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Hydrothermal Synthesis and Characterization of Two Organically Templated Cadmium Borophosphates with Novel Structures

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Two organically templated cadmium borophosphates, $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ (**1**) and $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$ (**2**), were synthesized hydrothermally in the presence of structure-directing amines. Compound **1** has a complex layered structure (orthorhombic, *Pbca* (No. 61); $a = 9.470(2)$, $b = 12.307(3)$, $c = 27.311(6)$ Å; $V = 3183(1)$ Å^3; $Z = 8$) with a 9MR channel system, while compound **2** (orthorhombic, *Pbca* (No. 61); $a = 9.286(3)$, $b = 12.459(3)$, $c = 21.626(6)$ Å; $V = 2502(1)$ Å^3; $Z = 8$) presents a 3-dimensional open framework structure of different types of intersecting channels. It is worth noting that both the Cl^- anions and the organic templates play important and interesting roles in the formation of the structures.

Introduction

Organically templated metal borophosphates are of great current interest because of their potential for novel structures and, correspondingly, catalytic applications.[1] Since the first such borophosphate with an open framework structure, $(C_2H_{10}N_2)[CoB_2P_3O_{12}(OH)]$,[2] was reported a few years ago, a broad spectrum of similar compounds with various dimensionalities and stoichiometries have been added to the list. A large number of them, $M^{II}(C_2H_{10}N_2)[B_2P_3O_{12}(OH)]$ (M^{II} = Mg, Mn, Fe, Ni, Cu, Zn),[3] $M^{II}(C_4H_{12}N_2)[B_2P_3O_{12}(OH)]$ (M^{II} = Co, Zn),[4] and $(C_6H_{14}N_2)_2[ZnB_6P_{13}O_{42}(OH)_{13}]$,[5] have 3-dimensional open framework structures, while some vanadium borophosphates show various anionic partial structures.[6] Recently, the first fluoroborophosphate, $(C_2H_{10}N_2)[BPO_4F_2]$ with an infinite and unbranched 1-D chain, and the first chloroborophosphate, $(C_6H_{14}N_2)\{Zn[ZnB_2P_4O_{15}(OH)_2]\cdot(C_6H_{13}N_2)Cl\}$, were also reported.[7,8] Surprisingly, however, despite the intensive studies of such systems involving various first-row transition metals, not much attention has been paid to similar compounds with cadmium. To our knowledge, known is only one class of such compounds, $MCd(H_2O)_2[BP_2O_8]\cdot nH_2O$ (M = Li, Na, K).[9] Their structures are quite interesting as they contain 6_1 or 6_5 helical anionic chains. Here we report the hydrothermal synthesis and the structures of the first two organically templated cadmium borophosphates, $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ (**1**) and $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$ (**2**).

Experimental Section

Synthesis. $CdCl_2$, B_2O_3, phosphoric acid (85 wt %), diethylenetriamine (DETA), and deionized water were mixed in molar ratio 1:1:8:5:80 for compound **1**. Similarly, $CdCl_2$, B_2O_3, phosphoric acid (85 wt %), ethylenediamine, and deionized water were mixed in molar ratio 1:1:8:10:80 for compound **2**. The mixtures were sealed

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Table 1. Crystal Structure Refinement Data for $(C_4H_{10}N_2)[CdClB_2P_3O_{12}(OH)]$ and $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$

struct param	**1**	**2**
empirical formula	$CdB_2P_3O_{13}Cl_1C_4N_3H_{17}$	$CdB_2P_3O_{13}C_2N_2H_{11}$
fw	577.59	498.1
wavelength (Å)	0.717 03	0.717 03
cryst system	orthorhombic	orthorhombic
space group	*Pbca* (No. 61)	*Pbca* (No. 61)
a (Å)	9.470(2)	9.286(3)
b (Å)	12.307(3)	12.459(3)
c (Å)	27.311(6)	21.626(6)
V (Å^3)	3183(1)	2502(1)
Z	8	8
D_{calc} (Mg/m^3)	2.411	2.639
μ(Mo Kα) (mm^{-1})	1.92	2.21
F(000)	2288	1952
θ range (deg)	1.49−26.01	2.89−27.04
tot. data collcd	13 778	11 555
unique data	3127	2751
obsd data	2154	2349
GOF on F^2	0.83	1.09
final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.036$, $wR_2{}^b = 0.053$	$R_1{}^a = 0.029$, $wR_2{}^b = 0.072$
R indices (all data)	$R_1 = 0.063$, $wR_2 = 0.058$	$R_1 = 0.038$, $wR_2 = 0.075$

[a] $R_1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_o{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (0.0302P)^2 + 5.74P]$ with $P = (F_o{}^2 + F_o{}^2)/3$.

Table 2. Selected Bond Distances and Bond Valence Sums in $(C_4N_3H_{16})[CdClB_2P_3O_{12}(OH)]$

moiety	dist/Å	moiety	dist/Å
Cd(1)−O(4)	2.266(3)	P(2)−O(9)	1.554(4)
Cd(1)−O(3)	2.274(3)	P(3)−O(4)	1.485(4)
Cd(1)−O(2)	2.279(3)	P(3)−O(13)	1.542(3)
Cd(1)−O(5)	2.282(3)	P(3)−O(12)	1.542(3)
Cd(1)−O(1)	2.332(3)	P(3)−O(10)	1.545(3)
Cd(1)−Cl(1)	2.476(1)	B(1)−O(1)	1.445(6)
P(1)−O(7)	1.482(3)	B(1)−O(11)[b]	1.460(6)
P(1)−O(2)	1.500(3)	B(1)−O(6)	1.480(6)
P(1)−O(6)	1.571(4)	B(1)−O(12)[c]	1.498(7)
P(1)−O(8)	1.589(4)	B(2)−O(1)	1.417(6)
P(2)−O(3)	1.503(3)	B(2)−O(9)	1.471(6)
P(2)−O(5)[a]	1.525(3)	B(2)−O(13)[c]	1.487(6)
P(2)−O(11)	1.542(3)	B(2)−O(10)	1.511(6)
org moiety		org moiety	
C(1)−N(1)	1.495(7)	C(3)−C(4)	1.479(8)
C(1)−C(2)	1.504(8)	C(3)−N(2)	1.479(7)
C(2)−N(2)	1.478(7)	C(4)−N(3)	1.490(6)

Bond Valence Sums (Σs)

[CdO_5Cl] octahedron, Σs[Cd−O/Cl] = 2.30
[$P(1)O_4$] tetrahedron, Σs[P(1)−O] = 4.87
[$P(2)O_4$] tetrahedron, Σs[P(2)−O] = 4.91
[$P(3)O_4$] tetrahedron, Σs[P(3)−O] = 4.94
[$B(1)O_4$] tetrahedron, Σs[B(1)−O] = 3.06
[$B(2)O_4$] tetrahedron, Σs[B(2)−O] = 3.06

[a] $-x + 1/2, y + 1/2, z$. [b] $-x + 1/2, y - 1/2, z$. [c] $x + 1/2, y, -z + 1/2$.

in 25 mL Teflon-lined stainless steel autoclaves and heated for 5 days under autogenous pressure at 473 and 443 K for compounds **1** and **2,** respectively. The resulting rodlike crystals from both reactions were recovered by filtration, washed with distilled water, and dried at room temperature. The yields were 60% and 45% based on Cd for **1** and **2**, respectively. The presence of Cl in **1** was confirmed by EDS analysis (EPMA_8705QH$_2$ electron microscope equipped with a LINKS ISIS).

Structure Determination. Crystals from each compound were selected under a polarizing microscope, glued to a thin glass fiber with cyanoacrylate (superglue) adhesive, and inspected for singularity. Two of them were chosen (0.40 × 0.20 × 0.20 mm for **1** and 0.40 × 0.15 × 0.15 mm for **2**), and data sets were collected on a Nonius Kappa CCD diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å). The data were corrected for absorption using the SADABS program. The structures were solved by direct methods and refined against $|F^2|$ with the aid of the SHELXTL-PLUS package.[10] All hydrogen positions were located from the difference map but were refined as riding in the final refinement. Additional information about the data collection and structure refinement is presented in Table 1, while selected distances for **1** and **2** are listed in Tables 2 and 3, respectively.

Other Characterizations. The products were examined also by powder X-ray diffraction (Rigaku D/max 2550V diffractometer, Cu Kα) to confirm their phase identity and purity. The diffraction patterns were consistent with those calculated from the structures determined by single-crystal X-ray diffraction. Thermogravimetric analyses were performed on a STA-409PC/4/H LUXX DSC-TGA instrument at a heating rate of 10 K min^{-1} in a flow of N_2 to a maximum temperature of 1273 K. IR spectra were collected on a Digilab-FTS-80 spectrophotometer using pressed KBr pellets of the samples.

Results and Discussion

Compound **1** is the first chloro−borophosphate with a layered structure. The layers are made of CdO_5Cl octahedra and BO_4 and PO_4 tetrahedra connected through common

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(10) Sheldrick, G. M. *SHELXTL Programs*, release version 5.1; Bruker AXS: Madison, WI, 1998.

Table 3. Selected Bond Distances and Bond Valence Sums in $(C_2N_2H_{10})[CdB_2P_3O_{12}(OH)]$

moiety	dist/Å	moiety	dist/Å
Cd(1)−O(8)	2.213(2)	P(2)−O(13)	1.571(3)
Cd(1)−O(6)	2.234(3)	P(3)−O(8)^b	1.504(3)
Cd(1)−O(3)	2.255(3)	P(3)−O(2)	1.510(3)
Cd(1)−O(2)	2.271(3)	P(3)−O(4)	1.556(3)
Cd(1)−O(7)	2.311(3)	P(3)−O(11)	1.565(3)
Cd(1)−O(12)	2.343(2)	B(1)−O(12)	1.440(4)
P(1)−O(7)	1.495(3)	B(1)−O(11)	1.467(4)
P(1)−O(10)	1.534(2)	B(1)−O(1)	1.474(4)
P(1)−O(5)	1.550(2)	B(1)−O(5)^c	1.496(4)
P(1)−O(9)	1.560(2)	B(2)−O(12)^b	1.418(4)
P(2)−O(3)	1.498(2)	B(2)−O(4)	1.444(4)
P(2)−O(6)^a	1.523(2)	B(2)−O(9)^d	1.491(4)
P(2)−O(11)	1.565(3)	B(2)−O(10)^b	1.508(4)
org moiety		org moiety	
C(1)−N(1)	1.480(5)	C(1)−C(2)	1.508(5)
C(2)−N(2)	1.482(5)		

Bond Valence Sums (Σs)

$[CdO_6]$ octahedron, $\Sigma s[Cd-O] = 2.24$
$[P(1)O_4]$ tetrahedron, $\Sigma s[P(1)-O] = 4.90$
$[P(2)O_4]$ tetrahedron, $\Sigma s[P(2)-O] = 4.85$
$[P(3)O_4]$ tetrahedron, $\Sigma s[P(3)-O] = 4.92$
$[B(1)O_4]$ tetrahedron, $\Sigma s[B(1)-O] = 3.06$
$[B(2)O_4]$ tetrahedron, $\Sigma s[B(2)-O] = 3.11$

^{a} $x + {}^1/_2, -y + {}^3/_2, -z + 2$. ^{b} $-x + {}^3/_2, y + {}^1/_2, z$. ^{c} $x + {}^1/_2, y, -z + {}^3/_2$. ^{d} $-x + 1, -y + {}^1/_2, -z + {}^3/_2$.

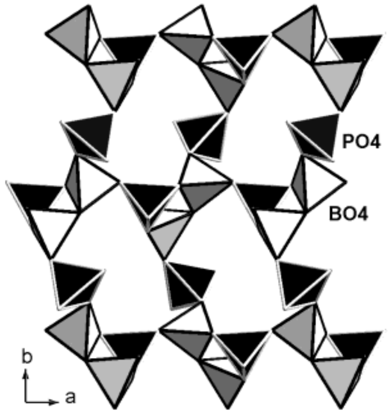

Figure 1. View of the layer of $_\infty{}^2\{[B_2P_3O_{12}(OH)]^{4-}\}$ in $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ showing the three- and nine-membered rings.

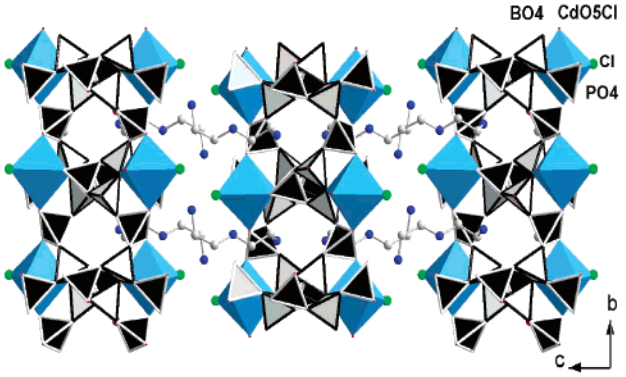

Figure 2. View along *a* of the structure of $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ showing the inorganic layers that alternate with organic molecules along the *c* axis.

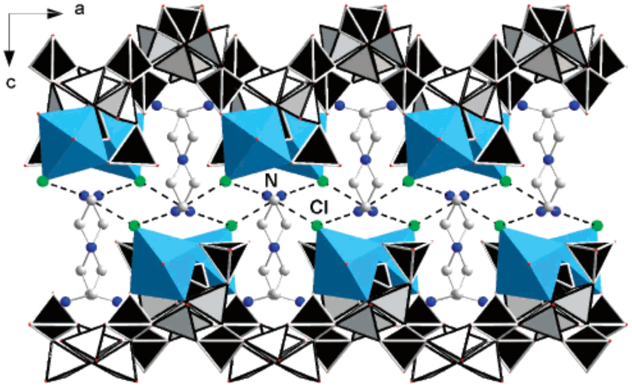

Figure 3. Arrangement of the organic templates between the inorganic layers of **1** where they act as "fasteners" for neighboring layers. The dotted lines represent the hydrogen bond interactions between N and Cl ions.

vertexes. The cadmium-centered octahedra share its five oxygen atoms with BO_4 and PO_4 tetrahedra while the latter are connected to each other and form three- and nine-membered rings (Figure 1) in the inorganic layer with repeating unit $[CdCl(B_2P_4O_{19})]^{3-}$. The Cd−Cl bonds, 2.476 Å, are arranged perpendicular to the layers. One of the phosphate groups, that of P(1), is two-bonded within the layer with P−O distances of 1.500 and 1.571 Å and has one terminal and one protonated oxygen atoms at distances of 1.482 and 1.589 Å, respectively. This makes the tetrahedron quite distorted. On the basis of bond strength calculations,[11] the bond valence sums for Cd, P, and B atoms are close to their normal valences of 2, 5, and 3, respectively, which indicates proper asignment of the anion groups (listed in Table 2).

The inorganic layers of cadmium chloro−borophosphate are separated by the organic templates (Figure 2). Each such inorganic layer is inverted with respect to its two neighboring layers which leads to a repeating arrangement of AB···AB layers along the *c* axis. The triprotonated DETA molecules are approximately perpendicular to the inorganic layers and participate in strong hydrogen bonding with them. One end of the molecules protrudes into the creases of the puckered layers and forms hydrogen bonds to oxygen atoms of P−O−B or Cd−O−P. The other end forms such bonds with oxygen and chlorine atoms from an adjacent layer (Figure 3), and thus, the templates act as fasteners between the layers to form an inorganic−organic framework.

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[11] Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

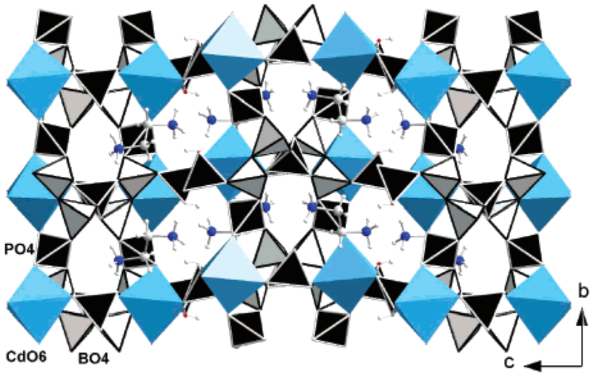

Figure 4. Polyhedral view of the structure of $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$ along the *c* axis, showing the 3-D structure made of distorted CdO_6 octahedra, BO_4 and PO_4 tetrahedra, and ethylenediamine molecules are located in the channels along the *c* axis.

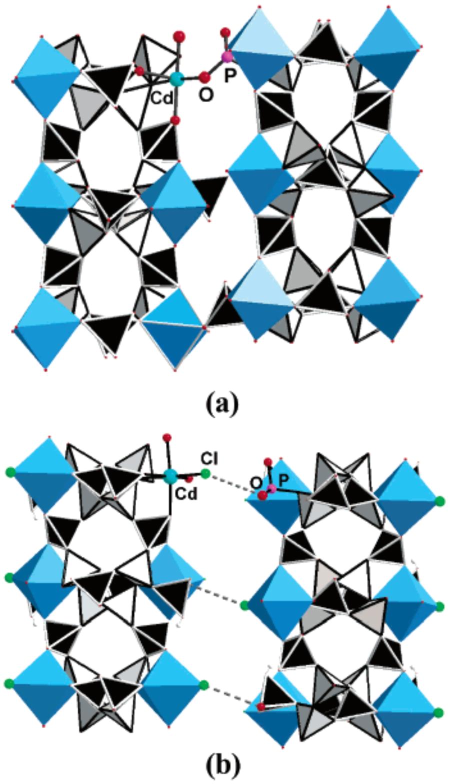

Figure 5. Comparison of the structures of **1** and **2** in similar views. (a) The borophosphate anions in compound **2** are linked together by CdO_6 octahedra via Cd−O−P bridges to form a 3-D network (details is shown). (b) A connection between the similar inorganic layers in **1** is impossible because of the existence of the terminal chlorine ions.

Structurally, compound **2** is closely related to the family of borophosphates with general formula $M^{II}(C_2H_{10}N_2)[B_2P_3O_{12}(OH)]$, where M^{II} = Mg, Mn, Fe, Ni, Cu, and Zn. Its three-dimensional structure is made of CdO_6 octahedra that share oxygen corners with BO_4 and PO_4 tetrahedra and form a system of intersecting channels along [100], [010], and [001] directions (Figure 4). They are occupied by the templates, diprotonated ethylenediamine molecules that are stacked along [100] and fixed via N−H...O hydrogen bonds to the framework. The effect of the bigger Cd ions compared to the metals in the prototypes structure (above) is only slight increase of the channel radius. The fact that the overall structure remains the same indicates that it might be possible to increase even further the size of the channels by introducing even larger metal ions to this type of borophosphate.

It is worth noting that both the Cl^- ions and the organic molecules play an important and interesting role in the formation of the structures of **1** and **2**. As shown in Figure 5, although the two compounds have different structures, they have almost identical borophosphate anionic units $[B_2P_3O_{12}(OH)]^{4-}$. These units in **2** are linked together by CdO_6 octahedra via Cd−O−P bridges and form the 3D framework. However, such connectivity is impossible in **1** because the oxygen atoms in the Cd−O−P bridges of **2** are replaced by terminal chlorine. Thus, the bridge is separated into two bonds, one of Cd−Cl and one of P−O. As a result of this, the 3D network of **2** is broken down to two-dimensional layers. It can be said, therefore, that the Cl^- ions act as a “tailor” in the formation of the structure of compound **1**.

The role of the organic molecules in the formation of the structures should not be ignored either. Thus, all attempts to synthesize a chloro−borophosphate with ethylenediamine instead of DETA produced compound **2**. This indicates that the organic template plays a very important role in directing the structure formation. Generally, small molecules can be placed in small spaces such as channels or holes to act as structure-directing agents in structures, while big molecules might be apt to break off some linkages and create larger spaces for themselves such as the space between layers. Therefore, compound **1** might be viewed as a derivative of compound **2** that has been “tailored” by the Cl^- ions and broken to layers by the space-creating DETA.

The TGA experiments for compound **1** showed weight loss in two steps followed by a long tail in the temperature range 623−923 K. The total weight loss of 26% corresponds to the release of the amine molecule (calcd 18.4%) and chlorine (calcd 5.4%) and the elimination of the hydroxyl groups from the PO_3OH units (calcd 3.1%). The same analysis for compound **2** showed three steps of decomposition in the range 713−1173 K. The weight loss within 713−783 K is 13.1%, which corresponds to the release of the ethylenediamine molecules (calcd 12.4%). The weight loss at the second step, 783−923 K, is 3.4%, and this agrees with the removal of 1 molar equiv of water through condensation of P−OH groups (calcd 3.6%). The third weight loss was observed in the range 923−1173 K, and it might be associated with the elimination of B_2O_3.

The IR spectrum of **1** showed a peak at 1619 cm^{-1} that corresponds to bending vibrations of O−H. The stretching and bending vibrations of N−H appeared at 3228−2992 and 1581−1515 cm^{-1}, respectively, while peaks in the 1454−1400 cm^{-1} range can be attributed to the bending vibrations of C−H. All these confirm the presence of protonated diethylenetriamine molecules. Compound **2** showed bands at 3280−3144 and 1529−1478 cm^{-1} that correspond also to N−H stretching and bending. Peaks observed at 3019−2870 cm^{-1} are in good agreement with C−H vibrations, and a peak at 1624 cm^{-1} can be attributed to bending vibrations of O−H groups.

Conclusion

The organically templated cadmium borophosphates $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ with a layered structure and $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$ with a 3-dimensional open framework structure have been hydrothermally synthesized for the first time. $(C_4H_{16}N_3)[CdClB_2P_3O_{12}(OH)]$ is the first example of chlorine atoms participating in the formation of the two-dimensional structure in borophosphates. By comparison of the two structures, it is found that both Cl ions and organic molecules play an important and interesting role in the formation of structures. The success of these syntheses might provide information about how to make more novel materials by introducing bigger template agents and halogen atoms.

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Supporting Information Available: Crystallographic and X-ray diffraction data for $(C_2H_{10}N_2)[CdB_2P_3O_{12}(OH)]$ and $(C_4H_{16}N_3)$-$[CdClB_2P_3O_{12}(OH)]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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