metal-organic papers

Pentaaqua(dichloromethylenebisphosphonato)-strontium(II)

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The title compound, [Sr{Cl$_2$C(PO$_3$H)$_2$}(H$_2$O)$_5$], is a monomer, the Sr atom being seven-coordinated by one chelating clodronate ligand and five aqua ligands. The coordination polyhedron can be described as a distorted monocapped trigonal prism. This compound is isostructural with hydrated calcium clodronate, [Ca{Cl$_2$C(PO$_3$H)$_2$}(H$_2$O)$_5$], described previously [Nardelli, Pelizzi, Staibano & Zucchi (1983). *Inorg. Chim. Acta*, **80**, 259–271].

Comment

Bisphosphonates are an interesting class of compounds because of their pharmaceutical applications (Fleisch, 1995; Fleisch *et al.*, 1969; Kanis & McCloskey, 1990; Bijvoet *et al.*, 1995) and their potential chemical applications in, for example, ion exchange, sorption and catalysis (Zhang & Clearfield, 1997; Alberti *et al.*, 1996; Snover *et al.*, 1996; Serre & Férey, 2002). Clodronate, the anion of disodium (dichloromethylene)bisphosphonate tetrahydrate, is one of the best documented methylenebisphosphonate derivatives and is used effectively in medical applications (Major *et al.*, 2000). Clodronate has six possible O-donor atoms, and we can therefore presume that it also forms polymeric structures that can be utilized in chemical applications. The previously reported crystal structure of hydrated calcium clodronate, [Ca{Cl$_2$C(PO$_3$H)$_2$}(H$_2$O)$_5$], revealed that clodronate itself acted only as a bidentate chelating ligand with Ca, forming a monomeric compound (Nardelli *et al.*, 1983). Our latest results, on the other hand, show that both clodronate and its partial ester derivative can also produce polymers (Kontturi *et al.*, 2002, 2004). The new strontium complex of clodronate, [Sr{Cl$_2$C(PO$_3$H)$_2$}(H$_2$O)$_5$], (I), is a monomer, and its preparation and crystal structure are reported here.

(I)
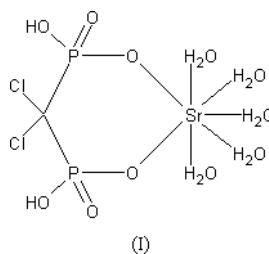
The title compound consists of one Sr^{2+} atom, one chelating Cl$_2$C(PO$_3$H)$_2$$^{2-}$ ligand and five aqua ligands (Fig. 1). The compound is isostructural with the corresponding calcium clodronate, [Ca{Cl$_2$C(PO$_3$H)$_2$}(H$_2$O)$_5$] (Nardelli *et al.*, 1983).
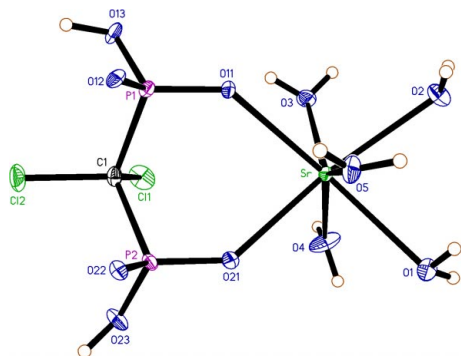
Figure 1
Molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.
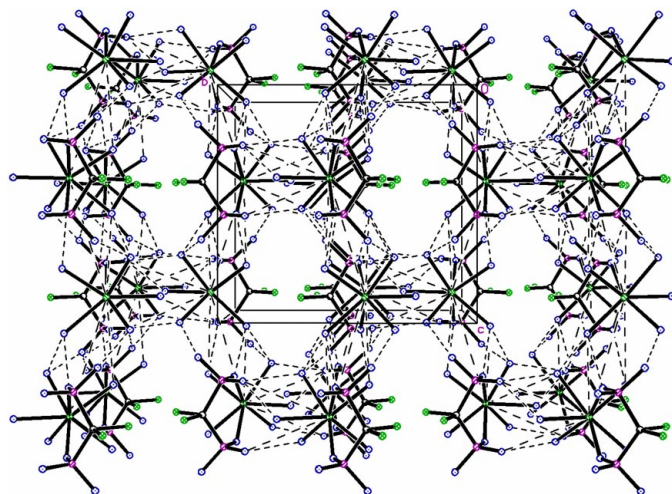

Figure 2
Packing diagram of (I), showing large pores in the direction of the a axis, formed between the hydrogen-bonded (dashed lines) units.

However, the methods of preparation of the compounds are different; the strontium compound was prepared with the gel method, while the calcium compound was prepared by slow evaporation at 333 K. On the other hand, we have also produced calcium clodronate using the gel method (Kontturi et al., 2004). In the Sr compound, the Sr atom is seven-coordinate, and the coordination polyhedron can be described as a distorted monocapped trigonal prism. One O atom from each of the phosphonate groups of the $Cl_2C(PO_3H)_2^{2-}$ ligand (O11 and O21) coordinates to the Sr atom to form a chelate ring, the 'bite' distance for O11···O21 being 3.136 (2) Å. The second O atom of the two phosphonate groups is doubly bonded to P, and the third is protonated. The monomeric units are packed through intermolecular hydrogen bonds. Twelve hydrogen bonds are present, the two strongest being formed by the protonated phosphonate atoms O13 and O23, which are donors to atoms O12 and O22 of the $Cl_2C(PO_3H)_2^{2-}$ ligands of adjacent molecules. The other hydrogen bonds involve all aqua ligands as donors and O atoms of $Cl_2C(PO_3H)_2^{2-}$ and aqua ligands as acceptors. The packing diagram (Fig. 2) shows large pores between the hydrogen-bonded units, in the direction of the a axis.

Experimental

Compound (I) was crystallized by the gel method (Kontturi et al., 2002, 2004) with disodium (dichloromethylene)bisphosphonate tetrahydrate (0.014 mmol, 5.0 mg) and $SrCl_2 \cdot 6H_2O$ (0.017 mmol, 4.6 mg) in water (0.9 ml, pH 4), using tetramethoxysilane (0.1 ml). Acetone (1.0 ml) was used as precipitant. Crystals formed in the shape of cubes above the gel, and were purified for characterization under the microscope. Analysis found: C 2.70, H 3.20, Sr 20.7%; calculated for $CH_{12}Cl_2O_{11}P_2Sr$: C 2.86, H 2.88, Sr 20.8%. IR (cm^{-1}): 1252 (s, b), 1193 (vs, b), 1124 (vs), 1085 (m), 1070 (w), 932 (vs), 863 (vw), 758 (m). ^{31}P CP/MAS–NMR: 7.13 p.p.m.

Crystal data

$[Sr(CH_2Cl_2O_6P_2)(H_2O)_5]$	D_m measured by flotation in cyclo-
$M_r = 420.57$	hexane/bromoform
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 10.5207$ (1) Å	Cell parameters from 2674
$b = 11.8587$ (1) Å	reflections
$c = 10.9164$ (2) Å	$\theta = 2.6-26.0°$
$V = 1361.95$ (3) Å^3	$\mu = 4.63$ mm^{-1}
$Z = 4$	$T = 120$ (2) K
$D_x = 2.051$ Mg m^{-3}	Cube, colourless
$D_m = 2.02$ (4) Mg m^{-3}	$0.35 \times 0.35 \times 0.35$ mm

Data collection

Nonius KappaCCD diffractometer	2674 independent reflections
φ and ω scans	2596 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.057$
(XPREP in SHELXTL; Bruker,	$\theta_{max} = 26.0°$
1998)	$h = -12 \rightarrow 12$
$T_{min} = 0.182$, $T_{max} = 0.198$	$k = -14 \rightarrow 14$
17 202 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
$wR(F^2) = 0.047$	$\Delta\rho_{min} = -0.56$ e Å^{-3}
$S = 1.08$	Extinction correction: SHELXL97
2674 reflections	Extinction coefficient: 0.0028 (4)
156 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1260 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2$	Flack parameter = 0.504 (5)
$+ 0.6P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Sr—O21	2.499 (2)	P1—O11	1.495 (3)
Sr—O11	2.500 (2)	P1—O12	1.503 (3)
Sr—O4	2.524 (2)	P1—O13	1.568 (2)
Sr—O5	2.542 (1)	P1—C1	1.849 (4)
Sr—O3	2.552 (2)	P2—O21	1.484 (2)
Sr—O2	2.576 (2)	P2—O22	1.499 (3)
Sr—O1	2.609 (2)	P2—O23	1.566 (2)
Cl1—C1	1.800 (2)	P2—C1	1.856 (4)
Cl2—C1	1.784 (2)		
O11—P1—C1	106.8 (1)	Cl2—C1—Cl1	109.3 (1)
O12—P1—C1	107.6 (1)	Cl2—C1—P1	108.6 (2)
O13—P1—C1	104.3 (1)	Cl1—C1—P1	107.4 (2)
O21—P2—C1	107.0 (1)	Cl2—C1—P2	108.6 (2)
O22—P2—C1	106.8 (1)	Cl1—C1—P2	106.9 (2)
O23—P2—C1	103.7 (1)	P1—C1—P2	115.9 (1)

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Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$A\cdots$O13[i]	0.85	2.03	2.865 (3)	168
O1—H1$B\cdots$O22[ii]	0.85	2.03	2.773 (3)	145
O2—H2$A\cdots$O12[ii]	0.85	1.97	2.755 (3)	153
O2—H2$B\cdots$O23[iii]	0.85	2.02	2.841 (3)	162
O3—H3$A\cdots$O21[iii]	0.85	2.01	2.793 (3)	152
O3—H3$B\cdots$O1[iii]	0.85	2.10	2.890 (3)	155
O4—H4$B\cdots$Cl1[iv]	0.85	2.72	3.554 (3)	167
O4—H4$A\cdots$O11[i]	0.85	1.93	2.768 (3)	167
O5—H5$A\cdots$O2[v]	0.85	2.11	2.955 (3)	171
O5—H5$B\cdots$O12[ii]	0.85	2.29	2.987 (3)	139
O13—H13$\cdots$O22[vi]	0.94	1.68	2.558 (4)	154
O23—H23$\cdots$O12[vii]	0.85	1.73	2.546 (3)	161

Symmetry codes: (i) $-x, 1-y, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, z$; (iii) $-x, 1-y, \frac{1}{2}+z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (vi) $1-x, 1-y, \frac{1}{2}+z$; (vii) $1-x, 1-y, z-\frac{1}{2}$.

There is a pseudo-centre of symmetry in the structure, and the structure was solved as an inversion twin in space group *Pna*2_1, as opposed to centrosymmetric *Pnma*. The solution in space group *Pnma* was not satisfactory; the displacements of the coordinated aqua ligands were, on average, larger in *Pnma* than in *Pna*2_1. In particular, the displacement ellipsoid of aqua ligand O3 was large and prolate. Also, the s.u. values of the bond distances and angles in *Pnma* were three times the s.u. values in *Pna*2_1; the *R* factor for observed reflections was three times greater and *wR* was four times greater in *Pnma* than in *Pna*2_1. H atoms of the aqua ligands were found in a difference map and then placed at optimized positions, taking into account potential hydrogen bonds [O—H = 0.85 Å]; a riding model was used, with $U_{iso}(H) = 1.5U_{eq}(O)$. Atoms H13 and H23 were found in difference maps, and a riding model was used, with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data

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