = 85\,(2)$ [299 (1)] K
Needle
$0.8 \times 0.15 \times 0.15$ mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
$\quad$ none
2941 measured reflections
2941 independent reflections
2157 observed reflections
$\quad$ [$I > 2\sigma(I)$]

$\theta_{max} = 26°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 7$
3 standard reflections
$\quad$ monitored every 100
$\quad$ reflections
$\quad$ intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0431$
$wR(F^2) = 0.1157$
$S = 1.096$
2157 reflections
342 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2$
$\quad + 2.69P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.078$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Atomic scattering factors
from *International Tables*
for Crystallography (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (2)

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

	x	y	z	U_{eq}
P	0.62657 (5)	0.04293 (6)	0.5	0.0103 (2)
O1	0.6450 (2)	0.1043 (2)	0.3698 (6)	0.0147 (8)
O2	0.6851 (2)	−0.0053 (2)	0.4762 (7)	0.0148 (7)
O3	0.5746 (2)	0.0040 (2)	0.4090 (6)	0.0139 (7)
O4	0.6181 (2)	0.0556 (2)	0.7411 (6)	0.0152 (8)
O5	0.7129 (2)	−0.1038 (2)	0.1809 (6)	0.0188 (8)
O6	0.7143 (2)	−0.1834 (2)	0.4412 (6)	0.0174 (8)
O7	0.6045 (2)	0.1700 (2)	−0.0023 (7)	0.0172 (7)
O8	0.7115 (2)	−0.2189 (2)	−0.1196 (7)	0.0229 (9)
O9	0.6743 (2)	0.2368 (2)	0.4303 (7)	0.0250 (9)
N1	0.4550 (2)	0.0301 (2)	0.4954 (9)	0.0121 (8)
N2	0.7082 (2)	0.0337 (2)	0.0369 (7)	0.0132 (9)
N3	0.8313 (2)	−0.2192 (2)	0.3479 (8)	0.0198 (10)
C1	0.7053 (2)	−0.1238 (3)	0.3719 (9)	0.0148 (11)
C2	0.6824 (2)	−0.0748 (3)	0.5419 (9)	0.0156 (11)
C11	0.4413 (2)	0.1033 (3)	0.4511 (8)	0.0120 (10)
C12	0.4588 (2)	0.1478 (3)	0.6409 (9)	0.0161 (10)
C13	0.4451 (3)	0.2223 (3)	0.5914 (10)	0.0200 (12)
C14	0.4774 (3)	0.2459 (3)	0.3843 (9)	0.0193 (12)
C15	0.4609 (3)	0.2008 (3)	0.1954 (9)	0.0162 (11)
C16	0.4739 (3)	0.1259 (3)	0.2448 (9)	0.0152 (11)
C21	0.7694 (2)	0.0554 (3)	−0.0239 (9)	0.0150 (10)
C22	0.8078 (3)	0.0578 (3)	0.1803 (9)	0.0199 (12)

C23	0.8705 (3)	0.0827 (3)	0.1259 (11)	0.0224 (12)
C24	0.8692 (3)	0.1516 (3)	0.0113 (13)	0.0245 (12)
C25	0.8306 (3)	0.1488 (3)	−0.1887 (11)	0.0265 (13)
C26	0.7673 (3)	0.1244 (3)	−0.1331 (11)	0.0227 (12)
C31	0.8641 (3)	−0.1528 (3)	0.3707 (10)	0.0178 (12)
C32	0.9261 (3)	−0.1607 (3)	0.2766 (11)	0.0227 (12)
C33	0.9614 (3)	−0.0946 (3)	0.3036 (13)	0.0325 (18)
C34	0.9633 (3)	−0.0718 (3)	0.5388 (13)	0.0378 (18)
C35	0.9016 (3)	−0.0651 (3)	0.6319 (12)	0.0317 (15)
C36	0.8657 (3)	−0.1314 (3)	0.6031 (11)	0.0242 (13)

Table 5. *Selected geometric parameters (Å, °) for* (2)

P—O1	1.507 (4)	C1—C2	1.516 (7)
P—O2	1.628 (3)	O2—C2	1.425 (6)
P—O3	1.508 (4)	O5—C1	1.259 (7)
P—O4	1.528 (4)	O6—C1	1.262 (6)
O1—P—O2	101.1 (2)	C2—O2—P	119.7 (3)
O1—P—O3	114.7 (2)	O5—C1—O6	125.9 (5)
O1—P—O4	115.4 (2)	O5—C1—C2	120.2 (4)
O2—P—O3	107.5 (2)	O6—C1—C2	113.9 (5)
O2—P—O4	106.5 (2)	O2—C2—C1	113.2 (4)
O3—P—O4	110.6 (2)		
O1—P—O2—C2	−168.0 (4)	P—O2—C2—C1	129.7 (4)
O3—P—O2—C2	−47.5 (4)	O5—C1—C2—O2	−14.1 (7)
O4—P—O2—C2	71.1 (4)	O6—C1—C2—O2	166.8 (4)

Table 6. *Hydrogen-bonding geometry (Å, °) for* (2)

D—H···A	H···A	D···A	D—H···A
O7—H7···O4^i	1.80 (4)	2.768 (5)	176 (5)
O7—H71···O1	1.85 (4)	2.796 (5)	166 (5)
O8—H8···O5	1.96 (4)	2.928 (5)	173 (5)
O8—H81···O6^i	1.89 (3)	2.812 (6)	157 (5)
O9—H9···O8^{ii}	1.82 (4)	2.732 (6)	155 (5)
O9—H91···O1	1.74 (3)	2.708 (5)	173 (5)
N1—H1N1···O4^{iii}	1.83 (5)	2.833 (5)	175 (5)
N1—H2N1···O3^{iv}	1.81 (4)	2.732 (6)	151 (4)
N1—H3N1···O3	1.79 (3)	2.792 (5)	175 (4)
N2—H1N2···O5	1.84 (3)	2.843 (5)	175 (5)
N2—H2N2···O4^i	1.78 (5)	2.767 (6)	168 (4)
N2—H3N2···O1	1.90 (5)	2.864 (5)	160 (4)
N3—H1N3···O9^v	1.74 (3)	2.732 (7)	173 (5)
N3—H2N3···O6	1.81 (4)	2.787 (6)	164 (5)
N3—H3N3···O7^{vi}	1.79 (5)	2.769 (6)	166 (5)

Symmetry codes: (i) $x, y, z-1$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iii) $1-x, -y, z-\frac{1}{2}$; (iv) $1-x, -y, \frac{1}{2}+z$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (vi) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$.

Preliminary examinations were by oscillation and Weissenberg photographs. For compound (2), initially, a room-temperature data set was collected. However, most of the final displacement parameters for the cyclohexylammonium C atoms had very high values and the C—C bond lengths were unrealistic. Therefore, new low-temperature diffractometer data were collected. A crystal fragment was mounted on a diffractometer equipped with an Oxford Cryosystem Cryostream Cooler and the temperature decreased slowly to 85 K. In the refinement of the 85 K data the positions of the C-bonded H atoms were deduced using stereochemical criteria and refined using a riding model. The remaining H atoms were found from a difference synthesis and refined with restraints for O—H (0.97 Å) and N—H (1.00 Å) bonds. All H atoms in compound (1) were found from a difference synthesis and refined isotropically.

Data collection: *XTL/XTLE Structure Determination System* (Syntex, 1976) for (1); Kuma KM-4 software (Kuma, 1987) for (2). Cell refinement: *XTL/XTLE Structure Determination System* for (1); Kuma KM-4 software for (2). Data reduction: *XTL/XTLE Structure Determination System* for

(1); Kuma KM-4 software for (2). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

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Potassium D-3-Phosphoglycerate and Cyclohexylammonium D-3-Phosphoglycerate Hydrate

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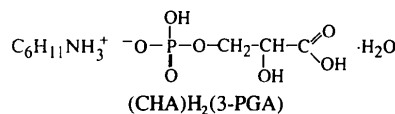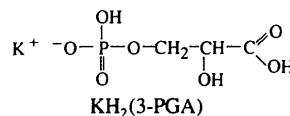## Abstract

The structures of the D-3-phosphoglycerate monoanions in the potassium [KH_2(3-PGA)] and cyclohexylammonium [(CHA)H_2(3-PGA)] salts [H_2(3-PGA) = $^-HO_3POCH_2CH(OH)(CO_2H)$] have been determined by X-ray analysis at 297 and 85 K, respectively. The C—C—C—OH torsion angles which define the relationship of the carboxylic group to the carbon backbone are $-120.2\,(2)$ and $60.1\,(3)°$, and the P—O(ester) bond lengths are 1.596 (2) and 1.600 (2) Å for KH_2(3-PGA) and (CHA)H_2(3-PGA), respectively. There are extensive networks of hydrogen bonds in both crystals in which all H atoms of the hydroxyl and ammonium groups are involved. The K^+ ion is octacoordinate.

Comment

The phosphate ester D-3-phosphoglycerate (3-PGA) is an essential intermediate in photosynthesis and glycolysis, as well as being a major building block in various biosynthetic pathways (Harper, Rodwell & Mayes, 1979). Knowledge of the three-dimensional structures of 3-PGA anions may be helpful, therefore, for complete interpretation of their interactions with macromolecules.

Unfortunately, up to now only three structures, all containing dianionic D-3-phosphoglycerate, have been published: disodium D-3-phosphoglycerate (Fewster & Fenn, 1982), barium D-3-phosphoglycerate dihydrate (Kamiya, Cruse & Kennard, 1983) and cadmium D-3-phosphoglycerate trihydrate (Mostad & Rosenqvist, 1971). In order to assess the influence of pH and chemical environment on the geometry of phosphoglycerates, we have begun a study of a number of crystal structures containing these anions in different ionization states. In this paper, the crystal structures of the potassium and cyclohexylammonium salts of monoionized phosphoglycerate, KH_2(3-PGA) and (CHA)H_2(3-PGA), respectively, are reported.

$$K^+ \;\; ^-O-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-CH_2-\overset{}{\underset{\underset{\displaystyle OH}{|}}{CH}}-C\overset{\diagup O}{\diagdown OH}$$

$$KH_2(3\text{-}PGA)$$

$$C_6H_{11}NH_3^+ \;\; ^-O-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-CH_2-\overset{}{\underset{\underset{\displaystyle OH}{|}}{CH}}-C\overset{\diagup O}{\diagdown OH} \;\; \cdot H_2O$$

$$(CHA)H_2(3\text{-}PGA)$$

The KH_2(3-PGA) crystal consists of phosphoglycerate monoanions and potassium cations whereas the (CHA)H_2(3-PGA) crystal is built up from phosphoglycerate monoanions, cyclohexylammonium cations and water of hydration. In each structure, the O(2) hydroxyl atom lies close to the plane of the adjacent carboxylic group. The main conformational difference between the two monoanions is in the relationship of O(2) to the carboxylic hydroxyl group, O(1)H (Figs. 1 and 2): O(1) and O(2) are *syn* in KH_2(3-PGA) but *anti* in (CHA)H_2(3-PGA). As a result, the C—C—C—O(1) torsion angle, which defines the twist of the carboxylic group with respect to the glycerate residue, is $-120.2\,(2)°$ in KH_2(3-PGA) and 60.1 (3)° in (CHA)H_2(3-PGA).

The geometry of the phosphate groups (Tables 2 and 4) does not depart from that commonly found in other monophosphate organic esters (Starynowicz, 1986; Lis & Jerzykiewicz, 1993; Jerzykiewicz & Lis, 1994). The ester P—O bond lengths of 1.596 (2) Å in KH_2(3-PGA) and 1.600 (2) Å in (CHA)H_2(3-PGA) are characteristic of monoionized phosphate. The orientation of the phosphate group with respect to the atom C(2) is almost *trans* in both structures, as shown by the P—O—C—C torsion angles (Tables 2 and 4).