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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aqua(L-O-serine phosphato)calcium(II)

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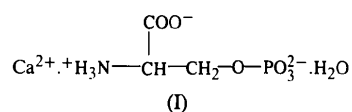
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Abstract

In the crystal structure of the title compound, [Ca(C₃H₆NO₆P)(H₂O)], the Ca ion is bonded to six O atoms, three from the phosphate group, two from the carboxyl group and one from the water molecule. The coordination geometry around the Ca ion is distorted octahedral. The L-O-serine phosphate molecules are connected in a three-dimensional manner through O—Ca—O bonds. The structural parameters also suggest the presence of intermolecular N—H···O hydrogen bonds.

Comment

Phosphorylated proteins have various important physiological functions in many hormonal regulatory systems, muscle, cells and organs (Taborsky, 1974; Rubin & Rosen, 1975; Cohen, 1982; Martin, Mayes & Rodwell, 1983). In some cases, the function of phosphoproteins has been explained in relation to their Ca-ion binding ability. In muscle, the calmodulin-mediated phosphorylation of light chains of muscle myosin begins the attachment–detachment contraction cycle of smooth muscle. It has been proposed that the phosphate on the myosin light chains may chelate with Ca ions. In milk, dephosphorylation of casein micelles containing Ca ions by phosphoprotein phosphatase causes extensive degradation of the micelles. In bones and/or teeth, phosphopeptide-bound collagen and/or phosphoryn bind Ca ions strongly. For these reasons, it is important to elucidate structurally the interaction between phosphoproteins and metal ions, especially Ca ions. We report here the structural features of the chelate compound of L-O-serine phosphate and the Ca ion, (I), as a useful model of the interaction of phosphoproteins with the Ca ion.



The crystal structures of L-serine phosphate (McCallum, Robertson & Sim, 1959) and DL-O-serine phosphate monohydrate (Putkey & Sundaralingam, 1970) have been reported previously. Fig. 1 shows the molecular structure and atom-numbering scheme of

the title compound. The Ca ion binds to six O atoms of *L*-O-serine phosphate and a water molecule in a distorted octahedral coordination geometry. The metal–ligand bond lengths are not equal, varying from 2.287 (3) Å for Ca(1)—O(3) to 2.413 (3) Å for Ca(1)—O(7). The intraligand O—Ca—O bond angles vary, ranging from 79.8 (1)° for O(4)—Ca(1)—O(7) to 98.01 (1)° for O(2)—Ca(1)—O(3). The crystal packing is shown in Fig. 2. *L*-O-Serine phosphate molecules connect together through O—Ca—O bonds. The O atom of the water molecule is not involved in this connection. Intermolecular hydrogen bonds are formed between the amino N atom and the carboxyl and phosphate O atoms: N(1)···O(6)(−1 + x, y, z) 2.748 (5) Å and N(1)···O(4)(−1 − x, $\frac{1}{2}$ + y, 1 − z) 2.985 (5) Å.

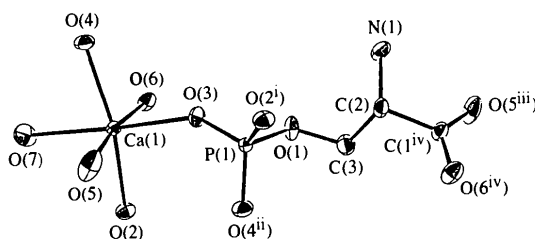


Fig. 1. An ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids correspond to 50% probability and H atoms have been omitted for clarity.

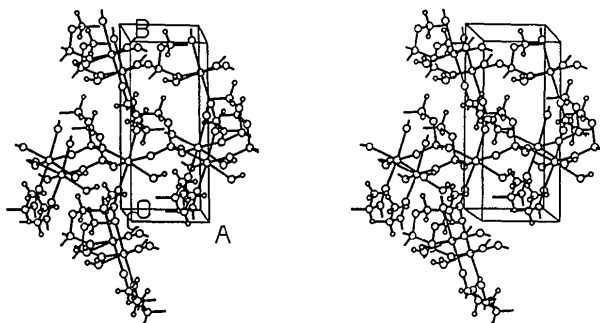


Fig. 2. A stereoview (ORTEP; Johnson, 1976) of the unit cell of the title compound.

Experimental

The title crystal was obtained by the slow evaporation at room temperature of an aqueous solution of a mixture of *L*-O-serine phosphate and CaCl₂·2H₂O in a 5:1 molar ratio at pH 7.0.

Crystal data

[Ca(C₃H₆NO₆P)(H₂O)]
M_r = 241.15
 Monoclinic
*P*2₁
a = 5.534 (2) Å
b = 12.759 (2) Å
c = 5.740 (2) Å
 β = 104.77 (2)°

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 20.05–23.25°
 μ = 0.989 mm^{−1}
T = 296 K
 Plate

V = 391.9 (2) Å³
Z = 2
D_x = 2.043 Mg m^{−3}
D_m not measured

0.2 × 0.1 × 0.05 mm
 Colorless

Data collection

Rigaku AFC-5R diffractometer
 ω –2 θ scans
 Absorption correction:
 ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.95, *T_{max}* = 1.00
 1035 measured reflections
 946 independent reflections
 884 observed reflections
 [*I* > 3 σ (*I*)]

R_{int} = 0.019
 θ_{\max} = 27.45°
h = 0 → 7
k = 0 → 16
l = −7 → 7
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.5%

Refinement

Refinement on *F*²
R = 0.024
wR = 0.029
S = 1.22
 884 reflections
 117 parameters
 H atoms refined isotropically
 $w = 4F_o^2/\sigma^2(F_o^2)$

(Δ/σ)_{max} = 0.16
 $\Delta\rho_{\max}$ = 0.24 e Å^{−3}
 $\Delta\rho_{\min}$ = −0.20 e Å^{−3}
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Ca(1)	0.0397 (1)	0.2911	0.5438 (1)	1.08 (2)
P(1)	−0.3734 (2)	0.34263 (9)	0.9322 (1)	1.21 (3)
O(1)	−0.3990 (5)	0.4674 (2)	0.9877 (5)	1.9 (1)
O(2)	0.3668 (4)	0.2953 (3)	0.8847 (4)	1.69 (8)
O(3)	−0.2690 (5)	0.3462 (3)	0.7149 (4)	2.2 (1)
O(4)	−0.2027 (4)	0.2927 (3)	0.1526 (4)	1.95 (8)
O(5)	−0.0758 (7)	0.1276 (2)	0.6427 (6)	3.1 (1)
O(6)	0.1424 (5)	0.4665 (2)	0.5020 (5)	2.0 (1)
O(7)	0.3310 (6)	0.2181 (3)	0.3384 (7)	2.8 (1)
N(1)	−0.8995 (7)	0.5664 (3)	0.9141 (6)	2.1 (1)
C(1)	0.1380 (7)	0.5344 (3)	0.3444 (7)	1.5 (1)
C(2)	−0.7829 (7)	0.4983 (3)	1.1238 (7)	1.5 (1)
C(3)	−0.4972 (8)	0.5014 (4)	1.1823 (8)	2.1 (1)

Table 2. Selected geometric parameters (Å, °)

Ca(1)—O(2)	2.303 (2)	P(1)—O(3)	1.503 (3)
Ca(1)—O(3)	2.287 (3)	P(1)—O(4 ⁱⁱ)	1.513 (3)
Ca(1)—O(4)	2.303 (2)	O(1)—C(3)	1.428 (5)
Ca(1)—O(5)	2.296 (3)	O(5 ⁱⁱⁱ)—C(1 ^{iv})	1.245 (5)
Ca(1)—O(6)	2.337 (3)	O(6 ^{iv})—C(1 ^{iv})	1.248 (5)
Ca(1)—O(7)	2.413 (3)	N(1)—C(2)	1.492 (5)
P(1)—O(1)	1.637 (3)	C(1 ^{iv})—C(2)	1.513 (5)
P(1)—O(2 ⁱ)	1.519 (3)	C(2)—C(3)	1.531 (5)
O(2)—Ca(1)—O(3)	98.01 (1)	O(1)—P(1)—O(4 ⁱⁱ)	108.3 (2)
O(2)—Ca(1)—O(4)	164.66 (9)	O(2 ⁱ)—P(1)—O(3)	114.2 (2)
O(2)—Ca(1)—O(5)	91.1 (1)	O(2 ⁱ)—P(1)—O(4 ⁱⁱ)	110.1 (2)
O(2)—Ca(1)—O(6)	84.6 (1)	O(3)—P(1)—O(4 ⁱⁱ)	114.6 (2)
O(2)—Ca(1)—O(7)	86.9 (1)	P(1)—O(1)—C(3)	121.1 (3)
O(3)—Ca(1)—O(4)	95.90 (1)	Ca(1 ⁱ)—O(2 ⁱ)—P(1)	131.7 (3)
O(3)—Ca(1)—O(5)	83.6 (1)	Ca(1)—O(3)—P(1)	146.5 (2)
O(3)—Ca(1)—O(6)	88.7 (1)	Ca(1 ⁱⁱ)—O(4 ⁱⁱ)—P(1)	154.6 (2)

O(3)—Ca(1)—O(7)	173.4 (1)	Ca(1 ^{III})—O(5 ^{III})—C(1 ^{IV})	168.9 (3)
O(4)—Ca(1)—O(5)	96.9 (1)	Ca(1 ^{IV})—O(6 ^{IV})—C(1 ^{IV})	141.1 (3)
O(4)—Ca(1)—O(6)	89.3 (1)	O(5 ^{III})—C(1 ^{IV})—O(6 ^{IV})	125.0 (4)
O(4)—Ca(1)—O(7)	79.8 (1)	O(5 ^{III})—C(1 ^{IV})—C(2)	118.9 (3)
O(5)—Ca(1)—O(6)	170.5 (1)	O(6 ^{IV})—C(1 ^{IV})—C(2)	116.0 (3)
O(5)—Ca(1)—O(7)	91.9 (1)	N(1)—C(2)—C(1 ^{IV})	109.9 (3)
O(6)—Ca(1)—O(7)	96.3 (1)	N(1)—C(2)—C(3)	111.8 (3)
O(1)—P(1)—O(2 ¹)	107.3 (2)	C(1 ^{IV})—C(2)—C(3)	108.2 (3)
O(1)—P(1)—O(3)	101.7 (2)	O(1)—C(3)—C(2)	113.5 (3)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Calcium Salts of *o*-Tolidine-6,6'-disulfonate

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Abstract

The dibasic and monobasic calcium salts of *o*-tolidine-6,6'-disulfonic acid, tetraaqua(4,4'-diamino-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonato-*O*:*O'*)calcium, [Ca(C₁₄H₁₄N₂O₆S₂)(H₂O)₄], (I), and hexaaqua(4-amino-4'-ammonio-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonato-*O*)calcium 4-amino-4'-ammonio-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonate hexahydrate, [Ca(C₁₄H₁₅N₂O₆S₂)(H₂O)₆](C₁₄H₁₅N₂O₆S₂).6H₂O, (II), have structures built upon layers of anions, with the calcium cations and water molecules between these layers. The calcium ions are seven-coordinate. The coordination sphere in compound (I) contains three sulfonate O atoms and four water molecules, while that in (II) contains one sulfonate O atom and six water molecules. Both structures are held together by a network of hydrogen bonds involving the amine, sulfonate and water groups. The biphenyl rings in the anions are approximately 75° out of parallel and the *ortho*-sulfonate groups are in an *anti* conformation.

Comment

We have previously examined the structural trends in various arenesulfonates (Gunderman & Squattrito, 1994) and naphthalenesulfonates (Gunderman & Squattrito, 1995). As an extension of this study of aromatic sulfonic acids and their salts, we have characterized two salts of an *ortho*-disulfonated biphenyl derivative. Despite the presence of numerous references to such compounds in the patent literature, no crystal structures of either the sulfonic acids or their salts have been reported. There are relatively few structural studies of *ortho*-substituted biphenyls of any kind (Lesser & Rabinovich, 1978). The closest reported compound to the title compounds, (I) and (II), is biphenyl-2,2'-dicarboxylic acid (Fronczek, Davis, Gehrig & Gandour, 1987). The dihedral angles between the phenyl rings of the *o*-tolidine-6,6'-disulfonate anions [(I) 78.8(2); (II) 72.5(4) and 75.0(4)°] are within the range reported for the two independent molecules of the dicarboxylic acid (71.3 and 83.6°). The torsion angles between the sulfonate groups [(I): C(6)—C(1)—C(7)—C(12)