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Synthesis, Structural Characterization, and Intercalation Chemistry of Two Layered Cadmium Organophosphonates

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The crystal structures of two cadmium organophosphonate monohydrates, $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$, were solved by single-crystal X-ray diffraction. $Cd(O_3PCH_3)\cdot H_2O$ is orthorhombic, space group $Pna2_1$ with $Z = 4$ and $a = 17.763(6)$, $b = 5.008(2)$, and $c = 5.912(3)$ Å, $V = 525.9(5)$ Å^3. The structure consists of layers of Cd atoms octahedrally coordinated by five phosphonate oxygen atoms and a water molecule. The methyl groups lie above and below the approximately planar Cd–O layer, and makes van der Waals contacts between layers. The structure of $Cd(O_3PC_6H_5)\cdot H_2O$ was refined in orthorhombic space group $Pmn2_1$, $Z = 2$, $a = 5.860(4)$, $b = 14.459(14)$, $c = 5.054(3)$ Å, $V = 428.2(6)$ Å^3. It is isostructural with previously reported $Mn(O_3PCH_3)\cdot H_2O$ and $Zn(O_3PCH_3)\cdot H_2O$. The layers in this structure are similarly constructed from octahedral coordination of Cd atoms by oxygen atoms. Both compounds dehydrate at elevated temperatures with no significant structural degradation. The dehydrated $Cd(O_3PCH_3)$ intercalates amines both from vapor and from nonaqueous solutions. As a result, a wide range of amine intercalation compounds (propylamine to *n*-octadecylamine) have been prepared. The intercalation reaction is shape-selective and is restricted to amines with no branching at the α-carbon position. This result is rationalized on the basis of steric restriction of the accessibility to the metal atoms. Such restriction is imposed by the methyl groups of the phosphonate which prevent amines that have α-branching from forming a Cd–N coordination bond. Dehydrated $Cd(O_3PC_6H_5)\cdot H_2O$ is also capable of intercalating very weakly basic alkanethiols.

Introduction

There has been continuous interest in metal organophosphonates.[1–6] Initially research activities were focused on organophosphonates of high-valent metals, such as Zr, Ti, and Sn, etc.[7] Tetravalent metal organophosphonates can be considered structural derivatives of the layered α-$Zr(HPO_4)\cdot H_2O$, with the organic group substituting for the hydroxyl group in the interlamellar region. Interest in these compounds stems from their properties as sorbents, catalysts, and catalyst supports. For example, microporosity is attained by pillaring apart the layered structure of these materials with rigid organic groups.[7f,h] Tetravalent metal organophosphonates have also served as structural models for the preparation of multilayer films that are analogous to Langmuir–Blodgett films.[8] Organophosphonates of other metals have since been discovered to have unique intercalation chemistry, in addition to their interesting structural chemistry. For example, vanadium organophosphonates $VO(O_3PR)\cdot H_2O$, prepared by the thermal removal of benzyl alcohol from $VO(O_3PR)\cdot H_2O\cdot C_6H_5CH_2OH$, bind a variety of primary alcohols while

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excluding secondary and tertiary alcohols.[6e] Some divalent metal organophosphonates, as first recognized by Clearfield *et al.*,[3e] and some trivalent metal organophosphonates have structures related to inorganic metal phosphates. For example, $M^{II}(O_3PCH_3)\cdot H_2O$ (M^{II}= Co, Mg, Mn, Ni, Zn)[4a,c] are structurally related to $M^IM^{II}(PO_4)\cdot H_2O$ (for $M^I = NH_4$, M^{II} = Cd, Co, Fe, Mg, Mn, Ni; and for M^I = K, M^{II} = Cd, Co, Mg, Mn, Ni).[9] Shape selectivity has also been found in the intercalation reactions of some divalent metal organophosphonates. Intercalation reaction of $M^{II}(O_3PCH_3)$ (M^{II} = Co, Zn), prepared by dehydration of $M^{II}(O_3PCH_3)\cdot H_2O$, is limited to amines that have no branching at the α-carbon position;[4c] and only ammonia can be intercalated into $M^{II}(O_3PC_6H_5)$.[3c] This has led to the possibility of utilizing this class of materials for selective chemical sensing based on molecular shape. Mallouk and co-workers have recently reported the fabrication of piezoelectric quartz crystal microbalance (QCM) derivatized with zinc organophosphonates and its use for sensitive and specific gas-phase sensing of ammonia and amines.[10] Other potential uses of these materials may be in the area of shape-selective separations. One limitation of using the Zn and Co organophosphonates for this purpose is that these materials react only with the vapor of an intercalant compound. Therefore, only small amine molecules with sufficient vapor pressure show significant reactivity. In this paper we report the synthesis, structural characterization, and dehydration of two cadmium organophosphonates, *i.e.*, $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$, and the intercalation reaction of $Cd(O_3PCH_3)$ with amines. Unlike cobalt and zinc organophosphonates, these cadmium compounds intercalate amines both from vapor and from nonaqueous solutions. Also reported are preliminary results of the intercalation behavior of $Cd(O_3PC_6H_5)$ with alkanethiols.

Experimental Section

Materials and Methods. Reagent and solvents used were of reagent grade quality and were obtained from commercial sources. Deionized water with resistivity of 17.8 MΩ cm was used as the sole source of water in all experiments. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Powder X-ray diffraction patterns were obtained with a Siemens D500 diffractometer with a voltage of 40 kV and current of 40 mA. The PXRD patterns were used to determine the interlayer spacings. No internal standard was used, but all the readily identified strong series of reflections corresponding to the layer spacing in each sample were used to attain self-consistency in calculating the reported values of the layer spacing. Thermogravimetric analyses were performed in flowing air at a rate of 10 °C/min on a du Pont 900 thermal analyzer. SEM micrographs were taken with a JEOL 840 scanning electron microscope.

Synthesis. Powder samples of $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$ were prepared by combining a 0.1–0.5 M aqueous solution of $Cd(NO_3)_2\cdot 4H_2O$ with an equimolar aqueous solution of the phosphonic acid. When 0.1 M NaOH aqueous solution was added dropwise to the stirred mixture solution to pH 3–4, white, poorly crystalline precipitate formed. The pH was further increased to 6 to ensure complete precipitation. The degree of crystallinity of the precipitate can be improved by stirring the mixture at 50–70 °C for about a day. The solids so prepared were then filtered and washed several times with copious amount of water and finally with ethanol, and dried in air at room temperature. Yield is almost quantitative (>95%).

Table I. Crystallographic Data for $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$

empirical formula	CH_5O_4PCd	$C_6H_7O_4PCd$
fw	224.42	286.49
a, Å	17.763(6)	5.860(4)
b, Å	5.008(2)	14.459(14)
c, Å	5.912(3)	5.054(3)
V, Å^3	525.9(5)	428.2(6)
Z	4	2
F(000)	424	276
crystal system	orthorhombic	orthorhombic
space group	$Pna2_1$ (No. 33)	$Pmn2_1$ (No. 31)
temp, °C	25	25
radiation	graphite monochromatized, Mo Kα (λ = 0.7107 Å)	
2θ range, (deg)	4–52.5	4–50
scan speed (deg/min)	6–12 (1° ω scan)	4–8 (1.5° ω scan)
ρ_{calc}, g/cm^3	2.83	2.22
reflections measured	2025	460
unique reflections	1012	460
R_{int}	0.023	not applicable
μ, cm^{-1}	43.47	26.95
transmission factor[a] range	0.3455–0.4769	
crystal size, mm	0.2 × 0.3 × 0.3	0.5 × 0.2 × 0.4
reflections used	1012	460
reflections rejected	0	0
secondary extinction[b] correction factor	$7.0(4) \times 10^{-5}$	$1.0(2) \times 10^{-4}$
R(*F*)[c]	0.0215	0.0320
$R_w(F)$	0.0284	0.0390
goodness of fit	1.117	1.604
parameters	64	67
max $\lvert\Delta/\sigma\rvert$	<0.1	<0.1
min, max peaks (e/Å^3)	–0.61, 1.41 (near Cd)	–0.93, 1.02 (near Cd)

[a] Absorption correction was based on measured crystal faces. [b] The correction for secondary extinction is of the form: $F_{corr} = F_{calc}/[(1 + X)(F_{calc})^2/\sin^2\theta]^{1/4}$ where *X* is the correction factor. [c] The function, $\sum w(|F_o| - |F_c|)^2$, was minimized and where $w = 1/(\sigma(F_o)^2 + (0.02F)^2)$.

Crystal Growth. Single crystals of $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$ were each grown from an aqueous solution containing equimolar $Cd(NO_3)_2\cdot 4H_2O$ and the corresponding phosphonic acid and 4 mol of urea/mol of the phosphonic acid. This clear solution was then held at 55 °C. After a week, colorless crystals of $Cd(O_3PCH_3)\cdot H_2O$ appeared as large plates (approximate dimensions 3 × 3 × 1 mm) and smaller prisms (0.3 × 0.3 × 0.3 mm). X-ray diffraction studies showed that the two forms of crystals were structurally identical. Crystals of $Cd(O_3PC_6H_5)\cdot H_2O$ formed within 3 days as very thin colorless plates.

Single-Crystal X-ray Diffraction. The crystal of $Cd(O_3PCH_3)\cdot H_2O$ used for data collection was a colorless prism of approximate dimensions 0.2 × 0.3 × 0.3 mm, and that of $Cd(O_3PC_6H_5)\cdot H_2O$ was a colorless plate of approximate dimensions 0.05 × 0.2 × 0.4 mm. Details of the crystal data, data collection, and refinement are listed in Table I. Data for both crystals were collected on a Nicolet P3 diffractometer equipped with a graphite monochromator using the ω scan technique. Lattice parameters of $Cd(O_3PCH_3)\cdot H_2O$ were obtained from the least-squares refinement of 14 reflections with $9.3 < 2\theta < 23.1°$, while lattice parameters of $Cd(O_3PC_6H_5)\cdot H_2O$ were obtained from the least-squares refinement of 21 reflections with $13.6 < 2\theta < 21.7°$. Data reduction and decay correction for both crystals were performed using the SHELXTL-PLUS software package.[11] Both structures were solved by direct methods and refined by full-matrix least-squares[11] methods with anisotropic thermal parameters for the non-H atoms. For both structures, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = \{0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}\}$. The intensity, *I*, is given by $(I_{peak} - I_{background}) \times$

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(scan rate); where 0.02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times \text{(scan rate)}]$. Neutral atom scattering factors for the Non-H atoms were taken from Cromer and Mann,[12] with the anomalous-dispersion corrections taken from the work of Cromer and Liberman.[13] The scattering factors for the H atoms were obtained from Stewart et al.[14] Values used to calculate the linear absorption coefficient are from the *International Tables for X-ray Crystallography* (1973).[15] All figures were generated using SHELXTL-PLUS.[11] Other computer programs used in this work are listed elsewhere.[16]

For the structure of $Cd(O_3PCH_3){\cdot}H_2O$, the C–H hydrogen atoms were calculated in idealized positions (C–H 0.96 Å) with isotropic thermal parameters fixed at $1.2U_{eq}$ of the relevant atom. The H atoms on the water molecule were found from a ΔF map. The O–H bond lengths did not refine to reasonable values and were, therefore, fixed at 0.85 Å with U_{iso} fixed at $1.2U_{eq}$ for O1W.

For the structure of $Cd(O_3PC_6H_5){\cdot}H_2O$, the diffraction peaks were quite broad, therefore a scan range of 1.5° in ω was used. The crystal was found to be isomorphous with that of $Mn(O_3PC_6H_5){\cdot}H_2O$[4a] and $Zn(O_3PC_6H_5){\cdot}H_2O$[3e] with the same unusual disorder of the phenyl rings and was therefore treated similarly. As in the case of $Mn(O_3PC_6H_5){\cdot}H_2O$, a few very faint and streaky diffraction spots were also found in the axial photographs taken along a^* and c^* indicating a doubling of both axes. But as in the case of $Mn(O_3PC_6H_5){\cdot}H_2O$, $Zn(O_3PC_6H_5){\cdot}H_2O$, and $LaH(O_3PC_6H_5)$[3b], the structural features such as bond lengths and bond angles and the final R value are refined better in the smaller cell. Most importantly there is no significant difference in structural features between the alternative treatments.

Dehydration and Intercalation Reactions. Both compounds were dehydrated before intercalation reaction. Dehydration was achieved at 150–170 °C under 5×10^{-2} Torr pressure for 3–6 h (until the pressure of the vacuum line reaches attainable minimum). The dehydrated compounds easily rehydrated when exposed to moist air; therefore, they were protected from exposure to air before and during intercalation reactions. Intercalation reactions with amines were effected either by exposing the dehydrated compounds to amine vapor, if the amine has adequately high vapor pressure, or by suspending the dehydrated compounds in a nonaqueous solution (or suspension in the case of long chain alkylamines) of an amine. Anhydrous ethanol and acetonitrile were used as solvents with no noticeable solvent effect on reaction rate or the product formed. The mixture was then allowed to stand at room temperature or at 50 °C with occasional shaking for an appropriate period of time, during which the suspended solid increased its apparent volume noticeably if the intercalation reaction had taken place. The solid was then filtered in air, washed thoroughly with ethanol, and dried in air.

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $Cd(O_3PCH_3){\cdot}H_2O$[a]

atom	x	y	z	U
Cd	0.265440(10)	0.17171(4)	0.2931	0.01981(11)
P	0.35036(4)	0.2376(2)	0.7933(5)	0.0183(2)
O1	0.33589(13)	−0.0592(5)	0.791(2)	0.0285(7)
O2	0.3155(4)	0.3842(10)	1.0048(10)	0.018(2)
O3	0.3182(5)	0.3762(11)	0.5901(12)	0.031(2)
C1	0.4497(2)	0.2940(9)	0.774(2)	0.032(2)
O1W	0.3577(2)	−0.1581(5)	0.297(2)	0.0294(8)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

Table III. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cd(O_3PCH_3){\cdot}H_2O$[a]

1	2	3	1–2	1–2–3
O3	Cd	O1W	2.238(7)	91.3(3)
O3	Cd	O3a		158.0(3)
O3	Cd	O2a		96.7(2)
O3	Cd	O2c		102.6(2)
O3	Cd	O1b		93.7(2)
O1W	Cd	O3a	2.327(3)	90.2(2)
O1W	Cd	O1b		170.60(9)
O1W	Cd	O2C		93.8(2)
O1W	Cd	O2a		89.5(2)
O1b	Cd	O2c	2.249(2)	91.73(2)
O1b	Cd	O2a		83.2(2)
O1b	Cd	O3a		82.7(2)
O2a	Cd	O3a	2.389(6)	61.4(2)
O2a	Cd	O2c		160.4(2)
O2c	Cd	O3a	2.198(6)	99.2(2)
O3a	Cd		2.417(7)	
O1	P	O2	1.508(2)	113.4(4)
O1	P	O3		112.6(5)
O2	P	O3	1.577(6)	105.7(3)
O2	P	C1		111.4(5)
O3	P	C1	1.501(7)	104.5(5)
C1	P	O1	1.790(4)	108.8(1)

[a] Atoms marked by a are related by $^1/_2 - x, -^1/_2 + y, -^1/_2 + z$. Atoms marked by b are related by $^1/_2 - x, ^1/_2 + y, -^1/_2 + z$. Atoms marked by c are related by $x, y, z - 1$.

Results and Discussion

Structure of $Cd(O_3PCH_3){\cdot}H_2O$. Positional and thermal parameters of atoms are given in Table II. Selected bond lengths and bond angles are given in Table III. The crystal packing is shown in Figures 1a and 2a. As can be seen from the figures the structure is layered and is composed of neutral slabs of $Cd(O_3PCH_3){\cdot}H_2O$ that are stacked along the a axis with only van der Waals interaction between the slabs. In the middle of each slab, Cd atoms are located approximately in a common plane, and are each octahedrally coordinated by five oxygen atoms of phosphonate groups and a water molecule. The methyl and phenyl groups are pointed approximately perpendicular to the plane and away from the inorganic layer. Figure 3a shows the distorted hexagonal coordination of the Cd atom by oxygen atoms in $Cd(O_3PCH_3){\cdot}H_2O$. Each Cd atom is bonded to four phosphonate groups, three of which are bonded to the Cd atom through one oxygen atom and the fourth which provides a pair of oxygen atoms to chelate the Cd atom. The sixth coordination site is occupied by a singly bonded H_2O molecule. This coordination scheme is found in $Cd(O_3PC_6H_5){\cdot}H_2O$ (Figure 3b) as well as in $Mn(O_3PC_6H_5){\cdot}H_2O$[4a] and $Zn(O_3PC_6H_5){\cdot}H_2O$[3e] and is the basis for the similarity between these compounds in their dehydration and intercalation behavior (*vide infra*).

Structure of $Cd(O_3PC_6H_5){\cdot}H_2O$. Positional and thermal parameters of atoms are given in Table IV. Selected bond lengths and bond angles are given in Table V. The overall structural features of $Cd(O_3PC_6H_5){\cdot}H_2O$ (Figures 1b and 2b) are very similar to those of $Cd(O_3PCH_3){\cdot}H_2O$. The coordination environment around the Cd atoms in $Cd(O_3PC_6H_5){\cdot}H_2O$ is shown in Figure 3b and is essentially the same as in that of $Cd(O_3PCH_3){\cdot}H_2O$. The in-plane arrangement of phosphonate groups and water molecules in relation to the metal atoms is also very similar, as compared in Figure 2a,b. The difference is that the CdO_6 octahedron in $Cd(O_3PC_6H_5){\cdot}H_2O$ possesses a mirror symmetry whereas the CdO_6 octahedron in $Cd(O_3PCH_3){\cdot}H_2O$ does not. The stacking of the layers along the b axis in $Cd(O_3PC_6H_5){\cdot}H_2O$ and the a axis in $Cd(O_3$-

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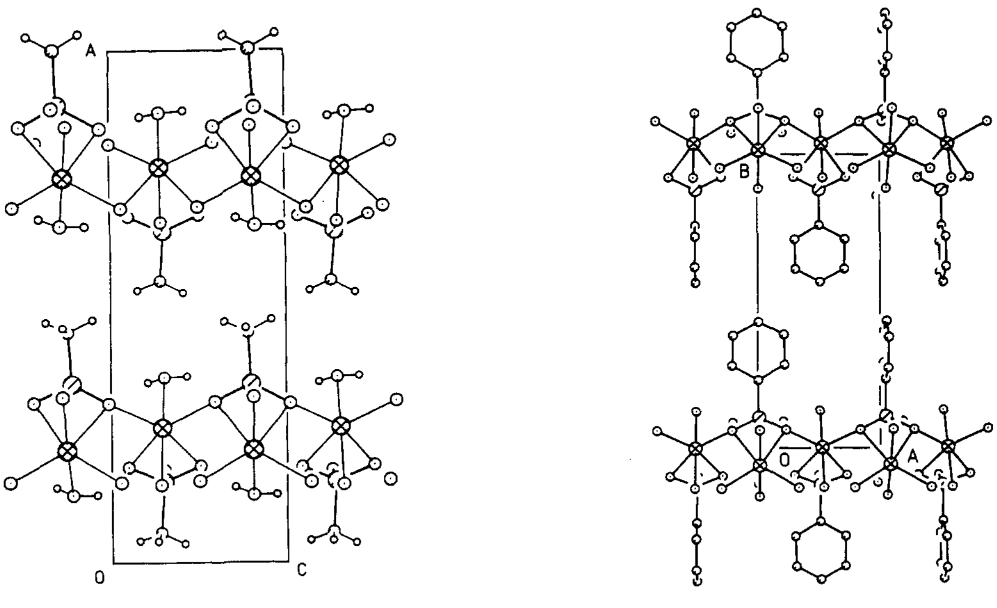
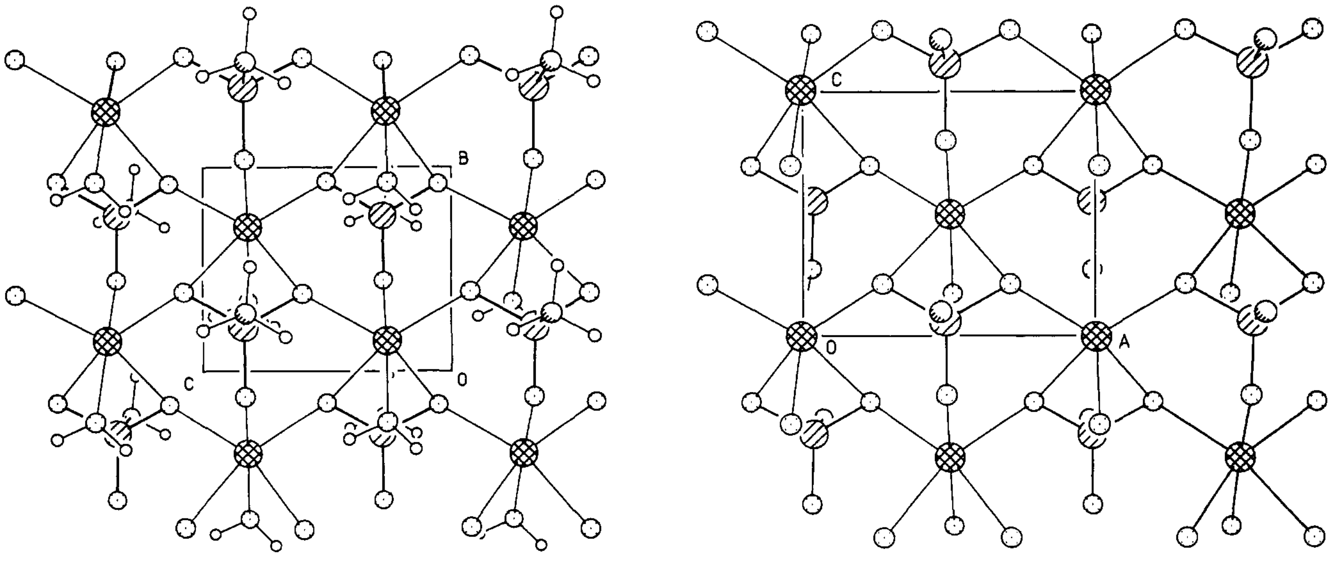


(a) (b)

Figure 1. Unit cell packing of (a) $Cd(O_3PCH_3)\cdot H_2O$ viewed along the *b*-axis and (b) $Cd(O_3PC_6H_5)\cdot H_2O$ viewed along the *c* axis. The disordered phenyl groups are presented as ordered with alternating and mutually perpendicular orientations. See text for discussions.



(a) (b)

Figure 2. Comparison of the $Cd{-}RPO_3{-}H_2O$ two-dimensional bonding network within one layer of $Cd(O_3PCH_3)\cdot H_2O$ and $Cd(O_3PC_6H_5)\cdot H_2O$. (a) The structure of $Cd(O_3PCH_3)\cdot H_2O$ viewed perpendicular to the layer plane (the *bc* plane). The angle between the P–C bond of the methyl group and the *bc* plane is 80°. (b) The structure of $Cd(O_3PC_6H_5)\cdot H_2O$ viewed along the *b* axis. The carbon atoms of the phenyl groups are deleted for clarity, except for the ones bonded to the phosphorus atoms.

$PCH_3)\cdot H_2O$ (Figure 1a,b) are different. In the former, the layers are translationally related along the *b* axis whereas in the latter the layers are related by an *a*-glide plane perpendicular to the *b* axis. The *a*-glide causes the layers to repeat in every other layer along the *a* axis, resulting in an *a*-axis dimension twice of the interlayer distance.

As mentioned above the structure of $Cd(O_3PC_6H_5)\cdot H_2O$ is isomorphous with that of $Mn(O_3PC_6H_5)\cdot H_2O$ and $Zn(O_3PC_6H_5)\cdot H_2O$. They have the same unusual disorder of the phenyl rings. The position of the phenyl rings are disordered among two orientations. In one orientation, the phenyl rings lie on a crystallographic mirror at $x = {}^1/_2$ and are perpendicular to this mirror in the other orientation. However, because of the dimensions of *a* and *c*, the disorder cannot be totally random. Along *a* and *c*, the phenyl rings must orient alternately to avoid extremely close CH···CH contacts. Along *c*, H···H contacts of 1 Å and C···C contacts of less than 2.7 Å would exist for adjacent phenyl ring atoms lying perpendicular to the mirror. Along *a*, H···H contacts of less than 2 Å would exist for adjacent phenyl ring atoms lying on the mirror. The C···C contacts, however, would be greater than 3.4 Å. There are no close

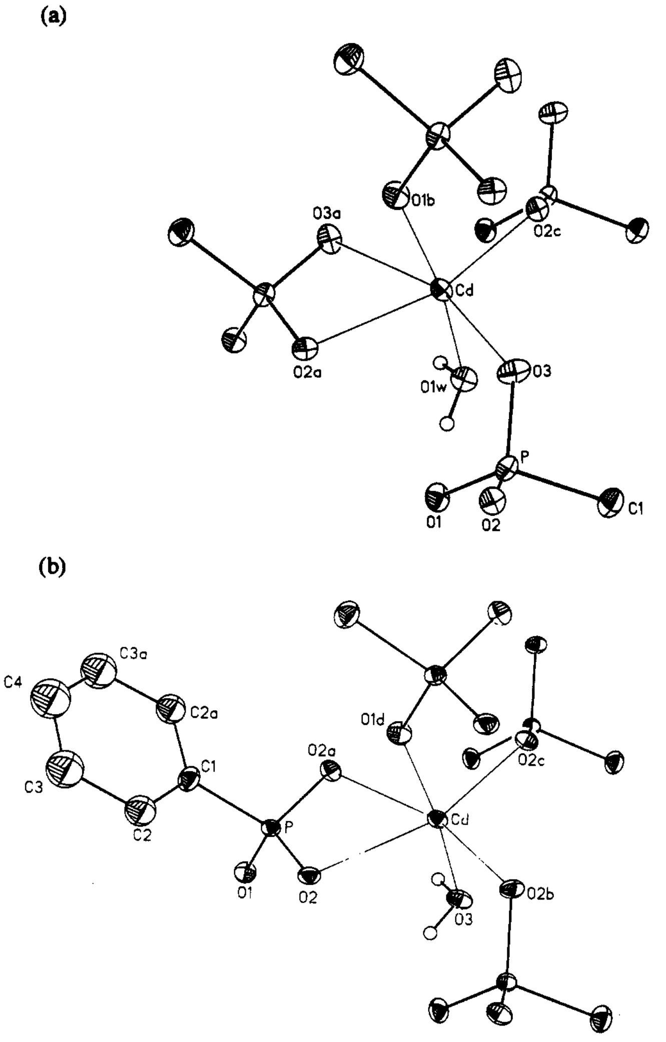


Figure 3. Coordination of Cd in (a) $Cd(O_3PCH_3)\cdot H_2O$ and in (b) $Cd(O_3PC_6H_5)\cdot H_2O$ along with the atom labeling scheme. H's have been omitted for clarity. Thermal ellipsoids are scaled to the 30% probability level in both cases. The Cd ion has a distorted octahedral coordination with one H_2O, three monodentate phosphonates and one bidentate phosphonate making up the coordination sphere. The coordination sphere for Cd is very similar in both compounds, except that the point symmetry is 1 for (a) and m for (b) at the Cd atom. For (b) the Cd ion and H_2O molecule have been transformed by $^1/_2 + x, -y, ^1/_2 + z$.

contacts between atoms in different layers. For comparison, the cell dimensions of $Mn(O_3PC_6H_5)\cdot H_2O$ are a = 5.734(5), b = 14.33(3), c = 4.945(4) Å, V = 406.4(9) Å^3, Z = 2, ρ_x = 1.87 g cm^{-3} (−110 °C) and the space group is $Pmn2_1$. The disorder, therefore, is likely occurring between layers with an ordered structure within each layer.

Table IV. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Atoms of $Cd(O_3PC_6H_5)\cdot H_2O$[a]

atom	x	y	z	U
Cd	0.0	−0.01928(5)	0.0	0.0188(3)
P	0.5	−0.1227(2)	0.0698(7)	0.0175(9)
O1	0.5	−0.1009(6)	−0.223(2)	0.025(3)
O2	0.7105(9)	−0.0835(4)	0.2152(13)	0.022(2)
O3	0.0	−0.1326(7)	−0.327(2)	0.028(3)
C1	0.5	−0.2451(8)	0.111(3)	0.030(4)
C4	0.5	−0.4357(15)	0.165(6)	0.075(7)
C2	0.705(4)	−0.2930(14)	0.131(5)	0.046(5)
C3	0.698(5)	−0.293(2)	0.145(6)	0.065(7)
C2A	0.5	−0.285(3)	0.362(9)	0.056(9)
C3A	0.5	−0.385(3)	0.395(9)	0.061(10)
C5A	0.5	−0.401(5)	−0.09(2)	0.12(2)
C6A	0.5	−0.297(3)	−0.105(9)	0.056(9)
H3	0.11(2)	−0.117(6)	−0.42(2)	0.04(3)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

Table V. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Cd(O_3PC_6H_5)\cdot H_2O$[a]

1	2	3	1–2	1–2–3
O2	Cd	O2a	2.409(6)	61.6(2)
O2	Cd	O1d		84.0(1)
O2	Cd	O3		90.6(1)
O2	Cd	O2b		99.2(2)
O2	Cd	O2c		160.5(2)
O3	Cd	O1d	2.326(1)	173.7(4)
O3	Cd	O2a		90.6(1)
O3	Cd	O2b		93.1(2)
O3	Cd	O2c		93.1(2)
O1d	Cd	O2a	2.234(9)	84.0(1)
O1d	Cd	O2b		91.0(2)
O1d	Cd	O2c		91.0(2)
O2a	Cd	O2b	2.409(6)	160.5(2)
O2a	Cd	O2c		99.2(2)
O2b	Cd	O2c	2.219(6)	99.7(2)
O2c	Cd		2.219(6)	
O1	P	O2	1.510(10)	112.9(3)
O2	P	C1	1.544(6)	108.0(4)
C1	P	O1	1.782(12)	108.8(6)
C2	C1		1.39(2)	
C2	C1	P		120.2(9)
C2A	C1	C6A	1.39(5)	121(3)
C2A	C1	P		121(2)
C6A	C1	P	1.32(5)	117(2)
C3	C4		1.32(3)	
C3A	C4	C5A	1.37(5)	126(4)
C5A	C4		1.39(9)	
C3	C2	C2A	1.44(3)	
C3	C2	C1		119(2)
C4	C3	C2		120(2)
C3A	C2A	C1	1.46(5)	121(3)
C4	C3A	C2A		116(4)
C6A	C5A	C4	1.51(8)	114(6)
C1	C6A	C5A		121(4)
H3	O3	H3′	0.83(10)	100(10)

[a] For the purposes of this table, the labels for the atoms bound to Cd are consistent with those shown in the figure. The relevant symmetry transformations for these atoms with respect to their coordinates are as follows: O1d is related by $^1/_2 - x, -y, ^1/_2 + z$. O2 is related by $^1/_2 - x, -y, -^1/_2 + z$. O2a is related by $-^1/_2 + x, -y, -^1/_2 + z$. O2b is related by $x - 1, y, z$. O2c is related by $1 - x, y, z$.

It is interesting to note that $Cd(O_3PC_6H_5)\cdot H_2O$ adds to the family of divalent metal organophosphonates $M^{II}(O_3PR)\cdot H_2O$ (M^{II} = Co, Mg, Mn, Ni, Zn) that are closely related to the inorganic metal phosphates $M^IM^{II}(PO_4)\cdot H_2O$.[9] For M^I = NH_4, M^{II} = Cd (phase A[9d]), Co, Fe, Mg, Mn, Ni; and for M^I = K, M^{II} = Cd, Co, Mg, Mn, Ni. They all crystallize in the same space group $Pmn2_1$. The structure of $Cd(O_3PCH_3)\cdot H_2O$ however, has no counterpart among the inorganic phosphates, although the structure of phase B of $NH_4Cd(PO_4)\cdot H_2O$[9c] (orthorhombic space group $Pnma$, a = 17.090 Å, b = 5.902 Å, c = 5.133 Å) is very similar with its a axis twice the interlayer spacing, also as a result of an a-glide. Palvadeau, Rouxel, and co-workers have recently reported the structure of monoclinic $Fe(O_3PC_2H_5)\cdot H_2O$[5d] that is related to that of orthorhombic $NH_4Fe(PO_4)\cdot H_2O$.

Dehydration and Intercalation Reactions. Because of the reported dehydration and shape-selective intercalation chemistry of $M^{II}(O_3PCH_3)$ (M^{II} = Co, Zn) with amine vapors[4c] and the similarity in the coordination environment around the metal atoms in the compounds $M^{II}(O_3PR)\cdot H_2O$ (M^{II} = Cd, Co, Zn), it is not surprising that Cd(O3

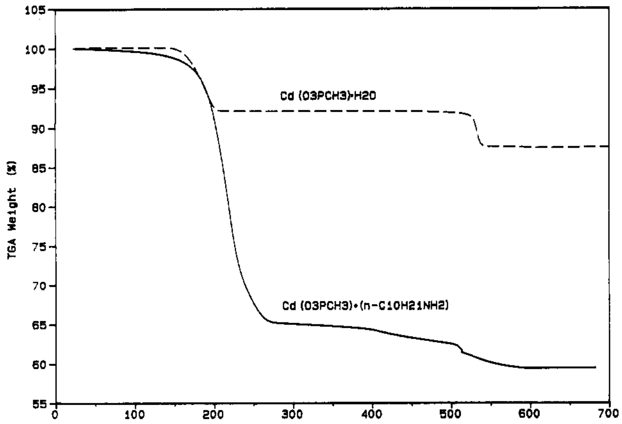


Figure 4. TGA traces of $Cd(O_3PCH_3){\cdot}H_2O$ and $Cd(O_3PCH_3)(n\text{-}C_{10}H_{21}NH_2)$. The experiments were performed in flowing air at a rate of 10 °C/min.

Table VI. List of Experiments for the Preparation of $Cd(O_3PCH_3)(RNH_2)$

amines	$d_{\text{interlayer}}$, Å	preparation conditions
n-C_3H_7–	13.27	1 day, *a*, *b*
n-C_4H_9–	14.40	1 day, *a*, *b*
n-C_6H_{13}–	18.90	2 days, *a*, *b*
n-C_4H_9–	14.40	4 hours, *b*, c
n-C_6H_{13}–	15.83	6 hours, *b*, *c*
n-C_8H_{17}–	18.70	1 day, 50 °C, *c*
n-$C_{10}H_{21}$–	21.60	2 days, 50 °C, *c*
n-$C_{12}H_{25}$–	24.24	3 days, 50 °C, *c*
n-$C_{14}H_{29}$–	26.85	3 days, 50 °C, *c*
n-$C_{16}H_{33}$–	29.16	5 days, 50 °C, *c*
n-$C_{18}H_{37}$–	32.00	5 days, 50 °C, *c*
3-methylbutyl–	16.20	3 days, 50 °C, *c*, *d*
2-methylbutyl	13.23	5 days at 50 °C, *c*, *e*
1-methylbutyl	no reaction	3 days at 50 °C, *c*
cyclohexyl-	no reaction	3 days at 50 °C, *c*
piperidine	no reaction	3 days at 50 °C, *c*

[a] Amine vapor. [b] Room temperature. [c] 0.5 g of $Cd(O_3PCH_3)$ suspended in 20 mL of acetonitrile containing 1.0 g of amine. [d] Reaction is incomplete in terms of product stoichiometry, but is nonetheless single phase. [e] Intercalated phase coexists with the anhydrous phosphonate when the reaction is terminated.

$PCH_3){\cdot}H_2O$ exhibits a similar dehydration step and intercalation chemistry with amines. $Cd(O_3PCH_3){\cdot}H_2O$ dehydrates beginning at 150 °C in flowing air (Figure 4) and the dehydrated phase shows strong peaks in the XRD powder pattern that indicate the retention of the layer structure with an interlayer spacing of 7.16 Å, a decrease of 1.72 Å from the 8.88-Å layer spacing of the monohydrate. There is, however, not enough evidence to establish whether the dehydration reaction is topotactic because the powder pattern does not contain enough peaks to permit indexing. But judging from the ready conversion of the dehydrated phase to the monohydrated phase when exposed to moisture in air, it is very likely that dehydration proceeds topotacticly.

$Cd(O_3PCH_3)$ forms intercalation compounds not only with amine vapor, as is the case for $Co(O_3PCH_3)$ and $Zn(O_3PCH_3)$, but it also reacts with amines in nonaqueous solution. This allows long-chain alkyl amines that have vapor pressures too low to be reactive in the vapor phase to be intercalated in the layered host. Table VI lists the experiments performed with various amines, the interlayer spacing of the intercalation compounds formed, and the reaction conditions used in the experiments. The interlayer spacings given in the table were calculated by using the different order of reflections corresponding to the same interlay distance that Figure 5 shows the X-ray powder diffraction patterns of some of the n-alkylamine intercalation compounds. TGA experiments and elemental analysis indicates that the reaction approaches equimolar stoichiometry when the reaction is allowed to proceed for 3–5 days, affording products that can be formulated as $Cd(O_3PCH_3)(RNH_2)$, but the initial reaction rate is rather fast. For example, 0.5 g of $Cd(O_3PCH_3)$ suspended in an acetonitrile solution containing 1.0 g of n-dodecylamine for 15 min afforded a single solid phase that had a stoichiometry of $Cd(O_3PCH_3)(n\text{-}C_{12}H_{25}NH_2)_{0.725}$. The molar content of n-$C_{12}H_{25}NH_2$ increased to 0.772 in 3 h, and to 0.806 in 24 h. The increase in amine content in the late stage of the intercalation reaction has little effect on the interlayer spacing of the intercalation compounds.

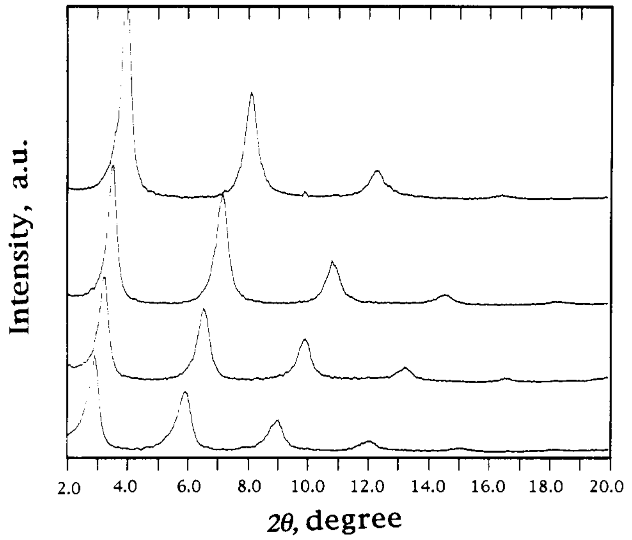


Figure 5. X-ray powder diffraction patterns of some n-alkylamine intercalation compounds $Cd(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$. From the top: n = 10, 12, 14, 16. All powder patterns are featureless above 20° (2θ), suggesting that the layers of the intercalation compounds have become turbostratic.

The stability of the amine intercalation compounds depends on the volatility of the amine involved. The intercalation compounds of lower molecular weight amines lose amine molecules gradually at room temperature in air, but they do not completely deintercalate. For example, $Cd(O_3PCH_3)(n\text{-}C_4H_9NH_2)$ loses about 49% of its amine after standing in air for 1 day and only loses an additional 8% after 2 weeks. The intercalation compounds of higher amines are quite stable. Figure 4 shows that TGA trace of $Cd(O_3PCH_3)(n\text{-}C_{10}H_{21}NH_2)$. The compound does not lose a significant amount of weight below 150 °C.

Figure 6 shows the SEM micrographs of $Cd(O_3PCH_3){\cdot}H_2O$ and $Cd(O_3PCH_3)(n\text{-}C_{10}H_{21}NH_2)$. Although the crystals of $Cd(O_3PCH_3){\cdot}H_2O$ are not platelike as most layered organophosphonates, the stacking of layers in the crystal can clearly be identified. Upon intercalation with amines, the layers are strikingly exfoliated. The degree of disorder can also be seen in the broadening of 00*l* diffraction peaks and the absence of any *hkl* ($h, k \neq 0$) peaks (Figure 5). The plot of interlayer spacing vs. the number of methylene groups in the n-alkylamine intercalation compounds is linear (Figure 7). It has a slope of 1.2913 Å/CH_2. Since the value 1.27 Å/CH_2 represents the distance between adjacent carbon atoms in an *all-trans*

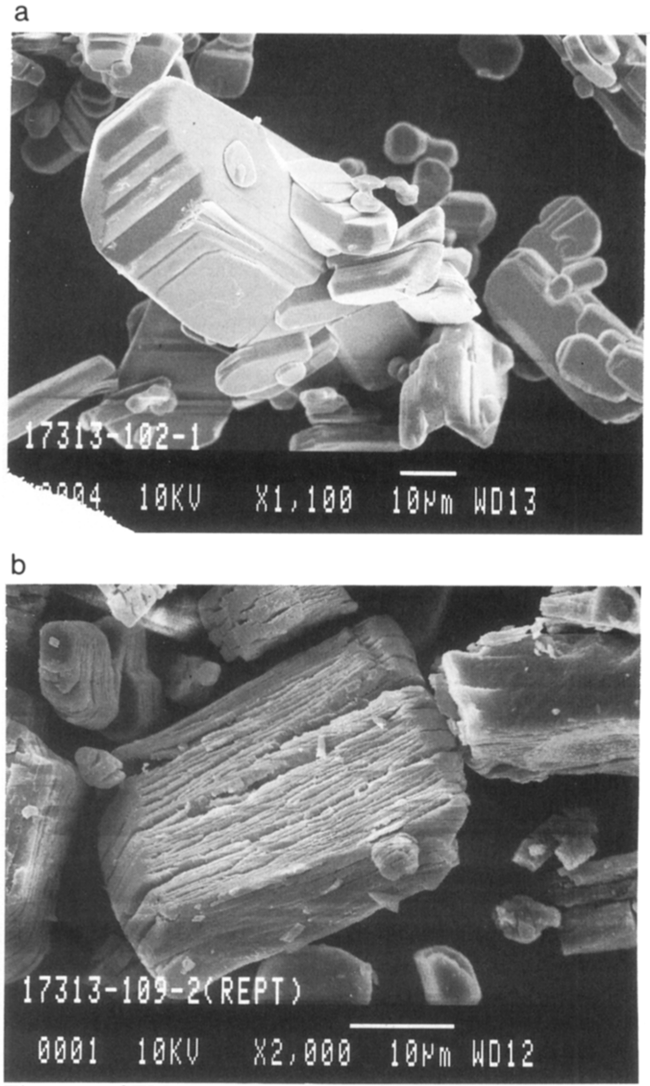


Figure 6. SEM micrographs of (a) $Cd(O_3PCH_3){\cdot}H_2O$ and (b) $Cd(O_3PCH_3)(n\text{-}C_{10}H_{21}NH_2)$ showing the exfoliation of layers upon intercalation.

fully extended alkyl chain along the chain axis,[17] the *n*-alkyl chains must be arranged as double layers in the interlamellar region, with a tilt angle of $\sin^{-1}[1.2913/2 \times 1.27]$, i.e., 30.6° with respect to the layer plane. Compared with an tilt angle of 31.4° for $Co(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$,[4c] the slightly lower value for $Cd(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$ can be explained by the larger in-plane cell dimensions of cadmium phosphonate (5.68×4.79 Å^2 for $Co(O_3PCH_3){\cdot}H_2O$ vs 5.91×5.01 Å^2 for $Cd(O_3PCH_3){\cdot}H_2O$).

As in the case of $Co(O_3PCH_3)$ and $Zn(O_3PCH_3)$, $Cd(O_3PCH_3)$ intercalates amines with the same kind of shape selectivity, *i.e.*, only those amines that have no branching at the α-carbon form intercalation compounds. Therefore this result can be similarly rationalized by assuming that the amine molecule occupies the site of the water molecule once the water molcule has been thermally removed. The four methyl groups surrounding the site (Figure 2a) restrict the accessibility of the site sterically so as to allow those amine molecules with the amine group attached only to a methylene group to form a dative bond between the nitrogen atom and the cadmium atom. Therefore coordination bond formation is the driving force for the intercalation reaction.

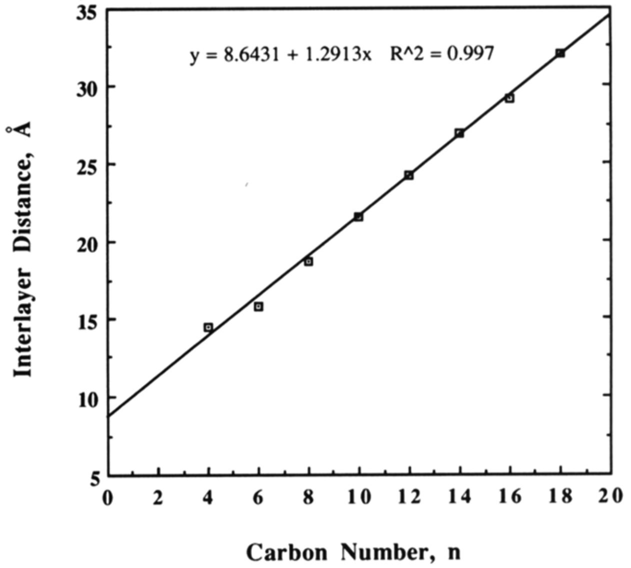


Figure 7. Plot of interlayer distance vs number of carbon atoms in the *n*-alkyl chain for $Cd(O_3PCH_3)(n\text{-}C_nH_{2n+1}NH_2)$. The equation is the least-squares fit of data.

It is quite surprising that $Cd(O_3PC_6H_5)$ also reacts with amines when dehydrated, although very slowly, contrary to the behavior of the isostructural cobalt and zinc phenylphosphonates whose bulky phenyl groups only allow enough space for ammonia molecules to intercalate.[3c] Therefore there must be structural changes associated with the reaction process. There is indication that the reaction might proceed through dissolution–recrystallization mechanism. The study to clarify this point is continuing.

It occurred to us that sulfur compounds might also form intercalation compounds because of the propensity of sulfur atoms to form Cd–S bonds. The exposure of $Cd(O_3PCH_3)$ to H_2S, however, leads to the formation of CdS. It was found that the very weakly basic alkanethiols intercalate into the dehydrated cadmium phenylphosphonates with layer expansion and that cadmium methylphosphonate reacts with alkanethiols with the destruction of its layer structure. The results of this research will be reported subsequently.

Acknowledgment. We thank Jim Pizzulli for SEM analyses and Jim Mumford for reacting cadmium phosphonate with hydrogen sulfide. Helpful discussions with Dr. Jack W. Johnson are gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms of $Cd(O_3PCH_3){\cdot}H_2O$, fractional coordinates and isotropic thermal parameters for the hydrogen atoms of $Cd(O_3PCH_3){\cdot}H_2O$, bond lengths and angles involving the hydrogen atoms in $Cd(O_3PCH_3){\cdot}H_2O$, and anisotropic thermal parameters for the ordered atoms of $Cd(O_3PC_6H_5){\cdot}H_2O$ (2 pages): observed and calculated structure factors for both structures (6 pages). Ordering information is given on any current masthead page.

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[17] Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; pp 48–62.