nificant overlap, the infrared band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1825 to 1725 cm^{-1} at 2-cm^{-1} intervals and entered into files on the university VAX 11/85 computer. Following base-line correction, the spectra were fit by a model consisting of Lorentzian band shapes, each characterized by a peak frequency (ν), maximum intensity (I), and half-width (fwhh) (Δ). Since the instrument resolution (2 cm^{-1}) is far less than the observed bandwidths (~20 cm^{-1}), it was unnecessary to convolute the model spectrum with a resolution (slit) function. The parameters were varied to minimize the squared deviation between the experimental and calculated intensities by using a standard nonlinear regression procedure.[54] A representative experimental and calculated spectrum of [**2**][Na] at −70 °C is shown in Figure 4. Given that the area of a Lorentzian peak is proportional to the product of the bandwidth and the maximum intensity, the area ratio of the different ion pairs is calculated easily as $A_2/A_1 = (I_2\Delta_2)/(I_1\Delta_1)$.

Thermodynamic Evaluation of the Ion-Pairing Equilibrium in [2][Na]. THF solutions 2.5×10^{-3} M in [**2**][Na] (vide supra) were used to measure the amount of contact and solvent-separated ion pairs in solution over the temperature range of −70 °C to room temperature. From the area associated with each antisymmetric carbonyl stretching band, the equilibrium constants were easily determined as defined by eq 3. The thermodynamic parameters were obtained by plotting ln K_{eq} vs T^{-1}, from which the slope and intercept afforded ΔH and ΔS, respectively. The error limits associated with the enthalpy and entropy for ion pairing were calculated by using the available least-squares regression program[55] and should not be taken to reflect uncertainties in sample preparation, band-area intensities, or temperature control but rather the deviation of the data points about the least-squares line.

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Supplementary Material Available: An ORTEP view of the [PPP^+] cation and a table of anisotropic thermal parameters (3 pages); a listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of Layered Calcium and Lanthanide Phosphonate Salts

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The crystal structures of two layered calcium phosphonate salts, $Ca(O_3PCH_3)\cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$, were solved by single-crystal X-ray diffraction. $Ca(O_3PCH_3)\cdot H_2O$ is monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 8.8562$ (13) Å, $b = 6.6961$ (10) Å, $c = 8.1020$ (10) Å, $\beta = 96.910$ (11)°, and $V = 476.97$ (12) Å^3. Ca atoms are coordinated by six oxygen atoms at a distance of ca. 2.4 Å, and by a seventh at 2.7 Å, making the coordination environment a distorted pentagonal bipyramid. In this salt, and in the structurally related $M(O_3PC_nH_{2n+1})\cdot H_2O$ ($n \leq 5$; M = Ca, Cd) series, the metal–phosphonate coordination is 5:5. $Ca(HO_3PC_6H_{13})_2$ is triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 5.606$ (2) Å, $b = 7.343$ (3) Å, $c = 21.158$ (7) Å, $\alpha = 97.31$ (3)°, $\beta = 96.98$ (3)°, $\gamma = 90.43$ (4)°, and $V = 857.2$ (6) Å^3. In this structure and the related $Ca(HO_3PC_nH_{2n+1})_2$ ($6 < n < 18$) series, the Ca atoms lie in approximately coplanar sheets and are coordinated by six oxygen atoms from different phosphonate groups lying above and below the plane. This structure is closely related to that of α-$Zr(HPO_4)_2\cdot H_2O$ and the tetravalent metal phosphonates $M(O_3PR)_2$ (M = Zr, Hf, Ti, Ce). Layered trivalent metal phosphonate salts $MH(O_3PR)_2$ (R = alkyl, phenyl; M = La, Sm, Ce) were also prepared. $LaH(O_3PCH_3)_2$ is triclinic with $Z = 2$, $a = 5.398$ (7) Å, $b = 8.168$ (18) Å, $c = 10.162$ (19) Å, $\alpha = 73.76$ (16)°, $\beta = 83.89$ (13)°, $\gamma = 73.50$ (14)°, and $V = 412.3$ (13) Å^3. The structure of the $MH(O_3PR)_2$ compounds appears to be closely related to that of the other 1:2 layered metal phosphonate salts $Ca(HO_3PC_nH_{2n+1})_2$ and $M(O_3PR)_2$.

Introduction

There has been considerable interest in the synthesis of new layered metal phosphonate salts,[1-6] because these materials have robust yet flexible structures. They are hybrid organic/inorganic materials in which the structure is directed by the choice of metal and reaction conditions and the nature of the interlayer region depends on the organic moiety. Since pillared[3] and intercalated[3,6] structures can be easily generated, they have been extensively investigated as catalysts, sorbents, and ion exchangers.

Frequently the structures of new metal phosphonates (which are often difficult to prepare as single crystals) can be related to those of known inorganic or mineral phosphates. For example, the structures of the tetravalent metal phosphonates $M(O_3PR)_2$ (M = Zr, Ti, Hf, Ce, Th) are believed[3-6] to be closely related to that of α-zirconium phosphate, $Zr(O_3POH)_2\cdot H_2O$, which was solved in 1969 by Clearfield and Smith.[7] Likewise, the vanadyl phosphonates $VO(RPO_3)\cdot H_2O\cdot R'OH$ described by Johnson and Co-workers[8] appear to be derived from the newberyite, $Mg(O_3POH)\cdot 3H_2O$, structure.[9]

Recently, we demonstrated that insoluble tetravalent and trivalent metal phosphonates, $M(O_3PR)_2$ and $MH(O_3PR)_2$, could

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be prepared as inorganic surface-bound multilayer structures analogous to Langmuir–Blodgett films.[6] This finding led us to carry out a systematic structural investigation of di- and trivalent metal phosphonates, for which detailed structural data were lacking. Cunningham et al.[10] had reported the synthesis of a group of divalent metal phenylphosphonates $M^{II}(O_3PC_6H_5)\cdot H_2O$ (M = Mg, Mn, Co, Cu, Ni) and had deduced that these compounds contained metal ions in octahedral coordination, but were unable to carry out X-ray structure determinations. The structures of $Mn(O_3PC_6H_5)\cdot H_2O$ and $Zn(O_3PC_6H_5)\cdot H_2O$ were subsequently solved by us[11] and independently by Clearfield and co-workers,[12] who pointed out the relationship between these structures and those of inorganic relatives $M(O_3PO\cdot NH_4)\cdot H_2O$ (M = Fe, Cd, Mn[13]). In our previous paper,[11] we described the syntheses of two series of divalent metal phosphonates, $M(O_3PR)\cdot H_2O$ (M = Mg, Mn, Zn, Ca, Cd; R = *n*-alkyl, aryl group) and $M(HO_3PR)_2$ (M = Ca). For M = Mg, Mn, or Zn in the first series, the phosphonates crystallize in the orthorhombic layered structure of $Mn(O_3PC_6H_5)\cdot H_2O$, with appropriate interlayer distances to accommodate the different R groups. For M = Ca or Cd in the same series, however, a different type of structure, apparently of lower symmetry, is adopted. In the second series, calcium forms 1:2 salts with phosphonic acids. The factor that determines the series into which the calcium phosphonates fall is the length of the *n*-alkyl chain, i.e. $Ca(O_3PC_nH_{2n+1})\cdot H_2O$ for $n = 1-5$ and $Ca(HO_3PC_nH_{2n+1})_2$ for $n > 5$ (n can be at least 18, which is the longest chain length we have used).

While it is not surprising that the 1:1 calcium phosphonates do not adopt the orthorhombic structure of $Mn(O_3PC_6H_5)\cdot H_2O$, because of the much larger ionic radius of Ca^{2+}, the new structural types of the 1:1 and 1:2 calcium phosphonates clearly warranted a structural investigation. In this paper, we present single-crystal X-ray structures of members of both the 1:1 and 1:2 calcium phosphonate families, $Ca(O_3PCH_3)\cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$. In addition, we report the synthesis and preliminary structural characterization of new family of trivalent metal phosphonates $LnH(O_3PR)_2$ (Ln = La, Sm, Ce). To our knowledge, the only trivalent metal phosphonate previously reported is $FeH(O_3PCH_3)_2$,[14] which is thought to be layered with an interlayer spacing of 12.09 Å The new crystallographic data presented here indicate a close structural relationship between the di-, tri-, and tetravalent metal phosphonate salts in which the metal:phosphonate ratio is 1:2.

Experimental Section

Materials and Methods. Reagents and solvents used were of reagent grade quality and were obtained from commercial sources. Alkyl- and arylphosphonic acids were available from a previous study.[11] Deionized water was purified to a resistivity of 18.3 MΩ cm with a Barnstead Nanopure II system (Sybron Corp.) and was used in all experiments. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. X-ray powder diffraction (XRD) patterns were obtained with a Phillips diffractometer using monochromatized Cu Kα radiation. Thermogravimetric analyses (TGA) were performed with a Perkin-Elmer 7 series thermal analysis system with a typical heating rate of 10 °C/min under flowing nitrogen. Infrared spectra were recorded on a Mattson CYGNUS 100 FTIR spectrophotometer with parameters adjusted to give 4 cm^{-1} resolution.

Table I. Crystallographic Data for $Ca(O_3PCH_3)\cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$

	$Ca(O_3PCH_3)\cdot H_2O$	$Ca(HO_3PC_6H_{13})_2$
a, Å	8.8562 (13)	5.606 (2)
b, Å	6.6961 (10)	7.343 (3)
c, Å	8.1020 (10)	21.158 (7)
α, deg	90.0	97.31 (3)
β, deg	96.910 (11)	96.98 (3)
γ, deg	90.0	90.43 (4)
V, $Å^3$	476.97 (12)	857.2 (6)
Z	4	2
fw	152.10	370.38
space group	$P2_1/c$	$P\bar{1}$
T, °C	25	−75
λ(Mo Kα), Å	0.7107	0.7107
ρ_{obs}, g/cm^3 (−75 °C)	2.12	1.43
μ, cm^{-1}	15.13	5.604
transm coeff	0.7364–0.7805	0.8145–0.9672
R	0.0402	0.0566
R_w	0.0654	0.0696

Compound Syntheses and Properties. The synthesis of divalent metal phosphonates have been described elsewhere.[11] The change in the homologous series from $Ca(O_3PC_nH_{2n+1})\cdot H_2O$ to $Ca(HO_3PC_nH_{2n+1})_2$ occurs at $n = 6$, where the phosphonic acids $C_nH_{2n+1}PO_3H_2$ begin to be insoluble in water. Since the longer chain phosphonic acids are dissolved in alcoholic (methanol or ethanol) aqueous media in the synthesis of compounds with $n \geq 6$, an experiment was carried out to determine whether the alcoholic medium drives the formation of 1:2 salts. Ca^{2+} was thus precipitated with *n*-pentylphosphonic acid in alcoholic aqueous media. The precipitate obtained was identified by elemental analysis, TGA, and XRD to be $Ca(O_3PC_5H_{11})\cdot H_2O$, indicating that the medium in which calcium phosphonates are prepared is not the sole cause of the difference in stoichiometry between the two groups. In a similar fashion, trivalent metal phosphonates were prepared by combining an aqueous solution of $Ln(NO_3)_3\cdot 5H_2O$ (Ln = La, Sm, Ce) with either an aqueous or an alcoholic aqueous solution of a phosphonic acid. In cases where precipitation did not occur upon combining the solutions, 0.1 M aqueous NaOH was added dropwise while the mixture was vigorously stirred. The resulting white precipitate in its mother liquor was kept at 70 °C for several days in order to promote Ostwald ripening of crystallites. The precipitate was filtered, washed with water and ethanol, and dried at 70 °C in air. Elemental analysis confirmed that the composition of these solids was $LnH(O_3PR)_2$. With comparable R groups, the solubility of the trivalent metal phosphonates is intermediate between that of divalent and tetravalent metal phosphonates, which are, respectively, soluble at pH 1–5 and are almost insoluble in any aqueous medium.

Crystal Growth. Single crystals of $Ca(O_3PCH_3)\cdot H_2O$ were grown in a U-tube half-filled with agar gel. One arm of the tube contained ca. 10 mL of an 0.1 M aqueous solution of $CaCl_2$, and the other contained the same volume of 0.1 M aqueous $CH_3PO_3H_2$ neutralized with NaOH to pH 6.5. After a period of 3 months, crystals of parallelpiped shape grew near the center of the tube. The crystals were taken out along with the gel and were isolated by dissolving the gel away in hot water. Single crystals of $Ca(HO_3PC_6H_{13})_2$ were grown by first mixing equal volumes of 0.1 M aqueous $CaCl_2$ and 0.2 M ethanolic *n*-hexylphosphonic acid. A white precipitation formed immediately, which was then dissolved by adding a few drops of 1 M HCl. To the clear solution so obtained was added 2 mol of urea/mol of *n*-hexylphosphonic acid. This clear solution was thermostated at 55 °C. After 2 weeks, clusters of colorless platelike crystals were formed from both the surface and the bottom of the solution. It was found that 55 °C was the best temperature for slow crystal growth. The urea served to increase the pH value of the solution homogeneously as it was hydrolyzed. The final pH of the solution after crystal growth was about 5. Single crystals of $LaH(O_3PCH_3)_2$ were grown similarly, except that HCl was not added because precipitation did not form when the solutions of $La(NO_3)_3\cdot 5H_2O$ and $CH_3PO_3H_2$ were combined.

Single-Crystal X-ray Diffraction. The data crystal for $Ca(O_3PCH_3)\cdot H_2O$ was a colorless block of approximate dimensions 0.19 × 0.20 × 0.23 mm. Data were collected at room temperature on a Nicolet R3 diffractometer equipped with a graphite monochromator. The crystal system is monoclinic and the space group is $P2_1/c$ (No. 14) as uniquely determined from systematically absent reflections. Lattice parameters were obtained from least-squares refinement of 46 reflections with 24.9

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Table II. Unit Cell Parameters and Elemental Composition of $MH(O_3PR)_2$ Salts

chem formula	$LaH(O_3PCH_3)_2$	γ, deg	73.50 (14)
a, Å	5.398 (7)	V, Å^3	412.3 (13)
b, Å	8.168 (18)	Z	2
c, Å	10.162 (19)	ρ_{calc}, g/cm^3	2.64 (1)
α, deg	73.76 (16)	ρ_{obs}, g/cm^3	2.65 (2)
β, deg	83.89 (13)		

chem formula	% C found (calcd)	% H found (calcd)	d_{001}, Å
$LaH(O_3PCH_3)_2$	7.40 (7.32)	2.09 (2.15)	9.6 (1)
$LaH(O_3PC_2H_5)_2$	12.70 (13.50)	2.89 (3.11)	12.1 (1)
$LaH(O_3PC_6H_5)_2$	31.77 (31.88)	2.46 (2.46)	15.6 (1)
$LaH(O_3PC_7H_{15})_2$	33.84 (33.88)	6.31 (6.30)	24.4 (2)
$SmH(O_3PC_7H_{15})_2$	33.00 (33.12)	6.17 (6.15)	24.8 (2)
$CeH(O_3PCH_3)_2$	7.24 (7.30)	2.10 (2.14)	9.6 (1)
$CeH(O_3PC_6H_5)_2$	31.89 (31.80)	2.45 (2.45)	15.6 (1)

$< 2\theta < 29.9°$. Data were collected out to 60° in 2θ by using the ω scan technique, with a 1.2° scan range in ω at 5–10°/min. A total of 5764 reflections were measured (−12 to +12 in h; −9 to +9 in k; −11 to +11 in l) of which 1400 were unique (R for averaging equivalent reflections = 0.0471). Four reflections were remeasured every 146 reflections to monitor instrument and crystal stability. The intensities of these reflections deviated by less than 1%. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located from a ΔF map and their positions were refined with isotropic thermal parameters. Crystal data and cell parameters for $Ca(O_3PCH_3)\cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$ are listed in Table I. The data crystal for $Ca(HO_3PC_6H_{13})_2$ was a colorless plate of approximate dimentions 0.06 × 0.21 × 0.64 mm. Data were collected at −75 °C on a Nicolet R3 diffractometer, equipped with a graphite monochromator and a Nicolet LT-2 low-temperature delivery system. The crystal system is triclinic and the space group is $P\bar{1}$ (No. 2). Lattice parameters were obtained from least-squares refinement of 37 reflections with $11.0 < 2\theta < 28.9°$. Data were collected out to 50° in 2θ by using the ω scan technqiue, with a 1.6° scan range in ω at 4–8°/min. A total of 3542 reflections were measured (0 to +6 in h; −8 to +8 in k; −25 to +25 in l) of which 3013 were unique (R for averaging equivalent reflections = 0.0277). Four reflections were remeasured every 96 reflections to monitor instrument and crystal stability. The intensities of these reflections deviated by less than 2%. The structure was solved by heavy-atom methods, as for $Ca(O_3PCH_3)\cdot H_2O$. Although $Ca(HO_3PC_6H_{13})_2$ has triclinic symmetry, the cell can be transformed by (102, 100, 010) into a C-centered cell of dimensions a = 42.005 (14) Å, b = 5.606 (2) Å, c = 7.343 (3) Å, α = 90.43 (4), β = 97.42 (3), γ = 89.36 (3)°, V = 1714 Å^3. While α and γ for this cell are nearly 90°, the diffraction symmetry is clearly not monoclinic as evidenced by an axial photograph of the 5.606-Å axis, an examination of the intensities of selected hkl and $h,-k,l$ reflections, and by the very high internal R for averaging reflections which would be equivalent in a monoclinic C-centered cell ($R_{internal}$ after the transformation was 31.9% for 1520 reflections). The data reduction, absorption correction, structure solution, and initial refinement for both structures were done by using SHELXTL-PLUS[15] and the final refinement was done by using SHELX76.[16] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_0) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$. Intensity, I, was given by $(I_{peak} - I_{bkgd})$ (scan rate); 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: $\sigma(I) = [(I_{peak} + I_{bkgd})^{1/2}$ (scan rate)]. For $Ca(O_3PCH_3)\cdot H_2O$ the final R = 0.0402 for 1272 reflections for which $F_o \geq 6\sigma(R_o)$,[17] R_w = 0.0654 (for all reflections, R = 0.0439, R_w = 0.0669) and a goodness of fit = 2.791. Maximum $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were −1.16 and 0.72 e/Å^3. For $Ca(HO_3PC_6H_{13})_2$ the final R = 0.0566 for 2239 reflections for which $F_o \geq 6\sigma(F_3)$, R_w = 0.0696 (for all reflections, R = 0.0723, R_w = 0.0729) and a goodness of fit = 2.133. Maximum $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were −0.83 and 0.95 e/Å^3. The scattering factors for the non-hydrogen atoms were taken from Cromer and Mann,[18] with anomalous dispersion corrections taken from Cromer and Liberman,[19] while scattering factors for the H atoms were obtained from Stewart, Davidson, and Simpson;[20] the linear absorption coefficient was calculated from values found in ref 21. Figures were generated by using SHELXTL-PLUS. Other computer programs used are listed in ref 11 of Gadol and Davis.[22]

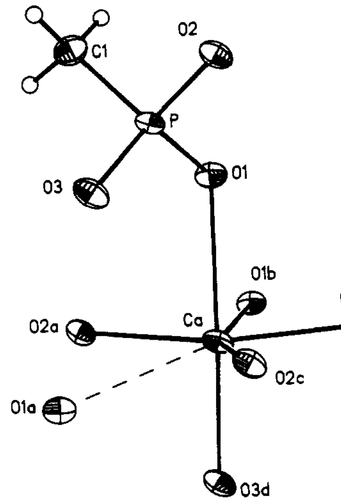

Figure 1. Thermal ellipsoid drawing showing the 7-coordination of Ca^{2+} in $Ca(O_3PCH_3)\cdot H_2O$. The dotted Ca–O bond length is 2.707 (2) Å, while all other Ca–O bonds are ca. 2.4 Å. Ellipsoids are shown with 50% probability. O atoms labeled with a are related by x, $^1/_2 - y$, $^1/_2 + z$, O atoms labeled with b are related by $-x$, $-y$, $-z$, O atoms labeled with c are related by $-x$, $1 - y$, $-z$, and O atoms labeled with d are related by $-x$, $^1/_2 + y$, $^1/_2 + z$.

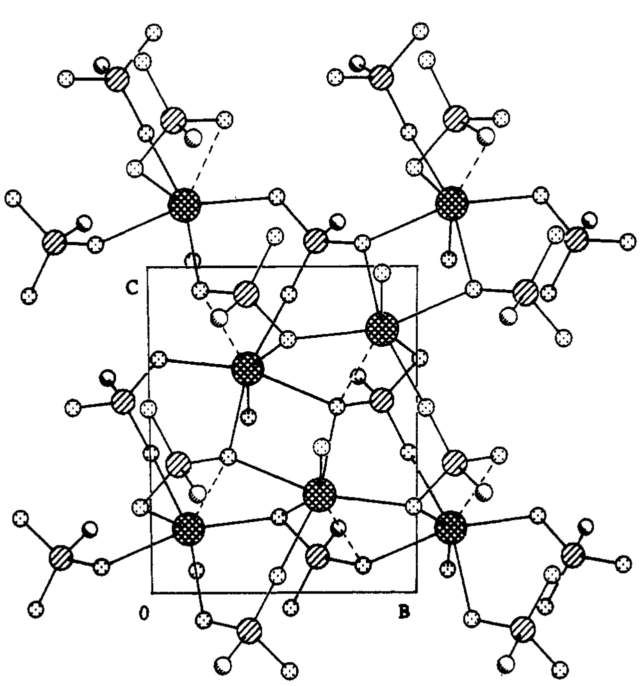

Figure 2. View down one sheet of $Ca(O_3PCH_3)\cdot H_2O$ down the a axis. Hydrogen atoms are omitted for clarity. The rectangular frame represents the unit cell in the plane of the figure.

Crystallites of $LaH(O_3PCH_3)_2$ and other $MH(O_3PR)_2$ derivatives grew as extremely fragile, thin flakes. It was difficult to find untwinned crystals of suitable size for single-crystal X-ray diffraction. After many tries, precession photographs (vide infra) were obtained with a LaH-

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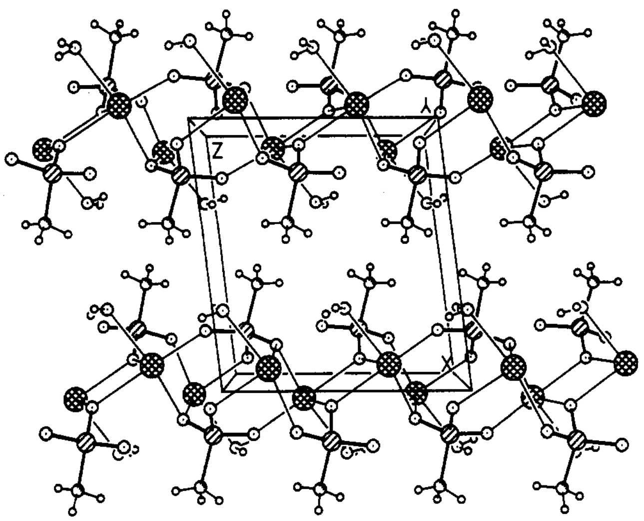

Figure 3. Packing diagram for $Ca(O_3PCH_3){\cdot}H_2O$ showing the layered structure and unit cell.

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

atom	*x*	*y*	*z*	*U*
Ca	0.07442 (5)	0.13443 (6)	0.19094 (5)	0.0145 (2)
P	−0.19306 (7)	0.37631 (8)	−0.08814 (7)	0.0122 (2)
O1	−0.0786 (2)	0.2013 (2	−0.0730 (2)	0.0163 (4)
O2	−0.1462 (2)	0.5215 (2)	0.2209 (2)	0.0165 (4)
O3	−0.2001 (2)	0.4803 (2)	0.0779 (2	0.0196 (5)
O4	0.2906 (2)	0.1433 (3)	0.0333 (3)	0.0238 (6)
C1	−0.3804 (3)	0.2907 (4	−0.1606 (3)	0.0210 (6)

[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 *i*th and *j*th direct space unit cell vectors.

$(O_3PCH_3)_2$ specimen, which showed triclinic symmetry. Unit cell parameters were determined with the Nicolet R3 diffractometer at −75 °C, from least-squares refinement of 24 reflections with $16.0 < 2\theta < 25.3°$. Crystallographic data for $LaH(O_3PCH_3)_2$ are summarized in Table II. Table II also lists elemental analysis results for the other trivalent metal phosphonates prepared and their interlayer distances as determined by X-ray powder diffraction. The accuracy of cell parameters derived for $LaH(O_3PCH_3)_2$ is supported by crystal density measurement (flotation method with mixture of CH_2I_2 and $CHCl_3$) as shown in Table II.

Results and Discussion

Structure of $Ca(O_3PCH_3){\cdot}H_2O$. Figure 1 shows the coordination environment of Ca and P in $Ca(O_3PCH_3){\cdot}H_2O$, while the crystal packing is shown in Figures 2 and 3. Positional and thermal parameters of atoms in the structure are given in Table III; selected bond lengths and angles are listed in Table IV. The Ca atoms in $Ca(O_3PCH_3){\cdot}H_2O$ have an approximately pentagonal-bipyramidal coordination, with five nearly coplanar oxygen atoms in the coordination sphere. One of the seven oxygen atoms (O1 related by x, $^1/_2 - y$, $^1/_2 + z$) surrounding the Ca atom has a bond length of 2.707 (2) Å, while all the others have bond lengths in the range 2.305 (2)–2.445 (2) Å. (The long Ca–O bond is shown as a dotted line in Figures 1 and 2). If this longer contact is ignored (although such distances are not uncommon for Ca–O bonds), the coordination of the Ca atom is a very distorted octahedron. The three oxygen atoms of the methylphosphonate group are all bonded to Ca atoms in different fashions. O1 is bonded to three Ca atoms (counting the long Ca–O bond), while O2 forms a 2.399 (2)-Å bond with the same Ca atom that is coordinated by O1 through the long Ca–O bond; the phosphonate group is therefore chelating. O2 also forms a bond at 2.395 (2) Å to a fourth Ca, and O3 is singly bonded to a fifth Ca atom. Therefore, the metal–phosphonate coordination in this compound is 5:5, in contrast to 4:4 for the orthorhombic $M(O_3PR){\cdot}H_2O$, in which a chelating phosphonate group is also found.[11,12] It is apparent from Figure 3 that $Ca(O_3PCH_3){\cdot}H_2O$ has a layered structure with sheets of neutral $Ca(O_3PCH_3){\cdot}H_2O$ units stacked along the crystallographic *a* axis. Rows of methyl groups running along the *c* direction and with P–C bonds pointing out of the sheets fall into the grooves formed by the identically arranged methyl groups on the adjacent sheet, making a very efficient space-filling packing. The methyl groups on the adjacent sheets are symmetry-related by 2-fold screw axes in the *b* direction.

Table IV. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Ca(O_3PCH_3){\cdot}H_2O$

atom				
1	2	3	1–2	1–2–3
O1	Ca	O4	2.432 (2)	85.64 (6)
O1	Ca	O2[a]		87.38 (6)
O1	Ca	O1[b]		81.88 (5)
O1	Ca	O2[c]		91.44 (5)
O1	Ca	O3[d]		163.92 (6)
O1	Ca	O1[a]		105.84 (5)
O2[a]	Ca	O4	2.399 (2)	152.84 (6)
O2[a]	Ca	O1[b]		76.53 (5)
O2[a]	Ca	O2[c]		127.19 (6)
O2[a]	Ca	O3[d]		83.92 (6)
O2[a]	Ca	O1[a]		58.10 (5)
O4	Ca	O1[b]	2.427 (2)	76.51 (6)
O4	Ca	O2[c]		79.24 (6)
O4	Ca	O3[d]		96.00 (7)
O4	Ca	O1[a]		148.85 (6)
O2[c]	Ca	O1[c]	2.395 (2)	155.25 (6)
O2[c]	Ca	O3[d]		104.60 (6)
O2[c]	Ca	O1[a]		71.75 (5)
O3[d]	Ca	O1[d]	2.305 (2)	82.95 (6)
O3[d]	Ca	O1[a]		80.88 (6)
O1[b]	Ca	O1[a]	2.445 (2)	133.01 (5)
O1[a]	Ca		2.707 (2)	
O1	P	O2	1.544 (2)	107.71 (10)
O1	P	O3		111.92 (9)
O2	P	O3	1.544 (2)	111.74 (9)
O2	P	C1		106.86 (11)
O3	P	C1	1.523 (2)	107.59 (12)
C1	P	O1	1.786 (3)	110.94 (10)

[a] Atom related by x, $0.5 - y$, $0.5 + z$. [b] Atom related by $-x$, $-y$, $-z$. [c] Atom related by $-x$, $1 - y$, $-z$. [d] Atom related by $-x$, $-0.5 + y$, $0.5 - z$.

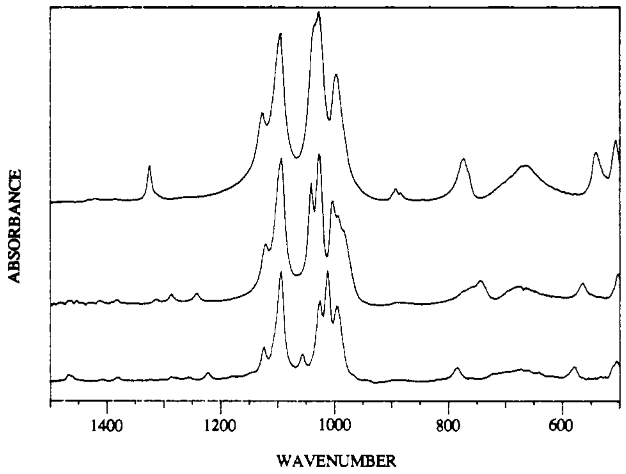

Figure 4. Infrared spectra of $Ca(O_3PCH_3){\cdot}H_2O$ (top), $Ca(O_3PC_2H_5){\cdot}H_2O$ (middle), and $Ca(O_3PC_5H_{11}){\cdot}H_2O$ (bottom). Similar spectra in the region of the P–O stretching frequencies (950–1150 cm^{-1}) are indicative of similar structural features. The absorption at 1324 cm^{-1} of $Ca(O_3PCH_3){\cdot}H_2O$ is attributed to ν_{P-CH_3}.

On the basis of the structure of $Ca(O_3PCH_3){\cdot}H_2O$, it is reasonable to assume that members of the homologous series $Ca(O_3PC_nH_{2n+1}){\cdot}H_2O$ (n = 1–5) have the same calcium–oxygen–phosphorus–water network as that shown in Figure 2. This conclusion is supported by similar P–O stretching features in the infrared spectra, which are very sensitive to local symmetry, for compounds in this series (Figure 4) and by the smooth increase of the interlayer distance with increasing n.[11b] The ideal procedure for establishing such a structural relationship would be to index

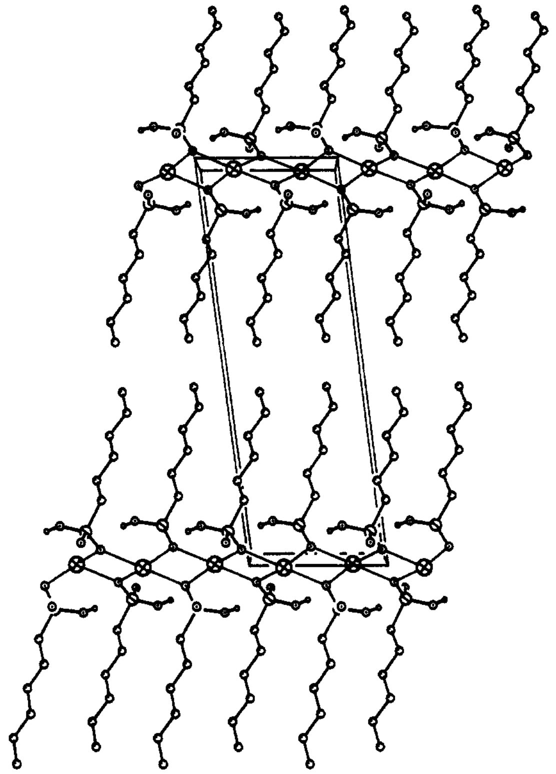

Figure 5. Packing diagram showing the unit cell and layered structure of $Ca(HO_3PC_6H_{13})_2$, viewed parallel to the *a* axis. Hydrogen atoms bonded to carbon are omitted for clarity.

Table V. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters ($Å^2$) for Non-Hydrogen Atoms of $Ca(HO_3PC_6H_{13})$

atom	*x*	*y*	*z*	*U*
Ca	0.1303 (2)	0.75023 (14)	0.00003 (5)	0.0122 (3)
P1	−0.2791 (2)	0.8936 (2)	0.09437 (6)	0.0128 (4)
P2	−0.3699 (2)	0.6040 (2)	−0.09378 (6)	0.0128 (4)
O1	−0.5497 (6)	0.8783 (5)	0.0752 (2)	0.0155 (11)
O2	−0.1649 (7)	0.7047 (5)	0.1062 (2)	0.0217 (13)
O3	−0.1431 (6)	0.9668 (5)	0.0459 (2)	0.0171 (12)
O4	−0.6262 (6)	0.6213 (5)	−0.0776 (2)	0.0152 (11)
O5	−0.2668 (7)	0.7924 (6)	−0.1072 (2)	0.0236 (14)
O6	−0.1946 (6)	0.5364 (5)	−0.0428 (2)	0.0162 (11)
C1	−.2217 (10)	1.0322 (8)	0.1715 (2)	0.018 (2)
C2	0.0072 (10)	0.9967 (8)	0.2146 (3)	0.018 (2)
C3	0.0412 (11)	1.1397 (9)	0.2742 (3)	0.026 (2)
C4	0.2529 (12)	1.1111 (9)	0.3233 (3)	0.026 (2)
C5	0.2736 (13)	1.2582 (10)	0.3818 (3)	0.038 (2)
C6	0.483 (2)	1.2317 (12)	0.4325 (4)	0.046 (3)
C7	−0.3617 (10)	0.4598 (7)	−0.1688 (2)	0.016 (2)
C8	−0.5536 (11)	0.4962 (8)	0.2226 (3)	0.021 (2)
C9	−0.5598 (11)	0.3559 (9)	−0.2821 (3)	0.025 (2)
C10	−0.7666 (12)	0.3818 (9)	−0.3337 (3)	0.030 (2)
C11	−0.7793 (14)	0.2385 (11)	−0.3928 (3)	0.042 (3)
C12	−0.989 (2)	0.2669 (14)	−0.4430 (4)	0.056 (3)

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

the X-ray powder patterns of all four compounds in the series, using the *b* and *c* cell dimensions of $Ca(O_3PCH_3)\cdot H_2O$, and allowing *a* and *β* values to vary (*a* and *β* are related to the interlayer distance *d* by $d = a \sin \beta$). We were unable to do this in the present case because, despite an easily identified progression of reflections corresponding to harmonics of interlayer distance, the powder patterns generally did not have a sufficient number of resolved *hkl* lines to permit accurate indexing. The interlayer spacings obtained in this series from powder data are given in ref 11b.

Structure of $Ca(HO_3PC_6H_{13})_2$. The structure of $Ca(HO_3PC_6H_{13})_2$ is also layered, as shown in the packing diagram, Figure 5. Positional and thermal parameters of atoms in the $Ca(HO_3PC_6H_{13})_2$ structure are given in Table V; bond lengths and angles are listed in Table VI. This structure is composed of neutral sheets of $Ca(HO_3PC_6H_{13})_2$ stacked along the crystallographic *c* axis. The Ca atoms within a single sheet lie almost in a common plane. The phosphonate groups are disposed above and below with the hexyl group pointing away from the Ca plane. A distorted octahedral coordination (Figure 6) around Ca^{2+} is achieved through the coordination of six $C_6H_{13}PO_3H^-$ groups, which are alternately displaced above and below the Ca plane.

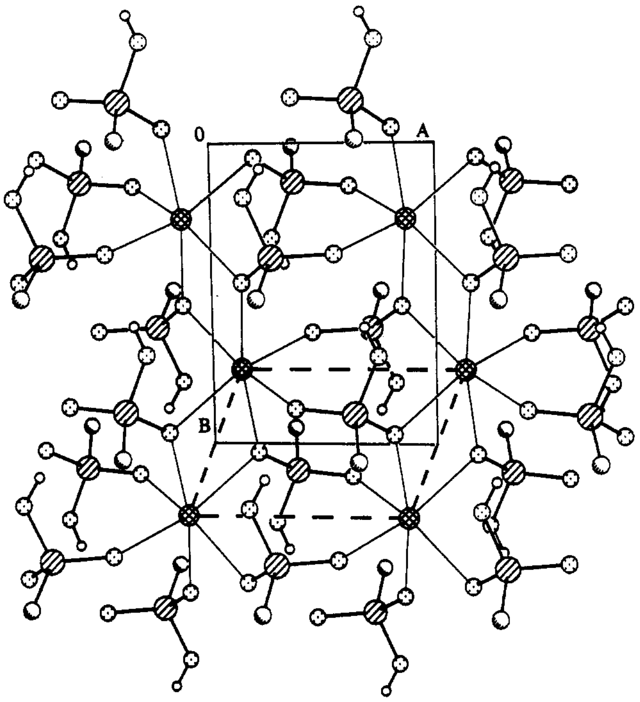

Figure 6. View down the *c* axis of a single sheet of $Ca(HO_3PC_6H_{13})_2$, showing the coordination environment around Ca^{2+}. Hydrogen and carbon atoms of the alkyl chain, except for the carbon atom bonded to phosphorus, are omitted for clarity. Solid lines show the unit cell in this projection. The dotted parallelogram is the portion compared to $Zr(O_3PR)_2$ in Figure 7.

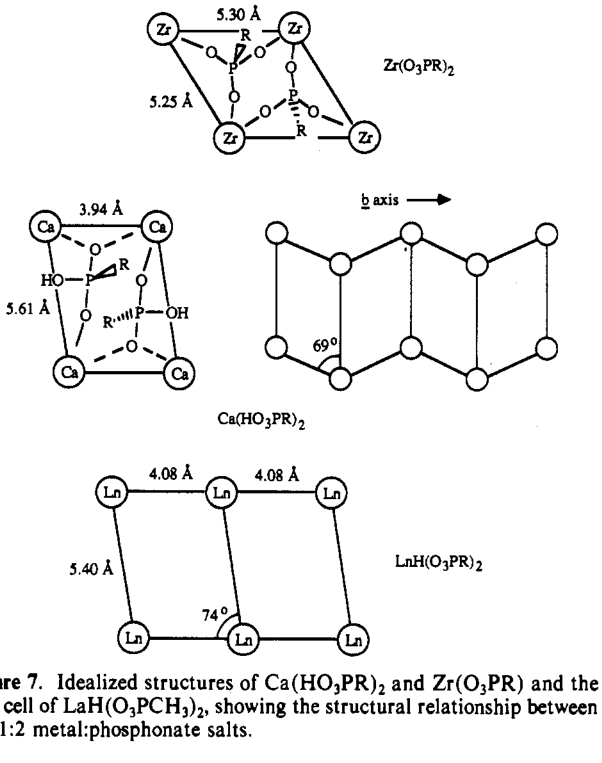

Figure 7. Idealized structures of $Ca(HO_3PR)_2$ and $Zr(O_3PR)$ and the unit cell of $LaH(O_3PCH_3)_2$, showing the structural relationship between the 1:2 metal:phosphonate salts.

Table VI. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Ca(HO_3PC_6H_{13})_2$

atom				
1	2	3	1–2	1–2–3
O1[a]	Ca	O3	2.353 (3)	90.77 (12)
O1[a]	Ca	O4[a]		95.84 (12)
O1[a]	Ca	O6		156.04 (12)
O1[a]	Ca	O3[b]		85.92 (12)
O1[a]	Ca	O6[c]		88.14 (12)
O3	A	O6	2.413 (4)	91.55 (12)
O3	Ca	O4[a]		156.14 (12)
O3	Ca	O3[b]		69.59 (12)
O3	Ca	O6[c]		119.35 (12)
O4*a*	Ca	O6	2.372 (3)	91.59 (12)
O4[a]	Ca	O3[b]		88.00 (12)
O4[a]	Ca	O6[c]		83.85 (12)
O6	Ca	O3[b]	2.408 (4)	117.15 (12)
O6	Ca	O6[c]		70.02 (11)
O3[b]	Ca	O6[c]	2.408 (4)	169.38 (12)
O6[c]	Ca		2.408 (4)	
O1	P1	O2	1.522 (3)	112.7 (2)
O1	P1	O3		114.1 (2)
O2	P1	O3	1.568 (4)	106.0 (2)
O2	P1	C1		104.0 (2)
O3	P1	C1	1.499 (4)	111.2 (2)
C1	P1	O1	1.801 (5)	108.3 (2)
O4	P2	O5	1.519 (4)	111.3 (2)
O4	P2	O6		114.9 (2)
O5	P2	O6	1.567 (5)	106.8 (2)
O5	P2	C7		102.9 (2)
O6	P2	C7	1.504 (4)	109.5 (2)
C7	P2	O4	1.798 (5)	110.6 (2)
C2	C1	P1	1.526 (7)	117.6 (4)
C3	C2	C1	1.527 (8)	110.5 (5)
C4	C3	C2	1.513 (8)	115.5 (5)
C5	C4	C3	1.529 (9)	112.5 (5)
C6	C5	C4	1.522 (10)	113.7 (6)
C8	C7	P2	1.519 (8)	115.2 (4)
C9	C8	C7	1.520 (8)	113.3 (5)
C10	C9	C8	1.523 (8)	113.3 (5)
C11	C10	C9	1.522 (9)	113.8 (6)
C12	C11	C10	1.520 (11)	112.6 (7)

[a] Atom related by $1 + x, y, z$. [b] Atom related by $-x, 2 - y, -z$. [c] Atom related by $-x, 1 - y, -z$.

The six Ca–O bond lengths are in the range 2.353 (3)–2.413 (4) Å. The most unusual feature of this crystal structure is that the hydroxyl group of $C_6H_{13}PO_3H^-$ is not involved in coordination to Ca, resulting in the sharing of one oxygen atom of $C_6H_{13}PO_3H^-$ between two calcium atoms. This arrangement of metal and phosphonate resembles the tetravalent metal phosphonates, which are structural relatives of α-$Zr(HPO_4)_2 \cdot H_2O$,[3-5,7] in that both structures have octahedral coordination of metal atoms by oxygen and the metal–phosphonate coordination in both is 6:3. A difference in the metal–oxygen–phosphorus network arises because the hydroxyl group is noncoordinating in the calcium structure, so that one of the other two oxygen atoms of the phosphonate group has to be bridging between two Ca atoms. This results in a compression of the distance between the Ca atoms. Therefore, the basal area per phosphonate group is only 20.8 Å^2 in the $Ca(HO_3PR)_2$ structures, compared to ca. 24 Å^2 for $Zr(O_3PR)_2$[7]. In Figure 7 the portion of the $Ca(HO_3PC_6H_{13})_2$ structure indicated by the dotted parallelogram in Figure 6 is compared to the related structural unit in $Zr(O_3PR)_2$. In the monoclinic $Zr(O_3PR)_2$ structure, these units are related by simple translation along the crystallographic *a* and *c* axes, while in $Ca(HO_3PC_6H_{13})_2$ the parallelogram is repeated in a zigzag fashion along the *b* axis.

Structure of $LaH(O_3PCH_3)_2$. The structure of $LaH(O_3PCH_3)_2$ is apparently layered, and c^* is identified as the stacking axis direction. From the cell parameters listed in Table II, the basal area occupied by each phosphonate group is calculated to be 21.13 Å^2. That this number falls between the 20.58 Å^2 found for $Ca(HO_3PR)_2$ and the 24 Å^2 for $Zr(O_3PR)_2$ suggests that the trivalent 1:2 metal phosphonates are structurally related in a manner similar to the relationship between $Ca(HO_3PR)_2$ and $Zr(O_3PR)_2$, although it is likely that the coordination number of La is higher than 6. We postulate that the other $MH(O_3PR)_2$ compounds, for which layer spacings are listed in Table II, have similar structures. Figure 7 shows schematically the relation between $LnH(O_3PR)_2$ and the other 1:2 metal:phosphonate structures. It is interesting to note that certain tetravalent metal phosphonates can be easily converted into trivalent metal phosphonates. For example, $Ce^{IV}(O_3PR)_2$ can be reduced with reducing agents such as 1,4-hydroquinone at room temperature, affording $Ce^{III}H(O_3PR)_2$. This reaction appears to occur by intercalation of hydroquinone into the structure, since $Ce^{IV}(O_3PC_2H_4PO_3)$ is unreactive under similar conditions. Establishment of the precise structural relationship between the trivalent structure and those of the other two 1:2 metal:phosphonate structural families awaits the elucidation of the structure of $LnH(O_3PR)_2$, which is currently under our investigation.

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Supplementary Material Available: Tables S1–S9, containing positional and thermal parameters for the H atoms, anisotropic thermal parameters for the non-H atoms, bond lengths and angles for the H atoms, the H-bonding geometry, and crystallographic data for both $Ca(O_3PCH_3) \cdot H_2O$ and $Ca(HO_3PC_6H_{13})_2$ (13 pages); Tables S10 and S11, listing observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.