

**Poly[[tetraaqua( $\mu_7$ -hydrogen dichloromethylenebisphosphonato)( $\mu_5$ -hydrogen dichloromethylenebisphosphonato)tribarium(II)] monohydrate]**

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Received 20 September 2004

Accepted 22 September 2004

Online 31 October 2004

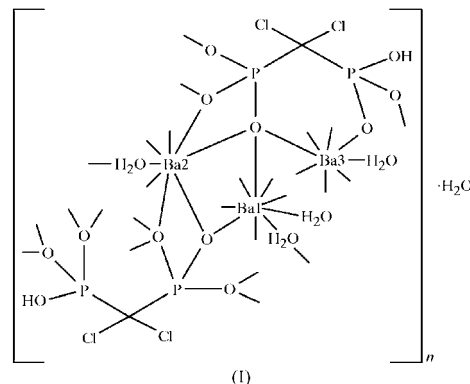
The title compound,  $\{[\text{Ba}_3(\text{CHCl}_2\text{O}_6\text{P}_2)_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$  or  $\{[\text{Ba}_3(\text{Cl}_2\text{CP}_2\text{O}_6\text{H})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ , is two-dimensional. The asymmetric unit contains three independent  $\text{Ba}^{2+}$  atoms, two chelating and bridging  $\text{Cl}_2\text{CP}_2\text{O}_6\text{H}^{3-}$  ligands and four aqua ligands, connected in layers parallel to the (100) plane. There are pores between the layers in the direction of the *b* axis filled with lattice water molecules.

**Comment**

Due to the chemical applications of metal bisphosphonates in, for example, ion exchange, sorption and catalysis, research on the chemistry of metal phosphonates has recently focused on the properties of solid materials. The effectiveness of these materials is related to the degree of porosity, and their structures consist of chains, layers or pillared layers. The dimensionality is dependent not only on the number of donor atoms of the ligand, but also on the length of the organic group between the phosphonate groups and on the degree of protonation of the phosphonate group (Clearfield, 1998; Zhang & Clearfield, 1997; Alberti *et al.*, 1996; Snover *et al.*, 1996; Serre & Férey, 2002). Bisphosphonates also have pharmaceutical applications (Fleisch, 1995; Fleisch *et al.*, 1969; Kanis & McCloskey, 1990; Bijvoet *et al.*, 1995) and one of the best documented methylene bisphosphonate derivatives in these applications is clodronate, or (dichloromethylene)bisphosphonate (Major *et al.*, 2000). Clodronate has six possible O-donor atoms and it also forms polymeric structures that can be utilized in chemical applications.

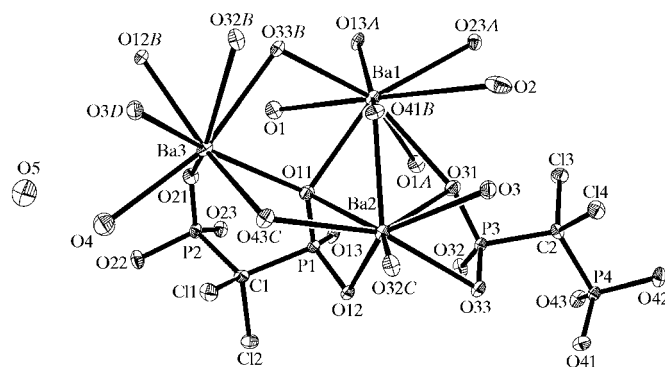
The previously reported crystal structures of Ca and Sr complexes of clodronate,  $[M\{\text{Cl}_2\text{C}(\text{PO}_3\text{H})_2\}(\text{H}_2\text{O})_5]$  (*M* is Ca or Sr), revealed that clodronate itself acts only as a bidentate chelating ligand, forming monomeric compounds (Nardelli *et al.*, 1983; Kontturi *et al.*, 2004a). On the other hand, our results

show that both clodronate and its partial ester derivative also produce polymers (Kontturi *et al.*, 2002, 2004b). The title novel Ba complex of clodronate,  $\{[\text{Ba}_3(\text{Cl}_2\text{CP}_2\text{O}_6\text{H})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$ , (I), is also a polymer, but its composition differs from the polymeric Ca complexes of clodronate described earlier (Kontturi *et al.*, 2004b). Its preparation and crystal structure are reported here.

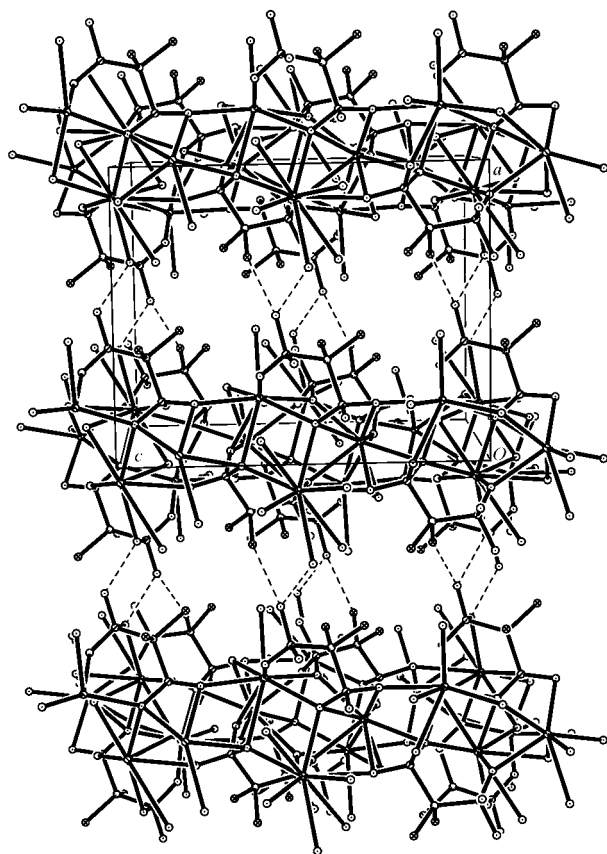


Compound (I) is a polymer, the asymmetric unit consisting of three independent  $\text{Ba}^{2+}$  atoms, two chelating and bridging  $\text{Cl}_2\text{CP}_2\text{O}_6\text{H}^{3-}$  ligands and four aqua ligands (Fig. 1). Five O atoms of both  $\text{Cl}_2\text{CP}_2\text{O}_6\text{H}^{3-}$  ligands are coordinated to Ba atoms, forming four- and six-membered chelate rings and acting as monoatomic bridges between the metal atoms. Two O atoms (O11 and O33) are coordinated simultaneously to all three Ba atoms, the P–O distances being 1.523 (3) and 1.522 (3) Å. The other coordinated O atoms have P–O distances in the range 1.492 (3)–1.515 (3) Å, and the P–O distances of the remaining, protonated, O atoms are 1.562 (3) and 1.575 (3) Å. The other bond distances and angles of the  $\text{Cl}_2\text{CP}_2\text{O}_6\text{H}^{3-}$  ligand are all typical (Nardelli *et al.*, 1983; Kontturi *et al.*, 2002, 2004a,b).

Of the three Ba atoms in (I), Ba1 is nine-coordinated, while Ba2 and Ba3 are eight-coordinated. The coordination spheres of all Ba atoms consist of four  $\text{Cl}_2\text{CP}_2\text{O}_6\text{H}^{3-}$  ligands, the remaining coordination sites being occupied by aqua ligands. The Ba–O bond distances range from 2.653 (3) to 3.292 (4) Å



**Figure 1**  
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms have been omitted. Atoms labelled with the suffixes *A, B, C* and *D* are at the symmetry positions  $(-x, -y, 1-z)$ ,  $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ ,  $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$  and  $(-x, 1-y, 1-z)$ , respectively.


**Figure 2**

A packing diagram for (I), viewed in the direction of the *b* axis, indicating the pores between the layers. For clarity, H atoms and the lattice water molecules have been omitted.

(Table 1). The layers of (I) are parallel to the (100) plane, and they are packed *via* intermolecular hydrogen bonds, the O...O/Cl distances being 2.606 (4)–3.081 (4) Å (146–173°) (Table 2). The packing diagram (Fig. 2) shows pores between the layers in the direction of the *b* axis. These pores are filled with lattice water molecules.

## Experimental

Compound (I) was crystallized by the gel method using Na<sub>2</sub>Cl<sub>2</sub>-C(PO<sub>3</sub>H)<sub>2</sub>·4H<sub>2</sub>O (0.014 mmol, 5.0 mg) and Ba(NO<sub>3</sub>)<sub>2</sub> (0.017 mmol, 4.5 mg). These compounds were dissolved in water (0.8 ml, pH 4), tetramethoxysilane (TMOS, 0.2 ml) was added, and the solution was shaken until homogenous. After gel formation, acetone (1.0 ml) was placed above the gel as precipitant. Needle-shaped crystals of (I) formed in and above the gel, and these were purified for characterization under the microscope. Analysis found: C 2.45, H 0.71, Ba 41.7%; calculated for C<sub>2</sub>H<sub>12</sub>Ba<sub>3</sub>Cl<sub>4</sub>O<sub>17</sub>P<sub>4</sub>: C 2.44, H 1.23, Ba 41.8%.

### Crystal data

|   |   |
|---|---|
| [Ba <sub>3</sub> (CHCl <sub>2</sub> O <sub>6</sub> P <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O | <i>D<sub>x</sub></i> = 3.089 Mg m <sup>-3</sup> |
| <i>M<sub>r</sub></i> = 985.82   | Mo <i>K</i> α radiation                         |
| Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>  | Cell parameters from 24 802 reflections         |
| <i>a</i> = 11.4147 (3) Å  | <i>θ</i> = 2.8–26.0°                            |
| <i>b</i> = 12.9907 (4) Å  | <i>μ</i> = 6.40 mm <sup>-1</sup>                |
| <i>c</i> = 14.2937 (5) Å  | <i>T</i> = 120 (2) K                            |
| <i>β</i> = 90.290 (2)°  | Needle, colourless                              |
| <i>V</i> = 2119.51 (11) Å <sup>3</sup>  | 0.25 × 0.10 × 0.10 mm                           |
| <i>Z</i> = 4  |   |

### Data collection

|  |   |
|--|---|
| Nonius KappaCCD area-detector diffractometer                                       | 4133 independent reflections                    |
| <i>φ</i> and <i>ω</i> scans  | 3746 reflections with <i>I</i> > 2σ( <i>I</i> ) |
| Absorption correction: multi-scan ( <i>XPREP</i> in <i>SHELXTL</i> ; Bruker, 1998) | <i>R</i> <sub>int</sub> = 0.054                 |
| <i>T</i> <sub>min</sub> = 0.277, <i>T</i> <sub>max</sub> = 0.528                   | <i>θ</i> <sub>max</sub> = 26.0°                 |
| 24 802 measured reflections  | <i>h</i> = -14 → 14                             |
|  | <i>k</i> = -16 → 16                             |
|  | <i>l</i> = -17 → 17                             |

### Refinement

|                                     |  |
|-------------------------------------|--|
| Refinement on <i>F</i> <sup>2</sup> | $w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 7.3351P]$        |
| $R[F^2 > 2\sigma(F^2)] = 0.026$     | where $P = (F_o^2 + 2F_c^2)/3$                           |
| $wR(F^2) = 0.057$                   | ( <i>Δ</i> / <i>σ</i> ) <sub>max</sub> < 0.001           |
| <i>S</i> = 1.13                     | <i>Δρ</i> <sub>max</sub> = 0.72 e Å <sup>-3</sup>        |
| 4133 reflections                    | <i>Δρ</i> <sub>min</sub> = -0.82 e Å <sup>-3</sup>       |
| 272 parameters                      | Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997) |
| H-atom parameters constrained       | Extinction coefficient: 0.00049 (6)                      |

**Table 1**

Selected geometric parameters (Å, °).

|                        |             |                        |             |
|------------------------|-------------|------------------------|-------------|
| Ba1—O13 <sup>i</sup>   | 2.704 (3)   | Ba3—O43 <sup>iii</sup> | 2.801 (3)   |
| Ba1—O41 <sup>ii</sup>  | 2.743 (3)   | Ba3—O4                 | 2.820 (4)   |
| Ba1—O33 <sup>ii</sup>  | 2.776 (3)   | Ba3—O11                | 2.833 (3)   |
| Ba1—O1                 | 2.821 (3)   | Ba3—O32 <sup>ii</sup>  | 2.898 (3)   |
| Ba1—O11                | 2.822 (3)   | Ba3—O33 <sup>ii</sup>  | 2.943 (3)   |
| Ba1—O1 <sup>i</sup>    | 2.880 (3)   | Ba3—O3 <sup>iv</sup>   | 2.957 (3)   |
| Ba1—O31                | 2.902 (3)   | P1—O13                 | 1.512 (3)   |
| Ba1—O23 <sup>i</sup>   | 3.032 (3)   | P1—O12                 | 1.514 (3)   |
| Ba1—O2                 | 3.292 (4)   | P1—O11                 | 1.523 (3)   |
| Ba2—O32 <sup>iii</sup> | 2.653 (3)   | P2—O21                 | 1.492 (3)   |
| Ba2—O41 <sup>ii</sup>  | 2.689 (3)   | P2—O23                 | 1.512 (3)   |
| Ba2—O12                | 2.742 (3)   | P2—O22                 | 1.562 (3)   |
| Ba2—O43 <sup>iii</sup> | 2.788 (3)   | P3—O31                 | 1.514 (3)   |
| Ba2—O3                 | 2.869 (3)   | P3—O32                 | 1.515 (3)   |
| Ba2—O11                | 2.871 (3)   | P3—O33                 | 1.522 (3)   |
| Ba2—O33                | 2.878 (3)   | P4—O41                 | 1.498 (3)   |
| Ba2—O31                | 2.909 (3)   | P4—O43                 | 1.500 (3)   |
| Ba3—O12 <sup>ii</sup>  | 2.658 (3)   | P4—O42                 | 1.575 (3)   |
| Ba3—O21                | 2.772 (3)   |                        |             |
| P2—C1—P1               | 114.4 (2)   | O22—P2—C1              | 105.89 (19) |
| P3—C2—P4               | 114.0 (2)   | O31—P3—C2              | 108.61 (19) |
| O13—P1—C1              | 104.15 (18) | O32—P3—C2              | 101.84 (18) |
| O12—P1—C1              | 105.98 (18) | O33—P3—C2              | 107.13 (17) |
| O11—P1—C1              | 106.39 (18) | O41—P4—C2              | 105.44 (18) |
| O21—P2—C1              | 106.25 (18) | O43—P4—C2              | 110.26 (18) |
| O23—P2—C1              | 106.63 (18) | O42—P4—C2              | 103.33 (18) |

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i>     | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O22—H22...O23 <sup>i</sup>  | 0.85        | 1.77          | 2.606 (4)             | 169                     |
| O42—H42...O2 <sup>ii</sup>  | 0.85        | 1.82          | 2.667 (4)             | 173                     |
| O1—H1A...O21                | 0.85        | 1.88          | 2.722 (4)             | 170                     |
| O1—H1B...O32 <sup>iii</sup> | 0.85        | 2.27          | 3.020 (4)             | 148                     |
| O2—H2A...O31                | 0.84        | 1.89          | 2.697 (5)             | 159                     |
| O2—H2B...O23 <sup>iii</sup> | 0.85        | 2.25          | 2.992 (5)             | 146                     |
| O3—H3A...O13 <sup>iv</sup>  | 0.85        | 1.91          | 2.744 (4)             | 166                     |
| O3—H3B...O5 <sup>v</sup>    | 0.85        | 2.13          | 2.893 (5)             | 150                     |
| O4—H4A...O5                 | 0.85        | 2.03          | 2.868 (5)             | 166                     |
| O5—H5A...O2 <sup>v</sup>    | 0.85        | 2.25          | 3.037 (5)             | 154                     |
| O5—H5B...O22 <sup>vi</sup>  | 0.85        | 2.35          | 3.081 (5)             | 146                     |

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

H atoms were located in difference Fourier maps, with O—H distances of approximately 0.85 Å, and a riding model was used, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1775). Services for accessing these data are described at the back of the journal.

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