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Ammonium, Potassium and Lithium Salts of D,L-Glyceric Acid

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(*Received 22 February 1996; accepted 29 May 1996*)

Abstract

The crystal structures of the ammonium, potassium and lithium salts of racemic glyceric acid (ammonium glycerate, $NH_4^+.C_3H_5O_4^-$, potassium glycerate, $K^+.C_3H_5O_4^-$, and lithium glycerate, $Li^+.C_3H_5O_4^-$) have been determined by X-ray analysis. The crystals of the potassium and ammonium salts are isomorphous. The α-hydroxy O atom lies almost in the plane of the carboxylate group in all three structures. There are networks of hydrogen bonds in all three crystals in which all the H atoms of the hydroxyl groups and the N-bonded H atoms in the ammonium salt are involved.

Comment

Glycerates are known to be intermediate compounds in many metabolic pathways. They are also the precursors of the 2-phospho-D-glycerates (Heinz & Lamprecht, 1967). Only two structures (of the Ca salts of glyceric acid) have been characterized to date, di(D,L-glycerate) dihydrate (Taga, Ohashi & Osaki, 1978) and di(L-glycerate) dihydrate (Lis & Popek, 1993). In this paper, the crystal structures of the ammonium (I), potassium (II), and lithium (III) salts of D,L-glyceric acid are presented. This work is a part of our systematic study of the structures of glycerate residues in different chemical environments (Lis & Jerzykiewicz, 1996).

$$CH_2(OH){-}CH(OH){-}COO^-.\ M^+$$

(I) $M = NH_4^+$
(II) $M = K^+$
(III) $M = Li^+$

The same numbering scheme has been used for the glycerate residues of all three compounds. The structures of the anions in (I) and (II) are essentially the same, so only the view of the glycerate anion in the potassium salt is included in this work. The D-isomers of the anions of the potassium and lithium salts are shown in Figs. 1 and 2.

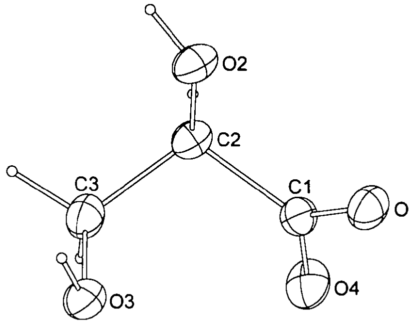

Fig. 1. The molecular structure and numbering scheme of the glycerate anion in the potassium D,L-glycerate crystal. Displacement ellipsoids are shown at the 50% probability level. The anion is shown as the D-isomer. The anion in the ammonium salt is essentially identical in structure and so is not shown as a separate figure.

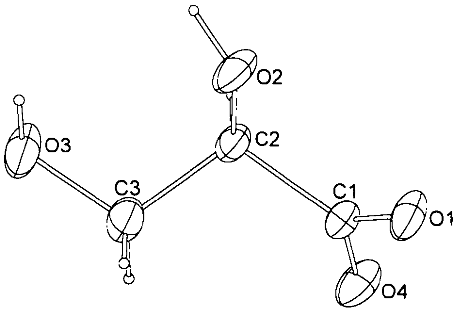

Fig. 2. The molecular structure and numbering scheme of the glycerate anion in the lithium D,L-glycerate crystal. Displacement ellipsoids are shown at the 50% probability level. The anion is shown as the D-isomer.

The crystals of (I) are composed of ammonium cations and the D- and L-glycerate anions. The structure of the crystal is stabilized by an extensive network of hydrogen bonds (Fig. 3). The NH_4^+ cation is bridged through O4, O2 and three O1 atoms to the four symmetry-related glycerate anions (Table 3). The O1 atom appears to be involved, as an acceptor, in the hydrogen-bond interaction with three different ammonium cations. The N-bonded atom H4 is involved in the bifurcated interaction with the O1 and O2 atoms of the same glycerate ion.

The crystal of (II) is isomorphous with the crystal of (I). Fig. 4 shows the crystal packing of (II). One glycerate ion chelates the K^+ ion through O1, O2 and

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

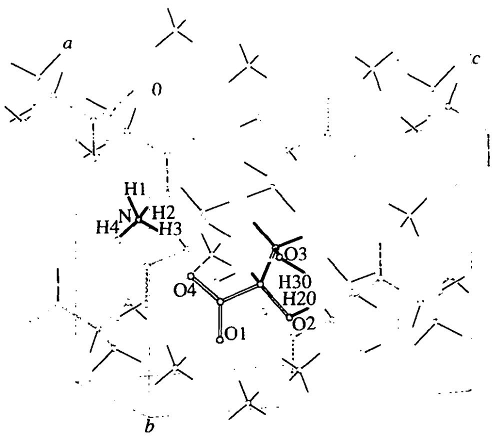

Fig. 3. The packing in the ammonium D,L-glycerate crystal.

O3, and the other one chelates through O1 and O2. Three other coordination positions are filled up by O1, O3 and O4 of three different glycerate anions. The eight-coordinated O atoms assume a distorted Archimedean antiprism. In one base of the polyhedron are atoms O1^{v}, O2^{vi}, O1^{vi} and O2^{v} and in the other, O4, O3^{v}, O1^{vii} and O3^{iv}. The K···O distances range from 2.703 (2) to 3.403 (2) Å (Table 5); the shortest K···K distance is 3.669 (2) Å. The hydroxyl groups are involved in the hydrogen bonds which form a two-dimensional network. The geometry of the hydrogen bonding in (II) is given in Table 6.

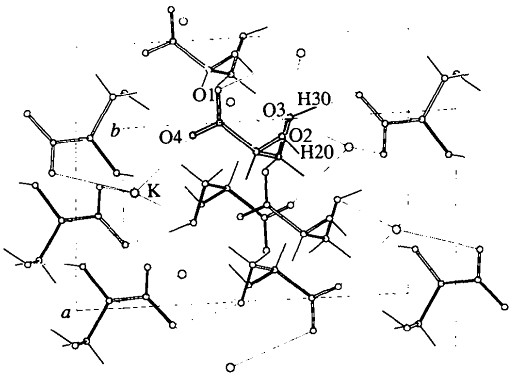

Fig. 4. The packing in the potassium D,L-glycerate crystal.

The crystals of (III) are composed of tetra-coordinated Li^{+} cations and glycerate anions. The crystal packing of (III) is shown in Fig. 5. One glycerate anion chelates the Li^{+} ion through O1 and O2 forming a five-membered ring. Another glycerate ion coordinates to the Li^{+} ion by the O4 (carboxylate) atom while the next coordinates by the O3 (β-hydroxyl) atom. These four different O atoms form a strongly distorted tetrahedral arrangement. The Li···O contacts range from 1.909 (2) to 1.934 (2) Å (Table 8). The shortest Li···Li distance is 4.465 (3) Å. The hydroxyl groups of the glycerate anion are involved as donors in the hydrogen bonds to the carboxylate O atoms of another glycerate anion. The glycerate anions linked by the hydrogen bonds form infinite chains. The hydrogen bonding geometry in (III) is given in Table 9.

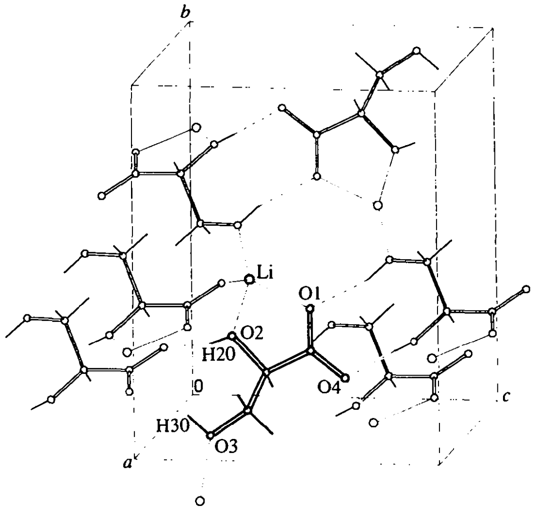

Fig. 5. The packing in the lithium D,L-glycerate crystal.

In all three structures, the α-hydroxy O atom lies almost in the plane of the carboxylate group, as in the structures of the Ca salts (Taga *et al.*, 1978; Lis & Popek, 1993). The deviations of O2 from the plane of the carboxylate group in (I), (II) and (III) are 0.015 (6), 0.084 (7) and 0.103 (5) Å, respectively.

The conformation of the glycerate ion in (III) is different from those found in (I) and (II). In (I) and (II), the β-hydroxy atom is −synclinal to the α-hydroxy atom with respect to the C2—C3 bond whereas in (III) it is +synclinal. The C3—O3 bond is +synclinal to C1—C2 with respect to the C2—C3 bond in (I) and (II) while in the lithium salt it is −antiperiplanar.

In the ammonium salt, the length of the C1—O1 bond is 0.015 (3) Å longer than that of C1—O4. In the structures of K and Li salts, the values of these bonds are comparable to within 3σ. There are no other significant differences in the values of the angles and bond lengths in the presented structures. They are in good agreement with the values reported for calcium di(D,L-glycerate) dihydrate (Taga *et al.*, 1978) and calcium di(L-glycerate) dihydrate (Lis & Popek, 1993).

Experimental

The ammonium salt of racemic glyceric acid was obtained using a significantly modified synthesis based on that described by Ott & Krämer (1933). Recrystallization of the crude product from water gave colourless crystals of the ammonium salt. Crystals of the potassium salt were obtained as follows: 0.5 g of ammonium D,L-glycerate was dissolved in 5 ml of water and passed over the Dowex 50 ion-exchange resin (H^+ form, 100 mesh, Acros Organics). $KHCO_3$ was added to the eluate in an equimolar ratio. The slow concentration of the obtained solution gave the colourless crystals of the potassium D,L-glycerate. The preparation and crystallization of the lithium salt was carried out as for the potassium salt described above, but using $LiHCO_3$.

Compound (I)

Crystal data

$NH_4^+.C_3H_5O_4^-$
$M_r = 123.11$
Monoclinic
$P2_1/c$
$a = 4.810 (3)$ Å
$b = 11.175 (5)$ Å
$c = 10.887 (5)$ Å
$\beta = 102.41 (4)°$
$V = 571.5 (5)$ Å^3
$Z = 4$
$D_x = 1.431$ Mg m^{-3}
$D_m = 1.40$ Mg m^{-3}
D_m measured by flotation in 1,2-dichloroethane/$CHCl_3$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 9–13°$
$\mu = 0.133$ mm^{-1}
$T = 300 (1)$ K
Needle
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Kuma KM4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
2572 measured reflections
2349 independent reflections
1306 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0301$
$\theta_{\rm max} = 35°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 18$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0418$
$wR(F^2) = 0.1127$
$S = 1.048$
1894 reflections
109 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.0283P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.06$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: none
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 (I)*

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

	x	y	z	$U_{\rm eq}$
N	0.7827 (3)	0.50851 (10)	0.14361 (12)	0.0288 (3)
O1	0.7350 (2)	0.87804 (8)	0.38414 (9)	0.0312 (3)
O2	0.4258 (3)	0.79077 (8)	0.53181 (10)	0.0317 (3)
O3	0.9956 (2)	0.68000 (10)	0.62888 (9)	0.0359 (3)
O4	0.8536 (3)	0.69884 (9)	0.32189 (9)	0.0341 (3)
C1	0.7272 (3)	0.76504 (11)	0.38444 (11)	0.0240 (3)
C2	0.5549 (3)	0.70309 (10)	0.46886 (12)	0.0257 (3)
C3	0.7484 (3)	0.62038 (12)	0.56066 (14)	0.0321 (3)

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

O1—C1	1.263 (2)	O3—C3	1.424 (2)
O4—C1	1.248 (2)	C1—C2	1.529 (2)
O2—C2	1.414 (2)	C2—C3	1.523 (2)
O1—C1—O4	124.9 (2)	C1—C2—C3	109.6 (2)
O1—C1—C2	118.31 (10)	O2—C2—C3	111.9 (2)
O4—C1—C2	116.7 (2)	C2—C3—O3	112.5 (2)
C1—C2—O2	109.21 (10)		
O1—C1—C2—O2	1.3 (2)	O4—C1—C2—C3	57.4 (2)
O1—C1—C2—C3	−121.6 (2)	O2—C2—C3—O3	−68.4 (2)
O4—C1—C2—O2	−179.71 (10)	C1—C2—C3—O3	52.8 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O1$^{\rm i}$	0.88 (3)	1.95 (3)	2.811 (2)	166 (2)
N—H2···O1$^{\rm ii}$	0.90 (2)	1.96 (3)	2.845 (2)	168 (2)
N—H3···O4	0.84 (3)	2.05 (3)	2.850 (2)	158 (2)
N—H4···O1$^{\rm iii}$	0.81 (3)	2.28 (3)	3.060 (2)	161 (3)
N—H4···O2$^{\rm iii}$	0.81 (3)	2.34 (3)	2.926 (2)	130 (3)
O2—H20···O3$^{\rm iv}$	0.84 (3)	1.97 (3)	2.806 (2)	176 (3)
O3—H30···O4$^{\rm v}$	0.92 (3)	1.79 (3)	2.708 (2)	175 (3)

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

Compound (II)

Crystal data

$K^+.C_3H_5O_4^-$
$M_r = 144.17$
Monoclinic
$P2_1/c$
$a = 4.790 (2)$ Å
$b = 10.506 (6)$ Å
$c = 10.851 (6)$ Å
$\beta = 103.69 (5)°$
$V = 530.5 (5)$ Å^3
$Z = 4$
$D_x = 1.805$ Mg m^{-3}
$D_m = 1.76$ Mg m^{-3}
D_m measured by flotation in CCl_4/C_2H_5I

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 10–15°$
$\mu = 0.918$ mm^{-1}
$T = 290 (1)$ K
Elongated prism
0.4 × 0.35 × 0.25 mm
Colourless

Data collection

Syntex $P2_1$ four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2343 measured reflections
2250 independent reflections
1782 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.05$
$\theta_{\rm max} = 35°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 16$
$l = -17 \rightarrow 16$
3 standard reflections monitored every 50 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 6\sigma(F^2)] = 0.0337$
$wR(F^2) = 0.0889$
$S = 1.089$

$(\Delta/\sigma)_{\rm max} = -0.04$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Extinction correction: none

1782 reflections
93 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.1168P]$
where $P = (F_o^2 + 2F_c^2)/3$

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 (Å²) for (II)*

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

	x	y	z	$U_{\rm eq}$
K	0.78367 (6)	0.50511 (3)	0.14694 (3)	0.02487 (8)
O1	0.7399 (3)	0.88842 (9)	0.39010 (10)	0.0265 (2)
O2	0.4226 (3)	0.80214 (9)	0.53924 (10)	0.02485 (19)
O3	1.0012 (3)	0.68665 (11)	0.64564 (10)	0.0282 (2)
O4	0.8405 (3)	0.69320 (10)	0.32967 (10)	0.0294 (3)
C1	0.7255 (3)	0.76942 (12)	0.39299 (11)	0.0203 (2)
C2	0.5551 (3)	0.70646 (11)	0.47950 (12)	0.0208 (2)
C3	0.7528 (3)	0.62122 (12)	0.57495 (13)	0.0252 (3)

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

K—O2$^{\rm v}$	2.739 (2)	K—O1$^{\rm vi}$	2.734 (2)
K—O4	2.767 (2)	O1—C1	1.253 (2)
K—O1$^{\rm i}$	2.964 (2)	O4—C1	1.264 (2)
K—O3$^{\rm v}$	3.403 (2)	O2—C2	1.424 (2)
K—O3$^{\rm iv}$	3.015 (2)	O3—C3	1.430 (2)
K—O2$^{\rm vi}$	2.943 (2)	C1—C2	1.532 (2)
K—O1$^{\rm vii}$	2.703 (2)	C2—C3	1.519 (2)
O1—C1—O4	125.8 (2)	C1—C2—C3	109.6 (2)
O1—C1—C2	119.1 (2)	O2—C2—C3	112.3 (2)
O4—C1—C2	115.1 (2)	C2—C3—O3	112.8 (2)
C1—C2—O2	109.48 (10)		
O1—C1—C2—O2	3.4 (2)	O4—C1—C2—C3	60.0 (2)
O1—C1—C2—C3	−120.1 (2)	O2—C2—C3—O3	−67.5 (2)
O4—C1—C2—O2	−176.5 (2)	C1—C2—C3—O3	54.4 (2)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O3$^{\rm i}$	0.82 (3)	2.01 (3)	2.825 (2)	174 (3)
O3—H3O···O4$^{\rm ii}$	0.96 (3)	1.67 (3)	2.627 (2)	175 (3)

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

Compound (III)

Crystal data

$\rm Li^+.C_3H_5O_4^-$
$M_r = 112.01$
Monoclinic
$P2_1/n$
$a = 5.099$ (4) Å
$b = 11.498$ (9) Å
$c = 8.728$ (8) Å
$\beta = 104.44$ (6)°
$V = 495.5$ (7) Å^3
$Z = 4$
$D_x = 1.501$ Mg m^{-3}
$D_m = 1.49$ Mg m^{-3}
D_m measured by flotation in 1,2-dichloroethane/CCl$_4$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 8$–12°
$\mu = 0.137$ mm^{-1}
$T = 293$ (1) K
Irregular plate
0.6 × 0.6 × 0.2 mm
Colourless

Data collection

Kuma KM4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
1627 measured reflections
1447 independent reflections
1113 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0346$
$\theta_{\rm max} = 30.07$°
$h = -7 \rightarrow 1$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 100 reflections
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0324$
$wR(F^2) = 0.0984$
$S = 1.048$
1447 reflections
94 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.0697P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.06$

$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.018 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)*

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

	x	y	z	$U_{\rm eq}$
Li	0.4809 (4)	0.39412 (15)	0.2831 (3)	0.0263 (4)
O1	0.49414 (16)	0.32181 (6)	0.48493 (9)	0.0281 (2)
O2	0.78828 (17)	0.29620 (7)	0.28452 (10)	0.0304 (3)
O3	0.9333 (3)	0.05412 (7)	0.23671 (10)	0.0365 (3)
O4	0.67372 (16)	0.17038 (7)	0.63242 (9)	0.0289 (2)
C1	0.65016 (19)	0.23626 (8)	0.51491 (11)	0.0213 (3)
C2	0.82532 (19)	0.20773 (8)	0.40082 (11)	0.0217 (3)
C3	0.7458 (3)	0.09042 (9)	0.32373 (14)	0.0316 (3)

Table 8. *Selected geometric parameters (Å, °) for (III)*

Li—O3$^{\rm i}$	1.909 (2)	O4—C1	1.256 (2)
Li—O4$^{\rm ii}$	1.925 (3)	O2—C2	1.416 (2)
Li—O2	1.927 (2)	O3—C3	1.424 (2)
Li—O1	1.934 (2)	C1—C2	1.530 (2)
O1—C1	1.251 (2)	C2—C3	1.517 (2)
O1—C1—O4	124.83 (9)	C1—C2—C3	110.15 (8)
O1—C1—C2	118.45 (9)	O2—C2—C3	110.3 (2)
O4—C1—C2	116.72 (10)	C2—C3—O3	110.89 (10)
C1—C2—O2	108.51 (9)		
O1—C1—C2—O2	5.3 (2)	O4—C1—C2—C3	63.9 (2)
O4—C1—C2—O2	−175.16 (9)	O2—C2—C3—O3	69.4 (2)
O1—C1—C2—C3	−115.6 (2)	C1—C2—C3—O3	−170.83 (9)

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

Table 9. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O4$^{\rm i}$	0.84 (3)	1.83 (3)	2.660 (2)	170 (2)
O3—H3O···O1$^{\rm i}$	0.85 (2)	1.89 (3)	2.702 (2)	159 (2)

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

Approximate unit-cell dimensions were determined by preliminary oscillation and Weissenberg photographs. For all compounds, the H atoms were located from difference Fourier maps. The diffraction data for (II) were measured some years ago and the processing involved the removal of reflections with zero or negative intensity. Refinement on F^2 using all data was therefore impossible.

Data collection: *KM*4 *Software* (Kuma Diffraction, 1987) for (I) and (III); *XTL/XTLE* (Syntex, 1976) for (II). Cell refinement: *KM*4 *Software* for (I) and (III); *XTL/XTLE* for (II). Data reduction: *KM*4 *Software* for (I) and (III); *XTL/XTLE* for (II). For all compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acid Salts of Phosphoenolpyruvic Acid (H_3PEP): $NaH_5(PEP)_2.2H_2O$ and $KH_5(PEP)_2$

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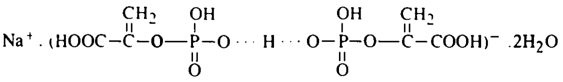
(*Received 12 April 1996; accepted 5 June 1996*)

Abstract

The crystal structures of two new salts of phosphoenolpyruvic acid (H_3PEP), sodium hydrogen bis[2-(phosphonooxy)propenoate, $Na^+.C_6H_9O_{12}P_2^-.2H_2O$, (I), and potassium hydrogen bis[2-(phosphonooxy)propenoate, $K^+.C_3H_4O_6P^-.C_3H_5O_6P$, (II), have been determined. In the crystal of (I), the phosphate groups of two PEP residues related by a center of symmetry are joined by a very short disordered hydrogen bond with an O···O distance of 2.456 (2) Å. As a result, the bis(phosphoenolpyruvate) monoanion can be distinguished. Crystals of (I) are almost isomorphous with crystals of zinc(II), manganese(II), magnesium and calcium bis(phosphoenolpyruvate) dihydrate and zinc(II) bis(phosphoglycolate) dihydrate. The crystal of (II) was found to be the 1:1 salt co-crystallized with the unionized molecular acid in the crystal chemical unit $K^+.H_2PEP^-.H_3PEP$. The P—O(ester) bond in the acid molecule [1.578 (2) Å] is shorter than in the monoanion [1.618 (2) Å]. In the sodium salt, this bond is 1.612 (2) Å. In both crystals, there are networks of strong hydrogen bonds.

Comment

This investigation was undertaken as part of a study of the structure of the phosphoenolpyruvate (PEP) moiety which may exist formally in four different forms, the tribasic acid, the monoanion, the dianion and the trianion. All of these forms have been characterized in the crystalline state (Weichsel & Lis, 1994; Souhassou, Schaber & Blessing, 1996). However, in the case of ammonium it is possible to obtain an acid salt, ammonium hydrogen bis(phosphoenolpyruvate) (Weichsel, Lis & Kuczek, 1991), and we report here the structures of two further salts of similar stoichiometry, $NaH_5(PEP)_2.2H_2O$, (I), and $KH_5(PEP)_2$, (II).



$$Na^+ . (HOOC-\overset{\overset{CH_2}{\|}}{C}-O-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-O \cdots H \cdots O-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-O-\overset{\overset{CH_2}{\|}}{C}-COOH)^- .2H_2O$$

(I)

$$K^+ \quad . \quad O=\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{P}}-O-\overset{\overset{CH_2}{\|}}{C}-COOH \quad . \quad O=\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{P}}-O-\overset{\overset{CH_2}{\|}}{C}-COOH$$

(II)

In the crystal of (I), the phosphate groups of two PEP residues related by a center of symmetry are joined by a very short hydrogen bond with an O···O distance of 2.456 (2) Å. As a result, the bis(phosphoenolpyruvate) monoanion may be distinguished with a symmetric hydrogen bond of equivalent double minima. However, since the bridging H3 atom is disordered, it may be also concluded that the crystal is built up of disordered acid molecules and phosphoenolpyruvate monoanions bridged by short hydrogen bonds. In such a case, the bond lengths in the phosphate group (Table 2) would be averaged values for these two PEP species. The enolpyruvate system is not quite planar, the angle between the carboxyl plane (C1, O5 and O6) and that formed by atoms C2, C3 and O4 being 2.9 (3)°.