A Novel Layered Structure of a New Cadmium Chlorophosphate with an Imidazolium Template

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A new organically templated cadmium chlorophosphate, $(C_3H_6N_2)[Cd_2Cl_2(HPO_4)_2]$ ($C_3H_6N_2$ = diprotonated imidazole) with a novel layered structure, was synthesized hydrothermally in the presence of imidazole as a structure-directing agent. This is the first example of a cadmium chlorophosphate with polymeric chains that consist of Cd–O/Cl–Cd units.

Considerable efforts have been made during the past decade to design and synthesize novel open-framework materials that might find their potential application in the fields of catalysis, ion exchange, electrical conduction, and magnetism.[1,2] A remarkable range of compounds and structures has been prepared under mild hydrothermal conditions ($T < 200\,^\circ C$, autogenous pressure) using organic molecules as structure-directing agents.[3–10] In addition, it was reported that fluorine and chlorine ions serve as mineralizers as well as linkers between metal atoms, and therefore they strongly affect the construction of the framework structures.[11,12] A broad spectrum of metal fluoro- and chlorophosphates has already been hydrothermally synthesized.[13–18] However, organically templated cadmium fluoro- and chlorophosphates have not been reported. Here we present the first example of such cadmium chlorophosphate $(C_3H_6N_2)[Cd_2Cl_2(HPO_4)_2]$ (**1**).

In a typical synthesis of compound **1**, a mixture of $CdCl_2$ (2.28 g), B_2O_3 (0.696 g) (initially aimed to produce a borophosphate), imidazole (3.09 g), and deionized water (15 mL) is heated at 100 °C. 5 mL of H_3PO_4 (85 wt %) is then gradually added to the former solution to adjust the pH at 1.0. The solution is then transferred to a Teflon-coated autoclave and is heated at 170 °C for 5 days. After slow cooling, colorless needles of **1** were obtained as a single-phase product (yield, 45% based on Cd). Found: Cd, 40.53; P, 11.08; C, 6.39; N, 5.08%. Calcd for $(C_3H_6N_2)[Cd_2Cl_2(HPO_4)_2]$: Cd, 40.03; P, 11.12; C, 6.46; N, 5.02%. The presence of Cl in the title compound was confirmed by EDS analysis.

The structure of the new compound was determined by single crystal X-ray diffraction.[19] Compound **1** has a two-dimensional layered structure made up of CdO_4Cl_2 octahedra and PO_4 tetrahedra (Figure 1). The asymmetric unit contains 10 non-hydrogen atoms, seven of which are shown in Figure 2 and the rest of which corresponds to the N and C atoms of an imidazolium cation in Figure 3. Each cadmium atom shares two oxygen corners with two bridging PO_4 tetrahedra (Cd–O = 2.253(3) and 2.353(3) Å), two chlorine corners with two neighboring cadmium octahedra (Cd–Cl = 2.555(3) and 2.573(5) Å), and two oxygen corners with both PO_4 tetrahedra and neighboring cadmium octahedra (Cd–O = 2.319(5) and 2.337(5) Å). This results in a fairly distorted octahedral geometry around cadmium. Each PO_4 tetrahedron shares three of the oxygen atoms with four cadmium octahedra (P–O = 1.507(4)–1.546(3) Å) while the fourth oxygen atom is protonated to an OH group (P–O = 1.577(4) Å). Interestingly, the distorted CdO_4Cl_2 octahedra form a straight chain by sharing opposite edges. This is the first example of a cadmium chlorophosphate derivative with such polymeric straight chains consisting of the Cd–O/Cl–Cd units in the crystal, though a zigzag cadmium octahedral chain was observed in $K_4[Cd_3(HPO_4)_4(H_2PO_4)_2]$.[20] The chains are connected by $PO_3(OH)$ tetrahedra and form the layers of the structure (Figure 3a). The chlorine vertices of the cadmium octahedra are found on the outside of the layers and their terminal nature can be considered as the reason for the lower dimensionality of the structure, i.e. it is impossible to form links between the layers via halogen atoms. Four-membered

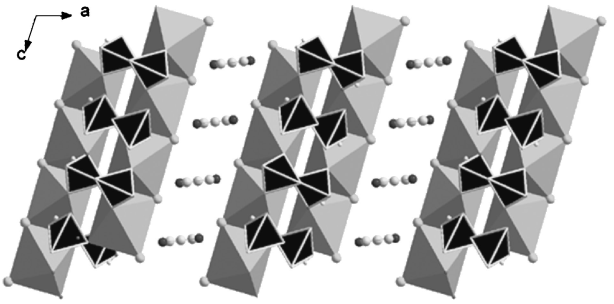


Figure 1. Polyhedral view of the structure $(C_3H_6N_2)[Cd_2Cl_2(HPO_4)_2]$ along the *b* axis, showing the layered structure constructed of distorted CdO_4Cl_2 octahedra and $PO_3(OH)$ tetrahedra. Templating imidazole dications are located between the layers and interact with them via hydrogen bonds. (CdO_4Cl_2: dark gray; PO_4: black; Cl^-: dark gray; N: black; C: light grey).

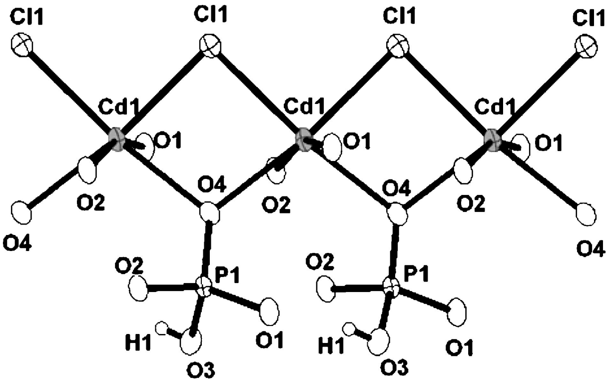
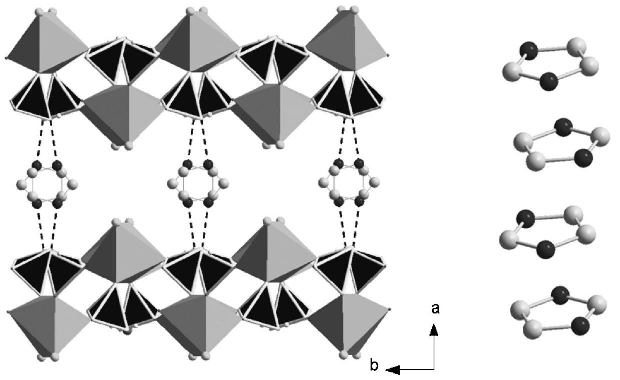


Figure 2. A closer view of the cadmium coordination (thermal ellipsoids at 50% probability).



(a) (b)

Figure 3. (a) Polyhedral view of the structure $(C_3H_6N_2)$-$[Cd_2Cl_2(HPO_4)_2]$ along the *c* axis, showing the four-membered channel system in the layers. Imidazole molecules located between layers via hydrogen bonds; (b) The parallel alignment of imidazole molecules, showing the reverse tactic direction of neighboring organic molecules. (CdO_4Cl_2 octahedra, dark gray; PO_4 tetrahedra, black; Cl^- ions, dark gray spheres; N, black spheres; C, light grey spheres; Hydrogen atoms are not shown).

rings of octahedra and tetrahedra in the layers are stacked on top of each other and form channel system along [001] direction.

The diprotonated imidazolium dications occupy the interlamellar spaces between the inorganic layers (interplanar separation is 3.75 Å) and satisfy the charge balance (Figures 3a and 3b). They interact with the inorganic layers via hydrogen bonds formed between the NH units of imidazolium cations and the oxygen atoms of phosphates (N1···O4 = 2.842(7) Å, O1···O4 = 2.618(6) Å).

Thermogravimetric analyses and differential scanning calorimetry (TGA and DSC) were performed using a STA–409PC/4/H LUXX DSC–TGA instrument at a heating rate of 5 °C/min in a flow of nitrogen gas from room temperature to 1000 °C. They showed two steps of decomposition in the range of 250 to 600 °C. The weight loss between 250–330 °C is 6.7% and indicates removal of 2 mol equiv. of water through condensation of P–OH groups (calcd 6.4%). The weight loss between 330–550 °C is 24.5% and corresponds to the release of the imidazole molecules (calcd 12.6%) and the chlorine atoms (calcd 12.7%). FTIR spectra of the compound, collected with a Digilab–FTS–80 spectrophotometer on a KBr pellet, showed bands at 3380 cm^{-1} (O–H stretching vibration), 1581 cm^{-1} (C=C bond), 2424–2316 cm^{-1} ($C{=}NH^+$ bending vibrations), and 3170–2856 and 1448–1411 cm^{-1} (N–H stretching and bending vibrations). These are consistent with the crystal structure of the compound determined by the X-ray diffraction.

In summary, a new cadmium chlorophosphate $[C_3H_6N_2]$-$[Cd_2Cl_2(PO_3(OH))_2]$ with a layered structure has been synthesized under mild hydrothermal conditions. This study presents the first example where chlorine atoms participate in the formation of 2-D structure in organically templated cadmium phosphates. It is clear that both the organic template and the chlorine atoms play important roles in the formation of the layered structure. We think this study would help further developing novel cadmium phosphates and related inorganic materials with use of different organic-templating agents and chlorine ions. Efforts to obtain such materials are now in progress in our laboratory.

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19 Crystal data for $\mathbf{(C_3H_6N_2)[Cd_2Cl_2(HPO_4)_2]}$: monoclinic, space group $C2/c$ (no. 15), $a = 22.976(5)$ Å, $b = 7.9077(17)$ Å, $c = 7.1929(16)$ Å, $\beta = 106.16(3)^\circ$, $V = 1255.3(5)$ Å^3, $Z = 4$, $M_r = 556.75$, $D_{calcd} = 2.946\,gcm^{-1}$, $\mu(Mo\,K\alpha) = 4.10\,mm^{-1}$, $\lambda = 0.71073$ Å. Data collection was performed using a Nonius Kappa CCD diffractometer at 283 K in the range of $1.85^\circ < \theta < 27.12^\circ$ using ω scan. A total of 3009 data were collected and were merged to give 1377 unique reflections ($R_{int} = 0.035$) of which 1283 were considered to be observed $[I > 2\sigma(I)]$. The structure was solved and refined using SHELXTL-PLUS package of program against $|F^2|$. Final $R = 0.0344$, $R_W = 0.0942$, S (goodness of fit) = 1.118 were obtained for all the data. The hydrogen atoms on the diprotonated imidazole were not located in this analysis (CCDC-247017).

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