Calcium D-3-Phosphoglycerate Tetrahydrate at 85 K

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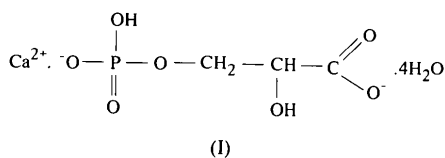14 Joliot-Curie St., 50-383 Wrocław, Poland. E-mail:
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Fig. 1. The coordination sphere of the calcium ion and numbering scheme of the 3-D-phospoglycerate dianion. Displacement ellipsoids are plotted at the 50% probability level.

Abstract

The structure determination of the D-3-phosphoglycerate dianion in the calcium salt is reported, $Ca^{2+}.C_3H_5O_7P^{2-}.4H_2O$. The P—O ester bond length is 1.602 (1) Å. The crystal structure is governed by calcium–oxygen interactions and hydrogen bonds. The Ca^{2+} cations are seven-coordinate, with Ca—O distances in the range 2.272 (2)–2.474 (2) Å.

Comment

As a continuation of our investigations on phosphoglycerates in various chemical environments (Lis & Jerzykiewicz, 1993, 1995, 1996; Jerzykiewicz & Lis, 1994), we report here the crystal structure of the Ca salt of D-3-phosphoglycerate, (I).

$$Ca^{2+}. \ ^-O—P—O—CH_2—CH—C\diagdown^{\nearrow O}_{O^-} \ .4H_2O$$

(with OH on P, O below P, OH on CH)

(I)

Crystals of the title compound consist of Ca^{2+} cations, D-3-phosphoglycerate dianions (Fig. 1) and water molecules. The geometrical parameters of the phosphoglycerate residue do not differ significantly from those found in previously described phosphoglycerates (Lis & Jerzykiewicz, 1993, 1995, 1996; Jerzykiewicz & Lis, 1994). The carboxylate group is twisted 73.1 (2)° relative to the carbon backbone, as the O(1)—C(1)—C(2)—C(3) torsion angle indicates. The orientation of the phosphate group with respect to the C-atom chain [defined by the P—O(3)—C(3)—C(2) torsion angle] is antiperiplanar. The P—O ester bond length of 1.602 (1) Å is characteristic of monoionized phosphate groups in phosphate esters (Starynowicz, 1986; Starynowicz, Lis & Weichsel, 1986; Weichsel & Lis, 1990).

The Ca atom is bonded to O atoms of two phosphoglycerate anions and of four water molecules so that its coordination number is seven; the Ca—O bond lengths range from 2.272 (2) to 2.474 (2) Å. Each phosphoglycerat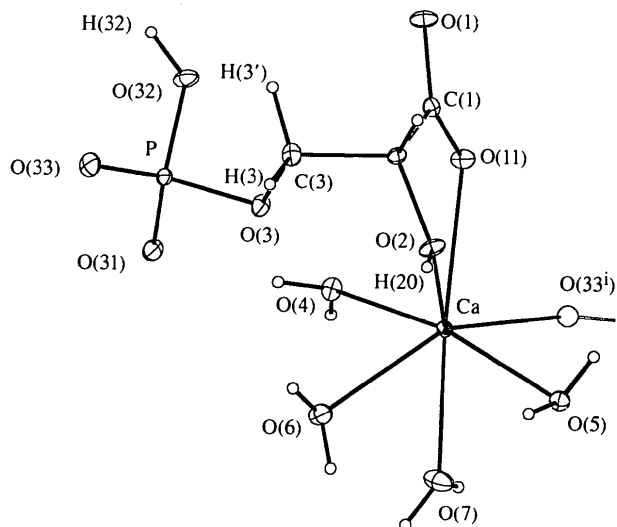e ligand is coordinated to two different Ca atoms, thereby forming chains along b. Each dianion chelates one Ca atom through O(2) and O(11) atoms, and coordinates a second through O(33). In addition to the polymeric structure, there is an extensive network of hydrogen bonds utilizing all the hydroxyl H atoms and holding the polymeric units together (Fig. 2, Table 3). The O(4) water molecules (as donors) link only to O phosphate atoms, whereas O(5) water molecules (as donors) bridge O atoms from carboxylate groups. The O(6) and O(7) water molecules join O atoms from phosphate groups and O atoms from other water molecules. The shortest hydrogen bond in the structure is that formed by O(2)—H(20) with O(1).
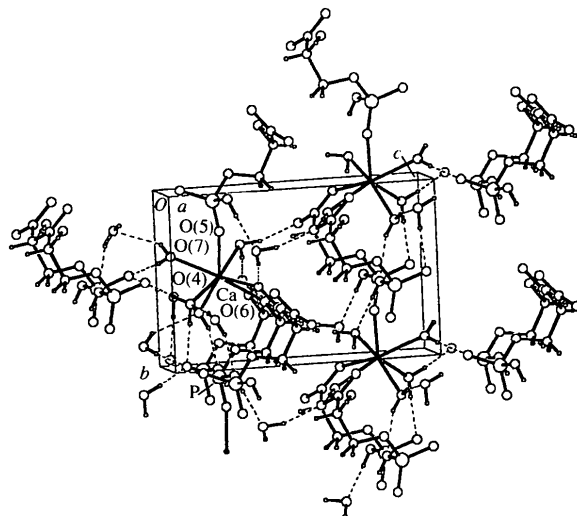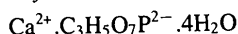

Fig. 2. The packing arrangement in the crystal.

O(5)	-0.01440 (16)	0.33976 (13)	0.32005 (8)	0.0078 (2)
O(6)	-0.06097 (17)	0.71108 (14)	0.15874 (8)	0.0107 (2)
O(7)	0.00134 (19)	0.38182 (15)	0.05749 (9)	0.0149 (2)
C(1)	0.6660 (3)	0.67847 (16)	0.41396 (9)	0.0066 (2)
C(2)	0.4422 (2)	0.76843 (16)	0.43376 (9)	0.0063 (2)
C(3)	0.4210 (3)	0.94490 (17)	0.37819 (10)	0.0084 (2)

Experimental

Crystals were grown by slow concentration of aqueous solutions of the commercial compound (Sigma). Note that earlier attempts to crystallize this compound (Mostad & Rosenqvist, 1971) failed.

Crystal data

Ca²⁺.C₃H₅O₇P²⁻.4H₂O
$M_r = 296.18$
Monoclinic
$P2_1$
$a = 5.751 (2)$ Å
$b = 7.718 (3)$ Å
$c = 12.469 (4)$ Å
$\beta = 102.76 (3)°$
$V = 539.8 (4)$ Å³
$Z = 2$
$D_x = 1.822 (2)$ Mg m⁻³
$D_m = 1.808$ Mg m⁻³ at room temperature
D_m measured by flotation in C_2H_5I/CCl_4 at room temperature

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 70 reflections
$\theta = 10–13°$
$\mu = 0.778$ mm⁻¹
$T = 85 (2)$ K
Block
$0.2 \times 0.1 \times 0.1$ mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4382 measured reflections
3910 independent reflections
3674 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

$\theta_{max} = 32.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -18 \rightarrow 18$
3 standard reflections every 100 reflections intensity decay: 2.3%

Refinement

Refinement on F^2
$R(F) = 0.023$
$wR(F^2) = 0.055$
$S = 1.078$
3910 reflections
196 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.283$

$\Delta\rho_{max} = 0.43$ e Å⁻³
$\Delta\rho_{min} = -0.35$ e Å⁻³
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: based on known stereochemistry at C(3)
Flack parameter = -0.03 (2) (Flack, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
Ca	0.24959 (4)	1/2	0.22274 (2)	0.00562 (5)
P	0.50170 (5)	1.06060 (5)	0.19242 (2)	0.00603 (6)
O(31)	0.42671 (16)	0.99230 (16)	0.07690 (7)	0.0097 (2)
O(32)	0.78241 (16)	1.04494 (14)	0.23198 (8)	0.0109 (2)
O(33)	0.42544 (17)	1.23728 (13)	0.21806 (9)	0.0109 (2)
O(3)	0.40082 (17)	0.91625 (12)	0.26249 (7)	0.0087 (2)
O(2)	0.24489 (17)	0.66059 (13)	0.39009 (8)	0.0092 (2)
O(11)	0.63600 (16)	0.55679 (15)	0.34483 (8)	0.0090 (2)
O(1)	0.86420 (16)	0.73498 (13)	0.46652 (8)	0.0100 (2)
O(4)	0.45310 (17)	0.63459 (13)	0.09718 (8)	0.0090 (2)

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

P—O(31)	1.505 (2)	C(2)—C(3)	1.521 (2)
P—O(32)	1.585 (2)	Ca—O(2)	2.432 (2)
P—O(33)	1.489 (2)	Ca—O(11)	2.440 (2)
P—O(3)	1.602 (1)	Ca—O(33ⁱ)	2.272 (2)
O(3)—C(3)	1.439 (2)	Ca—O(4)	2.389 (2)
O(2)—C(2)	1.416 (2)	Ca—O(5)	2.474 (2)
O(1)—C(1)	1.261 (2)	Ca—O(6)	2.419 (2)
O(11)—C(1)	1.261 (2)	Ca—O(7)	2.412 (2)
C(1)—C(2)	1.530 (2)		
O(31)—P—O(32)	109.2 (1)	O(3)—C(3)—C(2)	107.5 (1)
O(31)—P—O(33)	119.4 (1)	O(2)—C(2)—C(3)	112.0 (1)
O(32)—P—O(33)	109.3 (1)	C(3)—C(2)—C(1)	108.6 (1)
O(31)—P—O(3)	102.5 (1)	O(2)—C(2)—C(1)	107.6 (1)
O(32)—P—O(3)	104.1 (1)	O(1)—C(1)—C(2)	117.1 (2)
O(33)—P—O(3)	111.1 (1)	O(11)—C(1)—C(2)	117.1 (2)
C(3)—O(3)—P	118.8 (1)	O(11)—C(1)—O(1)	125.8 (2)
C(3)—O(3)—P—O(31)		-174.7 (1)	
C(3)—O(3)—P—O(32)		71.6 (1)	
C(3)--O(3)—P—O(33)		-46.0 (1)	
P—O(3)—C(3)—C(2)		-150.1 (1)	
O(2)—C(2)—C(3)—O(3)		-58.0 (2)	
O(11)—C(1)—C(2)—O(2)		15.9 (2)	
O(1)—C(1)—C(2)—O(2)		-165.5 (2)	
O(1)—C(1)—C(2)—C(3)		73.1 (2)	
O(11)—C(1)—C(2)—C(3)		-105.5 (2)	
C(1)—C(2)—C(3)—O(3)		60.7 (2)	

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O(2)—H(20)⋯O(1ⁱ)	0.79 (4)	1.85 (4)	2.637 (2)	170 (4)
O(32)—H(32)⋯O(5ⁱⁱ)	0.86 (3)	1.83 (3)	2.680 (2)	171 (3)
O(4)—H(4)⋯O(31ⁱⁱⁱ)	0.86 (3)	1.83 (3)	2.657 (1)	163 (3)
O(4)—H(41)⋯O(31)	0.87 (4)	1.92 (4)	2.774 (2)	166 (3)
O(5)—H(5)⋯O(1ⁱᵛ)	0.91 (3)	1.86 (3)	2.733 (2)	162 (3)
O(5)—H(51)⋯O(11ⁱ)	0.84 (3)	1.86 (3)	2.687 (1)	169 (3)
O(6)—H(6)⋯O(4ⁱ)	0.84 (4)	1.96 (4)	2.793 (2)	172 (4)
O(6)—H(61)⋯O(32ⁱ)	0.78 (3)	2.24 (3)	2.941 (2)	151 (3)
O(7)—H(7)⋯O(31ᵛ)	0.80 (4)	1.99 (4)	2.788 (2)	173 (4)
O(7)—H(71)⋯O(6ᵛ)	0.85 (4)	2.35 (4)	3.087 (2)	146 (3)

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

The space group and approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs. The collection of data was carried out at low temperature using an Oxford Cryosystems cooler; the (hkl) and $(\overline{hkl})$ reflections were measured. The crystal data at 294 (2) K are: $a = 5.745$ (2), $b = 7.715$ (3), $c = 12.541$ (5) Å, $\beta = 102.53$ (3)°, $V = 542.6$ (4) Å⁻³ and $D_x = 1.813$ (2) g cm⁻³.

Data collection: *Kuma KM-4 Users Guide* (Kuma Diffraction, 1989). Cell refinement: *Kuma KM-4 Users Guide*. Data reduction: *Kuma KM-4 Users Guide*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

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[Mo(C25H22P2)(C34H33P3)(CO)]

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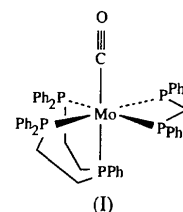
Abstract

The crystal structure of [bis(2-diphenylphosphino-ethyl)phenylphosphine-P,P',P''][bis(diphenylphosphino)-methane-P,P']carbonylmolybdenum(0), [Mo(dpepp)-(dppm)(CO)] [where dppm = $Ph_2PCH_2PPh_2$ and dpepp = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$], is reported. In the distorted octahedral complex, the tridentate ligand adopts a facial arrangement with the monodentate ligand *trans* to the central P atom. All Mo—P distances are statistically dissimilar.

Comment

Dinitrogen complexes of molybdenum and tungsten containing organophosphine ligands have played a key role in model studies of biological nitrogen fixation (George, 1983; Henderson, Leigh & Pickett, 1983; Hidai & Mizobe, 1995). We synthesized a series of mono(dinitrogen) complexes of molybdenum containing a tridentate phosphine and either two monodentate

phosphines or one bidentate phosphine (George & Tisdale, 1988). These complexes afforded ammonia upon treatment with acid demonstrating that it was not necessary to have two dinitrogen ligands per metal center in order to produce ammonia. There is some ambiguity about the structure of these complexes because of the various isomers that can be formed. For example, the tridentate ligand can be *fac* (facial) or *mer* (meridional). Previous structural assignments are based upon ^{31}P NMR spectroscopy. The crystal structure of [MoBr(dpepp)(dmpm)], (II) (dmpm = $Me_2PCH_2PMe_2$) (George, Ma, Shailh, Tisdale & Zubieta, 1990), was determined but since the complex is paramagnetic no relationship between the ^{31}P NMR spectrum and X-ray structure could be established.

(I)

The molecular structure of the title compound, (I), is shown with the atom-numbering scheme in Fig. 1. The structure is well resolved and shows several disordered atomic positions, bridging atoms C5 and P4, and the phenyl group bonded to the axial P atom (C91–C96). For clarity, lower occupancy sites are omitted in Fig. 1. The complex displays a distorted octahedral coordination environment about Mo with four P atoms
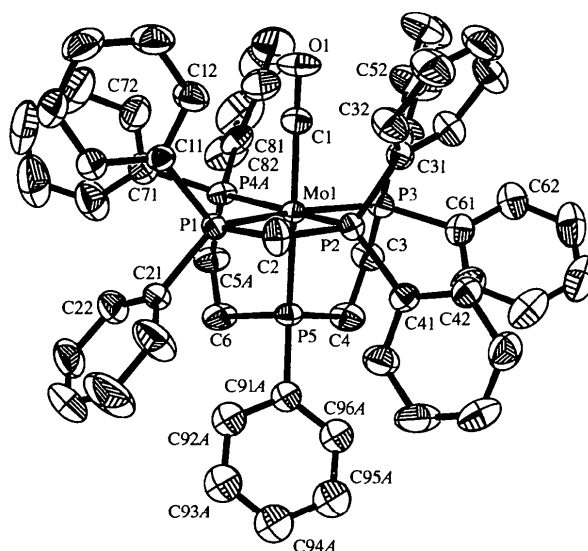

Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity and only high-occupancy sites are shown. All ring C atoms are numbered sequentially as shown explicitly in C91A–C96A.