

Synthesis, characterizations, and crystal structure of a novel 2D metal phosphonate: $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$

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Abstract

A novel cadmium phosphonate compound $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized by hydrothermal reaction at 120 °C and characterized by single-crystal X-ray diffraction as well as with infrared spectroscopy, elemental analysis and thermogravimetric analysis. The structure of compound **1** comprises CdO_6 octahedra and CdO_7 pentagonal bipyramid connected by $[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]^{3-}$ to form a 2D layered structure with a one-dimensional channel system and the charge-compensating Na^+ cations being located between two adjacent layers.

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Metal phosphonate chemistry has been an area of interest to both inorganic and materials chemists in recent years due to their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1–4]. The strategy of attaching additional functional groups such as amine, hydroxyl and carboxylate groups to the phosphonic acid has proven to be effective for the synthesis of metal phosphonates with open-framework and microporous structures. The introduction of these functional groups may not only result in new structure types of metal phosphonates, but also bring interesting functionalities. Recently, many metal phosphonates have been prepared through designing and synthesizing phosphonic acids with amine, hydroxyl, and carboxylate groups [5–13].

For example, 2-hydroxyphosphonoacetic acid (H_3L) with functional hydroxyl and carboxylate groups is an interesting ligand for the synthesis of metal phosphonates with open-framework structures, since it can adopt various kinds of coordination modes under different reaction conditions which may result in various interesting structures. By using 2-hydroxyphosphonoacetic acid (H_3L) with a chiral carbon atom and three functional groups ($-\text{OH}$, $-\text{COOH}$, and $-\text{PO}_3\text{H}_2$), we have recently reported a cadmium phosphonate $\text{Mg}_{0.5}\text{Cd}[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]$ [14], which comprises CdO_6 octahedra and MgO_6 octahedra connected by $[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]^{3-}$ to form 3D framework structure. To expand our studies in this respect, a novel 2D layered compound, $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ (**1**), has been synthesized by hydrothermal technique, using 2-hydroxyphosphonoacetic acid as ligand [15]. The compound structure was characterized by single-crystal X-ray diffraction [16], infrared spectroscopy, elemental analysis and thermogravimetric analysis.

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A single-crystal X-ray structure analysis of compound **1** revealed that compound $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ crystallizes in monoclinic space group $P2/c$. The asymmetric unit is shown in the Fig. 1.

Compound **1** contains two different types of cadmium atoms in the asymmetric unit. The occupancy of Cd 1 and Cd 3 atom is 0.5, respectively. The Cd 1 and Cd 3 atom are octahedrally coordinated by four phosphonate oxygen atoms from four separate L^{3-} ($\text{L} = \text{O}_3\text{PCH}(\text{OH})\text{CO}_2$) ligands and two carboxylate oxygen atoms from two L^{3-} ligands. The Cd 2 atom exhibits seven-coordinated environment. Three of the seven coordination positions are filled with three oxygen atoms (O13, O14, O15) from three water molecules. The remaining sites are occupied by two hydroxyl oxygen atoms (O4, O10) and two carboxylate oxygen atoms (O6, O12) from two L^{3-} ligands. To the best

of our knowledge, the reports about seven coordinated Cd(II) ion are rare. The Cd–O bond lengths (2.243(5)–2.384(3) Å) are comparable to those in the other Cd(II) phosphonate compounds [17–19]. The L^{3-} anion acts as a penta-dentate ligand, and it connects three Cd(II) atoms through two phosphonate oxygen atoms, two carboxylate oxygen atoms and one hydroxyl oxygen atom. On the other hand, two phosphonate oxygen atoms (O1, O7) from two L^{3-} ligands are not coordinated to the Cd(II) cations.

This compound shows a 2D layered structure, non-coordinated phosphonate oxygen atoms of the organic ligands are orientated toward the interlayer space, with the charge-compensating Na^+ cations being located between two adjacent layers (Fig. 2). Within the layer, each L^{3-} anion behaves as bridge ligands, one carboxylate oxygen atom together with one hydroxyl oxygen atom chelating

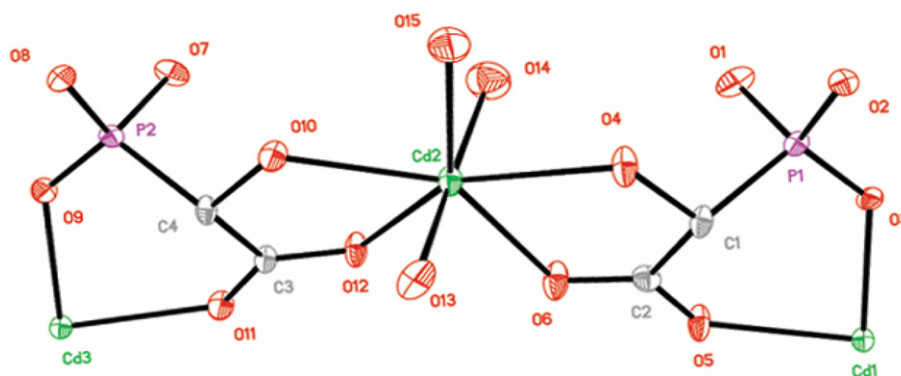


Fig. 1. Asymmetric unit of $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ (**1**) showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms, water molecules and Na^+ cations are omitted for clarity. Symmetry code for the generated atoms: (A) $x, -y + 1, z + 1/2$; (B) $-x + 1, -y + 1, -z$; (C) $-x + 1, y, -z + 1/2$; (D) $-x, -y + 1, -z$; (E) $-x, y, -z + 1/2$; (F) $x, y, z + 1$; (G) $x, y + 1, z + 1$; (H) $x, y + 1, z$; (I) $x, y, z - 1$; (J) $x, y - 1, z$; (K) $x, y - 1, z - 1$; (L) $x, -y + 1, z - 1/2$.

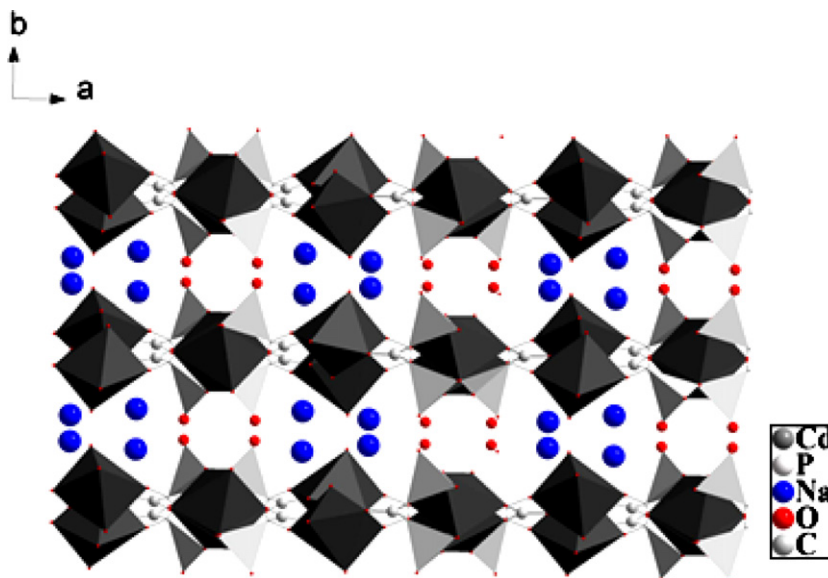


Fig. 2. The layered structure of compound **1** viewed in ab -plane. The light gray tetrahedra are O_3PC . The dark gray polyhedra are CdO_6 and CdO_7 . All H atoms are omitted for clarity.

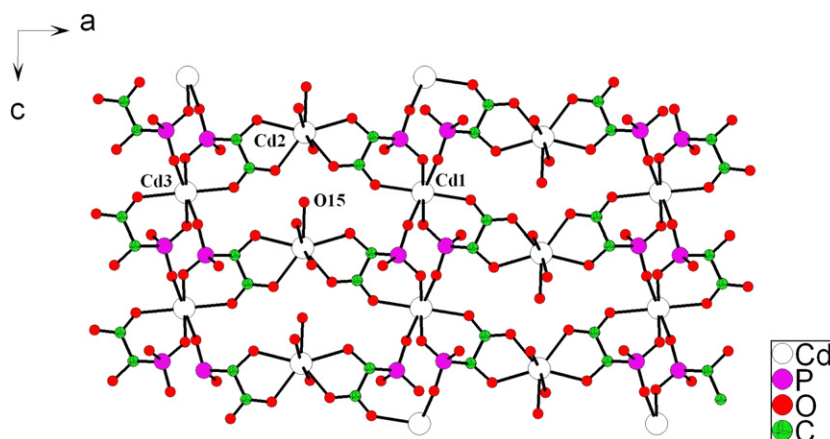


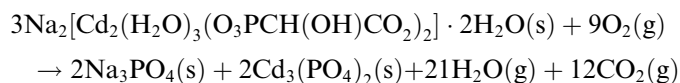
Fig. 3. Ball and stick representation of compound **1** viewed in *ac*-plane. All H atoms, water molecules and Na^+ cations are omitted for clarity.

one CdO_7 pentagonal bipyramid, one phosphonate oxygen atom and the other carboxylate oxygen atom chelating one CdO_6 octahedron (Fig. 3). As shown in Fig. 3, the connections of alternately arranged CdO_7 pentagonal bipyramid, CdO_6 octahedra and O_3PC tetrahedra result in a two-dimensional framework structure with a one-dimensional channel system along *b*-axis direction, and the layers are only held together by weak van der Waals interactions. The channel is assembled by 18-atom rings ($11.3 \text{ \AA} \times 4.3 \text{ \AA}$, estimated by measuring the distances between the centers of opposite atoms), which consist of four Cd(II), two P, four C and eight O atoms with the sequences Cd–O–C–O–Cd–O–C–O–Cd–O–P–C–O–Cd–O–C–P–O.

The IR spectrum [20] for compound **1** was recorded in the region $4000\text{--}400 \text{ cm}^{-1}$. A very strong absorption band around 3431 cm^{-1} corresponds to the O–H stretching vibrations of hydroxyl groups of the title compound, indicating that the hydroxyl oxygen atom is still protonated. This is in agreement with the result of the single-crystal X-ray diffraction study. A strong band at 1585 cm^{-1} is observed which is shifted at least 158 cm^{-1} from the expected value of uncoordinated carboxylic acid ($\nu(\text{C}=\text{O})$ typically around $1725\text{--}1700 \text{ cm}^{-1}$) [21]. This large shift is attributed to the carboxylate function coordinated to the metal. The medium absorption band around 1396 cm^{-1} is probably due to the stretching vibration of C–H. The set of bands between 1200 and 900 cm^{-1} are assigned to stretching vibrations of the tetrahedral O_3PC groups [22,23].

The thermogravimetric analysis [24] diagram of compound **1** indicates complicated overlapping steps of weight losses. The first step starts at $83 \text{ }^\circ\text{C}$ and completes at $272 \text{ }^\circ\text{C}$, corresponding to the release of two lattice water molecules. The observed weight loss of 5.52% is very close to the calculated value (5.40%). The weight loss (25.49%) in the temperature range $272\text{--}634 \text{ }^\circ\text{C}$ is attributed to the loss of the coordinated water and organic groups (the calculated value 25.58%). The DTA curve exhibits one weak endothermic peak and one strong endothermic peak at

approximately $382 \text{ }^\circ\text{C}$ and $596 \text{ }^\circ\text{C}$, respectively. The total weight loss (30.63%) is consistent with the theoretical value (30.89%) calculated for the following thermal decomposition reaction. The final product is assumed to be a mixture of $\text{Cd}_3(\text{PO}_4)_2$ and Na_3PO_4 in a molar ratio of 1:1.



In conclusion, a novel inorganic–organic hybrid material $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ (**1**) with a two-dimensional layered structure has been prepared under hydrothermal reaction conditions by the combination of Cd cation with 2-hydroxyphosphonoacetic acid. The structure of compound **1** comprises CdO_6 octahedra and CdO_7 pentagonal bipyramid connected by $[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]^{3-}$ to form a 2D layered structure with a one-dimensional channel system. The single-crystal X-ray structural analysis indicates that compound **1** crystallizes in achiral space groups.

Acknowledgements

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Appendix A. Supplementary data

CCDC 623379 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2006.11.005](https://doi.org/10.1016/j.inoche.2006.11.005).

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- [15] A mixture of 0.34 g (1.1 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.5 ml (2 mmol) 2-hydroxyphosphonoacetic acid (48.0 wt%), 0.17 g (4 mmol) NaF, 2.0 ml (35 mmol) acetic acid and 8 ml of deionized water was sealed in a Teflon-lined stainless steel autoclave, and then heated at 120 °C for 48 h. Colorless pillared crystals were obtained in ca. 33.61% yield based on Cd. Anal. Calcd. for $\text{C}_4\text{H}_{14}\text{Cd}_2\text{Na}_2\text{O}_{17}\text{P}_2$: C, 7.33; H, 2.09; P, 9.32; Cd, 33.58. Found: C, 7.20; H, 2.12; P, 9.29; Cd, 33.71%.
- [16] *Crystal structure analysis*: The data were collected at a temperature of 293 ± 2 K on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program with $T_{\text{max}} = 0.8822$ and $T_{\text{min}} = 0.6989$. The structure was solved in the space group P2/c by direct method and refined by the full-matrix least-squares fitting on F^2 using SHELXTL-97 [25]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms of organic ligands were generated geometrically, fixed isotropic thermal parameters, and included in the structure factor calculations. *Crystal data for 1*: $\text{C}_4\text{H}_{14}\text{Cd}_2\text{Na}_2\text{O}_{17}\text{P}_2$, $M = 666.87$, monoclinic, P2/c, $a = 22.660$ (2) Å, $b = 7.4822$ (6) Å, $c = 11.0247$ (10) Å, $\beta = 90.8990$ (10)°, $V = 1869.0$ (3) Å³, $Z = 4$, $D_c = 2.370$ g cm⁻³, $\mu = 2.572$ mm⁻¹. Data were collected on a single crystal with dimensions $0.15 \times 0.05 \times 0.05$ mm³. 10656 reflections were measured with ω -scans, in the range of $2.70^\circ \leq \theta \leq 26.50^\circ$ ($-28 \leq h \leq 23$, $-8 \leq k \leq 9$, $-13 \leq l \leq 13$), 3866 independent reflections ($R_{\text{int}} = 0.0570$). Final $R_1 = 0.0464$, $wR_2 = 0.1084$ [$I > 2\sigma(I)$], and the goodness-of-fit on F^2 is 1.029.
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