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Article

[Cd$_3$(H$_2$O)$_3$((O$_3$PCH$_2$)$_2$NH−CH$_2$C$_6$H$_4$−COOH)$_2$]·11H$_2$O: A Layered Cadmium Phosphonate with Reversible Dehydration/Hydration Properties

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In a recent systematic study on the influence of the reaction temperature on the structure formation in the system CdCl$_2$/H(HO$_3$PCH$_2$)$_2$NH−CH$_2$C$_6$H$_4$−COOH (H$_5$L) /NaOH, [Cd$_3$(H$_2$O)$_3$((O$_3$PCH$_2$)$_2$NH−CH$_2$C$_6$H$_4$−COOH)$_2$]·11H$_2$O was obtained as a microcrystalline compound. We have now been able to elucidate the structure from single-crystal data: triclinic, $P\bar{1}$; a = 5.4503(9), b = 12.880(2), and c = 16.417(3) Å; α = 67.841(6)°, β = 80.633(6)°, γ = 87.688(8)°, V = 1052.9(3) Å^3; Z = 1; R_1 = 0.1143, R_2 = 0.2108 (all data); 0.0705, 0.1823 ((I > 2$\sigma(I)$)). The structure of [Cd$_3$(H$_2$O)$_3$((O$_3$PCH$_2$)$_2$NH−CH$_2$C$_6$H$_4$−COOH)$_2$]·11H$_2$O is built up of cadmium phosphonate layers connected by water-mediated hydrogen bonds between aryl-carboxylic acid groups and water molecules coordinated to Cd^{2+} ions of adjacent layers (C−OH···H$_2$O···H$_2$O−Cd^{2+}). The title compound was characterized by IR spectroscopy and energy dispersive X-ray, elemental, and thermogravimetric analyses. Furthermore, temperature-dependent X-ray diffraction data are presented. [Cd$_3$(H$_2$O)$_3$((O$_3$PCH$_2$)$_2$NH−CH$_2$C$_6$H$_4$−COOH)$_2$]·11H$_2$O can be reversibly dehydrated, and mechanical stress and grinding in the presence of water leads to the intercalation of additional water molecules.

Introduction

The study of inorganic−organic hybrid compounds is an ongoing field of research, due to their ability to form interesting structures with potential applications such as sorbents, ion exchangers, catalysts, or charge-storage materials.[1−3] In this important class of materials, metal phosphonates were among the first to be investigated. On the basis of the work of Clearfield and Stynes on crystalline zirconium phosphates,[4] in 1978, Alberti and co-workers published a work on crystalline layered zirconium phosphonates,[5] which to date has stimulated numerous scientists to explore the chemistry of metal phosphonates in all its facets.[6,7] Thus, many phosphonic acid derivatives with and without additional functional groups, restrained only by the

limits of synthetic organic chemistry, have been employed for the synthesis of metal phosphonates.[3]

We have focused our attention on the reaction of di- and trivalent metal ions with functionalized polyphosphonic acids under hydrothermal conditions. Recently, we have started an investigation on the application of functionalized iminobis-(methylphosphonic acid) derivatives, (H$_2$O$_3$PCH$_2$)$_2$N−R, for the synthesis of metal phosphonates.[8−10] Special attention has been given to the chemistry of the ligand H(HO$_3$PCH$_2$)$_2$-NH−CH$_2$C$_6$H$_4$−COOH (later denoted H$_5$L). Employing our high-throughput (HT) methodology,[11] we have systematically investigated the influence of the counterion in different cobalt salts[12] and the pH level[13] as well as the reaction temperature[14]

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on the resulting structures. Thus, the counterions of the cobalt salts have an effect on the initial pH and, additionally, can take part in redox reactions, resulting in an in situ oxidation of the phosphonic acid. Second, an increasing amount of NaOH in the synthesis mixture leads to a gradual deprotonation of the ligand and therefore to an increasing molar ratio of metal/ligand in the reaction products. And finally, an increase in the reaction temperature leads to an increasing degree of condensation within the metal phosphonate layers.

Looking at the numerous compounds obtained with various metal cations (Co^{2+}, Ca^{2+}, Cd^{2+}, and Sm^{3+}), it becomes now clear that the rigid aryl-carboxylic acid group in $H(HO_3PCH_2)_2NH-CH_2C_6H_4-COOH$ has a determining impact on the structure formation. Thus, we observe metal phosphonate or metal hydrogenphosphonate layers with a varying degree of condensation, which are connected in a zipperlike fashion via hydrogen bonds between the aryl-carboxylic acid group and adjacent layers.[15]

In the course of the HT study on the influence of the reaction temperature on the formation of inorganic−organic hybrid compounds based on $H(HO_3PCH_2)_2NH-CH_2C_6H_4-COOH$, we obtained $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$ as a microcrystalline compound.[14] Now, we have been able to elucidate its structure from single-crystal X-ray diffraction (XRD). In this paper, we report on the structure, the detailed characterization, and the reversible water dehydration/hydration properties of this interesting compound.

Experimental Section

Materials and Methods. $CdCl_2\cdot H_2O$ (Merck, 98%) and NaOH (Merk, ≥99%) were used as obtained. The carboxyaryl-iminobis-(methylphosphonic acid), $H(HO_3PCH_2)_2NH-CH_2C_6H_4-COOH$, was synthesized by a Mannich-type reaction starting from 4-(aminomethyl)benzoic acid, phosphoric acid, and formaldehyde.[12,16] X-ray powder diffraction patterns were recorded with a STOE STADI P diffractometer using monochromated Cu $K\alpha_1$ radiation. IR spectra were recorded on an ATI Matheson Genesis instrument in the spectral range of 4000−400 cm^{-1} using the KBr disk method. Thermogravimetric (TG) analysis was carried out under oxygen on a TA instrument type 2050 analyzer apparatus with a heating rate of 1 °C/min. Carbon, hydrogen, and nitrogen contents were determined by elemental chemical analysis on an Eurovektor EuroEA elemental analyzer. Energy dispersive X-ray (EDX) analysis was performed on a Philips ESEM XL 30 instrument. X-ray thermodiffractometry was performed under air in the furnace of a Siemens D5000 diffractometer (Co K radiation, $\theta-\theta$ mode) from 20° to 500 °C with a 10 °C step from 20 to 400 °C.

Synthesis. Single crystals of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$ were obtained from a solution of 11.0 mg (0.0324 mmol) H_5L, 10 mL of H_2O, 81 μL (0.0324 mmol) of 0.4 M NaOH, and 108 μL (0.0324 mmol) of 0.3 M $CdCl_2\cdot H_2O$ at room temperature. The mixture was prepared in a 20 mL glass vial. From the clear solution, needles of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$ started to crystallize overnight. The pH before and after the crystallization was 6.

The bulk material of the title compound was obtained from a solution of 550 mg (1.62 mmol) H_5L, 490 mL of H_2O, 4.05 mL

Table 1. Crystallographic Data for $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$

formula	$Cd_3P_4O_{30}N_2C_{20}H_{52}$
space group	$P\bar{1}$
cryst syst	triclinic
a [Å]	5.4503(9)
b [Å]	12.880(2)
c [Å]	16.417(3)
α [deg]	67.841(6)
β [deg]	80.633(6)
γ [deg]	87.688(8)
V [Å^3]	1052.9(3)
Z	1
fw	1231.48
T [K]	250(2)
wavelength	0.71073
ρ [g/cm^3]	1.942
$F(000)$	600
cryst size [mm^3]	$0.12 \times 0.04 \times 0.02$
μ [mm^{-1}]	1.751
abs correction	semiempirical from equivalents
T_{min}/T_{max}	0.8174/0.9658
2θ range [deg]	1.36−24.93
range in hkl	$-6 \leq h \leq 6$, $-14 \leq k \leq 15$, $-19 \leq l \leq 19$
total data collected	10 209
unique/obs data [$I > 2\sigma(I)$]	3568/2437
R(int)	0.0812
R_1, R_2 [$I > 2\sigma(I)$]	0.0705, 0.1823
R_1, R_2 [all data]	0.1143, 0.2108
GOF	1.202
no. of parameters	287
$\Delta e_{min}/\Delta e_{max}$ [e·Å^{-3}]	1.934/2.01

(1.62 mmol) of 0.4 M NaOH, and 5.4 mL (1.62 mmol) of 0.3 M $CdCl_2\cdot H_2O$ at room temperature. Overnight, a colorless solid precipitates. The pH before and after the reaction was 5. After 2 days, the solid was filtered off and dried at ambient conditions (EDX: Cd/P = 3:4. Elemental anal. Calcd: C, 19.04; H, 4.15; N, 2.22. Found: C, 19.24; H, 3.95; N, 2.13).

X-ray Structure Analysis. A crystal of $[Cd_3(H_2O)_3((O_3PCH_2)_2-NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$ ($0.12 \times 0.04 \times 0.02$ mm^3) was mounted with Paratone-N oil (Hampton Research) on a nylon cryoloop and immediately placed under a cold nitrogen stream. X-ray intensity data were collected at 250 K on a Bruker-Nonius X8-APEX2 diffractometer with a CCD area-detector using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Two sets of narrow data frames (180 s per frame) were collected at different θ values for initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω. Data reduction was accomplished using *SAINT*, version 7.03.[17] The substantial redundancy in data (2.34) allowed a semiempirical absorption correction (*SADABS*, version 2.10)[17] to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least squares on all F^2 data using *SHELXTL*, version 6.14.[18] Four oxygen atoms corresponding to free water molecules (O3W, O4W, O5W, and O6W) have been refined with an occupancy of 0.5 leading to a total water content of 14 molecules per formula unit. This is in accordance with the results from TG and elemental chemical analysis. Hydrogen atoms connected to C atoms were included in calculated positions and allowed to ride on their parent atoms. Details on the structure determination are given in Table 1, and selected bond distances and angles are shown in Table 2.

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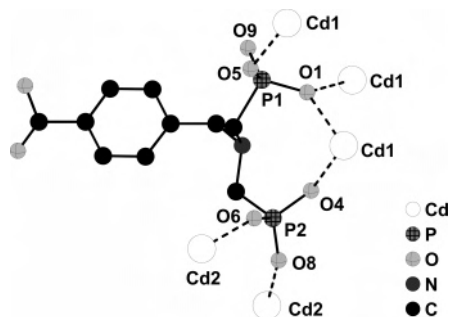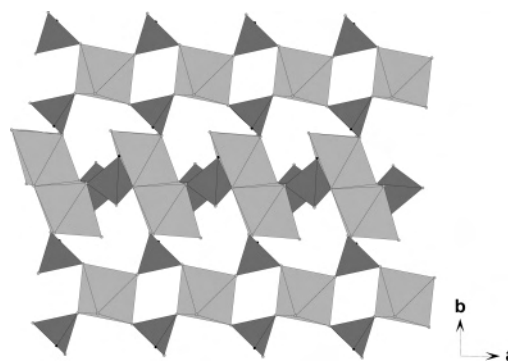(18) *SHELXTL*, version 6.14l; Bruker AXS: Madison, WI, 2001.

Table 2. Selected Bond Distances and Angles for
$[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$

Bond Distances/Å			
Cd−O	2.213(9)−2.425(11)	P−O	1.487(11)−1.520(9)
P−C	1.810(13), 1.817(14)	C−N	1.504(19)−1.549(17)
C−C$_{aryl}$	1.39(2)−1.38(2)	C−C$_{aliph}$	1.499(19)−1.52(2)
C−O	1.18(2), 1.33(2)		

Bond Angles/deg			
O−P−O	111.6(5)−114.4(5)	O−P−C	103.4(5)−107.9(6)
C−C−C	117.8(15)−122.5(14)	C−N−C	111.0(11)−112.4(10)
O−C−O	124.3(16)		

Results and Discussion

Structure Description. Since three water molecules coordinate to the Cd^{2+} ions, whereas the other water molecules are only involved in H bonds, the chemical formula is expressed as $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$. The asymmetric unit of $[Cd_3(H_2O)_3((O_3-PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$ is shown in Figure S1 in the Supporting Information. It consists of one Cd^{2+} ion on a general position (Cd1), one Cd^{2+} ion on a special position (Cd2), one $[(O_3PCH_2)_2NH-CH_2C_6H_4-COOH)]^{3-}$ zwitterion, and nine water molecules, of which four have an occupancy of 0.5. The coordination behavior of the organic molecule is given in Figure 1. All oxygen atoms of the phosphonate groups except oxygen atom O9 are involved in the coordination of the Cd^{2+} ions. An analysis of the P1−O distances and the N···O interactions shows that the N atom is protonated (Figure S2, Supporting Infomation). This is in agreement with other structures based on H_5L.[15] Whereas oxygen atoms O4, O5, O6, and O8 coordinate to only one Cd^{2+} ion, oxygen atom O2 bridges two Cd^{2+} ions (μ_2-oxygen). The Cd1 atoms form Cd_2O_{10} dimers of edge-sharing $Cd1O_6$ octahedra and Cd2-isolated CdO_6 octahedra (Figure S3). These are connected by phosphonate groups to form a Cd−phosphonate layer in the a,b plane (Figure 2). The aryl-carboxylic acid groups are oriented in a zipperlike fashion perpendicular to these layers. Interestingly, the Cd−phosphonate layers are held together by water-mediated hydrogen bonds between the carboxylic acid groups and water molecules coordinating to Cd^{2+} ions (C−OH···H_2O···H_2O−Cd^{2+}, Figure 3). Thus, channels along the a axis are formed that contain 11 hydrogen-bonded water molecules per formula unit.

Thermal Study. The thermal properties of the title compound were studied by TG measurements (Figure 4) as well as temperature-dependent powder XRD (Figure 5). In

Figure 2. In $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$, Cd_2O_{10} and isolated CdO_6 polyhedra (light gray) are connected by phosphonate groups (medium gray) to form a Cd−phosphonate layer in the a,b plane.
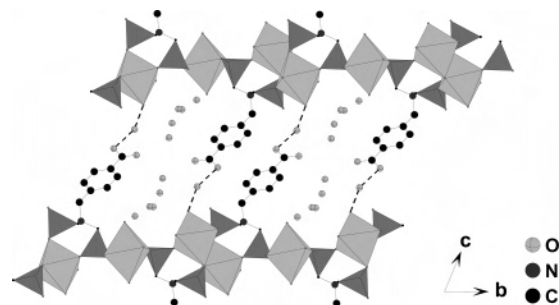
Figure 3. In $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$, the Cd−phosphonate layers are held together by water-mediated hydrogen bonding between the carboxylic acid groups and water molecules coordinating to Cd^{2+} ions (C−OH···H_2O···H_2O−Cd^{2+}). Thus, channels containing water molecules are formed. (CdO_6 octahedra are presented in light gray, and PO_3C tetrahedra are presented in medium gray.)
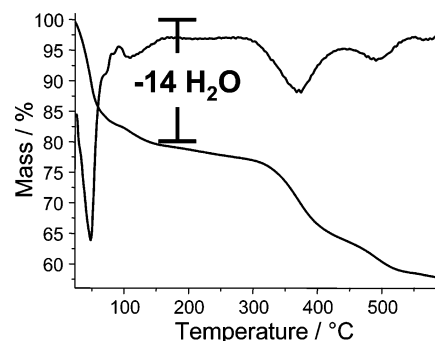
Figure 4. TG diagram with derivative of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$.
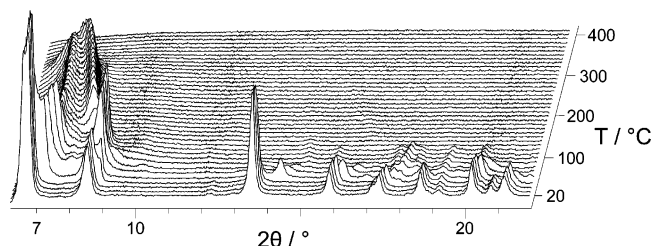
Figure 5. Results of the temperature-dependent powder XRD study of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$ (Co K radiation).

the TG diagram of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$, the water molecules are released in two steps. Thus, up to 90 °C, a weight loss of 17.3% is observed corresponding to the release of 12 water molecules (calcd, 17.1%). The remaining two water molecules are released up
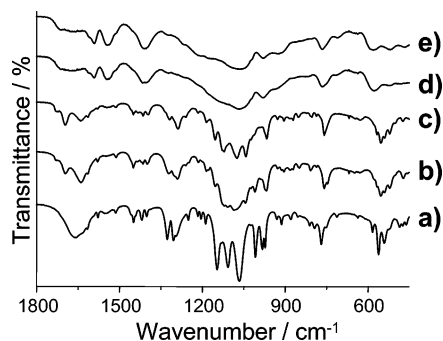

Figure 1. Coordination behavior of the organic molecule as observed in $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$.

Figure 6. IR spectra of as-synthesized $[Cd_3[(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$ (a), heated overnight to 60 °C (b), 100 °C (c), 150 °C (d), and 250 °C. (e). IR spectra showing the full range are given in Figure S4 in the Supporting Information.

Figure 7. XRD pattern obtained in the dehydration/hydration study of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$. The *d* values are given in Å and correspond to the position of the 001 reflection, reflecting the interlayer distance. Furthermore, the theoretical and observed powder patterns of $Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$ are given.

to 140 °C (20.1% total weight loss; calcd, 20.0% for 14 water molecules per formula unit). Upon further heating, a continuous weight loss up to 310 °C occurs, which might be due to further condensation of the Cd phosphonate layers leading to the release of water molecules. Starting from 310 °C, a steep weight loss shows the collapse of the structure and the pyrolysis of the organic molecules. These findings are in good agreement with temperature-dependent powder XRD measurements. Thus, three phases are observed. From room temperature to 60 °C, almost no change occurs and the powder patterns are in agreement with the theoretical pattern of the title compound. At 60 °C, a drastic change occurs and the first reflection (001 reflection) is moved to a higher 2θ value, indicating a smaller interlayer distance. Up to 120 °C, a slight continuous shift of the first reflection to higher degree 2θ value is observed. In the range from 120 to 310 °C a new continuous evolution, with the position of the first reflection almost unchanged, takes place. However, the shift of the second reflection to a lower degree 2θ value indicates a change within the layers. The XRD patterns obtained from the in situ thermodiffraction experiment differ at higher temperatures from the patterns of the ex situ study. The difference could be due to rehydration and relaxation processes occurring while the sample is cooled.

IR Spectrocopic Study. The as-synthesized title compound as well as the dehydrated samples at different temperatures (a sample was heated overnight to 60, 100, 150, and 250 °C) have been studied by IR spectroscopy (Figure 6). The broad band from 3000 to 3560 cm^{-1} in the IR spectrum of the as-synthesized compound clearly shows the presence of water molecules. The position and width suggests that it is loosely bonded and that interactions through hydrogen bonds are present. Additionally, a band at 3530 cm^{-1} can be attributed to O−H stretching vibrations of water molecules coordinated to Cd^{2+} ions. Sharp bands of low intensity at 3039 and 2859 cm^{-1} are due to aromatic and aliphatic C−H stretching vibrations, respectively. The broad bands of low intensity in the region from 2700 to 2400 cm^{-1} could be assigned to N−H and CO−H stretching vibrations involved in hydrogen bonds.[19] The C=O stretching vibration due the carboxylic acid group is located at 1656 cm^{-1}, which
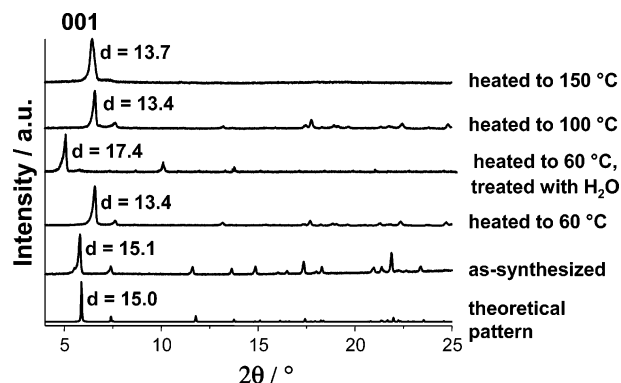
is typical for carboxylic acid groups involved in hydrogen bonds, as present in the crystal structure of the title compound. The broadness of the band is due to the interaction with water molecules in H bonds as well as the presence of the bending vibration of the water molecules. The band at 1450 cm^{-1} could be assigned to the C−C skeletal ring vibration mode. The set of bands between 1200 and 970 cm^{-1} are due to the stretching vibrations of the tetrahedral CPO$_3$ group.

Upon heating a sample of $Cd_3[(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot 11H_2O$ overnight to 60 or 100 °C, the broad band at 1656 cm^{-1} resolves into two sharper bands at 1695 and 1640 cm^{-1}, corresponding to the C=O stretching and the H$_2$O bending vibrations, respectively. On going to higher temperatures (150 and 250 °C), these bands disappear, and new bands between 1600 and 1400 cm^{-1} indicate the presence of carboxylate groups coordinating to Cd^{2+} ions accompanied by a H$^+$ transfer.[20] This could be explained by a condensation reaction between the carboxylic acid groups and the Cd−phosphonate layer, accompanied by the release of coordinatively bond water molecules. This hypothesis is further supported by thermodiffraction experiments, which show that up to 310 °C a layered compound is present. Furthermore, TG analysis shows that the last two water molecules are released above 100 °C.

Dehydration/Hydration Study. In order to study the dehydration/hydration properties of the title compound, a sample was heated to different temperatures (60, 100, 150, and 250 °C) overnight and then treated with water. The following results were obtained. The dehydration steps at 60 and 100 °C lead to compounds with an interlayer distance of 13.4 Å (based on the 2θ value of the 001 reflection). Upon stirring in water (i.e., 20 mg in 3 mL), no rehydration is observed, but levigating a sample with water in a mortar leads to an uptake of water. Surprisingly, the corresponding X-ray powder pattern collected on a wet sample shows that the interlayer distance is expanded by 2.3 Å to $d = 17.4$ Å in comparison with the as-synthesized material (interlayer

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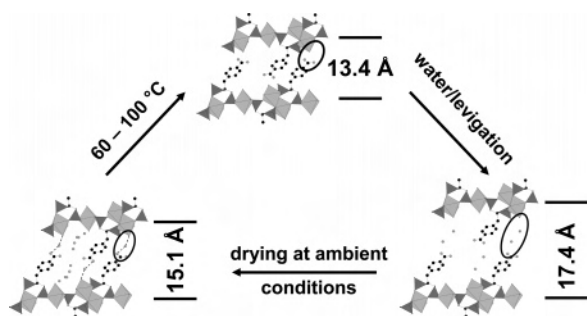(20) Milev, A. S.; Kannangara, G. S. K.; Wilson, M. A. *Langmuir* **2004**, *20*, 1888.

Figure 8. Schematic presentation of the results of the dehydration/ hydration studies on the compound $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$. The encircled areas are shown in more detail in Figure 9.
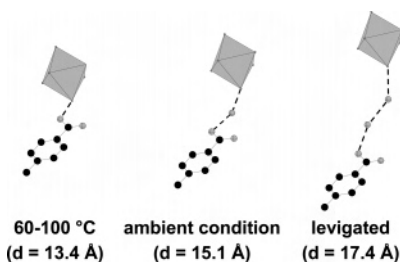

Figure 9. Proposed H-bond interaction of the carboxylic acid group in the title compound heated to $60-100\ °C$ (left) and in the levigated compound (right). According to single-crystal structure analysis, in the compound dried at ambient conditions, water-mediated hydrogen bonding between the carboxylic acid groups and water molecules coordinated to Cd^{2+} ion is observed (center).

distance $d = 15.1$ Å; Figure 7 and Figure 8). The value of 2.3 Å is in the range of an $O\cdots O$ distance in strong hydrogen bonds and consistent with studies on soil minerals where for the intercalation of a water monolayer in the interlayer space, an expansion of about 2.7 Å is observed.[21] Looking at the crystal structure of the title compound, one can imagine that an enlargement of the interlayer distance is achieved by the incorporation of another water molecule in the $C-OH\cdots H_2O\cdots H_2O-Cd^{2+}$ hydrogen-bonding scheme. Upon drying at ambient conditions, the material relaxes to the as-synthesized form. This change in the interlayer distance from $d = 13.4, 15.1,$ and 17.4 Å, respectively, is fully reversible. Samples heated to $150\ °C$ ($d = 13.7$ Å) and higher do not show rehydration properties. An explanation can be deduced from IR spectroscopic studies, which indicate that elevated temperatures lead to a condensation of the carboxylic acid groups with adjacent layers.

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Conclusion

The reaction of the aryl-carboxy phosphonic acid, $H(HO_3-PCH_2)_2NH-CH_2C_6H_4-COOH$, with $CdCl_2$ at room temperature results in the formation of $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$. In addition to the elucidation of the crystal structure, the title compound was characterized in detail and reversible dehydration/hydration properties were demonstrated. $[Cd_3(H_2O)_3((O_3PCH_2)_2NH-CH_2C_6H_4-COOH)_2]\cdot11H_2O$ is built up from cadmium phosphonate layers that are connected by water-mediated hydrogen bonds between aryl-carboxylic acid groups and water molecules coordinating to Cd^{2+} ions of adjacent layers ($C-OH\cdots H_2O\cdots H_2O-Cd^{2+}$). As observed in many other structures derived from $H(HO_3PCH_2)_2NH-CH_2C_6H_4-COOH$, the rigid aryl-carboxylic acid groups are arranged in a zipperlike fashion.[15] Thus, in the case of the title compound, large amounts of water molecules are located in channels along the *a* axis. These water molecules can be removed by heating the compound to $100\ °C$, resulting in a layered structure with interlayer spacing reduced by 1.7 Å. This compound can be rehydrated by levigation with water. Interestingly, the resulting X-ray powder pattern of the wet sample shows an increase in the interlayer distance of 2.3 Å in comparison with the as-synthesized compound. This can be explained by an intercalation of an additional monolayer of water molecules into the structure as observed in soil minerals.[21] Upon drying at ambient conditions, the expanded structure relaxes in its as-synthesized form. Since for possible applications, the toxicity due to cadmium is an obstacle, future work will be concerned with the substitution of Cd^{2+} ions by other divalent metal ions of similar ionic radii, such as Ca^{2+} ions. Furthermore, we will explore the intercalation chemistry of this interesting compound.