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Poly[[tri-μ-aqua-dodecaaquatris(μ_3-1-hydroxyethylidene-1,1-diphosphonato)tricalcium(II)tripalladium(II)] pentahydrate]

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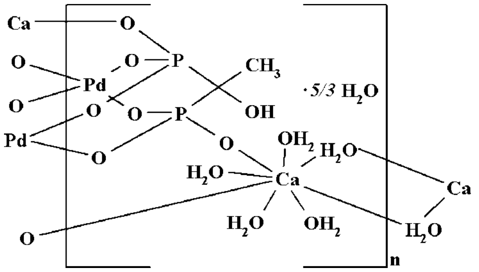
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(Pd–O) = 0.003 Å; H-atom completeness 84%; disorder in main residue; R factor = 0.031; wR factor = 0.071; data-to-parameter ratio = 15.3.

The asymmetric unit of the title compound, $\{[CaPd\{CH_3OHC(PO_3)_2\}(H_2O)_5]\cdot5/3H_2O\}_n$, consists of one half of the complex $[Pd\{CH_3OHC(PO_3)_2\}]^{2-}$ anion (point group symmetry m..), one Ca^{2+} cation [site symmetry (.2.)] that is surrounded by three water molecules (one of which is on the same rotation axis) and by three disordered lattice water molecules. The anions form a trinuclear metallocycle around a crystallographic threefold rotation axis. The cations are related by a twofold rotation axis to form a $[Ca_2(H_2O)_{10}]^{2+}$ dimer. The slightly distorted square-planar coordination environment of the Pd^{II} atoms in the complex anions is formed by O atoms of the bidentate chelating phosphonate groups of the 1-hydroxyethylidene-1,1-diphosphonate ligands. In the crystal, cations are bound to anions through —Ca—O—P—O— bonds, as well as through O—H⋯O hydrogen bonds, resulting in a three-dimensional polymer. The structure is completed by five disordered solvent molecules localized in cavities within the framework.

Related literature

For background to diphosphonic acids see: Zhang *et al.* (2007); Szabo *et al.* (2002); Matczak-Jon & Videnova-Adrabinska (2005). For background to the antitumor activity of palladium(II) complexes, see: Juribašić *et al.* (2011); Curic *et al.* (1996); Abu-Surrah *et al.* (2008); Ruiz *et al.* (2005, 2006); Tušek-Božić *et al.* (2008). For the structures of related complexes, see: Babaryk *et al.* (2012); Hammerl *et al.* (2002); Müller (1972).



Experimental

Crystal data

$[CaPd(C_2H_4O_7P_2)(H_2O)_5]\cdot1.67H_2O$
M_r = 468.58
Hexagonal, $P6/mcc$
a = 15.9731 (3) Å
c = 18.4149 (4) Å
V = 4068.91 (14) Å^3
Z = 12
Mo $K\alpha$ radiation
μ = 2.05 mm^{-1}
T = 296 K
0.39 × 0.07 × 0.06 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2009)
T_{min} = 0.502, T_{max} = 0.887
37638 measured reflections
1774 independent reflections
1410 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.071
S = 1.08
1774 reflections
116 parameters
28 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H1⋯O1^{i}	0.84 (1)	1.95 (2)	2.756 (3)	160 (4)
O5—H2⋯O5^{ii}	0.79 (2)	2.07 (2)	2.799 (5)	155 (4)
O6—H3⋯O2^{iii}	0.82 (2)	1.87 (2)	2.685 (3)	170 (4)
O7—H4⋯O3^{i}	0.82 (2)	2.07 (2)	2.865 (4)	166 (4)
O4A—H4A⋯O8	0.82	1.99	2.731 (16)	150

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: BR2239).

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Acta Cryst. (2014). E**70**, m291–m292   [doi:10.1107/S1600536814015189]

Poly[[tri-μ-aqua-dodecaaquatris(μ_3-1-hydroxyethylidene-1,1-diphosphonato)tricalcium(II)tripalladium(II)] pentahydrate]

Irina P. Kutsenko, Alexandra N. Kozachkova, Natalia V. Tsaryk, Vasily I. Pekhnyo and Julia A. Rusanova

S1. Comment

During the last decade, there has been a growing interest in the study of organic diphosphonic acids owing to their potentially very powerful chelating properties used in metal extractions and are tested by the pharmaceutical industry for use as efficient drugs preventing calcification and inhibiting bone resorption (Matczak-Jon & Videnova-Adrabinska, 2005). Diphosphonic acids and their metal complexes are used in the treatment of Pagets disease, osteoporosis and tumoral osteolysis (Szabo *et al.*, 2002). Also in the last years, there has been a surge of interest in palladium complexes as a prospective antitumor preparation (Abu-Surrah *et al.*, 2008, Curic *et al.*, 1996).

The title compound crystallized in centric space group P6/mcc. The square-planar environment of palladium atoms in the complex anion $[Pd_3\{CH_3OHC(PO_3)_2\}_3]^{6-}$is formed by coordination of the oxygen atoms of the chelating phosphonic groups of the ligand. By crystallographic threefold rotation axis it completed to trinuclear species with equilateral triangle geometry (Fig.1). Palladium atoms slightly deviate from the oxygen mean-planes towards the triangle center by 0.12 Å. The range of Pd – O bond distances of 2,006 (2) – 2,010 (2)Å as well *cis* O–Pd–O angles ranging from 85.78 (9)° to 92.91 (13)° are in a good agreement with literature values (Babaryk *et al.*, 2012 and references therein). CH_3 and OH groups of the HEDP are statistically disordered over two positions with equal occupation numbers.

As it shown on Fig. 2, each Ca atom of the complex binuclear cation is surrounded by eight oxygen atoms (six from water molecules, comprising two bridging ones, and two from phosphonic groups of the trinuclear clusters) in the form of a slightly distorted, bi-capped trigonal prism. (Hammerl *et al.*, 2002). The Ca – O bond distances were observed within the range of 2,416 (3) – 2,538 (3)Å. Calcium coordinated by eight water molecules is well known in the literature, and the distances of the bridging and nonbridging oxygen atoms found here agree well with the previously reported values (Müller *et al.*, 1972). Each binuclear cation linked to four trinuclear anions of adjacent layers through -Ca-O-P-O- bonds (Fig. 3) as well thought O-H···O hydrogen bonds. Moreover, each trinuclear anion is linked to six binuclear cations. In the crystal packing cations and anions stacked along the *c* axis into columns where layer of cations alternates with layer of anions. Resulting layered 3d polymer structure (Fig.4) completed by five disordered solvent water molecules which are located in cavities. The Ca – O and P-O bond distances (2.507 (2)Å and 1.498 (2)Å respectively) as well as D···A distances ranging from 2.756 (3)Å to 2.865 (4)Å are in a good agreement with literature values. Oxygen atom of one of the water solvent molecules O8 is statistically disordered over two positions and linked to cation thought CH_3-C-OH···O8 hydrogen bonds with D···A distance about 2.731 (16) Å. Another one water molecule oxygen atom O9 is situated at the origin (0, 0, 0) with 1/12 multiplicity. Remaining 3 oxygen atoms O10 of the water molecules are disordered around 6-fold rotation axis with centre of symmetry over 12 positions with an occupation number of 1/4. Considering this reasonable H-atom positions of the disordered solvent water molecules were not established

S2. Experimental

A solution of $AgNO_3$ (0.3398 g, 2.0 mmol) in H_2O (5 ml) was added to a solution of $PdCl_2$ (0.0885 g, 0.5 mmol) in hydrochloric acid (0.1*M*, 10 ml) and the resulting solution stirred at 276 K for 30 min under protection from light until AgCl was precipitated and filtered off. Hydroxyethylidenediphosphonic acid (0.112 g, 0.5 mmol) and $CaCO_3$ (0.05 g, 0.5 mmol) were added to filtrate. The resulting solution was stirred for 1 h at 276 - 277 K and left staying overnight at room temperature. The solvent was removed from resulting reaction mixture under reduced pressure leaving an yellow solid, which was washed twice with methanol and diethyl ether and dried under vacuum. Yellow rectangular crystals of the title compound suitable for crystallographic study were produced by slow evaporation of a water solution at room temperature.

S3. Refinement

The structure was solved by the direct method. H atoms of methyl groups were placed at calculated positions and treated as riding on the parent atoms, with $U_{\rm iso}(H) = 1.5\ U_{\rm eq}(C)$. H atoms near of the O4A and O4B atoms, and H atoms of water molecule were located in a difference Fourier map and further refined with SADI instruction to the restraint that they should be equal within about 0.02 Å and $U_{\rm iso}(H) = 1.5Ueq(O)$. The OH and CH_3 groups near C(1) carbon atom are disordered over two position with occupancy factor 0.25 and 0.25 respectively. Oxygen atoms of the water solvent molecules O8, O9, O10 were refined isotropically- O8 is statistically disordered with occupancy 1/2 and it position depends on the disorder of the above mentioned OH group; O9 is situated at the origin (0, 0, 0) with 1/12 multiplicity; three oxygen atoms O10 are disordered around 6-fold rotation axis with centre of symmetry over 12 positions with an occupation number of 1/4. Considering this reasonable H-atom positions of the disordered solvent water molecules were not established.

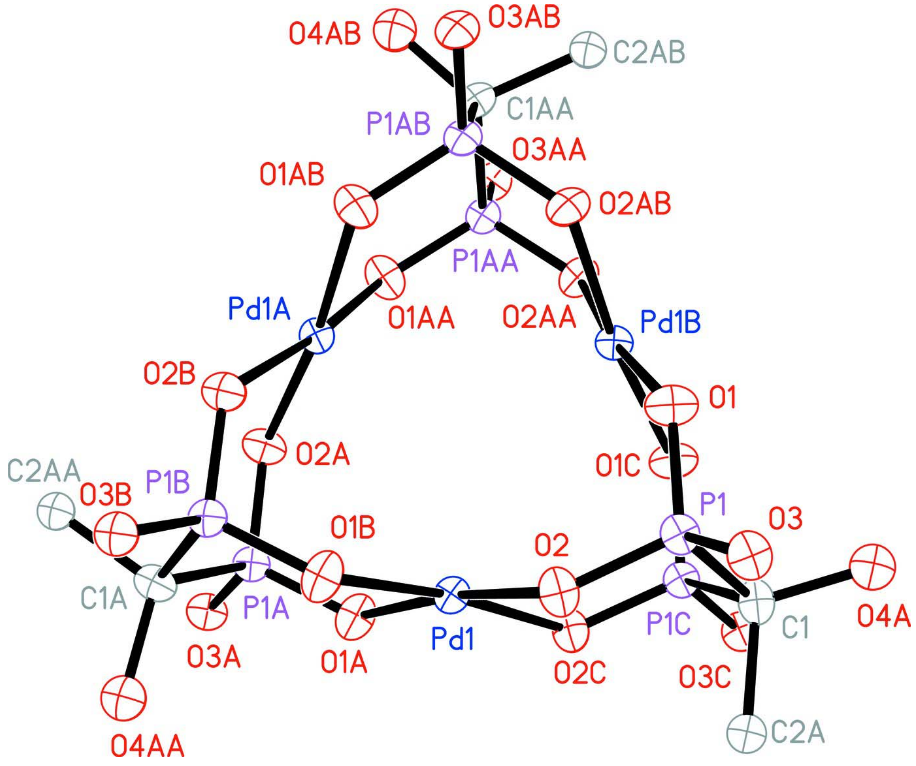

Figure 1

View of the anionic part of $[Pd_3\{O_3PC(OH)(CH_3)PO_3\}_3]^{6-}$ unit showing 50% probability displacement ellipsoids for the non-hydrogen atoms.

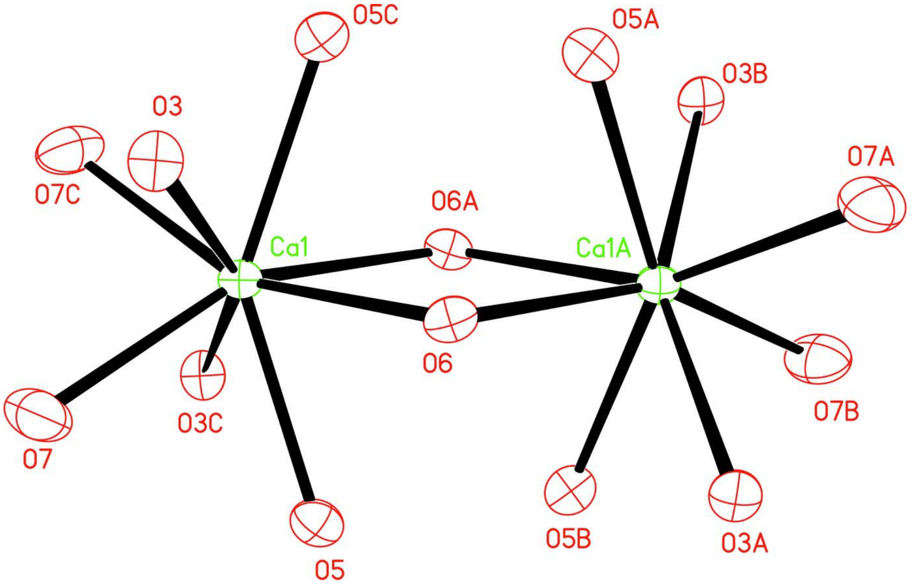

Figure 2

View of the cationic part of $[(4H_2O)O2Ca(2H_2O)CaO2(4H_2O)]^{2+}$ fragments showing 50% probability displacement ellipsoids for the non-hydrogen atoms.

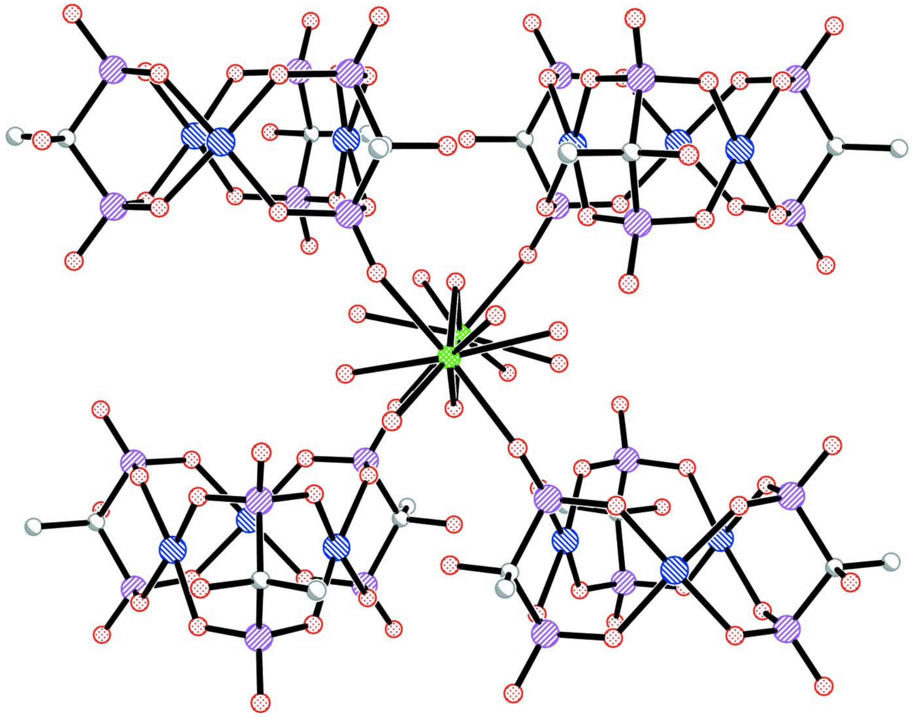

Figure 3

Linking of cations to anions of adjacent layers in crystal packing.

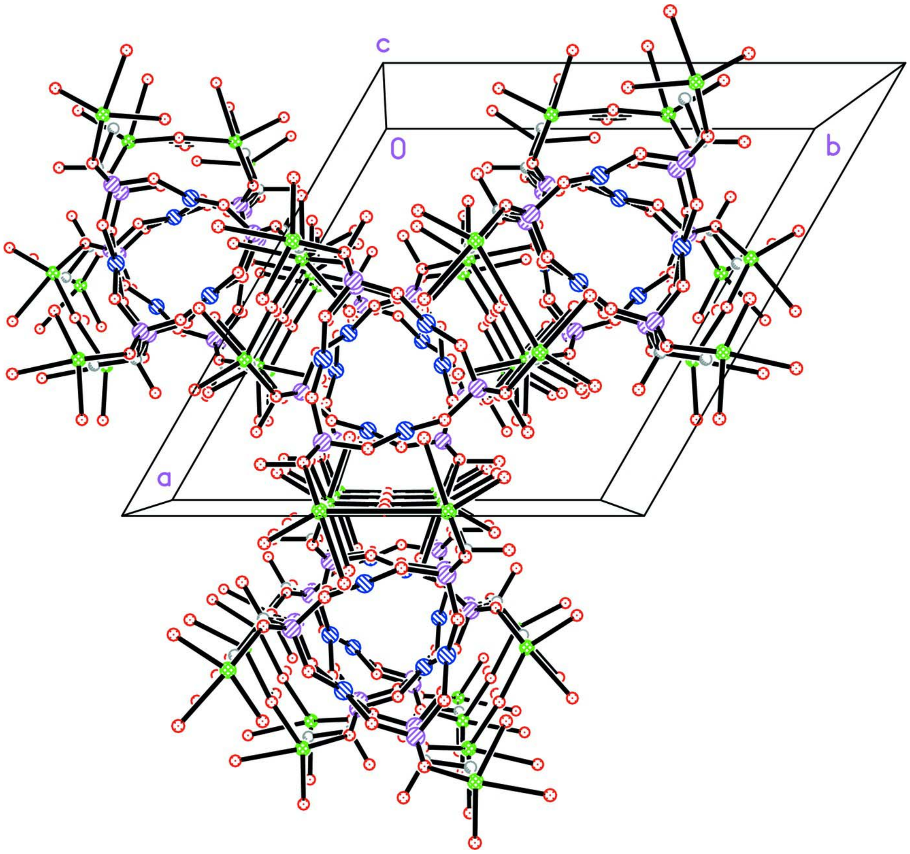

Figure 4

Crystal packing of title compound, in a projection along the *c* axis. Solvate molecules as well as hydrogen bonds are omitted for clarity.

Poly[[tri-μ-aqua-dodecaaquatris(μ_3-1-hydroxyethylidene-1,1-diphosphonato)tricalcium(II)tripalladium(II)] pentahydrate],

Crystal data

$[CaPd(C_2H_4O_7P_2)(H_2O)_5]\cdot1.67H_2O$	$F(000) = 2816$
$M_r = 468.58$	$D_x = 2.295$ Mg m^{-3}
Hexagonal, *P*6/*mcc*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 6 2c	$\mu = 2.05$ mm^{-1}
$a = 15.9731$ (3) Å	$T = 296$ K
$c = 18.4149$ (4) Å	Rectangular, yellow
$V = 4068.91$ (14) Å^3	0.39 × 0.07 × 0.06 mm
$Z = 12$	

Data collection

Bruker APEXII CCD area-detector diffractometer	37638 measured reflections
Radiation source: fine-focus sealed tube	1774 independent reflections
Graphite monochromator	1410 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\rm int} = 0.082$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2009)	$\theta_{\rm max} = 28.4°$, $\theta_{\rm min} = 2.6°$
	$h = -21\rightarrow21$
	$k = -21\rightarrow18$
$T_{\rm min} = 0.502$, $T_{\rm max} = 0.887$	$l = -22\rightarrow24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.071$
$S = 1.08$
1774 reflections
116 parameters
28 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 11.4857P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Pd1	0.63688 (3)	0.44960 (3)	0.0000	0.01659 (11)	
Ca1	0.37002 (6)	0.37002 (6)	0.2500	0.0182 (2)	
P1	0.45030 (6)	0.28992 (6)	0.08236 (4)	0.01779 (18)	
O1	0.48149 (18)	0.21370 (18)	0.08028 (12)	0.0246 (5)	
O2	0.53726 (17)	0.39316 (17)	0.07897 (12)	0.0223 (5)	
O3	0.38931 (18)	0.27739 (18)	0.14777 (12)	0.0218 (5)	
O5	0.33373 (19)	0.50409 (19)	0.22123 (13)	0.0243 (5)	
H1	0.327 (3)	0.507 (3)	0.1764 (6)	0.037*	
H2	0.367 (2)	0.5554 (18)	0.2384 (19)	0.037*	
O6	0.5000	0.5000	0.17187 (18)	0.0221 (7)	
H3	0.484 (3)	0.526 (3)	0.1407 (15)	0.033*	
O7	0.2157 (2)	0.2933 (2)	0.18857 (17)	0.0395 (7)	
H4	0.182 (3)	0.318 (3)	0.184 (2)	0.059*	
H5	0.238 (3)	0.291 (4)	0.1493 (16)	0.059*	
C1	0.3787 (3)	0.2740 (3)	0.0000	0.0224 (10)	
O4A	0.2883 (5)	0.1836 (5)	0.0000	0.0311 (19)*	0.50
H4A	0.253 (4)	0.185 (4)	−0.031 (6)	0.047*	0.25
C2A	0.3627 (7)	0.3633 (5)	0.0000	0.023 (2)*	0.50
H21	0.3251	0.3600	−0.0416	0.034*	0.25
H22	0.4242	0.4218	−0.0018	0.034*	0.50
H23	0.3291	0.3626	0.0434	0.034*	0.25
C2B	0.3085 (7)	0.1626 (5)	0.0000	0.019 (2)*	0.50
H24	0.2910	0.1403	0.0491	0.029*	0.25
H25	0.3399	0.1310	−0.0219	0.029*	0.25

H26	0.2515	0.1478	−0.0271	0.029*	0.25
O4B	0.3386 (6)	0.3370 (6)	0.0000	0.029*	0.50
H4B	0.298 (7)	0.321 (6)	−0.033 (5)	0.029*	0.25
O8	0.1458 (11)	0.1163 (12)	−0.1026 (9)	0.169 (6)*	0.50
O9	0.0000	0.0000	0.0000	0.40 (3)*	
O10	0.108 (2)	0.079 (3)	−0.2084 (13)	0.184 (14)*	0.25

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01985 (19)	0.0223 (2)	0.00785 (16)	0.01075 (16)	0.000	0.000
Ca1	0.0199 (3)	0.0199 (3)	0.0176 (4)	0.0119 (4)	−0.00021 (18)	0.00021 (18)
P1	0.0220 (4)	0.0215 (4)	0.0089 (4)	0.0101 (4)	0.0018 (3)	−0.0004 (3)
O1	0.0386 (15)	0.0328 (14)	0.0105 (11)	0.0240 (12)	0.0048 (10)	0.0016 (10)
O2	0.0237 (12)	0.0255 (12)	0.0119 (11)	0.0080 (10)	0.0043 (10)	−0.0021 (9)
O3	0.0261 (13)	0.0265 (13)	0.0106 (11)	0.0116 (11)	0.0045 (9)	−0.0005 (10)
O5	0.0261 (14)	0.0318 (14)	0.0165 (12)	0.0155 (12)	−0.0011 (10)	0.0024 (10)
O6	0.0280 (19)	0.0228 (18)	0.0194 (17)	0.0156 (15)	0.000	0.000
O7	0.0380 (17)	0.0476 (18)	0.0439 (18)	0.0297 (15)	−0.0130 (14)	−0.0102 (15)
C1	0.021 (2)	0.025 (3)	0.016 (2)	0.007 (2)	0.000	0.000

Geometric parameters (Å, º)

Pd1—O2^{i}	2.006 (2)	Ca1—O5^{iv}	2.538 (3)
Pd1—O2	2.006 (2)	Ca1—Ca1^{vi}	4.1524 (18)
Pd1—O1^{ii}	2.010 (2)	P1—O3	1.498 (2)
Pd1—O1^{iii}	2.010 (2)	P1—O1	1.529 (2)
Ca1—O7	2.416 (3)	P1—O2	1.537 (2)
Ca1—O7^{iv}	2.416 (3)	P1—C1	1.839 (3)
Ca1—O3	2.507 (2)	C1—O4B	1.438 (6)
Ca1—O3^{iv}	2.507 (2)	C1—O4A	1.444 (6)
Ca1—O6^{v}	2.526 (2)	C1—C2B	1.559 (6)
Ca1—O6	2.526 (2)	C1—C2A	1.569 (6)
Ca1—O5	2.538 (3)	C1—P1^{i}	1.839 (3)
O2^{i}—Pd1—O2	92.91 (13)	O6^{v}—Ca1—O5^{iv}	68.18 (6)
O2^{i}—Pd1—O1^{ii}	85.78 (9)	O6—Ca1—O5^{iv}	82.30 (7)
O2—Pd1—O1^{ii}	173.09 (10)	O5—Ca1—O5^{iv}	144.16 (13)
O2^{i}—Pd1—O1^{iii}	173.09 (10)	O7—Ca1—Ca1^{vi}	139.79 (8)
O2—Pd1—O1^{iii}	85.78 (9)	O7^{iv}—Ca1—Ca1^{vi}	139.79 (8)
O1^{ii}—Pd1—O1^{iii}	94.70 (14)	O3—Ca1—Ca1^{vi}	103.51 (6)
O7—Ca1—O7^{iv}	80.42 (16)	O3^{iv}—Ca1—Ca1^{vi}	103.51 (6)
O7—Ca1—O3	75.19 (9)	O3—P1—O1	111.26 (14)
O7^{iv}—Ca1—O3	84.19 (10)	O3—P1—O2	110.76 (13)
O7—Ca1—O3^{iv}	84.19 (10)	O1—P1—O2	111.95 (14)
O7^{iv}—Ca1—O3^{iv}	75.19 (9)	O3—P1—C1	109.08 (15)
O3—Ca1—O3^{iv}	152.97 (12)	O1—P1—C1	107.27 (16)
O7—Ca1—O6^{v}	153.43 (7)	O2—P1—C1	106.30 (16)

O7^{iv}—Ca1—O6^{v}	111.16 (10)	P1—O1—Pd1^{vii}	128.04 (14)
O3—Ca1—O6^{v}	128.30 (7)	P1—O2—Pd1	126.86 (14)
O3^{iv}—Ca1—O6^{v}	76.37 (7)	P1—O3—Ca1	142.04 (15)
O7—Ca1—O6	111.16 (10)	Ca1^{vi}—O6—Ca1	110.56 (13)
O7^{iv}—Ca1—O6	153.43 (7)	O4B—C1—O4A	97.3 (6)
O3—Ca1—O6	76.37 (7)	O4B—C1—C2B	118.7 (6)
O3^{iv}—Ca1—O6	128.30 (7)	O4A—C1—C2A	111.9 (6)
O6^{v}—Ca1—O6	69.44 (13)	C2B—C1—C2A	133.4 (6)
O7—Ca1—O5	74.02 (9)	O4B—C1—P1^{i}	111.5 (2)
O7^{iv}—Ca1—O5	138.18 (9)	O4A—C1—P1^{i}	112.3 (2)
O3—Ca1—O5	119.24 (8)	C2B—C1—P1^{i}	101.6 (3)
O3^{iv}—Ca1—O5	69.84 (8)	C2A—C1—P1^{i}	104.3 (2)
O6^{v}—Ca1—O5	82.30 (7)	O4B—C1—P1	111.5 (2)
O6—Ca1—O5	68.18 (6)	O4A—C1—P1	112.3 (2)
O7—Ca1—O5^{iv}	138.18 (9)	C2B—C1—P1	101.6 (3)
O7^{iv}—Ca1—O5^{iv}	74.02 (9)	C2A—C1—P1	104.3 (2)
O3—Ca1—O5^{iv}	69.84 (8)	P1^{i}—C1—P1	111.1 (2)
O3^{iv}—Ca1—O5^{iv}	119.24 (8)		

Symmetry codes: (i) *x*, *y*, −*z*; (ii) −*x*+*y*+1, −*x*+1, −*z*; (iii) −*x*+*y*+1, −*x*+1, *z*; (iv) *y*, *x*, −*z*+1/2; (v) −*y*+1, −*x*+1, −*z*+1/2; (vi) −*x*+1, −*y*+1, *z*; (vii) −*y*+1, *x*−*y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1···O1^{viii}	0.84 (1)	1.95 (2)	2.756 (3)	160 (4)
O5—H2···O5^{v}	0.79 (2)	2.07 (2)	2.799 (5)	155 (4)
O6—H3···O2^{vi}	0.82 (2)	1.87 (2)	2.685 (3)	170 (4)
O7—H4···O3^{viii}	0.82 (2)	2.07 (2)	2.865 (4)	166 (4)
O4*A*—H4*A*···O8	0.82	1.99	2.731 (16)	150

Symmetry codes: (v) −*y*+1, −*x*+1, −*z*+1/2; (vi) −*x*+1, −*y*+1, *z*; (viii) *x*−*y*, *x*, *z*.