

Poly[(acetone)tetraaqua[μ_6 -ethyl (dichloromethylene)diphosphonato]- μ_5 -ethyl (dichloromethylene)-diphosphonato]tribarium(II)

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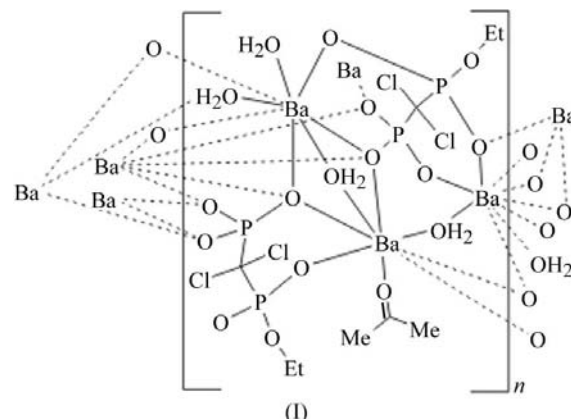
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The novel title compound, $[\text{Ba}_3(\text{C}_3\text{H}_5\text{Cl}_2\text{O}_6\text{P}_2)_2(\text{C}_3\text{H}_6\text{O})(\text{H}_2\text{O})_4]_n$, has a polymeric two-dimensional network structure which lies parallel to the $(10\bar{1})$ plane. The asymmetric unit consists of three independent Ba^{2+} ions, two of them eight-coordinated and the third nine-coordinated, and two independent ethyl (dichloromethylene)diphosphonate(3⁻) ligands, one acetone ligand and four aqua ligands. The coordination environments around the BaO_8 polyhedra are best described as bicapped trigonal prismatic, while the BaO_9 polyhedron is in a distorted tricapped trigonal prismatic geometry. The two diphosphonate ligands adopt different coordination modes. Both ligands chelate three metal cations, but one is coordinated to six metal cations in total and forms two six-membered and one four-membered chelate ring, while the other is coordinated to five metal cations in total and forms one six-membered and two four-membered chelate rings, the fifth unsubstituted O atom remaining uncoordinated.

Comment

Diphosphonic acids have attracted close attention because of their utility in supramolecular chemistry and crystal engineering (Clearfield *et al.*, 2001; Fu *et al.*, 2007). Usually, metal diphosphonates form polymeric materials and microporous solids, with properties that offer a diversity of practical applications in catalysis, ion-exchange and sorption (Clearfield, 1998, and references therein; Fu *et al.*, 2007; Serre *et al.*, 2006). Clodronate [(dichloromethylene)diphosphonate or Cl_2MBP] is one of the best documented diphosphonates since it is widely used in therapeutics (Russell, 2007; Rodan & Martin, 2000). Several metal diphosphonate complexes are known where the diphosphonate ligand is fully ionic, but studies of the complexation of their ester derivatives are limited. The introduction of these ester substituents on

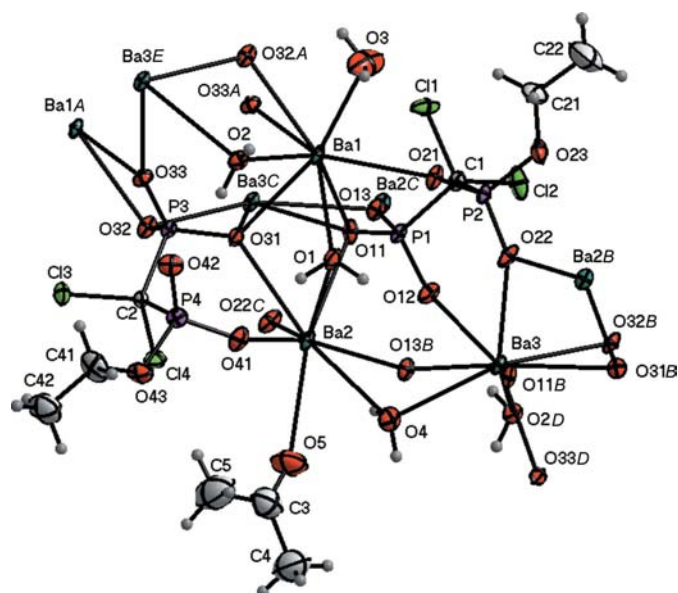
phosphorus groups can result in novel structures of metal diphosphonates and produce interesting functionalities. However, of the numerous metal phosphonate compounds now known, only a small number have been prepared with alkali earth metals.



In earlier work, we developed a method for the preparation of partial amide esters of Cl_2MBP (Jokiniemi *et al.*, 2006) and a novel synthesis for partial phenyl esters of Cl_2MBP (Jokiniemi *et al.*, 2009). Several metal complexes of amide ester derivatives of clodronic acid have been reported by our group (Jokiniemi *et al.*, 2007, 2008). We have also succeeded in preparing new Cd complexes with monophenyl, asymmetric diphenyl and monoethyl ester ligands of Cl_2MBP , and these will be reported shortly (Jokiniemi *et al.*, 2009).

In this work, using the monoethyl ester anion of Cl_2MBP , we obtained the title novel layered Ba diphosphonate complex, (I), whose structure is different from the structures reported for other metal complexes of ester derivatives of Cl_2MBP .

The asymmetric unit of (I) consists of three crystallographically independent Ba^{2+} ions, two independent ethyl (dichloromethylene)diphosphonate(3⁻) ligands, one acetone molecule and four aqua ligands. As shown in Fig. 1, there are two coordination modes for the $(\text{Cl}_2\text{CP}_2\text{O}_6\text{Et})^{3-}$ ligands. The methylenediphosphonate ligand containing atoms P1 and P2 is coordinated to six Ba^{2+} cations through five O atoms, forming two six-membered chelate rings with atoms Ba1 and Ba3, while atom P1 forms a four-membered chelate ring with adjacent atom Ba3C [symmetry code: $(C) \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The methylenediphosphonate ligand containing atoms P3 and P4 is coordinated to five Ba^{2+} cations through four O atoms, forming a six-membered chelate ring with atom Ba2, while atom P3 forms two four-membered chelate rings with atoms Ba1A [symmetry code: $(A) -x, 1 - y, -z$] and Ba3C. Thus, atom O42 of the phosphonate group containing atom P4 remains uncoordinated but is involved in hydrogen bonding. In both methylenediphosphonate ligands, two O atoms (O13/O22 and O32/O33) act as monoatomic bridges between two Ba atoms, and one O atom (O11 and O31) is coordinated simultaneously to three Ba atoms (Ba1, Ba2 and Ba3C). The $\text{Ba1} \cdots \text{Ba3C}$ contact of 4.1404 (8) Å is shorter than the sum of the van der Waals radii of Ba (4.28 Å; Guo & Zhang, 2008; Srinivasan *et al.*, 2007), indicating weak metal-to-metal interaction.

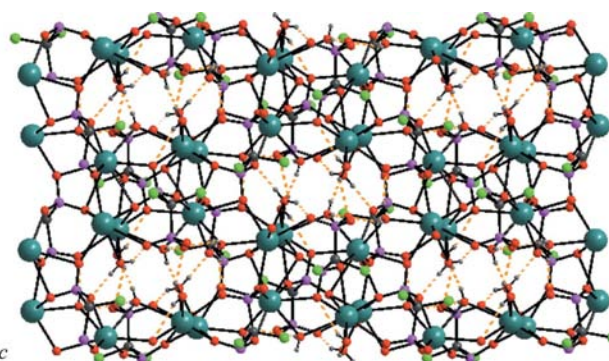

Figure 1

The structure of the asymmetric unit of (I), expanded to show relevant symmetry-related atoms, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffixes A–E are at the symmetry positions $(-x, 1-y, -z)$, $(\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z)$, $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$, respectively.

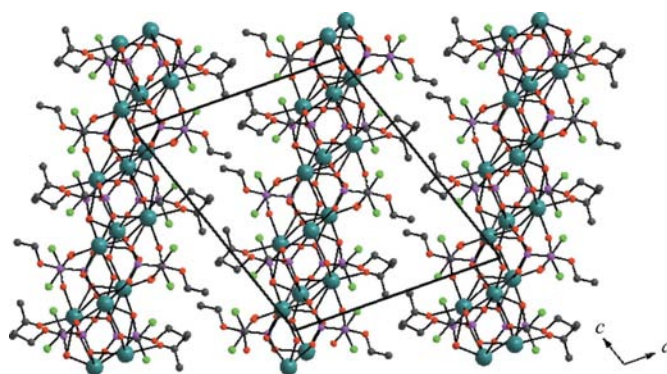
Both atoms Ba1 and Ba2 are eight-coordinated in a distorted bicapped trigonal prismatic geometry. The coordination environment around atom Ba1 consists of five phosphonate O atoms from three different methylenediphosphonate ligands and three aqua ligands. The Ba1–O bond distances range from 2.692 (3) to 2.889 (3) Å (Table 1). Aqua ligands O2 and O3 bridge atom Ba1 to adjacent atoms Ba2 and Ba3E [symmetry code: (E) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$], with a Ba1···Ba2 distance of 4.301 (1) Å and a Ba1···Ba3E distance of 4.502 (2) Å. The coordination environment around atom Ba2 consists of five phosphonate O atoms from four different methylenediphosphonate ligands, two bridging aqua ligands and one acetone ligand. The Ba2–O bond distances vary more widely, from 2.637 (3) to 3.226 (3) Å, compared with those involving atoms Ba1 and Ba3. Atom Ba3 is nine-coordinated in a distorted tricapped trigonal prismatic geometry. The coordination sites around the metal centre are occupied by seven phosphonate O atoms from five different methylenediphosphonate ligands, and two bridging aqua ligands. The Ba3–O bond distances range from 2.642 (3) to 3.023 (3) Å.

The infinite two-dimensional network of (I) can be thought of as formed through phosphonate atoms O12, O22 and O13, which link the Ba2 and Ba3 centres by acting as mono- and triatomic bridges. The O4 aqua ligand bridges atoms Ba2 and Ba3 [Ba2···Ba3 = 4.385 (1) Å] and is involved in forming the two-dimensional polymeric structure lying parallel to the (10 $\bar{1}$) plane (Fig. 2). As presented in Fig. 3, the Cl atoms and ethyl groups point away from the layers, with an interlayer distance of 14.5492 (4) Å.

The layered structure of (I) is stabilized by intralayer hydrogen bonds involving all the aqua ligands and coordi-


Figure 2

The two-dimensional network of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds. Ethyl groups and acetone molecules have been omitted for clarity.


Figure 3

The packing of the layers of (I) parallel to the (10 $\bar{1}$) plane, viewed along the *b* axis. H atoms have been omitted for clarity.

nated phosphonate O atoms (O12, O21, O32 and O41), and noncoordinated phosphonate atom O42 (Table 2, wherein the following symmetry codes are defined). Aqua ligands O1 and O4ⁱⁱ donate H atoms to phosphonate atoms O12ⁱⁱ and O21, respectively, thereby closing a Ba1–O1–H1B···O12ⁱⁱ–Ba3ⁱⁱ–O4ⁱⁱ–H4Aⁱⁱ···O21–Ba1 ring, which has a graph-set motif of $R_2^2(8)$ (Bernstein *et al.*, 1995). The O1 aqua ligand is also involved in hydrogen bonds with phosphonate atom O41 and aqua ligand O2^v, which results in two further ring motifs, *viz.* $S(4)$ (Ba2–O1–H1A···O41–Ba2) and $R_2^2(6)$ (Ba3ⁱⁱ–O2^v–H2A^v···O1–H1B···O12ⁱⁱ–Ba3ⁱⁱ). As aqua ligand O2 is involved in hydrogen bonding with atom O42, which further acts as an acceptor for two other H atoms of aqua ligands O3^v and O4^{vi} [symmetry code: (vi) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$], a hydrogen-bonding network with several combined rings is formed.

Experimental

The title compound was crystallized by the gel method. The starting materials Na₃Cl₂CP₂O₆Et (10 mg, 0.030 mmol) and BaCl₂·2H₂O (7.2 mg, 0.030 mmol) were dissolved separately in water (0.45 ml) and mixed, and tetramethoxysilane (0.1 ml) was added. The two-phase system was shaken until homogeneous. After gel formation, a precipitant, acetone (1 ml), was added above the gel to induce crystallization. Several months later, plate-like colourless crystals of (I) suitable for X-ray analysis had formed above the gel. Crystals suitable

Table 1
Selected bond lengths (Å).

Ba1—O21	2.692 (3)	Ba2—O31	2.833 (3)
Ba1—O11	2.721 (3)	Ba2—O4	3.036 (4)
Ba1—O31	2.724 (3)	Ba2—O1	3.226 (3)
Ba1—O32 ⁱ	2.731 (3)	Ba3—O12	2.642 (3)
Ba1—O3	2.748 (4)	Ba3—O33 ^{iv}	2.654 (3)
Ba1—O1	2.817 (3)	Ba3—O22	2.709 (3)
Ba1—O2	2.842 (3)	Ba3—O32 ⁱⁱ	2.772 (3)
Ba1—O33 ⁱ	2.889 (3)	Ba3—O13 ⁱⁱ	2.873 (3)
Ba2—O13 ⁱⁱ	2.637 (3)	Ba3—O4	2.892 (3)
Ba2—O41	2.723 (3)	Ba3—O2 ^{iv}	2.903 (3)
Ba2—O11	2.777 (3)	Ba3—O11 ⁱⁱ	2.910 (3)
Ba2—O22 ⁱⁱⁱ	2.793 (3)	Ba3—O31 ⁱⁱ	3.023 (3)
Ba2—O5	2.818 (5)		

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

for X-ray diffraction analysis were separated from the gel on a watch-glass under a microscope, washed with pure precipitant and dried in air.

Crystal data

[Ba ₃ (C ₃ H ₅ Cl ₂ O ₆ P ₂) ₂ (C ₃ H ₆ O)·(H ₂ O) ₄]	$\beta = 109.32 (3)^\circ$
$M_r = 1081.98$	$V = 3003.5 (10) \text{ \AA}^3$
Monoclinic, $P2_1/n$	$Z = 4$
$a = 16.635 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.814 (2) \text{ \AA}$	$\mu = 4.52 \text{ mm}^{-1}$
$c = 19.495 (4) \text{ \AA}$	$T = 150 \text{ K}$
	$0.25 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	41896 measured reflections
Absorption correction: multi-scan (XPREP in SHELXTL; Sheldrick, 2008)	5887 independent reflections
$T_{\min} = 0.550, T_{\max} = 0.805$	5446 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	$\Delta\rho_{\text{max}} = 2.99 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.92 \text{ e \AA}^{-3}$
5887 reflections	
346 parameters	

C-bound H atoms were placed in calculated positions and refined using the riding-model approximation, with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms, and C—H 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms. Water H atoms were located in a difference Fourier map and treated as riding, with O—H = 0.83–0.86 Å, and their isotropic displacement parameters were refined. The C atoms of the coordinated acetone molecule and ethyl substituent (C4, C5 and C22) all have relatively high thermal motion, indicating disorder in the methyl groups. However, no residual electron density suitable for a split-atom model was found. The highest peak (2.99 e Å⁻³) in the difference Fourier map is located 0.75 Å from atom H3B and the deepest hole (−0.92 e Å⁻³) is located 0.88 Å from Ba1.

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduc-

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O41	0.86	2.02	2.798 (5)	150
O1—H1B \cdots O12 ⁱⁱ	0.85	1.85	2.697 (4)	173
O2—H2B \cdots O42	0.83	1.99	2.813 (5)	172
O2—H2A \cdots O1 ^v	0.84	2.07	2.886 (5)	163
O3—H3A \cdots O42 ^v	0.85	2.11	2.796 (6)	137
O3—H3B \cdots O32 ⁱ	0.85	2.58	3.034 (6)	114
O4—H4A \cdots O21 ⁱⁱⁱ	0.85	1.96	2.806 (5)	170
O4—H4B \cdots O42 ^{iv}	0.85	2.28	2.957 (5)	137

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

tion: DENZO/SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2005); 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: LN3125). Services for accessing these data are described at the back of the journal.

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