Cadmium phosphates $Cd_2(PO_4)OH$ and $Cd_5(PO_4)_2(OH)_4$ crystallizing in mineral structures

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Single crystals of two basic cadmium phosphates, dicadmium orthophosphate hydroxide, $Cd_2(PO_4)OH$, and pentacadmium bis(orthophosphate) tetrakis(hydroxide), $Cd_5(PO_4)_2(OH)_4$, were obtained under hydrothermal conditions. $Cd_2(PO_4)OH$ adopts the triplite $[(Mn,Fe)_2(PO_4)F]$ structure type. Its asymmetric unit comprises two Cd, one P and five O sites, all situated at the general Wyckoff position 8f of space group $I2/a$; two of the O atoms are positionally disordered over two sites, and the H atom could not be localized. Disregarding the disorder, distorted $[CdO_6]$ polyhedra form a tri-periodic network by edge-sharing with neighbouring $[CdO_6]$ units and by vertex-sharing with $[PO_4]$ units. The site associated with the OH group is coordinated by four Cd atoms in a distorted tetrahedral manner forming $^1_\infty[(OH)Cd_{4/2}]$ chains parallel to [001]. The oxygen environment around the OH site suggests multiple acceptor atoms for possible O—H···O hydrogen-bonding interactions and is the putative reason for the disorder. $Cd_5(PO_4)_2(OH)_4$ adopts the arsenoclasite $[Mn_5(AsO_4)_2(OH)_4]$ structure type. Its asymmetric unit comprises five Cd, two P, and twelve O sites all located at the general Wyckoff position 4a of space group $P2_12_12_1$; the H atoms could not be localized. The crystal structure of $Cd_5(PO_4)_2(OH)_4$ can be subdivided into two main sub-units. One consists of three edge-sharing $[CdO_6]$ octahedra, and the other of two edge- and vertex-sharing $[CdO_6]$ octahedra. Each sub-unit forms corrugated ribbons extending parallel to [100]. The two types of ribbons are linked into the tri-periodic arrangement through vertex-sharing and through common $[PO_4]$ tetrahedra. Quantitative structure comparisons are made with isotypic $M_5(XO_4)_2(OH)_4$ crystal structures (M = Cd, Mn, Co; X = P, As, V).

1. Chemical context

In the quest for new oxidotellurates(IV) modified by incorporation of tetrahedral phosphate anions (Eder & Weil, 2020; Ok & Halasyamani, 2006; Yao *et al.*, 2021; Zhao *et al.*, 2021a,b; Zimmermann *et al.*, 2011), crystals of $Cd_2(PO_4)OH$ were serendipitously obtained under hydrothermal conditions when working in the system $Cd/Te^{IV}/P^V/O/(H)$. During a targeted synthesis of $Cd_2(PO_4)OH$ under Te-free conditions, another phosphate with composition $Cd_5(PO_4)_2(OH)_4$ had crystallized. We report here the synthesis conditions and crystal structure refinements of these two basic cadmium phosphates and their relationships with known mineral structures.

2. Structural commentary

So far, structural data for basic cadmium phosphates have only been reported for apatite-type $Cd_5(PO_4)_3(OH)$ (Hata *et al.*, 1978). The title compounds, which are described here for the first time, crystallize with known mineral structures. $Cd_2(PO_4)(OH)$ adopts the triplite structure, which was first reported by Waldrop (1968). Triplite is a mineral with

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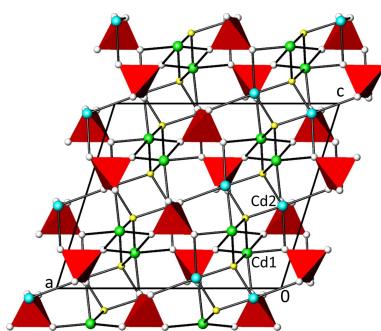
Table 1
Selected bond lengths (Å) for Cd₂(PO₄)OH.

Cd1—O3^{i}	2.224 (7)	Cd2—O1B^{iv}	2.242 (12)
Cd1—OH	2.256 (6)	Cd2—O4	2.251 (7)
Cd1—O4^{ii}	2.275 (6)	Cd2—O2B^{iii}	2.38 (5)
Cd1—O2B^{iii}	2.28 (5)	Cd2—O1B^{vi}	2.556 (14)
Cd1—O3^{iv}	2.350 (6)	P1—O2B^{vii}	1.51 (5)
Cd1—OH^{i}	2.484 (7)	P1—O3	1.519 (7)
Cd2—OH^{v}	2.101 (6)	P1—O1B	1.528 (11)
Cd2—OH	2.174 (7)	P1—O4	1.542 (7)

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

composition (Fe,Mn)₂(PO₄)F, and other natural and synthetic compounds with the composition $M_2(XO_4)Y$ share this structure type, where M = Mn, Fe, Cd, Co, Mg; X = P, As; Y = F, (F,OH) (Đorđević & Kolitsch, 2013). Cd₅(PO₄)₂(OH)₄ crystallizes isotypically with the mineral arsenoclasite [Mn₅(AsO₄)₂(OH)₄], the crystal structure of which was determined by Moore & Molin-Case (1971). Other isostructural compounds are synthetic Cd₅(VO₄)₂(OH)₄ (Karanović & Đorđević, 2022), Co₅(PO₄)₂(OH)₄ and Mn₅(PO₄)₂(OH)₄ (Ruszala *et al.*, 1977), as well as the natural variant of Mn₅(PO₄)₂(OH)₄ – the mineral gatehouseite (Elliott & Pring, 2011).

Cd₂(PO₄)OH is the first reported $M_2(XO_4)Y$ compound with exclusively OH⁻ ions at the Y site to crystallize in the triplite structure in space-group type $I2/a$. Such $M_2(XO_4)OH$ compounds usually adopt the triploidite structure in space-group type $P2_1/a$, like the arsenate analogue Cd₂(AsO₄)(OH) (Đorđević & Kolitsch, 2013). Triploidite-like structures have twice the unit-cell volume of triplite-like structures and show no centering of the monoclinic unit-cell. However, for Cd₂(PO₄)OH, reflections hinting at a doubled unit-cell volume or violating the reflection conditions for an I-centered unit-cell were not found in the diffraction data.

Cd₂(PO₄)OH. The asymmetric unit of Cd₂(PO₄)OH comprises two Cd, one P and five O sites (O1 and O2 being positionally disordered over two sites each). All atomic sites are situated at the general Wyckoff position $8f$ of space group $I2/a$. The resulting coordination polyhedra around Cd1, Cd2 and P are depicted in Fig. 1. For the sake of simplicity, the crystal structure of Cd₂(PO₄)OH will be described in the following without the disorder of atoms O1 and O2. Consid-

Figure 2
The idealized crystal structure of Cd₂(PO₄)OH without disorder of O1 and O2 in a projection along [0$\bar{1}$0]. The O atom of the OH group is given as a yellow sphere, the other O atoms as white spheres, the Cd atoms as green spheres; the [PO₄] unit is displayed as a red polyhedron.

ering Cd—O distances < 3.0 Å as relevant, both Cd sites are coordinated by six oxygen atoms forming significantly distorted [CdO₄(OH)₂] octahedra (Table 1, where only the bonds for O atoms with major occupancy are indicated). The mean Cd—O distances in the two polyhedra (Cd1—O = 2.31, Cd2—O = 2.28 Å) are in good agreement with the literature value of 2.302 (69) Å for six-coordinate Cd (Gagné & Hawthorne, 2020). Each [CdO₄(OH)₂] octahedron shares four of its edges with neighbouring [CdO₄(OH)₂] octahedra, two with each Cd (Cd1 and Cd2). Additionally, each [CdO₄(OH)₂]

Figure 1
Coordination polyhedra in the crystal structure of Cd₂(PO₄)OH showing the disordered atoms O1 and O2. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes refer to Table 1.
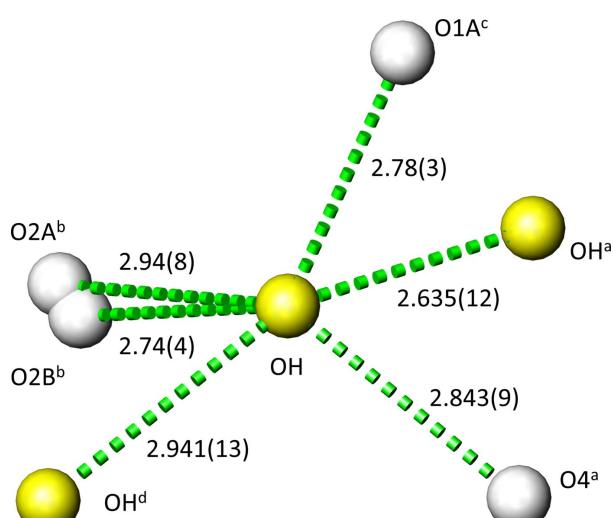
Figure 3
Cd₂(PO₄)OH. Environment of the OH site suitable for hydrogen-bonding interactions [d(OH···O) < 3.0 Å]; distances (Å) are indicated. Symmetry codes: (a) $-x + \frac{1}{2}, y, -z + 1$; (b) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (c) $-x + \frac{1}{2}, y - 1, -z + 1$; (d) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Comparison of bond lengths (Å) in the isotypic $M_5(XO_4)_2(OH)_4$ structures (M = Cd, Mn, Co; X = P, As, V) after standardization, and parameters of structural comparison with $Cd_5(PO_4)_2(OH)_4$ as the reference structure.

	$Cd_5(PO_4)_2(OH)_4$	$Mn_5(AsO_4)_2(OH)_4{}^a$	$Mn_5(PO_4)_2(OH)_4{}^b$	$Co_5(PO_4)_2(OH)_4{}^c$	$Cd_5(VO_4)_2(OH)_4{}^d$
$M1-O8$	2.245 (7)	2.19	2.156	2.063	2.295 (4)
$M1-O4^i$	2.267 (6)	2.25	2.193	2.132	2.317 (4)
$M1-O8^i$	2.269 (6)	2.17	2.157	2.050	2.271 (4)
$M1-O3$	2.312 (6)	2.20	2.214	2.207	2.287 (3)
$M1-O6^{ii}$	2.412 (7)	2.31	2.299	2.162	2.378 (4)
$M1-O10^i$	2.540 (6)	2.35	2.407	2.250	2.408 (3)
$M2-O8^i$	2.236 (6)	2.19	2.153	2.106	2.244 (4)
$M2-O4$	2.246 (6)	2.13	2.131	2.047	2.2469 (4)
$M2-O5$	2.258 (6)	2.19	2.166	2.107	2.265 (4)
$M2-O2^{iii}$	2.306 (6)	2.18	2.181	2.061	2.293 (4)
$M2-O6^{iv}$	2.319 (6)	2.19	2.229	2.171	2.321 (4)
$M2-O10$	2.335 (6)	2.25	2.244	2.152	2.329 (3)
$M3-O5$	2.202 (6)	2.07	2.076	1.998	2.193 (3)
$M3-O11$	2.226 (6)	2.06	2.076	1.983	2.212 (3)
$M3-O2$	2.300 (6)	2.26	2.225	2.232	2.302 (4)
$M3-O7^{iv}$	2.327 (6)	2.13	2.179	2.085	2.268 (4)
$M3-O1$	2.351 (6)	2.31	2.293	2.194	2.325 (3)
$M3-O3^{iv}$	2.599 (6)	2.69	2.583	2.410	2.849 (4)
$M4-O5$	2.184 (6)	2.15	2.107	2.029	2.241 (4)
$M4-O2^v$	2.196 (6)	2.14	2.116	2.031	2.252 (3)
$M4-O7^{vi}$	2.305 (6)	2.18	2.173	2.078	2.282 (3)
$M4-O12$	2.315 (6)	2.22	2.210	2.170	2.302 (3)
$M4-O10$	2.434 (6)	2.29	2.328	2.194	2.365 (4)
$M4-O6^{vi}$	2.555 (6)	2.36	2.453	2.340	2.413 (4)
$M5-O4^v$	2.240 (7)	2.17	2.165	2.110	2.245 (4)
$M5-O9^{vii}$	2.247 (6)	2.09	2.098	2.029	2.256 (4)
$M5-O3^{vi}$	2.334 (6)	2.32	2.297	2.260	2.299 (4)
$M5-O1^{viii}$	2.364 (6)	2.19	2.233	2.092	2.287 (3)
$M5-O9$	2.405 (6)	2.19	2.259	2.114	2.381 (4)
$M5-O12$	2.432 (6)	2.43	2.384	2.281	2.642 (4)
$X1-O9$	1.524 (6)	1.72	1.547	1.537	1.698 (3)
$X1-O6$	1.543 (7)	1.72	1.554	1.547	1.741 (4)
$X1-O12$	1.544 (6)	1.65	1.528	1.545	1.695 (4)
$X1-O1$	1.553 (6)	1.68	1.539	1.552	1.749 (3)
$X2-O11^v$	1.523 (6)	1.65	1.527	1.519	1.688 (3)
$X2-O7$	1.538 (7)	1.67	1.540	1.546	1.721 (3)
$X2-O10$	1.543 (7)	1.67	1.544	1.545	1.731 (4)
$X2-O3$	1.562 (6)	1.68	1.542	1.555	1.733 (4)
S		0.0118	0.0199	0.0394	0.0106
d_{max}		0.3033	0.1232	0.2613	0.2351
d_{av}		0.1378	0.0598	0.1123	0.1264
Δ		0.044	0.013	0.026	0.100
quotient $X{:}M$ of ionic radii	0.178	0.404	0.205	0.228	0.374

Notes: (a) Lattice parameter after standardization: a = 5.75 (1), b = 9.31 (2), c = 18.29 (2) Å, V = 979.1 Å^3. (b) Lattice parameters after standardization: a = 5.6923 (6), b = 9.110 (1), c = 18.032 (4) Å, V = 935.1 Å^3. (c) Lattice parameters after standardization: a = 5.5154 (4), b = 8.903 (2), c = 17.397 (2) Å, V = 854.3 Å^3. (d) Lattice parameters after standardization: a = 6.0133 (12), b = 9.5411 (19) Å, c = 19.011 (4) Å, V = 1090.7 (4) Å^3. Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (viii) $x + 1, y, z$.

unit shares four of its O atoms with [PO$_4$] tetrahedra, leading to a tri-periodic structure (Fig. 2).

Of the five oxygen sites, four (O1–O4) are bound to two Cd and one P atom each. The site associated with the OH group is bound to four Cd sites. This assignment is supported by bond-valence calculations (Brown, 2002), using the parameters of Brese & O'Keeffe (1991). The bond-valence sum (BVS) of the OH site amounts to 1.67 valence units (1.92–2.08 valence units for the other O sites). The OH site is the one occupied by the F$^-$ anion in the isotypic triplite-type structures. The [(OH)Cd$_4$] polyhedron has a distorted tetrahedral shape with bond lengths in the range 2.101 (6)–2.484 (7) Å. The [(OH)Cd$_4$] tetrahedra are linked to each other by sharing two edges with neighbouring tetrahedra forming $^1_\infty$[(OH)Cd$_{4/2}$] chains extending parallel to [001] (Fig. 2).

The environment of the OH site suggests multiple acceptor atoms for possible O—H$\cdots$O hydrogen-bonding interactions and is the putative reason why the hydrogen atom could not be localized and also for the disorder of O1 and O2. Taking into account hydrogen-bonding interactions with O$\cdots$O distances < 3.0 Å as significant, there are six O atoms in the vicinity of each OH site (Fig. 3). The shortest contact amounts to 2.635 (12) Å towards a symmetry-related OH site, the longest to 2.94 (8) Å to O2A. In the isotypic crystal structure of Cd$_2$(PO$_4$)F (Rea & Kostiner, 1974), the F site (corresponding to the OH site in the title structure) is not split and has four contacts < 3.0 Å to two F sites [2.756 (6) and 2.800 (7) Å] and to two O sites [2.828 (5) and 2.832 (5) Å].

Owing to the disorder present in Cd$_2$(PO$_4$)OH, a quantitative comparison with the ordered isotypic $M_2(XO_4)Y$ crystal

structures adopting the triplite-structure type was not undertaken.

$Cd_5(PO_4)_2(OH)_4$. The asymmetric unit of $Cd_5(PO_4)_2(OH)_4$ comprises five Cd, two P and twelve O sites, all located on the general Wyckoff position 4a of space group $P2_12_12_1$; the H-atom sites could not be localized. All five Cd sites are surrounded by six O atoms, resulting in a distorted octahedral environment for each metal atom. The Cd—O bond lengths are in a broad range between 2.184 (6) and 2.599 (6) Å (Table 2). The mean bond lengths are 2.341 Å (Cd1), 2.283 Å (Cd2), 2.222 Å (Cd3), 2.331 Å (Cd4) and 2.336 Å (Cd5), again in good agreement with the literature value specified above. The BVS values of the Cd atoms amount to 1.91, 2.16, 1.98, 2.00 and 1.90 valence units and thus show good agreement with the expected value of 2.

Of the twelve O sites present in the structure of $Cd_5(PO_4)_2(OH)_4$, four are occupied by the O atom of a hydroxide anion, as revealed by BVS calculations. O2, O4, O5, and O8 have considerably lower BVS values of 1.14, 1.17, 1.30 and 1.18 valence units, respectively, than the remaining O atoms [1.78 (O1), 1.96 (O3), 1.97 (O6), 1.90 (O7), 1.94 (O9), 1.95 (O10), 1.71 (O11) and 1.79 (O12) valence units]. Moreover, these four oxygen sites are the only ones that are not part of a phosphate group. Each of the hydroxide O atoms is connected to three Cd atoms in the form of a flat trigonal pyramid. According to the oxygen environments around the hydroxide O atoms, the closest possible acceptor groups for O—H···O hydrogen-bonding interactions are located at 2.997 (8) Å for O2···O1($-x, y + \frac{1}{2}, -z + \frac{1}{2}$), 2.986 (9) Å for O4···O9($-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$), 2.890 (9) Å for O5···O12($-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$), and 2.827 (9) Å for O8···O11($-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$), indicating rather weak hydrogen bonds in each case.

The [CdO_6] polyhedra {[Cd1O_3(OH)_3], [Cd2O_2(OH)_4], [Cd3O_4(OH)_2], [Cd4O_4(OH)_2] and [Cd5O_5(OH)]} define the structure by forming two main sub-units. Through edge-sharing, the octahedra around Cd1, Cd2 and Cd4 form corrugated double ribbons extending parallel to [100] as the first unit. The second unit is defined by the octahedra around Cd3 and Cd5. By sharing corners and edges, another corrugated ribbon is formed and also propagates parallel to [100]. The two types of ribbons are linked into a tri-periodic arrangement by sharing corners, as well as by sharing the two PO_4 tetrahedra (Fig. 4). The latter show deviations from an ideal tetrahedral arrangement, as revealed by slightly different bond lengths (Table 2) and by angular distortions, with O—P—O angles ranging from 106.2 (3) to 112.2 (3)° for P1 and 104.6 (4) to 114.0 (4)° for P2.

$Cd_5(PO_4)_2(OH)_4$ and the four isotypic $M_5(XO_4)_2(OH)_4$ crystal structures (M = Cd, Mn, Co; X = P, As, V) were quantitatively compared using the *compstru* software (de la Flor *et al.*, 2016) available at the Bilbao Crystallographic server (Aroyo *et al.*, 2006). For this purpose and for direct comparison of bond lengths (Table 2), the hydrogen atoms (if part of the model) were removed, and all crystal structures were standardized with *STRUCTURE-TIDY* (Gelato & Parthé, 1987). With $Cd_5(PO_4)_2(OH)_4$ as the reference structure, numerical values of parameter of comparison (degree of lattice distortion S, the arithmetic mean of the distance between paired atoms d_{av}, the maximum difference between the atomic positions of the matching atoms d_{max}, and the measure of similarity Δ) are collated in Table 2. As expected for isotypic structures, the low values for Δ indicate high similarities of $Cd_5(PO_4)_2(OH)_4$ with the four $M_5(XO_4)_2(OH)_4$ crystal structures. The differences in bond lengths of the individual structural units ([MO_6]; [XO_4]) are due to the different sizes of M^{II} and X^V, *viz*. 0.745 Å for Co (high spin), 0.83 Å for Mn (high spin), 0.95 Å for Cd, and 0.17 Å for P, 0.335 Å for As, 0.355 Å for V; all values were taken from Shannon (1976). As a simple measure, the quotient X:M can be used for correlation. The closer the quotient is to that of P: Cd = 0.178, the higher is the similarity.

3. Synthesis and crystallization

Crystals of $Cd_2(PO_4)OH$ and $Cd_5(PO_4)_2(OH)_4$ were both obtained from reactions under hydrothermal conditions. The starting materials were 0.1927 g (1.129 mmol) $CdCO_3$, 0.1784 g (1.118 mmol) TeO_2 and 0.1289 g (1.118 mmol) of 85%$_{wt}$ H_3PO_4 for the $Cd_2(PO_4)OH$ batch, and 0.1874 g (0.607 mmol) $Cd(NO_3)_2·4H_2O$, 0.0296 g (0.257 mmol) 85%$_{wt}$ H_3PO_4, and 0.2197 g (3.916 mmol) KOH for the $Cd_5(PO_4)_2(OH)_4$ batch. The reactants were weighed into small Teflon containers with a volume of *ca* 3 ml and mixed with deionized water so that the inner volume was filled to about two thirds with liquid. Then, the Teflon containers were placed into a steel autoclave and heated to 483 K for 7 d. Afterwards the autoclave was cooled down to room temperature within about 4 h. The formed solids were filtered off, washed with mother liquor, water and ethanol, and dried in air.

For the $Cd_2(PO_4)OH$ batch, the reaction product was a mixture of a white and bright-yellow solid. An X-ray powder diffraction measurement revealed α-TeO_2, which can be associated with the yellow solid, as a side product besides
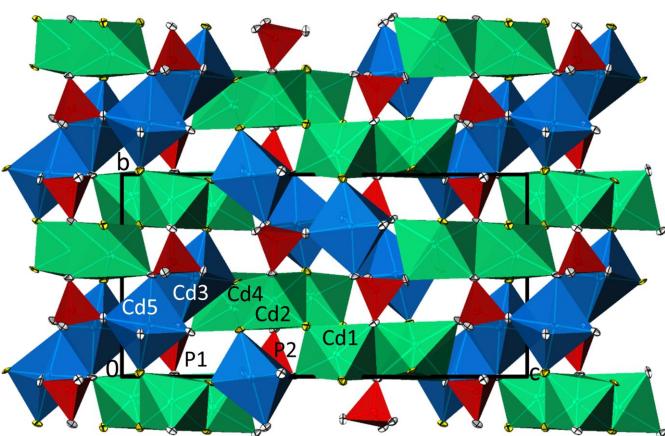
Figure 4
The crystal structure of $Cd_5(PO_4)_2(OH)_4$ in a projection along [100] in polyhedral representation. The [CdO_6] octahedra defining the first sub-unit are given in green, the [CdO_6] octahedra defining the second sub-unit are given in blue; [PO_4] tetrahedra are red. O atoms of OH groups are yellow, other O atoms are white. Displacement ellipsoids are displayed at the 74% probability level.

Table 3
Experimental details.

	Cd$_2$(PO$_4$)OH	Cd$_5$(PO$_4$)$_2$(OH)$_4$
Crystal data		
M_r	336.78	819.97
Crystal system, space group	Monoclinic, $I2/a$	Orthorhombic, $P2_12_12_1$
Temperature (K)	296	296
a, b, c (Å)	12.4307 (13), 6.6910 (6), 10.7087 (10)	5.8901 (4), 9.3455 (6), 18.7423 (13)
α, β, γ (°)	90, 107.506 (3), 90	90, 90, 90
V (Å^3)	849.43 (14)	1031.69 (12)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	10.30	10.51
Crystal size (mm)	$0.10 \times 0.08 \times 0.05$	$0.11 \times 0.07 \times 0.04$
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.600, 0.746	0.517, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7833, 1477, 1026	10057, 4493, 3588
R_{int}	0.065	0.051
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.747	0.806
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.100, 1.03	0.039, 0.059, 0.97
No. of reflections	1477	4493
No. of parameters	80	172
H-atom treatment	H-atom parameters not defined	H-atom parameters not defined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	2.91, −3.55	1.53, −1.76
Absolute structure	–	Flack x determined using 1284 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	−0.03 (4)

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), SHELXT (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

Cd$_2$(PO$_4$)OH. Small colourless block-shaped crystals of Cd$_2$(PO$_4$)OH could be isolated for single crystal X-ray diffraction.

For the Cd$_5$(PO$_4$)$_2$(OH)$_4$ batch, the reaction product was a white powder. Apart from Cd(OH)$_2$ and Cd$_5$(PO$_4$)$_2$(OH)$_4$ no other phases could be identified in the X-ray powder diffraction pattern. Colourless block-shaped crystals of Cd$_5$(PO$_4$)$_2$-(OH)$_4$ could be isolated for single crystal X-ray diffraction.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

For structure refinement of triplite-type Cd$_2$(PO$_4$)OH, labelling and fractional coordinates of atoms were adapted from the crystal structure of triplite (Waldrop, 1969). For direct comparison with other triplite-like structures (Waldrop, 1969; Đorđević & Kolitsch, 2013), the unconventional setting $I2/a$ of space-group type No. 15 was chosen. The conventional setting in $C2/c$ transforms with $-\mathbf{a} - \mathbf{c}, -\mathbf{b}, \mathbf{c}$ to the chosen unconventional setting. Oxygen atoms O1 and O2 were found to be positionally disordered over two sites. The pairs O1*A*/O1*B* and O2*A*/O2*B* were refined with common displacement parameters each. The site occupation factors were refined for the pair O1*A*/O2*A* and O1*A*/O2*A* to a ratio of 0.349 (18):0.651 (18). Remaining positive and negative residual electron density close to the Cd1 position suggests possible positional disorder of this atom as well. However, using split

positions for Cd1 led to a physically non-meaningful model and was not considered for the final refinement. H atoms could not be located for Cd$_2$(PO$_4$)OH.

For better comparison with the isotypic crystal structures of $M_5(XO_4)_2$(OH)$_4$ compounds (M = Cd, Mn, Co; X = P, As), structure data of Cd$_5$(PO$_4$)$_2$(OH)$_4$ were standardized with *STRUCTURE-TIDY* (Gelato & Parthé, 1987). H atoms could not be located reliably for Cd$_5$(PO$_4$)$_2$(OH)$_4$.

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Cadmium phosphates Cd$_2$(PO$_4$)OH and Cd$_5$(PO$_4$)$_2$(OH)$_4$ crystallizing in mineral structures

Felix Eder and Matthias Weil

Computing details

Dicadmium orthophosphate hydroxide (CdPO4OH)

Crystal data

Cd$_2$(PO$_4$)OH	$F(000) = 1216$
$M_r = 336.78$	$D_x = 5.267$ Mg m^{-3}
Monoclinic, $I2/a$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.4307\,(13)$ Å	Cell parameters from 1272 reflections
$b = 6.6910\,(6)$ Å	$\theta = 3.4–25.8°$
$c = 10.7087\,(10)$ Å	$\mu = 10.30$ mm^{-1}
$\beta = 107.506\,(3)°$	$T = 296$ K
$V = 849.43\,(14)$ Å^3	Block, colourless
$Z = 8$	$0.10 \times 0.08 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer	1477 independent reflections
	1026 reflections with $I > 2\sigma(I)$
ω– and φ–scan	$R_{int} = 0.065$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 32.1°$, $\theta_{min} = 3.4°$
	$h = -18 \rightarrow 18$
$T_{min} = 0.600$, $T_{max} = 0.746$	$k = -9 \rightarrow 9$
7833 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 36.2119P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 2.91$ e Å^{-3}
1477 reflections	$\Delta\rho_{min} = -3.55$ e Å^{-3}
80 parameters	

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cd1	0.20094 (5)	−0.00573 (10)	0.19098 (6)	0.01905 (15)	
Cd2	0.10811 (8)	0.15931 (10)	0.44546 (7)	0.0293 (2)	
P1	0.07732 (19)	0.6694 (3)	0.3759 (2)	0.0151 (4)	
O1A	0.123 (2)	0.856 (3)	0.469 (2)	0.028 (3)	0.349 (18)
O1B	0.0590 (13)	0.8402 (17)	0.4621 (11)	0.028 (3)	0.651 (18)
O2A	0.970 (8)	0.592 (15)	0.297 (10)	0.040 (7)	0.349 (18)
O2B	0.958 (4)	0.640 (7)	0.287 (5)	0.040 (7)	0.651 (18)
O3	0.1538 (6)	0.7093 (10)	0.2916 (7)	0.0299 (16)	
O4	0.1231 (6)	0.4933 (10)	0.4698 (6)	0.0261 (14)	
OH	0.2574 (6)	0.1685 (10)	0.3799 (6)	0.0265 (14)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0173 (3)	0.0217 (3)	0.0184 (3)	0.0027 (3)	0.0058 (2)	0.0029 (3)
Cd2	0.0639 (6)	0.0122 (3)	0.0167 (3)	0.0014 (3)	0.0197 (3)	−0.0001 (3)
P1	0.0196 (11)	0.0113 (8)	0.0157 (9)	0.0003 (8)	0.0072 (8)	−0.0014 (8)
O1A	0.043 (8)	0.017 (4)	0.025 (4)	0.009 (6)	0.012 (6)	−0.004 (3)
O1B	0.043 (8)	0.017 (4)	0.025 (4)	0.009 (6)	0.012 (6)	−0.004 (3)
O2A	0.011 (10)	0.08 (2)	0.029 (9)	0.002 (11)	0.000 (8)	0.033 (12)
O2B	0.011 (10)	0.08 (2)	0.029 (9)	0.002 (11)	0.000 (8)	0.033 (12)
O3	0.019 (4)	0.030 (4)	0.046 (4)	0.002 (3)	0.019 (3)	0.014 (3)
O4	0.041 (4)	0.018 (3)	0.020 (3)	0.007 (3)	0.011 (3)	0.005 (3)
OH	0.040 (4)	0.023 (3)	0.014 (3)	0.009 (3)	0.003 (3)	−0.003 (3)

Geometric parameters (Å, º)

Cd1—O3[i]	2.224 (7)	Cd2—O4	2.251 (7)
Cd1—OH	2.256 (6)	Cd2—O2B[ii]	2.38 (5)
Cd1—O2A[ii]	2.26 (10)	Cd2—O2A[ii]	2.52 (9)
Cd1—O4[iii]	2.275 (6)	Cd2—O1B[vi]	2.556 (14)
Cd1—O2B[ii]	2.28 (5)	Cd2—Cd2[v]	3.3659 (18)
Cd1—O3[iv]	2.350 (6)	P1—O2A[vii]	1.44 (11)
Cd1—OH[i]	2.484 (7)	P1—O2B[vii]	1.51 (5)
Cd1—Cd2[iii]	3.4339 (9)	P1—O3	1.519 (7)
Cd1—Cd2	3.4453 (10)	P1—O1B	1.528 (11)
Cd2—O1A[iv]	2.05 (2)	P1—O4	1.542 (7)
Cd2—OH[v]	2.101 (6)	P1—O1A	1.59 (2)
Cd2—OH	2.174 (7)	O1A—O1B	0.78 (2)
Cd2—O1B[iv]	2.242 (12)		
O3[i]—Cd1—OH	102.4 (3)	O1B[iv]—Cd2—Cd2[v]	104.7 (4)
O3[i]—Cd1—O2A[ii]	158 (3)	O4—Cd2—Cd2[v]	85.30 (18)
OH—Cd1—O2A[ii]	81.1 (17)	O2B[ii]—Cd2—Cd2[v]	111.2 (12)
O3[i]—Cd1—O4[iii]	100.9 (3)	O2A[ii]—Cd2—Cd2[v]	113 (2)

OH—Cd1—O4^{iii}	146.6 (2)	O1B^{vi}—Cd2—Cd2^{v}	139.0 (3)
O2A^{ii}—Cd1—O4^{iii}	86 (3)	O1A^{iv}—Cd2—Cd1^{viii}	125.3 (6)
O3^{i}—Cd1—O2B^{ii}	163.9 (15)	OH^{v}—Cd2—Cd1^{viii}	45.93 (19)
OH—Cd1—O2B^{ii}	74.4 (8)	OH—Cd2—Cd1^{viii}	96.04 (17)
O2A^{ii}—Cd1—O2B^{ii}	9 (2)	O1B^{iv}—Cd2—Cd1^{viii}	128.2 (3)
O4^{iii}—Cd1—O2B^{ii}	89.0 (13)	O4—Cd2—Cd1^{viii}	40.91 (16)
O3^{i}—Cd1—O3^{iv}	76.9 (2)	O2B^{ii}—Cd2—Cd1^{viii}	140.2 (11)
OH—Cd1—O3^{iv}	93.5 (3)	O2A^{ii}—Cd2—Cd1^{viii}	148 (2)
O2A^{ii}—Cd1—O3^{iv}	81 (3)	O1B^{vi}—Cd2—Cd1^{viii}	80.1 (3)
O4^{iii}—Cd1—O3^{iv}	114.9 (3)	Cd2^{v}—Cd2—Cd1^{viii}	70.04 (2)
O2B^{ii}—Cd1—O3^{iv}	87.5 (14)	O1A^{iv}—Cd2—Cd1	75.0 (7)
O3^{i}—Cd1—OH^{i}	110.1 (2)	OH^{v}—Cd2—Cd1	110.3 (2)
OH—Cd1—OH^{i}	76.5 (2)	OH—Cd2—Cd1	39.81 (17)
O2A^{ii}—Cd1—OH^{i}	92 (3)	O1B^{iv}—Cd2—Cd1	85.5 (3)
O4^{iii}—Cd1—OH^{i}	73.2 (2)	O4—Cd2—Cd1	111.95 (16)
O2B^{ii}—Cd1—OH^{i}	84.8 (13)	O2B^{ii}—Cd2—Cd1	41.3 (12)
O3^{iv}—Cd1—OH^{i}	168.8 (2)	O2A^{ii}—Cd2—Cd1	41 (2)
O3^{i}—Cd1—Cd2^{iii}	123.70 (17)	O1B^{vi}—Cd2—Cd1	144.2 (3)
OH—Cd1—Cd2^{iii}	106.25 (17)	Cd2^{v}—Cd2—Cd1	73.08 (3)
O2A^{ii}—Cd1—Cd2^{iii}	75 (3)	Cd1^{viii}—Cd2—Cd1	134.96 (3)
O4^{iii}—Cd1—Cd2^{iii}	40.40 (16)	O2A^{vii}—P1—O2B^{vii}	14 (4)
O2B^{ii}—Cd1—Cd2^{iii}	71.9 (16)	O2A^{vii}—P1—O3	110 (4)
O3^{iv}—Cd1—Cd2^{iii}	145.72 (17)	O2B^{vii}—P1—O3	108 (2)
OH^{i}—Cd1—Cd2^{iii}	37.43 (15)	O2A^{vii}—P1—O1B	110 (5)
O3^{i}—Cd1—Cd2	125.92 (19)	O2B^{vii}—P1—O1B	101 (2)
OH—Cd1—Cd2	38.11 (19)	O3—P1—O1B	117.5 (6)
O2A^{ii}—Cd1—Cd2	47 (2)	O2A^{vii}—P1—O4	102 (3)
O4^{iii}—Cd1—Cd2	132.32 (18)	O2B^{vii}—P1—O4	114.4 (14)
O2B^{ii}—Cd1—Cd2	43.4 (12)	O3—P1—O4	110.3 (4)
O3^{iv}—Cd1—Cd2	73.04 (18)	O1B—P1—O4	105.7 (5)
OH^{i}—Cd1—Cd2	95.77 (14)	O2A^{vii}—P1—O1A	138 (4)
Cd2^{iii}—Cd1—Cd2	105.90 (2)	O2B^{vii}—P1—O1A	126 (2)
O1A^{iv}—Cd2—OH^{v}	84.3 (7)	O3—P1—O1A	93.8 (10)
O1A^{iv}—Cd2—OH	90.8 (8)	O1B—P1—O1A	29.0 (8)
OH^{v}—Cd2—OH	76.1 (3)	O4—P1—O1A	101.5 (9)
O1A^{iv}—Cd2—O1B^{iv}	20.4 (7)	O1B—O1A—P1	71 (2)
OH^{v}—Cd2—O1B^{iv}	96.9 (4)	O1B—O1A—Cd2^{ix}	94 (2)
OH—Cd2—O1B^{iv}	109.4 (4)	P1—O1A—Cd2^{ix}	134.3 (14)
O1A^{iv}—Cd2—O4	165.7 (7)	O1A—O1B—P1	80 (2)
OH^{v}—Cd2—O4	81.5 (2)	O1A—O1B—Cd2^{ix}	66 (2)
OH—Cd2—O4	87.7 (2)	P1—O1B—Cd2^{ix}	124.8 (7)
O1B^{iv}—Cd2—O4	162.0 (4)	O1A—O1B—Cd2^{vi}	152 (2)
O1A^{iv}—Cd2—O2B^{ii}	93.8 (13)	P1—O1B—Cd2^{vi}	121.4 (8)
OH^{v}—Cd2—O2B^{ii}	150.0 (12)	Cd2^{ix}—O1B—Cd2^{vi}	107.6 (4)
OH—Cd2—O2B^{ii}	74.0 (12)	P1^{x}—O2A—Cd1^{xi}	142 (7)
O1B^{iv}—Cd2—O2B^{ii}	90.9 (11)	P1^{x}—O2A—Cd2^{xi}	123 (5)
O4—Cd2—O2B^{ii}	99.5 (12)	Cd1^{xi}—O2A—Cd2^{xi}	92 (3)
O1A^{iv}—Cd2—O2A^{ii}	87 (3)	P1^{x}—O2B—Cd1^{xi}	135 (2)

OH^v—Cd2—O2A^{ii}	151 (2)	P1^x—O2B—Cd2^{xi}	128 (3)
OH—Cd2—O2A^{ii}	77 (2)	Cd1^{xi}—O2B—Cd2^{xi}	95.3 (19)
O1B^{iv}—Cd2—O2A^{ii}	83 (2)	P1—O3—Cd1^i	118.7 (4)
O4—Cd2—O2A^{ii}	107 (2)	P1—O3—Cd1^{ix}	134.6 (4)
O2B^{ii}—Cd2—O2A^{ii}	8 (3)	Cd1^i—O3—Cd1^{ix}	103.1 (2)
O1A^{iv}—Cd2—O1B^{vi}	90.4 (8)	P1—O4—Cd2	133.0 (4)
OH^v—Cd2—O1B^{vi}	100.2 (3)	P1—O4—Cd1^{viii}	127.5 (4)
OH—Cd2—O1B^{vi}	175.9 (3)	Cd2—O4—Cd1^{viii}	98.7 (2)
O1B^{iv}—Cd2—O1B^{vi}	72.4 (4)	Cd2^v—OH—Cd2	103.8 (3)
O4—Cd2—O1B^{vi}	90.2 (3)	Cd2^v—OH—Cd1	137.1 (3)
O2B^{ii}—Cd2—O1B^{vi}	109.8 (12)	Cd2—OH—Cd1	102.1 (3)
O2A^{ii}—Cd2—O1B^{vi}	107 (2)	Cd2^v—OH—Cd1^i	96.6 (3)
O1A^{iv}—Cd2—Cd2^v	84.9 (8)	Cd2—OH—Cd1^i	113.6 (3)
OH^v—Cd2—Cd2^v	38.84 (19)	Cd1—OH—Cd1^i	103.5 (2)
OH—Cd2—Cd2^v	37.31 (16)		

Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1/2$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $x, -y+1/2, z-1/2$; (iv) $x, y-1, z$; (v) $-x+1/2, y, -z+1$; (vi) $-x, -y+1, -z+1$; (vii) $x-1, y, z$; (viii) $x, -y+1/2, z+1/2$; (ix) $x, y+1, z$; (x) $x+1, y, z$; (xi) $-x+1, y+1/2, -z+1/2$.

Pentacadmium bis(orthophosphate) tetrakis(hydroxide) (Cd5PO42OH2)

Crystal data
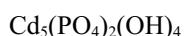
Cd$_5$(PO$_4$)$_2$(OH)$_4$	$D_x = 5.279$ Mg m^{-3}
$M_r = 819.97$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 2236 reflections
$a = 5.8901 (4)$ Å	$\theta = 3.9–33.6°$
$b = 9.3455 (6)$ Å	$\mu = 10.51$ mm^{-1}
$c = 18.7423 (13)$ Å	$T = 296$ K
$V = 1031.69 (12)$ Å^3	Block, colourless
$Z = 4$	$0.11 \times 0.07 \times 0.04$ mm
$F(000) = 1480$	

Data collection

Bruker APEXII CCD diffractometer	4493 independent reflections
ω– and φ–scan	3588 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.051$
	$\theta_{max} = 35.0°$, $\theta_{min} = 2.2°$
$T_{min} = 0.517$, $T_{max} = 0.747$	$h = -9 \rightarrow 9$
10057 measured reflections	$k = -14 \rightarrow 11$
	$l = -28 \rightarrow 30$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0115P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.039$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.059$	$\Delta\rho_{max} = 1.53$ e Å^{-3}
$S = 0.97$	$\Delta\rho_{min} = -1.76$ e Å^{-3}
4493 reflections	Absolute structure: Flack x determined using 1284 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
172 parameters	
0 restraints	
H-atom parameters not defined	Absolute structure parameter: $-0.03 (4)$

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.05007 (11)	0.10420 (7)	0.52815 (3)	0.01113 (12)
Cd2	0.05248 (11)	0.37573 (7)	0.37637 (4)	0.01083 (12)
Cd3	0.08667 (9)	0.49327 (7)	0.17892 (4)	0.01161 (13)
Cd4	0.56114 (11)	0.34489 (7)	0.27458 (3)	0.01154 (12)
Cd5	0.76352 (10)	0.25492 (7)	0.06812 (4)	0.01085 (12)
P1	0.3047 (3)	0.1745 (2)	0.12271 (13)	0.0081 (4)
P2	0.3795 (3)	0.0690 (2)	0.37363 (13)	0.0084 (4)
O1	0.0817 (9)	0.2510 (7)	0.1450 (3)	0.0120 (12)
O2	0.1169 (10)	0.7316 (6)	0.2081 (3)	0.0111 (12)
O3	0.2013 (10)	0.0034 (7)	0.4260 (3)	0.0130 (12)
O4	0.2237 (11)	0.5202 (7)	0.4556 (3)	0.0126 (13)
O5	0.2489 (11)	0.4695 (6)	0.2841 (3)	0.0117 (12)
O6	0.2772 (10)	0.0109 (7)	0.1297 (4)	0.0126 (12)
O7	0.2995 (10)	0.0217 (7)	0.2992 (3)	0.0146 (13)
O8	0.3482 (10)	0.2500 (7)	0.5450 (3)	0.0130 (12)
O9	0.3680 (11)	0.2095 (7)	0.0458 (3)	0.0128 (13)
O10	0.3790 (9)	0.2340 (7)	0.3772 (3)	0.0113 (12)
O11	0.3843 (10)	0.5159 (7)	0.1066 (3)	0.0134 (13)
O12	0.5088 (9)	0.2213 (7)	0.1688 (3)	0.0115 (13)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0100 (2)	0.0129 (3)	0.0104 (3)	−0.0005 (2)	−0.0002 (2)	0.0010 (2)
Cd2	0.0097 (2)	0.0114 (3)	0.0114 (3)	−0.0002 (2)	0.0002 (2)	−0.0006 (2)
Cd3	0.0107 (2)	0.0103 (3)	0.0139 (3)	−0.0001 (2)	−0.0008 (2)	−0.0001 (3)
Cd4	0.0108 (2)	0.0135 (3)	0.0103 (3)	0.0018 (2)	0.0004 (2)	0.0008 (2)
Cd5	0.0124 (2)	0.0096 (3)	0.0105 (3)	−0.0012 (2)	0.0008 (2)	0.0005 (3)
P1	0.0085 (8)	0.0067 (10)	0.0090 (10)	−0.0001 (7)	−0.0006 (7)	0.0002 (9)
P2	0.0078 (8)	0.0085 (10)	0.0089 (10)	0.0015 (7)	0.0008 (7)	0.0013 (9)
O1	0.008 (2)	0.012 (3)	0.016 (3)	0.002 (3)	0.000 (2)	−0.004 (3)
O2	0.011 (2)	0.007 (3)	0.015 (3)	−0.003 (2)	0.002 (2)	−0.003 (3)
O3	0.015 (3)	0.007 (3)	0.016 (3)	−0.003 (2)	0.006 (2)	0.001 (3)
O4	0.013 (3)	0.012 (3)	0.013 (3)	0.000 (2)	−0.003 (2)	−0.002 (3)
O5	0.016 (3)	0.006 (3)	0.013 (3)	−0.001 (2)	0.001 (2)	0.006 (2)
O6	0.016 (3)	0.007 (3)	0.016 (3)	−0.003 (3)	−0.004 (2)	0.000 (3)
O7	0.017 (3)	0.020 (4)	0.007 (3)	0.004 (3)	−0.001 (2)	−0.005 (3)
O8	0.016 (3)	0.012 (3)	0.011 (3)	0.001 (3)	0.002 (2)	0.001 (3)
O9	0.013 (3)	0.017 (4)	0.008 (3)	0.001 (2)	0.000 (2)	0.000 (3)

O10	0.007 (2)	0.010 (3)	0.016 (3)	−0.004 (2)	−0.001 (2)	0.004 (3)
O11	0.011 (2)	0.015 (3)	0.015 (3)	−0.003 (2)	0.001 (2)	−0.001 (3)
O12	0.010 (3)	0.011 (3)	0.014 (3)	0.000 (2)	−0.003 (2)	−0.004 (3)

Geometric parameters (Å, º)

Cd1—O8	2.245 (7)	Cd4—O2^v	2.196 (6)
Cd1—O4^i	2.267 (6)	Cd4—O7^{vi}	2.305 (6)
Cd1—O8^i	2.269 (6)	Cd4—O12	2.315 (6)
Cd1—O3	2.312 (6)	Cd4—O10	2.434 (6)
Cd1—O6^{ii}	2.412 (7)	Cd4—O6^{vi}	2.555 (6)
Cd1—O10^i	2.540 (6)	Cd5—O4^v	2.240 (7)
Cd2—O8^i	2.236 (6)	Cd5—O9^{vii}	2.247 (6)
Cd2—O4	2.246 (6)	Cd5—O3^{vi}	2.334 (6)
Cd2—O5	2.258 (6)	Cd5—O1^{viii}	2.364 (6)
Cd2—O2^{iii}	2.306 (6)	Cd5—O9	2.405 (6)
Cd2—O6^{iv}	2.319 (6)	Cd5—O12	2.432 (6)
Cd2—O10	2.335 (6)	P1—O9	1.524 (6)
Cd3—O5	2.202 (6)	P1—O6	1.543 (7)
Cd3—O11	2.226 (6)	P1—O12	1.544 (6)
Cd3—O2	2.300 (6)	P1—O1	1.553 (6)
Cd3—O7^{iv}	2.327 (6)	P2—O11^v	1.523 (6)
Cd3—O1	2.351 (6)	P2—O7	1.538 (7)
Cd3—O3^{iv}	2.599 (6)	P2—O10	1.543 (7)
Cd4—O5	2.184 (6)	P2—O3	1.562 (6)
O8—Cd1—O4^i	162.9 (2)	O3^{vi}—Cd5—O1^{viii}	85.2 (2)
O8—Cd1—O8^i	97.50 (11)	O4^v—Cd5—O9	79.9 (2)
O4^i—Cd1—O8^i	86.8 (2)	O9^{vii}—Cd5—O9	97.25 (17)
O8—Cd1—O3	93.6 (2)	O3^{vi}—Cd5—O9	105.6 (2)
O4^i—Cd1—O3	103.2 (2)	O1^{viii}—Cd5—O9	150.6 (2)
O8^i—Cd1—O3	86.9 (2)	O4^v—Cd5—O12	92.8 (2)
O8—Cd1—O6^{ii}	80.2 (2)	O9^{vii}—Cd5—O12	157.8 (2)
O4^i—Cd1—O6^{ii}	91.3 (2)	O3^{vi}—Cd5—O12	98.4 (2)
O8^i—Cd1—O6^{ii}	165.0 (2)	O1^{viii}—Cd5—O12	90.79 (19)
O3—Cd1—O6^{ii}	108.0 (2)	O9—Cd5—O12	60.93 (19)
O8—Cd1—O10^i	81.4 (2)	O9—P1—O6	108.6 (4)
O4^i—Cd1—O10^i	82.8 (2)	O9—P1—O12	106.2 (3)
O8^i—Cd1—O10^i	81.8 (2)	O6—P1—O12	108.3 (3)
O3—Cd1—O10^i	166.9 (2)	O9—P1—O1	111.3 (4)
O6^{ii}—Cd1—O10^i	83.2 (2)	O6—P1—O1	110.2 (3)
O8^i—Cd2—O4	97.0 (2)	O12—P1—O1	112.2 (3)
O8^i—Cd2—O5	169.9 (2)	O11^v—P2—O7	114.0 (4)
O4—Cd2—O5	92.5 (2)	O11^v—P2—O10	108.5 (3)
O8^i—Cd2—O2^{iii}	85.0 (2)	O7—P2—O10	109.0 (4)
O4—Cd2—O2^{iii}	178.0 (2)	O11^v—P2—O3	109.5 (4)
O5—Cd2—O2^{iii}	85.6 (2)	O7—P2—O3	104.6 (4)
O8^i—Cd2—O6^{iv}	82.4 (2)	O10—P2—O3	111.3 (4)

O4—Cd2—O6^{iv}	94.7 (2)	P1—O1—Cd3	120.4 (3)
O5—Cd2—O6^{iv}	100.3 (2)	P1—O1—Cd5^{ix}	120.9 (3)
O2ⁱⁱⁱ—Cd2—O6^{iv}	85.5 (2)	Cd3—O1—Cd5^{ix}	99.2 (2)
O8ⁱ—Cd2—O10	98.1 (2)	Cd4^{vi}—O2—Cd3	124.7 (3)
O4—Cd2—O10	88.1 (2)	Cd4^{vi}—O2—Cd2^{iv}	101.1 (2)
O5—Cd2—O10	78.7 (2)	Cd3—O2—Cd2^{iv}	111.7 (2)
O2ⁱⁱⁱ—Cd2—O10	91.7 (2)	P2—O3—Cd1	128.3 (4)
O6^{iv}—Cd2—O10	177.1 (2)	P2—O3—Cd5^v	111.1 (3)
O5—Cd3—O11	102.3 (2)	Cd1—O3—Cd5^v	113.6 (3)
O5—Cd3—O2	81.4 (2)	P2—O3—Cd3ⁱⁱⁱ	88.7 (3)
O11—Cd3—O2	89.5 (2)	Cd1—O3—Cd3ⁱⁱⁱ	113.0 (2)
O5—Cd3—O7^{iv}	106.1 (2)	Cd5^v—O3—Cd3ⁱⁱⁱ	93.3 (2)
O11—Cd3—O7^{iv}	150.1 (2)	Cd5^{vi}—O4—Cd2	118.2 (3)
O2—Cd3—O7^{iv}	85.6 (2)	Cd5^{vi}—O4—Cd1^x	120.0 (3)
O5—Cd3—O1	98.6 (2)	Cd2—O4—Cd1^x	99.3 (3)
O11—Cd3—O1	86.4 (2)	Cd4—O5—Cd3	110.2 (3)
O2—Cd3—O1	175.8 (2)	Cd4—O5—Cd2	106.7 (2)
O7^{iv}—Cd3—O1	98.4 (2)	Cd3—O5—Cd2	120.2 (3)
O5—Cd3—O3^{iv}	164.7 (2)	P1—O6—Cd2ⁱⁱⁱ	128.6 (3)
O11—Cd3—O3^{iv}	92.9 (2)	P1—O6—Cd1^{xi}	109.3 (3)
O2—Cd3—O3^{iv}	101.2 (2)	Cd2ⁱⁱⁱ—O6—Cd1^{xi}	94.1 (2)
O7^{iv}—Cd3—O3^{iv}	59.42 (19)	P1—O6—Cd4^v	128.5 (3)
O1—Cd3—O3^{iv}	79.8 (2)	Cd2ⁱⁱⁱ—O6—Cd4^v	90.9 (2)
O5—Cd4—O2^v	166.4 (2)	Cd1^{xi}—O6—Cd4^v	97.2 (2)
O5—Cd4—O7^{vi}	88.1 (2)	P2—O7—Cd4^v	129.9 (4)
O2^v—Cd4—O7^{vi}	97.3 (2)	P2—O7—Cd3ⁱⁱⁱ	99.9 (3)
O5—Cd4—O12	102.9 (2)	Cd4^v—O7—Cd3ⁱⁱⁱ	111.8 (3)
O2^v—Cd4—O12	90.1 (2)	Cd2^x—O8—Cd1	101.2 (3)
O7^{vi}—Cd4—O12	83.8 (2)	Cd2^x—O8—Cd1^x	115.6 (3)
O5—Cd4—O10	78.0 (2)	Cd1—O8—Cd1^x	133.6 (3)
O2^v—Cd4—O10	93.3 (2)	P1—O9—Cd5^{xii}	149.7 (4)
O7^{vi}—Cd4—O10	159.4 (2)	P1—O9—Cd5	96.3 (3)
O12—Cd4—O10	113.9 (2)	Cd5^{xii}—O9—Cd5	113.8 (3)
O5—Cd4—O6^{vi}	86.1 (2)	P2—O10—Cd2	124.6 (3)
O2^v—Cd4—O6^{vi}	82.4 (2)	P2—O10—Cd4	113.0 (3)
O7^{vi}—Cd4—O6^{vi}	81.5 (2)	Cd2—O10—Cd4	96.7 (2)
O12—Cd4—O6^{vi}	162.5 (2)	P2—O10—Cd1^x	128.6 (3)
O10—Cd4—O6^{vi}	82.4 (2)	Cd2—O10—Cd1^x	89.6 (2)
O4^v—Cd5—O9^{vii}	87.0 (2)	Cd4—O10—Cd1^x	97.1 (2)
O4^v—Cd5—O3^{vi}	168.8 (2)	P2^{vi}—O11—Cd3	127.1 (4)
O9^{vii}—Cd5—O3^{vi}	82.7 (2)	P1—O12—Cd4	136.4 (3)
O4^v—Cd5—O1^{viii}	94.6 (2)	P1—O12—Cd5	94.7 (3)
O9^{vii}—Cd5—O1^{viii}	111.4 (2)	Cd4—O12—Cd5	121.2 (2)

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