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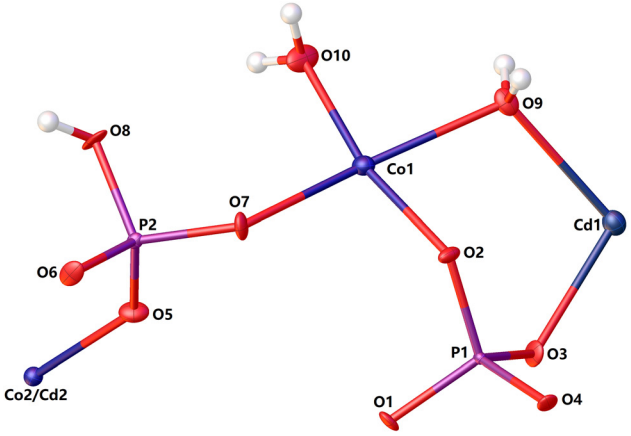
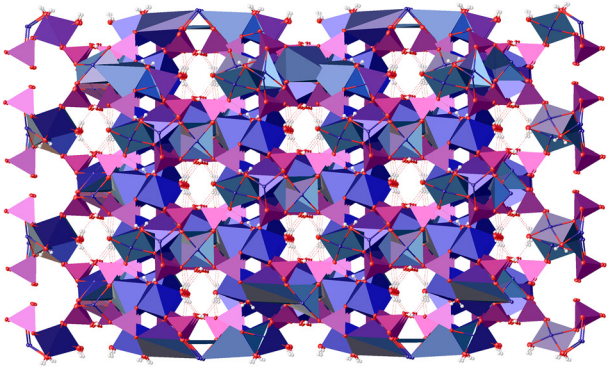
The crystal structure of cobalt cadmium bis(hydrogenphosphate) bis(phosphate(V)) tetrahydrate, $H_{10}O_{20}P_4Co_{3.14}Cd_{1.86}$





Abstract

$H_{10}O_{20}P_4Co_{3.14}Cd_{1.86}$, monoclinic, $C2/c$ (no. 15), a = 17.5779(6) Å, b = 9.0747(3) Å, c = 9.4946(3) Å, β = 96.636(3)°, V = 1504.38(9) Å^3, Z = 1, $R_{gt}(F)$ = 0.0273, $wR_{ref}(F^2)$ = 0.0646, T = 293(2) K.

CCDC no.: 2157686

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Purple needle
Size:	0.32 × 0.06 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.52 mm^{-1}
Diffractometer, scan mode:	New Xcalibur, ω
θ_{max}, completeness:	29.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3496, 1737, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1612
$N(param)_{refined}$:	145
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Olex2 [4]

Source of material

A mixture containing $CoSO_4{\cdot}7H_2O$ (0.840 g), $Cd(NO_3){\cdot}4H_2O$ (0.680 g), H_3PO_4 (aq. 85%) (0.35 mL), and deionized water (H_2O) (16.0 mL), with pH value 6.0, was prepared by mixing these components and sealing in a 25 mL Teflon-lined stainless steel autoclave (70% of the total volume of the autoclave). Then, the resulting slurry was heated to 458 K in an oven and maintained at the temperature for one week. Then, the dark purple purity-phase crystals of the title compound (about 31% yield based on Co) were obtained. The results of elemental analyses provided the chemical compositions: (wt.%) for the title compound: H, 1.24; P, 14.06; Co, 20.98; Cd, 25.04 (in contrast, anal. calcd. (wt.%): H, 1.18; P, 14.61; Co, 21.80; Cd, 24.70; O, 37.71).

https://doi.org/10.1515/ncrs-2022-0068
Received February 9, 2022; accepted March 11, 2022;
published online April 4, 2022

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1[a]	0.82478 (2)	0.02895 (4)	0.63265 (3)	0.01053 (13)
Co1[b]	0.82478 (2)	0.02895 (4)	0.63265 (3)	0.01053 (13)
Co2[c]	0.68240 (3)	0.08560 (6)	0.31409 (6)	0.0104 (2)
Cd2[d]	0.68240 (3)	0.08560 (6)	0.31409 (6)	0.0104 (2)
Co3[e]	0.5000	0.60654 (6)	0.2500	0.0103 (2)
Cd3[f]	0.5000	0.60654 (6)	0.2500	0.0103 (2)
P1	0.83862 (6)	0.26486 (11)	0.37391 (11)	0.0094 (3)
P2	0.58188 (6)	0.31913 (11)	0.09070 (11)	0.0102 (3)
O1	0.79877 (16)	0.4095 (3)	0.3268 (3)	0.0141 (6)
O2	0.79559 (16)	0.1362 (3)	0.2952 (3)	0.0144 (6)
O3	0.83591 (17)	0.2462 (3)	0.5347 (3)	0.0158 (6)
O4	0.92300 (16)	0.2669 (3)	0.3425 (3)	0.0134 (6)
O5	0.57549 (18)	0.4356 (3)	0.2025 (3)	0.0188 (7)
O6	0.58378 (17)	0.3848 (3)	−0.0565 (3)	0.0168 (7)
O7	0.65331 (17)	0.2275 (3)	0.1376 (3)	0.0162 (6)
O8	0.51077 (18)	0.2139 (4)	0.0821 (3)	0.0201 (7)
H8	0.4872	0.2184	0.0025	0.030*
O9	0.73606 (19)	−0.0815 (4)	0.4633 (3)	0.0176 (7)
O10	0.57932 (18)	−0.0038 (4)	0.3424 (4)	0.0228 (7)
H10A	0.5798	−0.0365	0.4280	0.034*
H10B	0.5691	−0.0766	0.2844	0.034*
H9A	0.709 (3)	−0.118 (7)	0.519 (6)	0.06 (2)*
H9B	0.759 (3)	−0.141 (5)	0.415 (5)	0.029 (15)*

[a]Occupancy: 0.740 (6); [b]Occupancy: 0.260 (6); [c]Occupancy: 0.974 (5); [d]Occupancy: 0.026 (5); [e]Occupancy: 0.666 (6); [f]Occupancy: 0.334 (6).

Experimental details

The hydrogen atoms were placed at calculated positions with the SHELX program. Coordinates of hydrogen atoms were refined without any constraints or restraints.

Comment

In recent decades, transition metal phospates and phosphonates have attracted great attention for its outstanding physicochemical properties (such as heterogeneous catalysis, ion exchange, optical, magnetic, etc.) and potential real-world applications. In the phosphates the relatively high charge in $(PO_4)^{3-}$ tetrahedra is not only favor of the formation of anionic frameworks, but also favor of the high degree of mechanical and thermal stability [5, 6]. Moreover, cobalt phosphates have received more interest owing to its feasibility for catalytic properties [7–10]. The 3d transition element Co can offer a wide variety of frameworks to perform diverse redox reactions under conventional catalytic conditions [11]. Herein, we report a new hureaulite ($Mn_5[PO_3(OH)]_2(PO_4)2{\cdot}4H_2O$)-type Co/Cd phosphate, $Co_{2.56}Cd_{2.44}[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$. In general, Mn element in hureaulite being replaced by diverse transition-metal elements will lead to different physicochemical properties. Although some hurealite-type compounds, e.g. $Co_5[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [12], $Mn_5[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [13], $Cd_5[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [14], $Mn_{3.75}Co_{1.25}[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [15], $Mn_3Co_2[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [15], $Mn_{2.5}Co_{2.5}[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [15], $Mn_2Co_3[PO_3(OH)]_2(PO_4)_2{\cdot}4H_2O$ [15], have been synthesized and studied, analogous isostructural compound, which Co and Cd elements collectively replace Mn element, has never been reported.

Single-crystal X-ray diffraction structure study reveals that the title compound is isostructural with hureaulite, showing a 3D-network structure. Compared to hureaulite, all the five Mn sites in $Mn_5[PO_3(OH)]_2(PO_4)2{\cdot}4H_2O$ are replaced collectively by Co and Cd atoms. The title structure contains two and a half Co/Cd sharing sites, with the total Co/Cd atom occupancy rate about 3.14:1.86, two hydrogen phospate ion $[PO_3(OH)]^{2-}$, two phosphate ions $(PO_4)^{3-}$, and four coordinated waters (H_2O). The Co/Cd phosphate is constructed by penta–Co/Cd ($[Co_{3.14}Cd_{1.86}(HPO_4)_2(PO_4)_2(H_2O)_4]$) 0D neutral clusters as secondary building units. The five-membered $Co_{3.14}Cd_{1.86}$ clusters were terminated by water molecule O(9) (H_2O), which is then connected by the O(1) from P(1) phosphate and the water molecule O(10) (H_2O) to form a 2D layer. The layers are further linked by monohydrate phosphates and phosphates in $\nu^1{:}\nu^2{:}\nu^2{:}\mu_5$ and $\nu^2{:}\nu^2{:}\nu^2{:}\nu^1{:}\mu_7$ modes to construct a 3D structure [13]. Each Co^{II}/Cd^{II} ion possesses a distorted Co/CdO_6 octahedron geometry and it is noteworthy that Co(3)/Cd(3) is on the mirror plane. The Co(1)/Cd(1)–O, Co(2)/Cd(2)–O and Co(3)/Cd(3)–O bond lengths vary in the range of 2.198(3)–2.333(3) Å, 2.031(3)–2.211(3) Å, 2.124(3)–2.235(3) Å. The P(1)–O and P(2)–O bond lengths are in the normal range of 1.530(3)–1.546(3) Å and 1.511(3)–1.568(3) Å respectively. Bond valence sum (BVS) calculations show that all P atoms have the oxidation state of +5 respectively. The angles of Co/Cd–O–Co/Cd are from 98.03(11)–110.40(14)° and the intracluster metal-metal separations through ν–O bridges are 3.384 and 3.731 Å for Co(1)/Cd(1)···Co(2)/Cd(2) and Co(1)/Cd(1)···Co(3)/Cd(3). The P(1) phosphate links seven Co/Cd ions, while the P(2) one connects five Co/Cd ions. The $Co_{3.14}Cd_{1.86}$ penta-nuclear clusters are connected through O(1) and O(9) (H_2O) to form the 3D configuration.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The work was supported by the Natural Science Foundation of Fujian Province (No. 2020J01367) and the Qimai Science and Technology Innovation Foundation of Xinluo County (No. 2022XLQM04).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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