$a = 7.134\ (3)$ Å
$b = 20.971\ (6)$ Å
$c = 7.635\ (2)$ Å
$\beta = 122.28\ (1)^\circ$
$V = 965.9\ (5)$ Å^3
$Z = 2$
$D_x = 1.787$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

$T = 293$ K
Bar
$0.27 \times 0.12 \times 0.12$ mm
Yellow
Crystal source: solution of K_2PdCl_4 and metronidazole (SPECIA, Paris) in acetone/water (Bales *et al.*, 1983)

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian
$T_{min} = 0.70$, $T_{max} = 0.85$
4345 measured reflections
2203 independent reflections
1508 observed reflections $[F > 4\sigma(F)]$

$R_{int} = 0.021$
$\theta_{max} = 27.5^\circ$
$h = -9 \rightarrow 9$
$k = -27 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity variation: 0.4%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.034$
$S = 1.252$
1508 reflections
160 parameters
All H-atom parameters refined
$w = 4F^2/[\sigma^2(F^2) + (0.02F^2)^2]$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1) (Pd, Cl, O, N, C) and Stewart, Davidson & Simpson (1965) (H)

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP-Plus* (Frenz, 1985). Molecular graphics: *FRODO* (Jones, 1978).

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

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

	x	y	z	U_{eq}
Pd	0	0	0	0.02975 (5)
Cl	0.2548 (2)	−0.06635 (5)	−0.0014 (1)	0.0548 (2)
N1	0.1885 (4)	0.1476 (1)	−0.2367 (4)	0.0371 (6)
C2	0.0648 (5)	0.0964 (2)	−0.2546 (4)	0.0360 (7)
N3	0.1267 (4)	0.0737 (1)	−0.0680 (3)	0.0331 (5)
C4	0.2954 (5)	0.1114 (2)	0.0741 (5)	0.0366 (7)
C5	0.3353 (5)	0.1566 (2)	−0.0271 (5)	0.0377 (7)
C11	0.1796 (5)	0.1804 (2)	−0.4128 (5)	0.0471 (8)
C12	0.3682 (6)	0.1604 (2)	−0.4365 (5)	0.0521 (9)
O13	0.3669 (5)	0.0938 (1)	−0.4684 (4)	0.0584 (7)
C21	−0.1204 (6)	0.0698 (2)	−0.4510 (5)	0.056 (1)
N51	0.4900 (5)	0.2073 (2)	0.0637 (5)	0.0528 (7)
O52	0.6084 (5)	0.2076 (2)	0.2542 (5)	0.0726 (9)
O53	0.4972 (5)	0.2473 (2)	−0.0489 (5)	0.087 (1)

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

Pd—Cl	2.293 (1)	N3—C4	1.362 (3)
Pd—N3	1.994 (2)	C4—C5	1.345 (6)
N1—C2	1.349 (4)	C5—N51	1.418 (5)
N1—C5	1.379 (3)	C11—C12	1.509 (6)
N1—C11	1.481 (5)	C12—O13	1.416 (4)
C2—N3	1.334 (4)	N51—O52	1.231 (4)
C2—C21	1.479 (4)	N51—O53	1.221 (6)
Cl—Pd—N3	89.8 (1)	N3—C4—C5	108.6 (2)
C5—N1—C11	128.8 (3)	N1—C5—C4	107.9 (3)
C2—N1—C11	124.6 (2)	C4—C5—N51	126.5 (3)
C2—N1—C5	106.0 (2)	N1—C5—N51	125.4 (3)
N1—C2—C21	125.7 (3)	N1—C11—C12	111.7 (2)
N1—C2—N3	110.4 (2)	C11—C12—O13	111.7 (3)
N3—C2—C21	123.7 (3)	C5—N51—O53	119.0 (3)
Pd—N3—C2	128.1 (2)	C5—N51—O52	116.4 (3)
C2—N3—C4	106.9 (2)	O52—N51—O53	124.5 (3)
Pd—N3—C4	124.9 (1)		

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71454 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1010]

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Acta Cryst. (1994). C**50**, 181-185

Zinc(II) Bis(phosphoglycolate) Dihydrate and Calcium Bis(phosphoglycolate) Dihydrate

TADEUSZ LIS

Institute of Chemistry, University of Wrocław, ul. Joliot-Curie 14, 50-383 Wrocław, Poland

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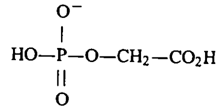
Abstract

Crystals of zinc(II) bis(phosphoglycolate) dihydrate, $Zn^{2+}.2C_2H_4O_6P^-.2H_2O$, are almost isomorphous with crystals of zinc(II) bis(phosphoenolpyruvate) dihydrate. The Zn atoms occupy centres of symmetry and are six-coordinate (through two water molecules and four phos-

phate O atoms). Two terminal O atoms of each phosphate group bridge pairs of Zn atoms, thereby forming linear chains along the *b* axis. In crystals of calcium bis(phosphoglycolate) dihydrate, $Ca^{2+}.2C_2H_4O_6P^-.2H_2O$, the Ca atoms are coordinated by two *trans* water molecules and four phosphate O atoms. One of the terminal atoms of each phosphate group bridges pairs of Ca atoms, thereby forming linear chains along the *a* axis. The orientation of the phosphate group relative to the glycolate moiety is different in the two salts. All O-atom-bonded H atoms (in both crystals) participate in hydrogen bonding.

Comment

The preparation and structure determination of the title compounds were undertaken as a continuation of the structural study of phosphoglycolate (PG) in different ionization states and different chemical environments (Lis, 1993).



$$\begin{array}{l} \quad\;\;\; O^- \\ \quad\;\;\; | \\ HO-P-O-CH_2-CO_2H \\ \quad\;\;\; \| \\ \quad\;\;\; O \end{array}$$

(PG)

Figs. 1 and 3 show the structures and numbering schemes for the phosphoglycolate monoanions in the Zn, (I), and Ca, (II), salts, respectively. In the Ca crystal there are two crystallographically independent monoanions, *A* and *B*. The molecular shapes of anions *A* and *B* are almost mirror images of each other, the mirror being about the glycolate group (Fig. 3). The C—COO group of each PG monoanion is quite planar. There is also a tendency for the ester atom O(2) to lie in this plane. Similar trends have been observed in other structures containing the PG moiety (Lis, 1993). Differences are visible in the deformations of the phosphate groups from ideal tetrahedral geometry (Tables 2 and 5) and in the orientations of the phosphate groups relative to the acetoxy moieties, described by the P—O(2)—C(2)—C(1) torsion angles of 163.1 (6)° in the Zn salt and −125.8 (5)° in *A* and 128.8 (4)° in *B* of the Ca salt. The P—O(ester) bond lengths are similar to those found in sodium and potassium salts of PG monoanions. The carboxylic OH group is *trans* to the ester O atom in both salts. The same situation was also observed in the Na salt, but in the K salt these groups were situated *syn* to one another (Lis, 1993).

The crystals of the Zn compound are almost isomorphous with those formed by zinc(II) bis(phosphoenolpyruvate) dihydrate (Lis, 1992). The Zn^{2+} ions are located at the centres of distorted octahedra, each formed by two water and four phosphate O atoms. These octahedra are doubly connected in the [010] direction by terminal phosphate O atoms, forming a linear polymer (Fig. 2) with a Zn···Zn distance of 5.223 (3) Å. The Zn—O distances are in the range 2.025 (2)-2.162 (2) Å.

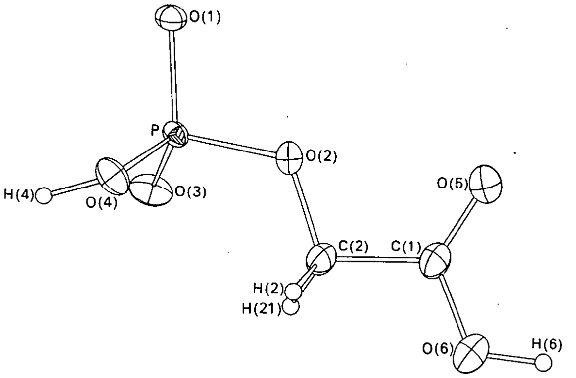


Fig. 1. The molecular structure of the phosphoglycolate monoanion in zinc(II) bis(phosphoglycolate) dihydrate.

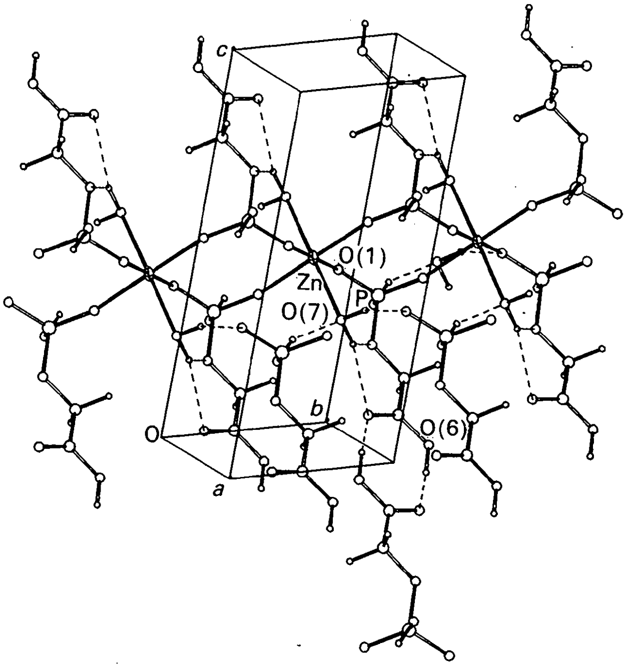


Fig. 2. The packing arrangement in the crystal of zinc(II) bis(phosphoglycolate) dihydrate.

Thus, both the Zn polyhedra and the Zn-PG interactions are different from those found in the inhibitory complex of Zn-PG, in which the PG moieties coordinate with the carboxylic group in a monodentate mode and the Zn-ion coordination is trigonal bipyramidal (Lebioda, Stec, Brewer & Tykarska, 1991).

Hydrogen-bond distances and angles for the Zn compound are listed in Table 3; the hydroxyl O(4)—H(4) group is involved in a bond (as donor) with a water molecule and pairs of centrosymmetrically related carboxylic groups interact with each other in the usual way. Furthermore, the water H atom H(71) forms a hydrogen bond with the phosphate O atom O(1^{iii}) and the second water H atom, H(7), is used in weak bifurcated hydrogen bonds.

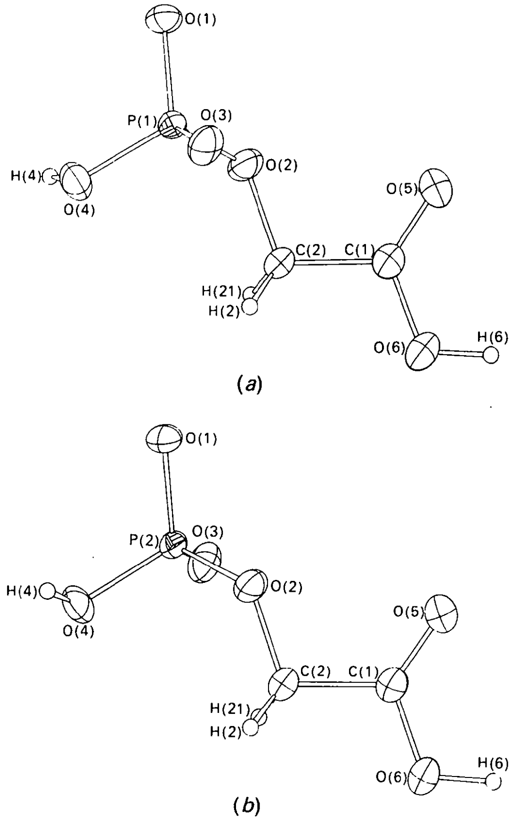


Fig. 3. The molecular structure of the two crystallographically independent monoanions, (*a*) anion *A* and (*b*) anion *B*, in calcium bis(phosphoglycolate) dihydrate.

The Ca^{2+} ions are bound to two water molecules (*trans* oriented) and four phosphoglycolate anions. One of the terminal O atoms in each crystallographically independent phosphoglycolate anion bridges two Ca atoms. Thus, the crystal structure of calcium bis(phosphoglycolate) dihydrate consists of infinite, almost linear chains of Ca^{2+} ions parallel to *a* with Ca···Ca distances of 3.716 (2) Å (Fig. 4).

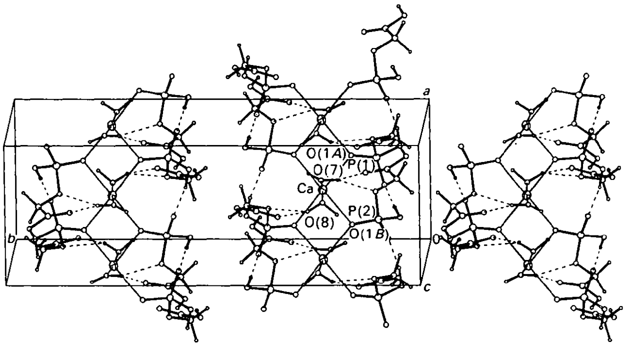


Fig. 4. The packing arrangement in the crystal of calcium bis(phosphoglycolate) dihydrate.

The phosphate hydroxyl group of anion *B* forms a hydrogen bond with the phosphate group of anion *A*, and the phosphate hydroxyl group of anion *A* forms a hydrogen bond with the phosphate group of anion *B*, translated by the distance of *a* (Table 6). Thus, linear chains along *a* are formed. The carboxylic hydroxyl groups (as donors) form hydrogen bonds with phosphate O atoms. In addition, the water molecules (as donors) form hydrogen bonds with ester and carbonyl O atoms. The total effect of this arrangement is to produce two-dimensional nets parallel to the (010) plane. Interactions between these nets are by van der Waals forces only (Fig. 4).

Experimental

Compound (I)

Crystal data

$[Zn(C_2H_4O_6P)_2].2H_2O$
$M_r = 411.45$
Triclinic
$P\bar{1}$
$a = 5.215\ (4)$ Å
$b = 5.223\ (3)$ Å
$c = 11.935\ (6)$ Å
$\alpha = 79.06\ (4)^\circ$
$\beta = 87.52\ (5)^\circ$
$\gamma = 85.15\ (6)^\circ$
$V = 317.9\ (4)$ Å^3
$Z = 1$

$D_x = 2.149\ (3)$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9\text{-}16^\circ$
$\mu = 2.32$ mm^{-1}
$T = 300\ (2)$ K
Plate shaped
0.3 × 0.3 × 0.04 mm
Colourless

Data collection

Kuma KM-4 automated four-circle κ-axis diffractometer
$\omega/2\theta$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.94$, $T_{max} = 1.09$
2074 measured reflections
1880 independent reflections

1513 observed reflections $[F > 6.0\sigma(F)]$
$R_{int} = 0.018$
$\theta_{max} = 30^\circ$
$h = -7 \rightarrow 1$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 50 reflections
intensity variation: 3%

Refinement

Refinement on *F*
$R = 0.0327$
$wR = 0.0453$
1352 reflections
122 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o) + 0.00027F_o^2]$
$(\Delta/\sigma)_{max} = 0.034$

$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Extinction correction: $1-xF_c^2/\sin\theta$
Extinction coefficient: $x = 3.9\ (23) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
Zn	1/2	1/2	1/2	0.0128 (2)
P	0.25411 (13)	1.06032 (13)	0.35495 (6)	0.0119 (2)
O(1)	0.2255 (5)	0.7956 (5)	0.42819 (19)	0.0168 (5)
O(2)	0.4277 (5)	0.9964 (5)	0.24821 (19)	0.0201 (5)
O(3)	0.3664 (5)	1.2655 (5)	0.40241 (21)	0.0228 (6)
O(4)	−0.0113 (5)	1.1676 (5)	0.29972 (21)	0.0208 (5)
O(5)	0.8027 (6)	0.8789 (6)	0.10780 (24)	0.0333 (6)
O(6)	0.8006 (7)	1.2899 (6)	0.01153 (26)	0.0427 (7)
O(7)	0.7904 (5)	0.6046 (5)	0.36824 (20)	0.0171 (5)
C(1)	0.7171 (7)	1.1064 (7)	0.09011 (27)	0.0227 (7)
C(2)	0.4934 (7)	1.2053 (7)	0.15962 (27)	0.0214 (7)

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

Zn—O(1)	2.097 (2)	Zn—O(7)	2.162 (2)
Zn—O(3$^{\rm i}$)	2.025 (2)	P—O(2)	1.601 (2)
P—O(1)	1.504 (2)	P—O(4)	1.572 (2)
P—O(3)	1.475 (2)	C(2)—C(1)	1.514 (5)
O(2)—C(2)	1.421 (4)	C(1)—O(6)	1.297 (5)
C(1)—O(5)	1.216 (4)		
O(1)—P—O(2)	103.6 (2)	O(1)—P—O(3)	120.0 (2)
O(1)—P—O(4)	109.0 (2)	O(2)—P—O(3)	109.5 (2)
O(2)—P—O(4)	102.9 (2)	O(3)—P—O(4)	110.3 (2)
P—O(2)—C(2)	119.2 (2)	O(2)—C(2)—C(1)	108.2 (3)
C(2)—C(1)—O(5)	122.3 (4)	C(2)—C(1)—O(6)	112.3 (4)
O(5)—C(1)—O(6)	125.4 (4)	O(1)—Zn—O(3$^{\rm i}$)	88.4 (1)
O(1)—Zn—O(7)	94.5 (1)	O(3$^{\rm i}$)—Zn—O(7)	88.2 (1)
Zn—O(1)—P	131.5 (2)	Zn$^{\rm ii}$—O(3)—P	167.8 (1)
O(1)—P—O(2)—C(2)	179.7 (5)	O(3)—P—O(2)—C(2)	−51.2 (5)
O(4)—P—O(2)—C(2)	66.1 (5)	P—O(2)—C(2)—C(1)	163.1 (6)
O(2)—C(2)—C(1)—O(5)	4.6 (7)	O(2)—C(2)—C(1)—O(6)	−175.9 (7)

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

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

D	H	A	H···A	D···A	D—H···A
O(4)	H(4)	O(7)$^{\rm i}$	1.79 (4)	2.680 (3)	151 (4)
O(6)	H(6)	O(5)$^{\rm ii}$	1.69 (6)	2.645 (4)	166 (6)
O(7)	H(7)	O(2)	2.17 (6)	2.879 (3)	129 (4)
O(7)	H(7)	O(5)	2.25 (4)	3.167 (4)	157 (4)
O(7)	H(71)	O(1)$^{\rm iii}$	1.80 (5)	2.729 (3)	160 (4)

Symmetry codes: (i) $x-1, 1+y, z$; (ii) $2-x, 2-y, -z$; (iii) $x+1, y, z$.

Compound (II)

Crystal data

$[Ca(C_2H_4O_6P)_2].2H_2O$
$M_r = 386.16$
Monoclinic
$P2_1/a$
$a = 7.431$ (3) Å
$b = 21.300$ (9) Å
$c = 8.838$ (5) Å
$\beta = 90.42$ (4)°
$V = 1398.8$ (12) Å^3
$Z = 4$

$D_x = 1.833$ (2) Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 6.81$ mm^{-1}
$T = 295$ (2) K
Plate shape
0.35 × 0.10 × 0.30 mm
Colourless

Data collection

Kuma KM-4 automated four-circle κ-axis diffractometer
$\omega/2\theta$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{\rm min} = 0.81$, $T_{\rm max} = 1.29$
2987 measured reflections
2880 independent reflections

2302 observed reflections [$F > 6.0\sigma(F)$]
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 75°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 26$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity variation: 2.5%

Refinement

Refinement on F
$R = 0.0418$
$wR = 0.0678$
2223 reflections
239 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o) + 0.0015F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.15$

$\Delta\rho_{\rm max} = 0.44$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.54$ e Å^{-3}
Extinction correction: $1-xF_c^2/\sin\theta$
Extinction coefficient: $x = 5.4$ (13) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
Ca	0.47305 (8)	0.24959 (2)	0.35650 (6)	0.0237 (2)
P(1)	0.73182 (10)	0.11678 (3)	0.44402 (7)	0.0191 (2)
P(2)	0.22909 (9)	0.11839 (3)	0.26764 (7)	0.0188 (2)
O(1A)	0.7224 (3)	0.18027 (8)	0.3707 (3)	0.0232 (5)
O(2A)	0.9017 (4)	0.12286 (9)	0.5526 (3)	0.0274 (5)
O(3A)	0.5681 (3)	0.09654 (10)	0.5286 (3)	0.0287 (5)
O(4A)	0.7756 (4)	0.06383 (9)	0.3288 (3)	0.0288 (5)
O(5A)	0.9383 (6)	0.15343 (12)	0.8430 (3)	0.0583 (10)
O(6A)	1.0230 (5)	0.05663 (11)	0.9058 (3)	0.0478 (8)
O(1B)	0.2196 (3)	0.18094 (8)	0.3455 (3)	0.0244 (5)
O(2B)	0.3956 (4)	0.12789 (9)	0.1577 (3)	0.0281 (5)
O(3B)	0.0653 (4)	0.09804 (10)	0.1821 (3)	0.0286 (5)
O(4B)	0.2806 (3)	0.06423 (8)	0.3778 (3)	0.0272 (5)
O(5B)	0.4345 (6)	0.15886 (12)	−0.1325 (3)	0.0623 (11)
O(6B)	0.5287 (5)	0.06321 (11)	−0.1923 (3)	0.0450 (8)
O(7)	0.4552 (5)	0.26024 (12)	0.0925 (3)	0.0474 (8)
O(8)	0.4649 (6)	0.24395 (11)	0.6211 (3)	0.0470 (9)
C(1A)	0.9699 (5)	0.10002 (14)	0.8113 (4)	0.0289 (7)
C(2A)	0.9563 (5)	0.07379 (13)	0.6524 (4)	0.0285 (7)
C(1B)	0.4696 (5)	0.10618 (14)	−0.0992 (4)	0.0300 (7)
C(2B)	0.4545 (6)	0.07960 (14)	0.0576 (4)	0.0338 (8)

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

Ca—O(1A)	2.372 (2)	Ca—O(1B)	2.386 (2)
Ca—O(1$A^{\rm i}$)	2.392 (2)	Ca—O(1$B^{\rm ii}$)	2.358 (2)
Ca—O(7)	2.347 (2)	Ca—O(8)	2.343 (2)
P(1)—O(1A)	1.501 (2)	P(2)—O(1B)	1.501 (2)
P(1)—O(2A)	1.585 (2)	P(2)—O(2B)	1.592 (2)
P(1)—O(3A)	1.496 (2)	P(2)—O(3B)	1.492 (2)
P(1)—O(4A)	1.556 (2)	P(2)—O(4B)	1.556 (2)
O(2A)—C(2A)	1.425 (3)	O(2B)—C(2B)	1.428 (4)
C(2A)—C(1A)	1.514 (4)	C(2B)—C(1B)	1.502 (4)
C(1A)—O(5A)	1.195 (4)	C(1B)—O(5B)	1.189 (4)
C(1A)—O(6A)	1.305 (4)	C(1B)—O(6B)	1.309 (4)

O(1A)—P(1)—O(2A)	102.8 (2)	O(1B)—P(2)—O(2B)	101.9 (2)
O(1A)—P(1)—O(3A)	116.1 (2)	O(1B)—P(2)—O(3B)	116.7 (2)
O(1A)—P(1)—O(4A)	112.3 (2)	O(1B)—P(2)—O(4B)	112.5 (2)
O(2A)—P(1)—O(3A)	111.6 (2)	O(2B)—P(2)—O(3B)	111.2 (2)
O(2A)—P(1)—O(4A)	106.6 (2)	O(2B)—P(2)—O(4B)	106.7 (2)
O(3A)—P(1)—O(4A)	107.0 (2)	O(3B)—P(2)—O(4B)	107.3 (2)
P(1)—O(2A)—C(2A)	122.5 (2)	P(2)—O(2B)—C(2B)	122.0 (2)
O(2A)—C(2A)—C(1A)	108.7 (3)	O(2B)—C(2B)—C(1B)	109.0 (3)
C(2A)—C(1A)—O(5A)	123.8 (3)	C(2B)—C(1B)—O(5B)	124.5 (4)
C(2A)—C(1A)—O(6A)	110.5 (3)	C(2B)—C(1B)—O(6B)	110.1 (3)
O(5A)—C(1A)—O(6A)	125.7 (4)	O(5B)—C(1B)—O(6B)	125.4 (4)
Ca—O(1A)—Ca$^{\mathrm{ii}}$	102.5 (1)	Ca—O(1B)—Ca$^{\mathrm{i}}$	103.1 (1)
O(1A)—Ca—O(1A$^{\mathrm{i}}$)	174.0 (1)	O(1A)—Ca—O(1B)	103.7 (1)
O(1A)—Ca—O(1B$^{\mathrm{ii}}$)	77.6 (1)	O(1A)—Ca—O(7)	98.7 (1)
O(1A)—Ca—O(8)	86.6 (1)	O(1A$^{\mathrm{i}}$)—Ca—O(1B)	76.7 (1)
O(1A$^{\mathrm{i}}$)—Ca—O(1B$^{\mathrm{ii}}$)	102.5 (1)	O(1A$^{\mathrm{i}}$)—Ca—O(7)	87.3 (1)
O(1A$^{\mathrm{i}}$)—Ca—O(8)	87.4 (1)	O(1B)—Ca—O(1B$^{\mathrm{ii}}$)	175.2 (1)
O(1B)—Ca—O(7)	88.8 (1)	O(1B)—Ca—O(8)	89.0 (1)
O(1B$^{\mathrm{ii}}$)—Ca—O(7)	86.4 (1)	O(1B$^{\mathrm{ii}}$)—Ca—O(8)	95.7 (1)
O(7)—Ca—O(8)	174.6 (1)		

O(1A)—P(1)—O(2A)—C(2A)	176.6 (5)
O(3A)—P(1)—O(2A)—C(2A)	51.4 (5)
O(4A)—P(1)—O(2A)—C(2A)	−65.1 (5)
P(1)—O(2A)—C(2A)—C(1A)	−125.8 (5)
O(2A)—C(2A)—C(1A)—O(5A)	0.2 (6)
O(2A)—C(2A)—C(1A)—O(6A)	−178.8 (5)
O(1B)—P(2)—O(2B)—C(2B)	−179.2 (3)
O(3B)—P(2)—O(2B)—C(2B)	−54.2 (3)
O(4B)—P(2)—O(2B)—C(2B)	62.6 (3)
P(2)—O(2B)—C(2B)—C(1B)	128.8 (4)
O(2B)—C(2B)—C(1B)—O(5B)	−1.2 (5)
O(2B)—C(2B)—C(1B)—O(6B)	178.1 (4)

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

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

D	H	*A*	H···*A*	*D*···*A*	*D*—H···*A*
O(4A)	H(4A)	O(3B$^{\mathrm{i}}$)	1.67 (4)	2.624 (3)	169 (4)
O(6A)	H(6A)	O(3B$^{\mathrm{ii}}$)	1.69 (4)	2.613 (3)	158 (5)
O(4B)	H(4B)	O(3A)	1.65 (4)	2.602 (3)	166 (4)
O(6B)	H(6B)	O(3A$^{\mathrm{iii}}$)	1.63 (4)	2.585 (3)	166 (4)
O(7)	H(7)	O(5A$^{\mathrm{iv}}$)	1.95 (5)	2.874 (3)	158 (5)
O(7)	H(71)	O(5B)	1.99 (4)	2.939 (3)	165 (5)
O(7)	H(71)	O(2B)	2.32 (4)	2.912 (3)	118 (5)
O(8)	H(8)	O(2A$^{\mathrm{v}}$)	2.37 (4)	2.938 (3)	116 (3)
O(8)	H(8)	O(5A$^{\mathrm{v}}$)	2.04 (4)	2.944 (3)	155 (4)
O(8)	H(81)	O(5B$^{\mathrm{vi}}$)	2.22 (7)	2.843 (3)	121 (5)

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

Colourless crystals of the title compounds were grown from aqueous solutions containing a 1:1 molar ratio of $CaCl_2$ or $ZnCl_2$ and phosphoglycolic acid. Furthermore, the Ca crystals were also obtained from stoichiometric water solution of CaO and phosphoglycolic acid.

For both compounds, data collection used *Kuma KM-4 Software* (Kuma Diffraction, 1989). Oscillation and Weissenberg photographs as well as preliminary diffractometer data collection suggested the isomorphism of the Zn salt with zinc(II) phosphoenolpyruvate dihydrate crystals. The refinement was started by using the published coordinates for heavy atoms of the $Zn(PEP)_2.2H_2O$ crystal (Lis, 1992). The structure of the Ca salt was solved by the heavy-atom method. In both structures, the H atoms were found from difference maps and refined with constraints (O—H = 0.97 and C—H = 1.08 Å). Both structures were refined using *SHELX76* (Sheldrick, 1976)

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71510 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1054]

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Dicalcium 1,4,5,8-Naphthalenetetracarboxylate Pentahydrate

LAWRENCE J. FITZGERALD AND ROGER E. GERKIN*

Chemistry Department, The Ohio State University, Columbus, Ohio 43210, USA

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Abstract

In the title structure, the 1,4,5,8-naphthalenetetracarboxylate anion possesses 2/*m* symmetry with the twofold axis coincident with the central C—C bond of the naphthalene rings. The ten atoms comprising the naphthalene core have a mean deviation of 0.033 Å from the best least-squares plane describing these atoms, with the carboxyl C atom 0.395 (2) Å removed from the plane. The dihedral angle between the carboxylate plane and the least-squares plane of the naphthalene rings is 46.2 (3)°. The O—C—O angle of the carboxylate group, 121.13 (12)°, is smaller than normally expected, presumably due to the bidentate interaction with the Ca ion. The Ca ion is coordinated by eight O atoms: six carboxylate O atoms and two water O atoms. Because the Ca ion resides on a twofold axis there are only four independent Ca—O distances, which are in the range 2.368 (1)–2.681 (1) Å. In this structure, the organic anions are separated by Ca ions and water molecules such that there are no short-range organic–organic interactions. One of the water molecules separating the organic anions is not involved in coordination with Ca, and is disordered.

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