Synthesis and X-ray Powder Structure of a New Pillared Layered Cadmium Phosphonate, Giving Evidence that the Intercalation of Alkylamines into $Cd(O_3PR)\cdot H_2O$ Is Topotactic

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A new pillared layered phosphonate, cadmium 2-aminoethylphosphonate, $Cd(O_3PC_2H_4NH_2)$ (**1**), has been synthesized, and its structure was solved ab initio from X-ray powder diffraction data and refined by Rietveld methods. Compound **1** is orthorhombic: space group $Pna2_1$, $a = 15.4643(2)$ Å, $b = 5.16512(7)$ Å, $c = 6.27650(8)$ Å, and $Z = 4$. Its layer arrangement is similar to that in $Cd(O_3PR)\cdot H_2O$, except that the water molecule coordinated to cadmium in $Cd(O_3PR)\cdot H_2O$ is replaced by the nitrogen atom from the amino ends of the ethyl chains borne by phosphorus of the upper and lower layers. The strong similarity of the IR, ^{31}P, and ^{113}Cd NMR data for $Cd(O_3PC_2H_4NH_2)$ and $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$ clearly shows the topotactic character of the intercalation of *n*-alkylamines in the dehydrated form of $Cd(O_3PR)\cdot H_2O$ to yield $Cd(O_3PR)\cdot n\text{-}NH_2R'$.

Introduction

A variety of metal phosphonate compounds have been synthesized and examined in view of their applications in catalysis, sorption, ion exchange, magnetic studies, intercalation chemistry, etc.[1]

The composition of the divalent metal phosphonates is generally $M^{II}(O_3PR)\cdot H_2O$, conforming to the same structure type for Mn, Zn, Ni, Co, Mg, Cd, and Fe.[2] The metal is six-coordinated; one site is occupied by the water molecule and the five others are phosphonate oxygen atoms, resulting in a 122 connectivity for the RPO_3 blocks. It has been shown that some of these compounds (Zn, Co, Cd) can be dehydrated thermally and that *n*-alkylamine sorption takes place in the corresponding dehydrated phases when exposed to gaseous amines to yield $M^{II}(O_3PR)\cdot NH_2R'$.[2d,3] The question was raised as to whether this dehydration/intercalation proceeds in a topotactic manner (substitution of the water molecule by the amine). In the case of zinc, in parallel studies, Clearfield et al.[3c] $[Zn(O_3PC_6H_5)\cdot H_2O]$ and Bujoli et al.[3d] $[Zn(O_3PCH_3)\cdot H_2O]$ have clearly demonstrated that a layer restructuring occurs during the two consecutive steps. In fact, the zinc atoms are tetrahedrally coordinated in both the anhydrous and intercalated compounds, due to a decrease in the connectivity of the RPO_3 groups. However, while zinc can be found in ZnO_4, ZnO_5, or ZnO_6 geometries in phosphonates, our experience in the field of cadmium phosphonates has shown that more often than not this metal assumes a coordination of 6 (in agreement with the effect of size, considering the radius of Cd^{2+} compared to Zn^{2+}).[4] It was thus of interest to verify if a layer rearrangement similar to that observed in the case of zinc was also present in the $Cd(O_3PR)\cdot H_2O$ system.

In this paper we describe the synthesis and structure of a new cadmium phosphonate $Cd(O_3PC_2H_4NH_2)$, the structure of which provides additional information relevant to the problem discussed above.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical Co. and were used as received. FTIR spectra were obtained on a Bruker IFS-85 FTIR spectrometer with the usual KBr pellet technique. The solid state ^{31}P and ^{113}Cd NMR spectra were recorded on a DSX 300 Bruker spectrometer as previously described.[5] The principal components of the chemical shift tensors were measured using the spinning sidebands fitting routine,[6,7] for the different observation conditions (static and MAS at various spinning rates). The chemical analyses were performed by the CNRS Analysis Laboratory (Vernaison, France).

Synthesis Procedures. $Cd(O_3PCH_3)\cdot H_2O$, $Cd(O_3PCH_3)$, and $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$ were prepared as reported in the literature by Cao et al.[2d] Cadmium 2-aminoethylphosphonate, $Cd(O_3PC_2H_4NH_2)$, was prepared by mixing cadmium nitrate (1 mmol), (2-aminoethyl)phosphonic acid (1 mmol), and 2 mL of a 1 M sodium hydroxide

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(1) Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Eds.; John Wiley and Sons: New York, 1998; Vol. 47, p 371.

(2) (a) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781. (b) Cao, G.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics* **1988**, *26*, 63. (c) Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 7. (d) Cao, G.; Lynch, V. M.; Yacullo, L. N. *Chem. Mater.* **1993**, *5*, 1000. (e) Bujoli, B.; Pena, O.; Palvadeau, P.; Le Bideau, J.; Payen, C.; Rouxel, J. *Chem. Mater.* **1993**, *5*, 583.

(3) (a) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434. (b) Zhang, Y.; Scott, K. J.; Clearfield, A. *J. Mater. Chem.* **1995**, *5*, 315. (c) Poojary, D. M., Clearfield, A. *J. Am. Chem. Soc.* **1995**, *117*, 11278. (d) Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *J. Mater. Chem.* **1996**, *6*, 1843.

(4) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988.

(5) Massiot, D.; Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *Chem. Mater.* **1997**, *9*, 6.

(6) Massiot, D.; Thiele, H.; Germanus, A. *Bruker Rep.* **1994**, *140*, 1762.

(7) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

10.1021/ic981248g CCC: $18.00

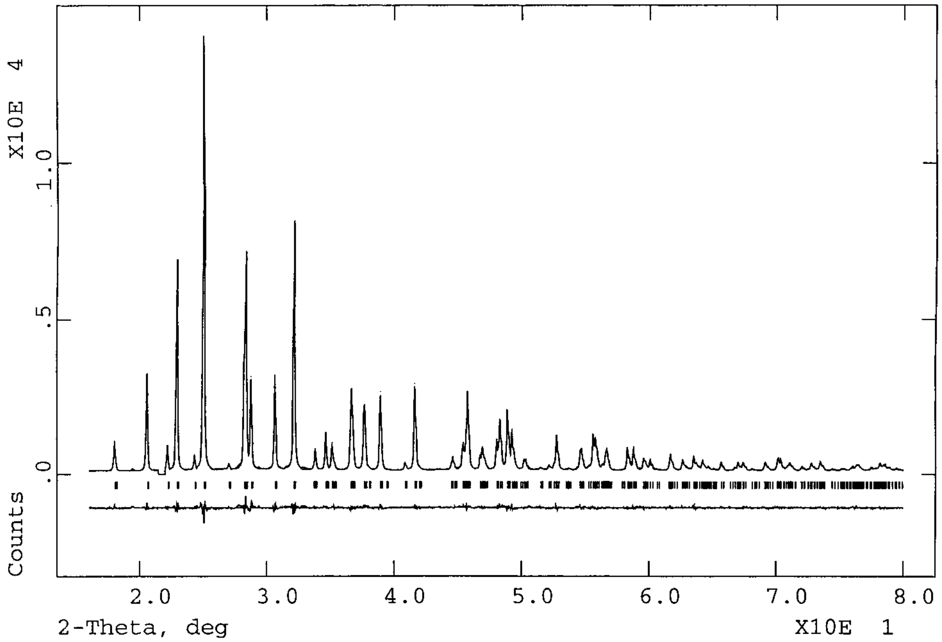

Figure 1. Observed (·) and calculated (−) profiles for the Rietveld refinement of $Cd(O_3PC_2H_4NH_2)$. The difference plot is on the same intensity scale.

solution with water (15 mL). The mixture was placed in the PTFE cell (23 mL capacity) of an autoclave, sealed, and placed in a drying oven at 175 °C for 3 days. The desired compound was obtained as a white crystalline powder that was collected by filtration, washed with water and acetone, and dried at room temperature (yield: 80%). Anal. Found: N, 5.88; C, 10.24; H, 2.63; Cd, 47.78. Calcd: N, 5.93; C, 10.20; H, 2.57; Cd, 47.74. TGA, room temperature to 250 °C, 0%.

X-ray Data Collection. Step-scanned X-ray powder data for the sample were collected on the finely ground sample (using a tubular aerosol suspension chamber to reduce preferred orientation) by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation ($\lambda_{K\alpha 1}$ = 1.540 598, $\lambda_{K\alpha 2}$ = 1.544 380). Data were collected between 2 and 80° in 2θ with a step size of 0.02° and a count time of 20 s/step. The powder pattern was indexed by the TREOR program[8] on the basis of the first 20 observed lines. The best solution which indexed all the peaks indicated an orthorhombic cell with lattice parameters a = 15.48 Å, b = 5.17 Å, and c = 6.28 Å. The systematic absences were consistent with the space group $Pna2_1$.

Structure Solution and Refinement. The raw pattern data were transferred to the GSAS program package.[9] The powder pattern was refined with the Le Bail technique using the following parameters: unit cell constants, background (shifted Chebyshev function, 12 variables), Kα1/Kα2 ratio, profile (Pseudovoigt with Finger−Cox−Jephcoat asymmetry), 6 variables including line width, strain broadening, sample shift, and FCJ asymmetry.[9] Integrated intensities were extracted from the profile over the range $16° < 2\theta < 80°$. A direct methods calculation was then computed using this data set in the SHELX program.[10] The positions of the Cd, P, O_1, O_2, N, C_1, and C_2 atoms were derived from this calculation. A Rietveld method was then used to refine those atomic positions. Soft constraints were imposed in a first refinement series for the P−O, P−C, C−C, and N−C bond distances. In addition, further restrictions were introduced between nonbonded atoms to preserve the tetrahedral geometry about the P atom and angles in the organic chain. A difference Fourier map computed at this stage revealed the position of the remaining oxygen atom O_3. Neutral atomic scattering factors were used for all atoms. A correction was made for the preferred orientation effect (bc plane) by using the March−Dollase model[9] implemented in the GSAS programs. No corrections were made for the absorption effects. The cadmium atom was refined anisotropically, all others isotropically. The weight of the constraints was progressively reduced as the refinement progressed and finally completely removed in the last stage. The final cycle of refinement, based upon 55 variable parameters, smoothly converged with agreement factors of $R_p = 0.057$, $wR_p = 0.040$, and $R(F^2) = 0.030$. A final Rietveld refinement plot is given in Figure 1.

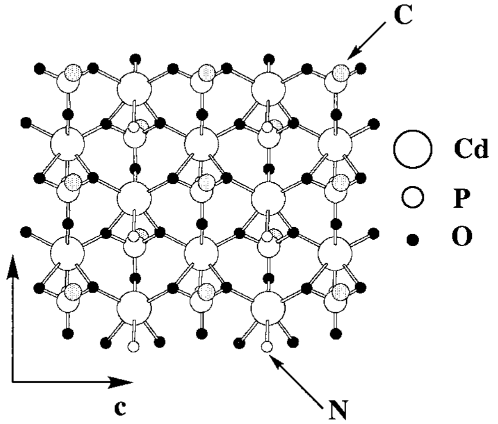

Figure 2. Schematic representation of a $Cd(O_3PC_2H_4NH_2)$ layer as seen perpendicular to the a axis. The carbon atoms that are not bound to phosphorus have been omitted for clarity. Important distances (Å): Cd−O = 2.189(8), 2.266(6), 2.339(8), 2.373(9), 2.516(9); Cd−N = 2.320(7).

Results

Structure of $Cd(O_3PC_2H_4NH_2)$ (1). The crystal packing is presented in Figures 2 and 3, showing a pillared layered structure. In the middle of each slab, Cd atoms are octahedrally coordinated by five oxygen atoms of phosphonate groups and a nitrogen atom coming alternatively from aminoethyl chains of the upper and lower layers. Two of the phosphonate oxygen atoms are each bridging two adjacent cadmium atoms, while the third one is only bonded to one metal atom (connectivity:

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(8) Werner, P. E.; Erikson, L.; Westdahl, M. J. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(9) (a) Larson, A.; von Dreele., R. B. *GSAS: Generalized Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1985. (b) Dollase, W. A. *J. Appl. Crystallogr.* **1986**, *19*, 267.

(10) Sheldrick, G. M. *SHELXTL PLUS 4.0*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

Table 1. Compared IR and NMR Data for $Cd(O_3PC_2H_4NH_2)$ and $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$[a]

	$Cd(O_3PC_2H_4NH_2)$	$Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$
IR	ν(NH) 3306, 3255, 3166 cm^{-1} + [1599] $\nu(PO_3)$ 1100 (m), 1074 (s), 996 (vs), 969 (s) cm^{-1}	ν(NH) 3302, 3257, 3168 cm^{-1} + [1600] $\nu(PO_3)$ 1100 (m), 1076 (s), 991 (vs), 972 (s) cm^{-1}
^{31}P MAS NMR	$\delta_{11} = 90.6$, $\delta_{22} = 18.5$, $\delta_{33} = -25.3$, $\delta_{iso} = 27.9$ ppm $\Omega = 115.9$ ppm, $\kappa = -0.2$	$\delta_{11} = 90.9$, $\delta_{22} = 20.6$, $\delta_{33} = -26.3$, $\delta_{iso} = 28.4$ ppm $\Omega = 117.2$ ppm, $\kappa = -0.2$
^{113}Cd MAS NMR	$\delta_{11} = 251.1$, $\delta_{22} = 173.1$, $\delta_{33} = 65.9$, $\delta_{iso} = 163.4$ ppm $\Omega = 185.2$ ppm, $\kappa = 0.2$	$\delta_{11} = 256.8$, $\delta_{22} = 181.2$, $\delta_{33} = 67.2$, $\delta_{iso} = 168.4$ ppm $\Omega = 189.6$ ppm, $\kappa = 0.2$

[a] $\delta_{iso} = {}^1/_3(\delta_{11} + \delta_{22} + \delta_{33})$, $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{iso})/(\delta_{11} - \delta_{33})$ with $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. All values are given with respect to the following references: 85% H_3PO_4 (^{31}P) and $Cd(NO_3)_2\cdot 4H_2O$ (^{113}Cd).

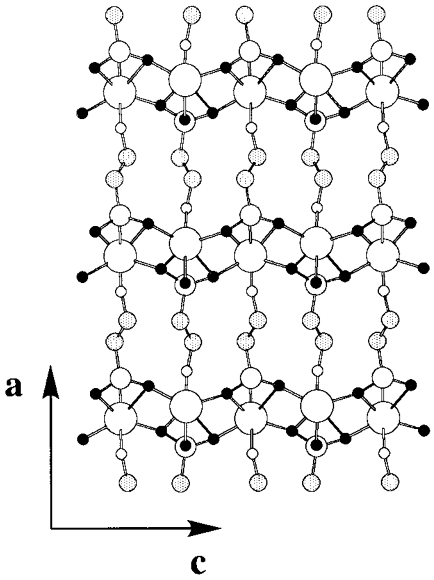

Figure 3. Schematic representation of $Cd(O_3PC_2H_4NH_2)$ as seen perpendicular to the *b* axis, showing the pillared layered structure.

122). Each phosphonate group provides a pair of oxygen atoms to chelate a Cd atom, resulting in a small O−Cd−O angle (60.9(2)°). The in-plane arrangement of phosphonate groups in relation to the metal atoms is similar to that found in $Cd(O_3PR)\cdot H_2O$ [$R = C_6H_5$, CH_3], except that the water molecule coordinated to Cd is replaced by a primary amine end. This is the second example (with $Zn(O_3PC_2H_4NH_2)$)[11] of pillared layered phosphonate in which the organic pillars are based on 2-aminoethylphosphonic acid blocks.

Discussion

A first point that is worth noting is the strong similarity between the inorganic frameworks in $Cd(O_3PC_2H_4NH_2)$ and $Cd(O_3PR)\cdot H_2O$. The only difference between these two phases is that the water molecule coordinated to cadmium in $Cd(O_3PR)\cdot H_2O$ is replaced by a nitrogen atom for the pillared layered $Cd(O_3PC_2H_4NH_2)$. The structure of the slabs in this latter product corresponds exactly to that expected for the amine intercalate $Cd(O_3PR)\cdot NH_2R'$, if the "dehydration/amine intercalation" process in $Cd(O_3PR)\cdot H_2O$ is fully topotactic (replacement of the water molecule by the nitrogen atom of the intercalated amine, with no other structural modification). For this reason, a combination of FTIR, ^{31}P, and ^{113}Cd MAS NMR spectroscopies was used to compare $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$ and $Cd(O_3PC_2H_4NH_2)$ (Table 1).

(i) The IR spectrum of the intercalate in the ν(NH) region shows the coordination of the nitrogen atom of the *n*-butylamine to the cadmium atoms (by similarity with the spectrum of **1**). Moreover, the IR spectra of the two compounds are nearly superimposable in the PO_3 vibration domain.

(ii) The ^{31}P MAS NMR spectrum of $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$ indicates a single phosphorus site, the chemical shift tensor of which is quasi-identical to that of $Cd(O_3PC_2H_4NH_2)$. Only one cadmium site is observed on the ^{113}Cd MAS NMR spectra, with again very close chemical shift tensors for the two compounds.

FTIR and NMR spectroscopies are highly sensitive techniques, capable of providing detailed local information about the metal−O_3P arrangement in metal phosphonates. In this study, the strong similarities observed in the data collected for $Cd(O_3PCH_3)\cdot n\text{-}NH_2C_4H_9$ and **1** give clear evidence that the structural features in both compounds are entirely similar. Thus, the main conclusion is that the "dehydration/amine intercalation" in $Cd(O_3PCH_3)\cdot H_2O$ proceeds topotactically, via the displacement of the water molecule by the amine. To obtain information about the cadmium environment in the anhydrous phase using high-resolution solid-state NMR, $Cd(O_3PCH_3)\cdot H_2O$ was dehydrated in the ZrO_2 rotor [180 °C], thus avoiding its rehydration. For the resulting $Cd(O_3PCH_3)$ phase, ^{113}Cd could not be observed through crosspolarization due to the removal of the water molecule, nor could it be detected directly, possibly because of long relaxation times. On the other hand, the ^{31}P MAS NMR spectrum revealed a single phosphorus site [$\delta_{iso} = 39.1$ ppm, $\Omega = 87.4$ ppm, $\kappa = -0.15$], confirming that no degradation occurred during the dehydration process [^{31}P NMR data for the starting $Cd(O_3PCH_3)\cdot H_2O$: $\delta_{iso} = 34.4$ ppm, $\Omega = 89.4$ ppm, $\kappa = 0.05$].

In conclusion, this work has unambiguously demonstrated, contrary to the case of $Zn(O_3PR)\cdot H_2O$, the topotactic character of the intercalation of *n*-alkylamines in the dehydrated form of $Cd(O_3PR)\cdot H_2O$ to yield $Cd(O_3PR)\cdot n\text{-}NH_2R'$. The interest of solid state NMR combined with infrared spectroscopy to characterize efficiently diamagnetic metal phosphonates with low crystallinity is also emphasized.

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Supporting Information Available: Figure S1 containing the ^{31}P MAS NMR spectrum of $Cd(O_3PCH_3).n\text{-}NH_2C_4H_9$ and $Cd(O_3PC_2H_4NH_2)$; tables of crystallographic data and refinement conditions, atomic coordinates and thermal parameters, selected bond lengths and angles for $Cd(O_3PC_2H_4NH_2)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Drumel, S.; Janvier, P.; Deniaud, D.; Bujoli, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1051.