

Structure of Calcium Bis(phosphoenolpyruvate) Dihydrate

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Abstract. $\text{Ca}^{2+} \cdot 2(\text{C}_3\text{H}_4\text{O}_6\text{P})^- \cdot 2\text{H}_2\text{O}$, $M_r = 410.18$, triclinic, $P\bar{1}$, $a = 5.424(4)$, $b = 5.594(6)$, $c = 12.078(9)$ Å, $\alpha = 83.00(8)$, $\beta = 85.73(6)$, $\gamma = 85.18(7)^\circ$, $V = 361.7(6)$ Å³, $Z = 1$, $D_m = 1.87$, $D_x = 1.883(4)$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 7.2$ cm⁻¹, $F(000) = 210$, $T = 302(2)$ K, final $R = 0.0307$ for 1199 observed reflections. The Ca^{2+} ions occupy centres of symmetry and are six coordinated (by two water and four phosphate O atoms). Two terminal O atoms of each phosphate group bridge pairs of Ca atoms, thereby forming linear chains along **b**. The P—O—C—C(carboxyl) torsion angle is $163.8(5)^\circ$ and the phosphate ester P—O bond length is $1.616(2)$ Å.

Introduction. We are currently investigating the crystal structures of phosphoenolpyruvate (PEP) salts and complexes (Weichsel & Lis, 1990) to see how PEP geometries depend on protonation, on the cations present and on the solvent used during crystallization. As part of this study we now report the crystal structure of $\text{Ca}(\text{PEP})_2 \cdot 2\text{H}_2\text{O}$.

Experimental. Clear plate-like crystals of the compound were grown from aqueous solutions containing 1:1 or 1:2 molar ratios of CaCl_2 and phosphoenolpyruvic acid. D_m measured by flotation in $\text{CCl}_4/\text{C}_2\text{H}_4\text{Br}_2$ mixture. Weissenberg and oscillation photographs showed the crystals to be triclinic. A fragment of approximate dimensions $0.4 \times 0.25 \times 0.1$ mm was cut from a larger crystal. Syntex $P2_1$ diffractometer with graphite monochromator and $\text{Mo } K\alpha$ radiation were used for lattice parameters (15 reflections in range $18 \leq 2\theta \leq 25^\circ$) and intensity measurements; ω - 2θ scan technique. 2144 reflections [1627 with $I > 3\sigma(I)$] were collected below $\theta = 27^\circ$ ($-6 \leq h \leq 2$, $-7 \leq k \leq 7$, $-15 \leq l \leq 15$). After each group of 50 reflections two standards were measured; variation $\pm 4\%$. 428 symmetry-related reflections were averaged; $R_{\text{merge}} = 0.018$. Scattering factors for Ca^{2+} , P, O, C and H were from *International Tables for X-ray Crystallography*

(1974, Vol. IV); anomalous dispersion was included for all non-H atoms. The structure was solved by direct methods and refined on F by *SHELX76* (Sheldrick, 1976). The H atoms were found from a difference map and refined with constraints $d(\text{O—H}) = 0.97$, $d(\text{C—H}) = 1.08$ Å. Final refinement was performed using anisotropic thermal parameters (isotropic for H atoms). No absorption or extinction corrections. Final $R = 0.0307$, $wR = 0.0375$ for 1199 reflections with $I > 3\sigma(I)$ and 130 refined parameters, where $w = 1/\sigma^2(F_o)$; max. $\Delta/\sigma = 0.05$. Residual electron density in final difference Fourier map within -0.38 and 0.34 e Å⁻³.

Discussion. Final atomic parameters are listed in Table 1* and principal interatomic distances, bond angles and torsion angles in Table 2. The structure of the phosphoenolpyruvate monoanion and the atom-numbering scheme are shown in Fig. 1 and the packing of the crystal in Fig. 2.

The Ca^{2+} ions are located at the centres of distorted octahedra 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 $\text{Ca} \cdots \text{Ca}$ distance of $5.594(6)$ Å. The Ca—O (water) distances [$2.451(3)$ Å] lie in the normally observed range (Einspahr & Bugg, 1980). The Ca—O (phosphate) distances are $2.259(3)$ and $2.326(3)$ Å.

The enolpyruvate system is not quite planar. The angle between the carboxyl plane and that formed by the C(2), C(3) and O(4) atoms of $4.9(8)^\circ$ is intermediate between the corresponding values in the monopotassium salt [$0.7(7)^\circ$] and in the orthorhombic form of the monocyclohexylammonium PEP salt [$13.9(9)^\circ$] (Weichsel & Lis, 1991). The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53957 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic parameters for calcium bis(phosphoenolpyruvate) dihydrate

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
Ca	0.5	0.5	0.5	0.0188 (3)
P	0.24315 (16)	1.03580 (12)	0.35311 (6)	0.0182 (2)
O(1)	-0.0135 (5)	1.1276 (4)	0.30442 (19)	0.0282 (6)
O(2)	0.2244 (5)	0.7810 (4)	0.40641 (17)	0.0231 (6)
O(3)	0.3353 (5)	1.2164 (4)	0.41623 (17)	0.0271 (6)
O(4)	0.4263 (5)	1.0010 (4)	0.24356 (18)	0.0287 (6)
O(5)	0.7995 (6)	0.8843 (4)	0.10325 (21)	0.0428 (7)
O(6)	0.8413 (6)	1.2707 (5)	0.03632 (23)	0.0484 (7)
O(7)	0.8150 (5)	0.5832 (4)	0.34696 (18)	0.0256 (5)
C(1)	0.7332 (7)	1.1019 (6)	0.10024 (26)	0.0299 (8)
C(2)	0.5189 (7)	1.1899 (6)	0.17224 (26)	0.0267 (7)
C(3)	0.4330 (8)	1.4187 (6)	0.16444 (30)	0.0345 (9)
H(1)	-0.098 (10)	1.274 (6)	0.329 (5)	0.111 (21)
H(6)	0.981 (7)	1.198 (9)	-0.006 (5)	0.120 (23)
H(3)	0.267 (4)	1.484 (7)	0.210 (3)	0.051 (12)
H(31)	0.534 (6)	1.541 (5)	0.105 (3)	0.032 (10)
H(7)	0.762 (9)	0.668 (7)	0.277 (2)	0.072 (15)
H(71)	0.931 (7)	0.656 (8)	0.388 (4)	0.080 (17)

Table 2. Principal interatomic distances (Å), interatomic angles (°), torsion angles (°) and hydrogen-bonding data in calcium bis(phosphoenolpyruvate) dihydrate

P—O(1)	1.573 (3)	O(4)—C(2)	1.383 (4)
P—O(2)	1.499 (2)	O(5)—C(1)	1.237 (4)
P—O(3)	1.477 (2)	O(6)—C(1)	1.296 (4)
P—O(4)	1.616 (2)	C(1)—C(2)	1.486 (5)
C(2)—C(3)	1.320 (5)	Ca—O(2)	2.326 (3)
Ca—O(3 ⁱ)	2.259 (3)	Ca—O(7)	2.451 (3)
O(1)—P—O(2)	107.9 (2)	O(5)—C(1)—O(6)	124.1 (4)
O(1)—P—O(3)	111.4 (2)	O(5)—C(1)—C(2)	121.4 (3)
O(1)—P—O(4)	104.0 (2)	O(6)—C(1)—C(2)	114.5 (3)
O(2)—P—O(3)	119.9 (2)	O(4)—C(2)—C(1)	110.7 (3)
O(2)—P—O(4)	102.4 (2)	O(4)—C(2)—C(3)	126.7 (4)
O(3)—P—O(4)	109.8 (2)	C(1)—C(2)—C(3)	122.5 (4)
P—O(4)—C(2)	124.0 (3)	O(2)—Ca—O(3 ⁱ)	87.0 (1)
O(2)—Ca—O(7)	89.2 (1)	O(3 ⁱ)—Ca—O(7)	93.8 (1)
P—O(2)—Ca	133.4 (2)	P—O(3)—Ca ⁱⁱ	175.0 (2)
P—O(1)—H(1)	118 (3)	C(1)—O(6)—H(6)	109 (3)
O(1)—P—O(4)—C(2)	74.1 (5)	P—O(4)—C(2)—C(1)	163.8 (5)
O(2)—P—O(4)—C(2)	-173.6 (5)	P—O(4)—C(2)—C(3)	-17.4 (7)
O(3)—P—O(4)—C(2)	-45.2 (5)	C(3)—C(2)—C(1)—O(5)	-174.7 (7)
O(4)—C(2)—C(1)—O(5)	4.2 (7)	C(3)—C(2)—C(1)—O(6)	5.6 (8)
O(4)—C(2)—C(1)—O(6)	-175.5 (7)	H(1)—O(1)—P—O(3)	-10 (4)
O—H...O	O...O (Å)	H...O (Å)	O—H...O (°)
O(1)—H(1)...O(7 ⁱⁱⁱ)	2.734 (3)	1.79 (4)	163 (5)
O(6)—H(6)...O(5 ^{iv})	2.641 (5)	1.69 (5)	167 (5)
O(7)—H(71)...O(2 ^v)	2.741 (3)	1.83 (4)	155 (4)
O(7)—H(7)...O(4)	3.213 (4)	2.51 (5)	129 (4)
O(7)—H(7)...O(5)	3.211 (4)	2.29 (4)	158 (4)

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

carboxylic hydroxyl group is *trans* planar to the ester O(4) atom as was observed earlier in other PEP salts crystallized from water solutions (Weichsel & Lis, 1991). The P—O(ester) and the enolic bond lengths [1.616 (2) and 1.383 (4) Å] are in agreement with values in other PEP structures. All other bond lengths and angles do not differ significantly from those found in other monoionized PEP moieties. The

torsion angle P—O(4)—C(2)—C(3), defining the phosphate group orientation with respect to the enolpyruvate system, is $-17.4 (7)^\circ$. The values of this torsion angle in ten known crystals of PEP (Weichsel & Lis, 1991) are in the $\pm 90^\circ$ range indicating flexibility about the enolic bond and suggesting also that the conformation about the enolic bond may depend both on the cation and on the solvent used in crystallization.

The hydrogen-bond distances and angles are listed in Table 2; the hydroxyl O(1)—H(1) group is involved (as donor) with a water molecule and pairs of centrosymmetrically related carboxyl groups interact with each other in the usual way. Furthermore, the water H(71) atom forms a hydrogen bond with

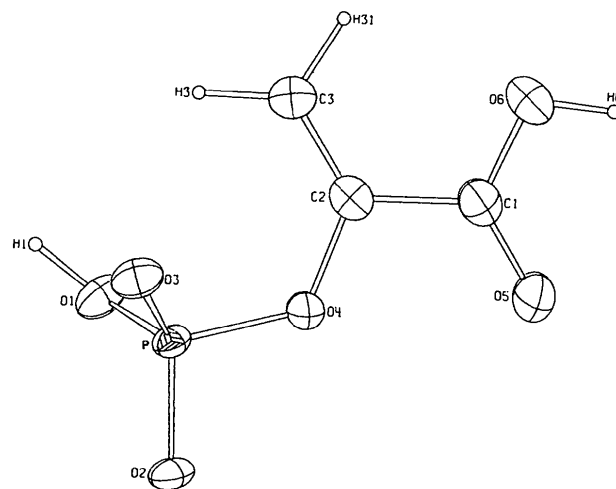


Fig. 1. Molecular geometry and numbering scheme of the phosphoenolpyruvate monoanion in calcium bis(phosphoenolpyruvate) dihydrate.

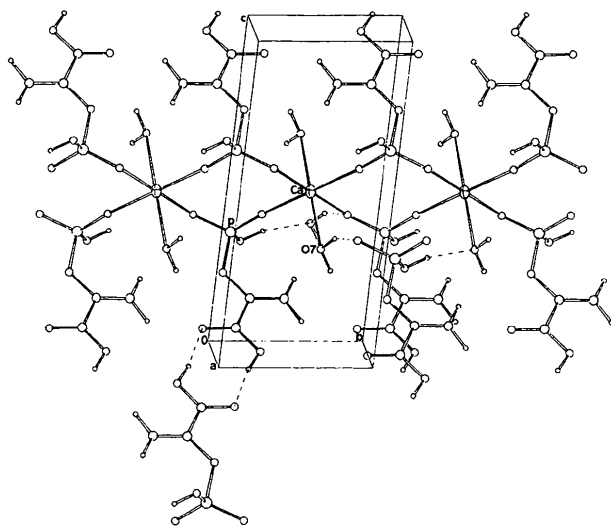


Fig. 2. The packing arrangement. Dashed lines show strong hydrogen bonds.

the phosphate atom O(2) and the second [H(7)] water atom is used in weak bifurcated hydrogen bonds.

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Synthesis and Structure of $[P(C_6H_5)_4]_4[M_2(WSe_4)_4]$ ($M = Pb, Sn$)

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Abstract. Tetrakis(tetraphenylphosphonium) bis(μ -tetraselenidotungstato-*Se, Se', μ -Se''*)-bis[(tetraselenidotungstato-*Se, Se'*)plumbate], $M_r = 3770.7$, triclinic, $P\bar{1}$, $a = 12.963$ (1), $b = 14.430$ (2), $c = 14.705$ (1) Å, $\alpha = 105.26$ (1), $\beta = 99.88$ (1), $\gamma = 94.06$ (1)°, $V = 2595$ (1) Å³, $Z = 1$, $D_x = 2.40$ g cm⁻³, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $\mu = 218.0$ cm⁻¹, $F(000) = 1673.5$ (including anomalous dispersion), $T = 153$ K, $R[\text{on } F \text{ for } F_o^2 > 3\sigma(F_o^2)] = 0.047$, $wR[\text{on } F \text{ for } F_o^2 > 3\sigma(F_o^2)] = 0.048$, $R(F^2) = 0.075$, $wR(F^2) = 0.101$ for 10 498 unique reflections, 7747 having $F_o^2 > 3\sigma(F_o^2)$. The centrosymmetric $[Pb_2(WSe_4)_4]^{4-}$ ion is composed of two independent W atoms tetrahedrally coordinated by Se atoms and one independent Pb atom in a distorted octahedral coordination of Se atoms. Tetrakis(tetraphenylphosphonium) bis(μ -tetraselenidotungstato-*Se, Se', μ -Se''*)-bis[(tetraselenidotungstato-*Se, Se'*)stannate], $[PPh_4]_4[Sn_2(WSe_4)_4]$, is isostructural with $[PPh_4]_4[Pb_2(WSe_4)_4]$, $M_r = 3593.7$, triclinic, $P\bar{1}$, $a = 12.981$ (3), $b = 14.412$ (6), $c = 14.644$ (7) Å, $\alpha = 105.26$ (4), $\beta = 99.79$ (3), $\gamma = 94.56$ (3)°, $V = 2583$ (1) Å³, $Z = 1$, $D_x = 2.31$ g cm⁻¹, $\lambda(Cu K\alpha_1) = 1.54056$ Å, $T = 153$ K.

Introduction. The reaction of various divalent metal cations with the tetrathiometalates MoS_4^{2-} or WS_4^{2-} affords the bis(thiometalate) anions $[M'(MS_4)_2]^{2-}$ ($M' = Fe, Co, Ni, Pd, Zn, \text{etc.}$, $M = Mo, W$) (Müller, Diemann, Jostes & Bögge, 1981). In contrast, the reaction of Sn^{2+} with WS_4^{2-} affords $[Sn_2(WS_4)_4]^{4-}$ (Müller, Paulat-Böschchen, Krebs & Dornfeld, 1976).

Until quite recently, little related chemistry of the $MoSe_4^{2-}$ and WSe_4^{2-} ions was known (Ansari & Ibers, 1990). It was recently found that reaction of WSe_4^{2-} with Ni^{2+} affords not only $[Ni(WSe_4)_2]^{2-}$ {analogous to $[Ni(WS_4)_2]^{2-}$ } but also $[Ni(Se_2)-$

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$(WSe_4)]^{2-}$ for which there is no known sulfur analogue (Ansari, Chau, Mahler & Ibers, 1989). Thus the chemistry of the soluble selenides need not parallel that of the sulfides. In the present study, the reactions of Pb^{2+} and Sn^{2+} with WSe_4^{2-} were investigated. These reactions afford the $[M_2(WSe_4)_4]^{4-}$ ($M = Pb, Sn$) species.

Experimental. All reactions were carried out under a dry dinitrogen atmosphere with the use of standard Schlenk techniques. Solvents were dried and distilled before use. $[PPh_4]_4[M_2(WSe_4)_4]$ ($M = Pb, Sn$) was prepared by the reaction in DMF of $PbCl_2$ or $SnCl_2$ with $[NH_4]_2[WSe_4]$ in the presence of $[PPh_4]Br$. The ⁷⁷Se NMR spectrum of a DMF solution of the Pb complex exhibits resonances at δ 1653, 1563, 964, 938 and 894 (relative to Me_2Se at δ 0). These may be assigned to terminal W—Se at δ 1653 and 1563 and bridging W—Se at δ 964, 938 and 894 (Wardle, Mahler, Chau & Ibers, 1988). Such an assignment is consistent with a structure for an anion analogous to that of $[Sn_2(WS_4)_4]^{4-}$.

A tabular crystal $0.081 \times 0.139 \times 0.061$ mm was mounted in the cold stream ($T = 153$ K) of an Enraf–Nonius CAD-4 diffractometer. Cell constants were obtained from 23 reflections in the range $25 < \theta(Cu K\alpha_1) < 26^\circ$. Intensity data were collected by the ω - 2θ technique in the range $3 \leq \theta(Cu K\alpha_1) \leq 75^\circ$ ($-16 \leq h \leq 0$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$). The basic scan speed was 4° min^{-1} in ω but reflections having $F_o^2 < 3\sigma(F_o^2)$ were scanned more slowly up to a maximum time of 60 s. The scan range was 0.5° in ω below $K\alpha_1$ to 0.5° in ω above $K\alpha_2$. Six standards (081, 081, 643, 308, 600, 101) chosen from diverse regions of reciprocal space were monitored every 3 h during data collection and remained constant within