

Hydrothermal synthesis, crystal structures and characterizations of a novel 3D metal phosphonate: $\text{Mg}_{0.5}\text{Cd}[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]$

Zhen-Gang Sun ^{a,*}, Lian-Yi Cui ^a, Zhong-Min Liu ^b, Lei Meng ^a, Hui Chen ^a,
Da-Peng Dong ^a, Lan-Cui Zhang ^a, Zai-Ming Zhu ^a, Wan-Sheng You ^a

^a Institute of Chemistry for Functionalized Materials, Faculty of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, Liaoning 116029, PR China

^b Laboratory of Natural Gas Chemistry & Applied Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, PR China

Received 4 May 2006; accepted 18 June 2006
Available online 27 June 2006

Abstract

A novel cadmium and magnesium phosphonate compound $\text{Mg}_{0.5}\text{Cd}[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]$ (**1**) has been synthesized by hydrothermal reaction at 110 °C and characterized by single-crystal X-ray diffraction as well as with infrared spectroscopy, elemental analysis and thermogravimetric analysis. The structure of **1** 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 with one-dimensional channel system in the *a*-axis direction.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Metal phosphonates; Crystal structure; Hydrothermal synthesis; Cadmium; Magnesium

Metal phosphonates have received a great deal of attention in recent years due to the possibility to form interesting structures with potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry [1–4]. Great efforts have been devoted to the synthesis of novel inorganic–organic hybrid materials based on metal phosphonates, which exhibit a variety of structures such as one-dimensional (1D) chain, two-dimensional (2D) layer, and three-dimensional (3D) network [5–7]. The use of bi- and trifunctional phosphonic acids in the synthesis of metal phosphonates can result in the formation of porous materials. During the past few years, several strategies have been adopted for functionalizing phosphonates, including adding a second unique functional group such as an amine, hydroxyl or carboxylic acid [8–15].

In the point of view of structural construction of inorganic–organic hybrid compounds, phosphonic acids with hydroxyl and carboxyl groups are useful ligands, because they could together provide various kinds of coordination modes under different reaction conditions which may result in various interesting structures. Therefore, we are interested in the use of 2-hydroxyphosphonoacetic acid (H_3L) with a chiral carbon atom and three functional groups ($-\text{OH}$, $-\text{COOH}$, and $-\text{PO}_3\text{H}_2$) in the synthesis of new metal phosphonates, with the goal of obtaining 3D channel structures. In this paper, we report the synthesis [16] of a novel 3D open-framework coordination compound, $\text{Mg}_{0.5}\text{Cd}[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]$ (**1**) by hydrothermal technique, using 2-hydroxyphosphonoacetic acid as ligand. The compound structure was characterized by single-crystal X-ray diffraction [17], infrared spectroscopy, elemental analysis and thermogravimetric analysis.

A single-crystal X-ray structure analysis of **1** revealed that compound $\text{Mg}_{0.5}\text{Cd}[\text{O}_3\text{PCH}(\text{OH})\text{CO}_2]$ crystallizes in monoclinic space group $\text{P}2(1)/n$. The asymmetric unit is shown in the Fig. 1.

* Corresponding author. Tel.: +86 411 82156568; fax: +86 411 82156858.

E-mail address: szg188@163.com (Z.-G. Sun).

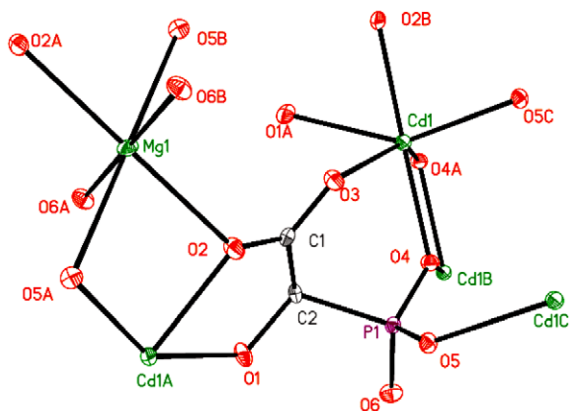


Fig. 1. ORTEP view of the coordination geometries of cadmium, magnesium and phosphorus of **1**, showing the asymmetric unit (ellipsoids at 50% probability). All H atoms were omitted for clarity. Symmetry code for the generated atoms: (A) $-x + 1, -y, -z + 1$; (B) $2x - 1/2, -y + 1/2, z - 1/2$; and (C) $-x, -y, -z + 1$.

It consists of one Cd atom, one L^{3-} ligand and one Mg atom of which occupancy is 0.5. The Cd(II) atom has a distorted octahedral environment. Three of the six coordination sites are filled with three phosphonate oxygen atoms (O4, O4A, O5C) from three separate L^{3-} ligands. The remaining sites are occupied by the hydroxyl oxygen atom (O1A) and the two carboxylate oxygen atoms (O3, O2B). The Cd—O distance ranges from 2.252(3) to 2.362(3) Å, in agreement with those reported for other Cd(II) phosphonates $Cd(O_3PC_2H_4NH_2)$ [18], $Cd_2(O_3PCH_2C_6H_4CH_2PO_3) \cdot 2H_2O$ [19] and $Cd_2(OH)(O_3PC_2H_4CO_2)$ [20]. It is noted that the Cd—O (hydroxyl oxygen) distance (2.362 Å) is much longer than the other Cd—O distances in compound **1** (2.252(3)–2.307(3) Å), attributed to the presence of the hydroxyl proton. A long Cd—O (hydroxyl oxygen) distance is also observed in $Cd(O_3PC_2H_4NH_2)$ (2.516 Å), $Cd_2(O_3PCH_2C_6H_4CH_2PO_3) \cdot 2H_2O$ (2.493 Å), and $Cd_2(OH)(O_3PC_2H_4CO_2)$ (2.369 Å).

It is interesting that the Mg(II) in compound **1** is also in an octahedral environment, being coordinated by six oxygen atoms from the three separate L^{3-} ligands, two of the six oxygen atoms are carboxylate oxygen atoms from two different L^{3-} ligands and the remaining four atoms are phosphonate oxygen atoms from two L^{3-} ligands, the Mg—O distance varies from 2.229(3) to 2.491(3) Å. To the best of our knowledge, the reports about Mg atom involved in coordination are rare. The L^{3-} anion acts as a ennead-dentate ligand, O1, O3 and O6 atom act as monodentate, O1 and O3 are coordinated by one Cd(II) atom, respectively, O6 is coordinated by one Mg(II) atom, O2, O5 and O4 act as bidentate with two metal atoms, O2 and O5 are coordinated by one Cd(II) and Mg(II) atom, respectively, and O4 links with two Cd(II) atoms. Therefore, all the oxygen atoms of the 2-hydroxyphosphonoacetic acid ligand are involved in metal coordination.

The overall structure can be described as a 3D open-framework type with channels running along the *a*-axis. The 3D framework is based on two crystallographically

distinct Cd centered octahedra CdO_6 and Mg centered octahedra MgO_6 (Fig. 2). Two CdO_6 octahedra share the O4—O4 edge to form a subunit. These subunits and the MgO_6 octahedra are connected each other by edge-sharing (O2—O5) to form zigzag chains along *c*-axis, these chains are linked *via* carboxylate oxygens (O2 and O3) and hydroxyl oxygen atom (O1) to form layers in *bc*-plane. The layers are then connected *via* O4, O5 and O6 from the O_3PC tetrahedra to form 3D open-framework structure (Fig. 3).

The IR spectrum [21] for compound **1** was recorded in the region from 4000 to 400 cm^{-1} . A very strong absorption band around 3448 cm^{-1} corresponds to the O—H stretching vibrations of hydroxyl groups of the title compound, indicating 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 1610 cm^{-1} is observed which is shifted at least 90 cm^{-1} from the expected value of uncoordinated carboxylic acid ($\nu(C=O)$ typically around 1725–1700 cm^{-1}) [22]. This large shift is due to the carboxylate function coordinated to the metal. The medium absorption band around 1399 cm^{-1} is

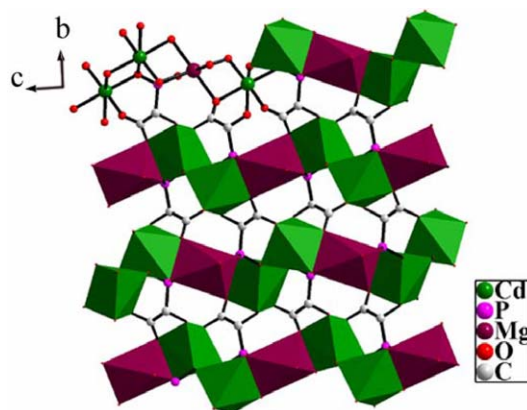


Fig. 2. A ball-and-stick and polyhedral representation of the framework structure of **1** in the *bc*-plane.

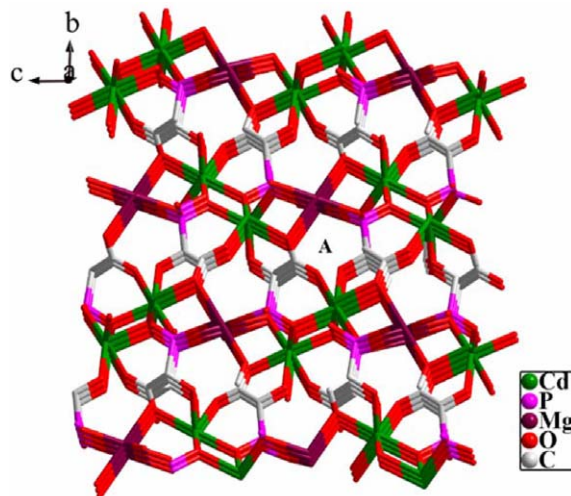
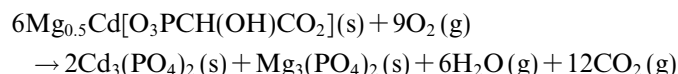


Fig. 3. View of the 3D framework structure of **1** along the *a*-axis.

probably due to the stretching vibration of C–H. The set of bands between 1200 and 900 cm^{-1} (1129, 1054 and 922 cm^{-1}) are due to stretching vibrations of the tetrahedral O_3PC groups [23,24]. Additional weak bands at low energy (576, 531, and 460 cm^{-1}) are found. These bands are probably due to bending vibrations of the tetrahedral O_3PC groups and M–O (M = Cd and Mg) stretching vibrations.

Thermogravimetric analysis [25] of compound **1** in the 50–800 °C temperature range in static air atmosphere revealed that it is thermally stable up to 316 °C. Above this temperature, it gradually loses weight until 618 °C. The total weight loss (21.1 wt%) is consistent with theoretical value (21.0%) calculated for the following thermal decomposition reaction. The final product is assumed to be mixture of $\text{Cd}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$ in a molar ratio of 2:1



In conclusion, a novel inorganic–organic hybrid material with a three-dimensional framework has been prepared under hydrothermal reaction conditions by the combination of Cd and Mg cation with 2-hydroxyphosphonoacetic acid. The structure of **1** 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 with one-dimensional channel system in the *a*-axis direction. The single-crystal X-ray structural analysis indicates that compound **1** crystallizes in achiral space groups.

Acknowledgments

This research was supported by grants from the Natural Science Foundation of Liaoning Province of China (20032104) and the Education Department of Liaoning Province of China (05L214).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.06.015.

References

- [1] S.Y. Song, J.F. Ma, J. Yang, M.H. Cao, K.C. Li, *Inorg. Chem.* 44 (2005) 2140.
- [2] B. Bujoli, S.M. Lane, G. Nonglaton, M. Pipelier, J. Léger, D.R. Talham, C. Tellier, *Chem. Eur. J.* 11 (2005) 1980.
- [3] K. Maeda, *Micropor. Mesopor. Mater.* 73 (2004) 47.
- [4] A.K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem., Int. Ed.* 38 (1999) 3268.
- [5] Y. Fan, G.H. Li, Z. Shi, D. Zhang, J.N. Xu, T.Y. Song, S.H. Feng, *J. Solid State Chem.* 177 (2004) 4346.
- [6] S. Bauer, H. Muller, T. Bein, N. Stock, *Inorg. Chem.* 44 (2005) 9464.
- [7] S.S. Bao, T.W. Wang, Y.Z. Li, L.M. Zheng, *J. Solid State Chem.* 179 (2006) 413.
- [8] A. Clearfield, *Prog. Inorg. Chem.* 47 (1998) 371–510, and references therein.
- [9] J.G. Mao, Z.K. Wang, A. Clearfield, *Inorg. Chem.* 41 (2002) 6106.
- [10] J.G. Mao, A. Clearfield, *Inorg. Chem.* 41 (2002) 2319.
- [11] F. Serpaggi, G. Férey, *Inorg. Chem.* 38 (1999) 4741.
- [12] C. Serre, N. Stock, T. Bein, G. Férey, *Inorg. Chem.* 43 (2004) 3159.
- [13] S.J. Hartman, E. Todorov, C. Cruz, S.C. Sevon, *Chem. Commun.* (2000) 1213.
- [14] R.B. Fu, H.S. Zhang, L.S. Wang, S.M. Hu, Y.M. Li, X.H. Huang, X.T. Wu, *Eur. J. Inorg. Chem.* (2005) 3211.
- [15] X. Shi, G.S. Zhu, S.L. Qiu, K.L. Huang, J.H. Yu, R.R. Xu, *Angew. Chem., Int. Ed.* 43 (2004) 6482.
- [16] A mixture of 0.34 g (1.1 mmol) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.10 g (0.5 mmol) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 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 110 °C for 48 h. Colorless prism-shaped crystals were obtained in ca. 40.3% yield based on Cd. Anal. Calcd for $\text{C}_2\text{H}_2\text{CdMg}_{0.5}\text{O}_6\text{P}$: C, 8.65; H, 0.72; Mg, 4.38; P, 11.26; Cd, 40.50. Found: C, 8.73; H, 0.67; Mg, 4.29; P, 11.35; Cd, 40.38%.
- [17] *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 $T_{\text{max}} = 0.8526$ and $T_{\text{min}} = 0.6835$. The structure was solved in the space group $P2(1)/n$ by direct method and refined by the full-matrix least-squares fitting on F^2 using SHELXTL-97 [26]. 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. The final Fourier map had a minimum and maximum electron density of -0.547 and $0.796 \text{ e} \text{ \AA}^{-3}$. *Crystal data for 1*: $\text{C}_2\text{H}_2\text{CdMg}_{0.5}\text{O}_6\text{P}$, $M = 277.56$, monoclinic, $P2(1)/n$, $a = 5.1877(5)$ Å, $b = 12.4176(11)$ Å, $c = 9.1107(8)$ Å, $\beta = 102.886(2)^\circ$, $V = 572.12(9)$ Å³, $Z = 4$, $D_c = 3.222 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 4.119 \text{ mm}^{-1}$. Data were collected on a single crystal with dimensions $0.10 \times 0.08 \times 0.04 \text{ mm}^3$. 3272 reflections were measured with ω -scans, in the range of $2.82^\circ \leq \theta \leq 26.50^\circ$ ($-6 \leq h \leq 5$, $-15 \leq k \leq 15$, $-11 \leq l \leq 11$), 1191 independent reflections ($R_{\text{int}} = 0.0261$). Final $R_1 = 0.0269$ [$I > 2\sigma(I)$], $wR_2 = 0.0623$, and the goodness-of-fit on F^2 is 1.068. CCDC reference no. is 602596. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).
- [18] F. Frdoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield, B. Bujoli, *Inorg. Chem.* 38 (1999) 1831.
- [19] N. Stock, T. Bein, *J. Solid State Chem.* 167 (2002) 330.
- [20] F. Frdoueil, M. Evain, D. Massiot, M. Bujoli-Doeuff, P. Janvier, A. Clearfield, B. Bujoli, *J. Chem. Soc., Dalton Trans.* (2002) 1508.
- [21] The infrared spectrum was recorded from a KBr pellet by use of a Bruker AXS TENSOR-27 FT-IR spectrometer in the range 4000–400 cm^{-1} .
- [22] N. Stock, T. Bein, *J. Mater. Chem.* 15 (2005) 1384.
- [23] Z.M. Sun, J.G. Mao, B.P. Yang, S.M. Ying, *Solid State Sci.* 6 (2004) 295.
- [24] A. Cabeza, X.Q. Yang, C.V.K. Sharma, M.A.G. Aranda, S. Bruque, A. Clearfield, *Inorg. Chem.* 41 (2002) 2325.
- [25] TG and DTA analysis was performed on a Perkin–Elmer Pyris Diamond TG-DTA thermal analyses system in static air with a heating rate of 10 K min^{-1} from 50 to 800 °C.
- [26] G.M. Sheldrick, SHELXS 97, Program for X-ray Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.