

Polymeric bis(phosphonomethyl-carboxylato)calcium(II) at 85 K

Katarzyna Ślepokura* and Tadeusz Lis

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St, 50-383 Wrocław, Poland

Correspondence e-mail: slep@wchuwr.chem.uni.wroc.pl

Received 13 November 2002

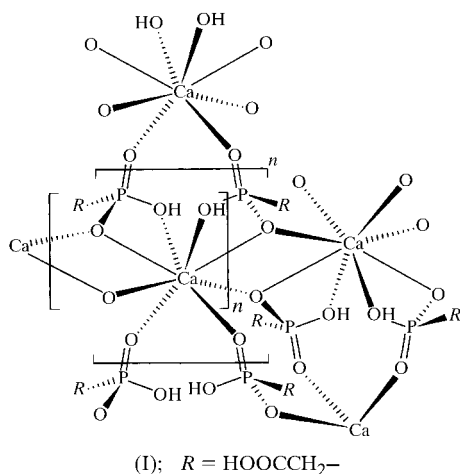
Accepted 19 December 2002

Online 11 February 2003

In the crystal structure of the title compound, alternatively called poly[calcium(II)-di- μ -carboxymethylphosphonato], $[\text{Ca}(\text{C}_2\text{H}_4\text{O}_5\text{P})_2]_n$ or $[\text{Ca}(\text{H}_2\text{AP})_2]_n$, one of the phosphonate O atoms of the phosphonocarboxylate monoanion lies nearly antiperiplanar (*ap*) to the carboxylic acid C atom. The phosphonate P atom is located $-sc$ and $+ac$ relative to the carboxylic acid O atoms. The overall structure has a layered architecture. The Ca^{2+} cations lie on a twofold axis and are bridged by the phosphonate O atoms to form chains along the *c* axis, giving layers parallel to (100). There are medium-strength $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions stabilizing the layers, and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds connect adjacent layers.

Comment

Metal phosphonates have applications in many fields of chemistry, *e.g.* in catalysis and ion exchange (Bhardwaj *et al.*, 1993; Alberti *et al.*, 1996). The first structurally studied

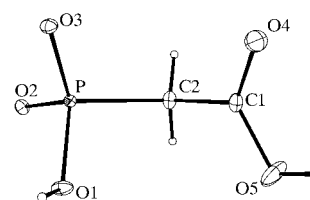


complex of phosphonoacetic acid (H_3AP) was $\text{K}_4[\text{Cu}(\text{C}_2\text{H}_4\text{O}_5\text{P})_2(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ (Afonin *et al.*, 1998), in which the Cu^{2+} ion is five-coordinated by four O atoms of two bidentate chelating phosphonoacetate trianions and the O atom of the water

molecule. Other crystal structures of M^{2+} phosphonoacetates (all with layered architectures) have been reported in the literature, namely $[\text{Al}(\text{O}_3\text{PCH}_2\text{COO})]\cdot 3\text{H}_2\text{O}$ (Hix *et al.*, 1998), $[\text{Mn}_3(\text{O}_3\text{PCH}_2\text{COO})_2]$ (Stock *et al.*, 2000), and the isomorphous series $[\text{M}(\text{C}_2\text{H}_4\text{O}_5\text{P})_2(\text{H}_2\text{O})]$, with $M = \text{Mg}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}$ and Cu^{II} (Ślepokura *et al.*, 2002). Crystal structure studies of this last compound and of the title compound, (I), were undertaken as a continuation of a previous structural study of phosphonoacetic acid and its Na^+ , K^+ , Li^+ and NH_4^+ salts (Lis, 1997).

Phosphonoacetic acid may exist in four different forms, namely the tribasic acid, a monoanion (with one of the phosphonic acid O atoms deprotonated), a dianion (with the phosphonic and carboxylic acid O atoms deprotonated) and a trianion (with all hydroxyl O atoms, *viz.* two phosphono and one carboxyl, deprotonated) (Lis, 1997). In (I), the anion occurs in the monoionized state. The molecular structure and atom-numbering scheme for the monoanion are shown in Fig. 1.

The overall structure of the carboxymethylphosphonate monoanion in (I) is similar to that observed previously in phosphonoacetic acid and its M^+ and M^{2+} salts (Lis, 1997;


Figure 1

The molecular structure and atom-numbering scheme of the phosphono-carboxylate monoanion in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure 2

The three-dimensional structure of (I). Displacement ellipsoids are drawn at the 50% probability level. For clarity, only one chain of Ca^{2+} cations connected *via* oxygen bridges is shown. From adjacent chains (above and below that shown), only O3 atoms are marked [symmetry code: (i) $x, -y, \frac{1}{2} + z$]. Dashed lines show intralayer $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

Ślepokura *et al.*, 2002), with the carboxylic acid atom C1 lying nearly antiperiplanar, *-ap* (*trans*), to one of the phosphonate O atoms (O2) and nearly *gauche* (*+sc* and *-sc*) with respect to the remaining phosphonate O atoms (O1 and O3). The O2–P–C2–C1, O1–P–C2–C1 and O3–P–C2–C1 torsion angles are listed in Table 1.

The orientation of the phosphonate group in relation to the acetate group is one of the main points of interest in the structures of phosphonoacetic acid and its derivatives, and may be described by the above-mentioned torsion angles, in combination with P–C2–C1–O4 and P–C2–C1–O5. The values of these last two angles show that the carboxylic acid O atoms are in *-sc* and *+ac* positions in relation to the P atom.

The conformation of the phosphonocarboxylate monoanion in (I) lies between that found in free phosphonoacetic acid (Lis, 1997) and its M^{2+} salts (Ślepokura *et al.*, 2002), and that found for the H₃AP salts of monovalent cations (Lis, 1997) or in the potassium, ammonium and dicyclohexylammonium salts of (2-oxopropyl)phosphonic acid (Mazurek & Lis, 1999). The values of the appropriate P–C2–C1–O4 and P–C2–C1–O5 torsion angles in the former group of compounds are about 50 and -132° , respectively; in the latter (for analogous P–C–O and P–C–C–C angles), regardless of the degree of ionization of the anion, the values are close to 90° , which means that the phosphonate group prefers a disposition almost perpendicular to the rest of molecule, while in the structure of (I) presented here, the relevant angles are $-72.14(9)$ and $107.20(7)^\circ$, respectively.

In the phosphonate group of (I), a deformation from the ideal tetrahedral shape is observed, especially in the O2–P–O3 angle, in which the deprotonated O atoms are involved; the C2–P–O1(H) angle is the smallest of all the phosphonate group angles, which is consistent with other monoionized phosphonate groups. The P–O1(H) bonds are longer than the P–O bonds.

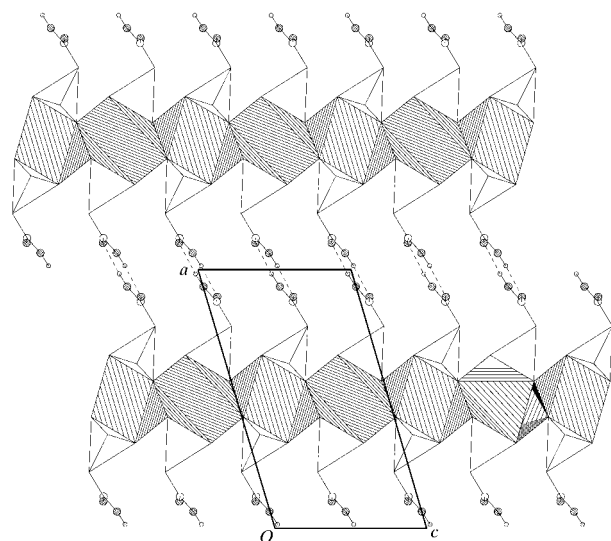


Figure 3
The layered structure of (I), viewed along [010]. Dashed lines show interlayer O–H...O hydrogen bonds.

The crystals of (I) are built up from Ca^{2+} ions and phosphonocarboxylate monoanions, which act as bridging as well as chelating ligands. The Ca^{2+} cations are situated on a twofold axis and their eight-coordinate polyhedra are composed of the phosphonate O atoms only. Every metal cation is chelated by two phosphonocarboxylate monoanions *via* atoms O1 and O2, and bridged by atom O2 from another monoanion, which in turn chelates an adjacent Ca^{2+} cation. Thus, a chain is formed along the *c* axis (Fig. 2). The metal coordination sphere is completed by two O3 atoms from adjacent chains, forming layers parallel to (100). The shortest Ca...Ca distances are 3.938(2) and 5.516(2) Å within and between the chains, respectively.

On the whole, the structure of (I) fits into the known structural pattern for metal phosphonates. Many of them, as for (I) described here, are layered compounds, in which inorganic groups build up the layer backbone, while the organic parts protrude into the interlamellar spaces. The common structural motif, occurring here as well, is the planar network of tetra- or divalent metal ions (here Ca^{2+}), knitted together by phosphonate O atoms above and below the layer plane (Cao *et al.*, 1990, 1992; Dines & DiGiacomo, 1981; Hix *et al.*, 1998). The structure of the layers is additionally stabilized by moderately strong O–H...O and C–H...O hydrogen bonds formed by both phosphonate and carboxylic acid moieties (Table 2). Situated in the interlamellar spaces, the carboxylic acid groups from adjacent layers are connected to each other *via* O–H...O hydrogen-bonding interactions (Fig. 3).

We have recently obtained crystals of a new magnesium salt of phosphonoacetic acid, in which a phase transition is observed at 230–240 K. The measurements for both phases were taken at 85 and 250 K, and their structures will be published elsewhere.

Experimental

Crystalline calcium phosphonocarboxylate was obtained from the reaction of commercially available (Aldrich) phosphonoacetic acid (aqueous solution) with solid CaCO_3 . The title polymeric bis-(phosphonomethylcarboxylato)calcium(II) compound crystallized in the form of colourless needles.

Crystal data

[Ca(C₂H₄O₅P)₂]
 $M_r = 318.12$
Monoclinic, $P2_1/c$
 $a = 13.021(3)$ Å
 $b = 5.516(2)$ Å
 $c = 7.358(2)$ Å
 $\beta = 106.50(3)^\circ$
 $V = 506.7(3)$ Å³
 $Z = 2$

$D_x = 2.085$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 6172 reflections
 $\theta = 4\text{--}37^\circ$
 $\mu = 0.98$ mm⁻¹
 $T = 85(2)$ K
Needle, colourless
 $0.30 \times 0.30 \times 0.05$ mm

Data collection

Kuma KM-4 CCD κ -geometry diffractometer
 ω scans
Absorption correction: Gaussian (SHELXTL; Bruker, 1997)
 $T_{\min} = 0.782$, $T_{\max} = 0.950$
8195 measured reflections

2437 independent reflections
2269 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 37.4^\circ$
 $h = -22 \rightarrow 21$
 $k = -9 \rightarrow 9$
 $l = -10 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.051$
 $S = 1.13$
 2437 reflections
 95 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.1327P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ca—O2 ⁱ	2.3740 (8)	P—O3	1.5160 (8)
Ca—O3 ⁱⁱ	2.4039 (8)	P—O1	1.5758 (7)
Ca—O2	2.4229 (8)	P—C2	1.8098 (10)
Ca—O1	2.8639 (8)	O4—C1	1.2229 (11)
Ca \cdots Ca ⁱ	3.9376 (10)	O5—C1	1.3091 (10)
Ca \cdots Ca ⁱⁱ	5.5160 (11)	C1—C2	1.5053 (10)
P—O2	1.5095 (6)		
O2—P—O3	114.86 (3)	O1—P—C2	102.63 (4)
O2—P—O1	106.03 (4)	O4—C1—O5	124.27 (7)
O3—P—O1	112.47 (3)	O4—C1—C2	122.61 (7)
O2—P—C2	108.24 (4)	O5—C1—C2	113.11 (7)
O3—P—C2	111.75 (3)	C1—C2—P	112.86 (5)
O4—C1—C2—P	−72.14 (9)	O3—P—C2—C1	58.74 (6)
O5—C1—C2—P	107.20 (7)	O1—P—C2—C1	−62.00 (6)
O2—P—C2—C1	−173.82 (5)		

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

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3 ⁱ	0.81 (2)	1.83 (2)	2.637 (2)	173 (2)
O5—H5 \cdots O4 ⁱⁱ	0.85 (2)	1.84 (2)	2.687 (2)	173 (2)
C2—H21 \cdots O1 ⁱⁱⁱ	0.92 (2)	2.62 (2)	3.231 (2)	124 (1)
C2—H22 \cdots O3 ^{iv}	1.00 (2)	2.60 (2)	3.426 (2)	140 (1)
C2—H22 \cdots O4 ^{iv}	1.00 (2)	2.60 (2)	3.432 (2)	142 (1)

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

The H atoms were found in difference Fourier maps and were refined.

Data collection: *KM-4 CCD Software* (Kuma, 1995–1999); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1003). Services for accessing these data are described at the back of the journal.

References

- Afonin, E. G., Sergienko, V. S. & Aleksandrov, G. G. (1998). *Zh. Neorg. Khim.* **43**, 1463–1468. (In Russian.)
- Alberti, G., Cascioli, M., Costantino, U. & Vivani, R. (1996). *Adv. Mater.* **8**, 291–303.
- Bhardwaj, C., Hu, H. & Clearfield, A. (1993). *Inorg. Chem.* **32**, 4294–4299.
- Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cao, G., Hong, H.-G. & Mallouk, T. E. (1992). *Acc. Chem. Res.* **25**, 420–427.
- Cao, G., Lynch, V. M., Swinnea, S. & Mallouk, T. E. (1990). *Inorg. Res.* **29**, 2112–2117.
- Dines, M. B. & DiGiacomo, P. (1981). *Inorg. Chem.* **20**, 92–97.
- Hix, G. B., Wragg, D. S., Wright, P. A. & Morris, R. E. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3359–3361.
- Kuma (1995–1999). *KM-4 CCD Software*. Versoin 1.161. Kuma Diffraction, Wrocław, Poland.
- Lis, T. (1997). *Acta Cryst.* **C53**, 28–42.
- Mazurek, J. & Lis, T. (1999). *J. Mol. Struct.* **474**, 143–155.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stock, N., Frey, S. A., Stucky, G. D. & Cheetham, A. K. (2000). *J. Chem. Soc. Dalton Trans.* pp. 4292–4296.
- Ślepokura, K., Piątkowska, A. & Lis, T. (2002). *Z. Kristallogr.* **217**, 614–621.