Preparation of Lanthanide Arylphosphonates and Crystal Structures of Lanthanum Phenyl- and Benzylphosphonates

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A series of phenyl- and benzylphosphonates of the lanthanide elements has been prepared. In the lanthanum system single crystals have been obtained and the crystal structures determined. Lanthanum phenylphosphonate, $La(O_3PC_6H_5)(HO_3PC_6H_5)$, is triclinic, space group $P\bar{1}$, $a = 8.410$ (3), $b = 15.696$ (7), $c = 5.636$ (1) Å^3, $\alpha = 90.24$ (4)°, $\beta = 108.99$ (1)°, $\gamma = 85.59$ (4)°, $Z = 2$, $R(F) = 0.056$ for 1591 observations $[I > 3\sigma(I)]$ and 172 variables. The structure is a layered one in which the lanthanum atoms are eight-coordinate. Both phosphonate groups chelate the metal atom. One oxygen of each chelate ring then bridges to an adjacent La atom, while the third oxygen bridges to lanthanum at right angles to the bridging of the chelating oxygens. The phenyl rings protrude into the interlamellar space but are disordered. This disorder arises because the true unit cell has a doubled c axis. Thus, the phenyl rings in any one row are parallel to each other in the a-axis direction but are inclined to each other in adjacent rows in the c-axis direction at an angle of 58°. A short hydrogen bond (2.41 Å O–O distance) is present within the layers. $La(O_3PCH_2C_6H_5)(HO_3PCH_2C_6H_5)\cdot 2H_2O$ is orthorhombic, space group $Pbcn$, $a = 10.801$ (2), $b = 10.301$ (2), $c = 33.246$ (8) Å, $Z = 8$, $V = 3699$ (1) Å^3, $R(F_o) = 0.033$ for 1207 observations with $I > 3\sigma(I)$ and 277 variables. This structure is also a layered one with 8-fold coordination about the lanthanum atom. There are six phosphonate and two water oxygens in the La coordination sphere in a distorted dodecahedral arrangement. One phosphonate group chelates the lanthanum, while the remaining oxygen bridges to an adjacent La atom. One of the chelating oxygens also bonds to an adjacent lanthanum atom. The second phosphonate group bridges across two La atoms with two of its oxygens, while the third bonds to hydrogen. This acid proton and the water molecules form an extensive system of intralayer hydrogen bonds. A second type of rare-earth phosphonate of composition $Ln_2(O_3PC_6H_5)_3$ was prepared in slightly alkaline media.

Introduction

Recently, there has been increased activity in the field of metal phosphonate chemistry. Originally the bulk of these studies was directed toward four-valent metals,[1-5] but more recently derivatives of di-[6-10] and trivalent metals[10] have also been prepared. The interest in these compounds stems from their versatility. Many of these compounds are layered and can act as hosts in intercalation reactions.[5,11,12] In addition metal phosphonates can be prepared in which the organic moiety contains functional groups[2,3,13-15] than can participate in novel interlayer chemistry.[16,17] By utilizing diphosphonates it is possible to cross-link the layers and to space the cross-links to create porous structures.[3,18,19] These features suggest their use as catalysts, sorbants and ion exchangers.[19,20] The wide choice of metals and the variety of organic ligands than can be utilized to prepare the metal phosphonate suggests the possibility of rational design of structures for highly specific functions.[19]

Research into the chemical modification of surfaces has also become a more actively pursued field of research in recent years. The impetus for much of this research is to prepare microstructures that can impart desirable properties to bulk materials.[21] Among these are catalytic properties, electron-transfer reactions, light-induced vectoral electron transport, corrosion inhibition, and properties relevant to solid-state microelectronics. In this connection it has recently been shown that well-ordered zirconium phosphonate films can be formed on several substrates.[21-23] To understand the nature of such films it is essential to have prototype crystal structures of model metal phosphonates.

Another reason for providing structural information on model phosphonates is their possible relationship to the structure of known inorganic or mineral phosphates. For example, the four-valent phenylphosphonates are thought to have the same layer structure as α-zirconium phos-

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Table I. X-ray Powder Patterns of Cerium Phenylphosphonates

$Ce_2(O_3PC_6H_5)_3 \cdot 3H_2O$		$CeH(O_3PC_6H_5)$-$(HO_3PC_6H_5)$	
d (Å)	I/I_0	*d* (Å)	I/I_0
15.2	100	15.9	100
7.51	10	7.85	15
		5.24	10
5.05	5	5.03	5
3.73	2	4.37	2
3.55	2	3.86	2
3.08	1	3.72	2
3.01	1	3.14	1

phate,[1] while the divalent $Mn(O_3PC_6H_5) \cdot H_2O$ and Zn-$(O_3PC_6H_5) \cdot H_2O$ structures[8,9] are related to divalent phosphates of composition $M(O_3PONH_4) \cdot H_2O$ (M = Fe, Cd, Mn).[24,25] Likewise, the vanadyl phosphonates appear to be derived from the newberyite structure,[5c,26] $Mg(O_3PO$-$H) \cdot 3H_2O$.

In this paper we describe the preparation of lanthanide phenyl- and benzylphosphonates and their structures. Cao et al.[10] have prepared the cerium and lanthanum phenylphosphonates of composition $M(O_3PC_6H_5)(HO_3PC_6H_5)$ and a series of alkylphosphonates. From the unit-cell dimension measurements they deduced that the structure of the lanthanide phosphonates is most likely related to those of $Ca(HO_3PR)_2$ and $Zr(O_3PC_6H_5)_2$. We were able to prepare two types of phenylphosphonates, a 1:2 compound and 2:3 type compound of general composition Ln_2-$(O_3PC_6H_5)_3 \cdot 3H_2O$. The structures of the former type were also determined.

Experimental Section

Synthesis of Lanthanide Phenylphosphonates. Two types of compounds, one at low pH (~2.0) and the other at pH = 8.0, were prepared. The examples provided are for the Ce(III) derivatives. A solution of 1.70 g (3.9 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$ in 9 mL of deionized water was added with stirring to a solution of 0.94 g (6.0 mmol) of phenylphosphonic acid, $C_6H_5PO_3H_2$, in 10 mL of water at room temperature. The reaction mixture was stirred for 40 min, during which time a white solid formed. The solid was filtered off and washed with water until free of nitrate ion. Elemental analysis of the air dried solid gave Ce, 30.78%; P, 13.49%; C, 31.9%; H, 2.38%. Calculated for $Ce(O_3PC_6H_5)$-$(HO_3PC_6H_5)$: Ce, 30.91%, P, 13.67%; C, 31.80%; H, 2.45%. Yield 1.2 g or 68%.

In the second preparation a solution of sodium phenylphosphonate was prepared by adding 0.92 g (23 mmol) of NaOH in 5 mL of water to 7 mL of a 1.64 M solution of phenylphosphonic acid (11.5 mmol). This solution was then added to a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (3.32 g, 7.6 mmol) in 10 mL of water at room temperature. Stirring was continued for 30 min, followed by filtration and washing of the recovered solid. Elemental analysis of the air dried solid gave: Ce, 35.17%, P, 11.34%; C, 27.4%; H, 2.6%; H_2O (TGA), 6.8%. Calculated for $Ce_2(O_3PC_6H_5)_3 \cdot 3H_2O$: Ce, 34.92%; P, 11.58%; C, 26.95%; H, 2.64%; H_2O, 6.73%. The X-ray powder pattern of this solid is similar to but distinct from that of $Ce(O_3PC_6H_5)(HO_3PC_6H_5)$ as shown in Table I. Similar procedures were used to obtain phenylphosphonates of La, Sm, Dy, and Yb.

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Table II. Crystallographic Data for $La(O_3PC_6H_4)(HO_3PC_6H_5)$ and $La(O_3PCH_2C_6H_5)(HO_3PCH_2C_6H_5) \cdot 2H_2O$

	$LaP_2C_{12}H_{11}O_6$		$LaP_2C_{14}H_{18}O_8$
	small cell	large cell	
fw	452.07	452.07	516.16
cryst syst	triclinic	triclinic	orthorhombic
a (Å)	8.410 (3)	8.399 (4)	10.801 (2)
b (Å)	15.696 (7)	15.651 (9)	10.301 (2)
c (Å)	5.636 (1)	11.246 (4)	33.246 (8)
α (deg)	90.24 (3)	90.35 (4)	90
β (deg)	108.99 (1)	108.98 (3)	90
γ (deg)	85.59 (4)	85.60 (4)	90
V (Å³)	701.3 (4)	1393.5 (9)	3699 (1)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Pbcn$ (No. 60)
Z	2	4	8
D_{calc} (g/cm³)	2.141	2.155	1.854
λ (Å)	0.710 69	0.710 69	0.710 69
μ(Mo Kα), cm⁻¹	33.04	33.25	25.24
T (°C)	23 (1)	23 (1)	24 (1)
trans coeff	0.94–1.07	0.839–1.15	0.668–1.00
R (F_o)	0.056	0.058	0.033
R_w (F_o)	0.062	0.062	0.056
GOF	1.380	1.440	1.207

Synthesis of Benzylphosphonic Acid. Benzylphosphonic acid was obtained by hydrolysis of the diethyl ester (Aldrich Chemical Co.) with concentrated HCl: 97.7 g (0.43 mol) was refluxed for 4 h in a round-bottomed flask containing 100 mL of concentrated HCl. The resulting precipitate was recrystallized from water (mp 167–169, lit. 168 °C). The solid obtained weighed 50 g or 68% isolated yield.

Synthesis of Lanthanum Benzylphosphonate, $La(O_3PC$-$H_2C_6H_5)(HO_3PCH_2C_6H_5) \cdot 2H_2O$. A 0.2 M solution of lanthanum chloride (20 mL) was added dropwise to 20 mL of a 0.6 M solution of benzylphosphonic acid. The mixture was stirred for 4 h, and the white powder collected by filtration washed and air dried. Found: C, 32.2%; H, 3.8%; H_2O (TGA), 6.56%. Calculated for $LaH(O_3PCH_2C_6H_5) \cdot 2H_2O$, C, 32.57%; H, 3.71%; H_2O, 6.98%.

Growth of Single Crystals. An aqueous solution of 0.1 M benzylphosphonic acid (50 mL) was added to 50 mL of a 0.1 M aqueous solution of $LaCl_3$. This solution was kept at room temperature for 3 days while water was allowed to evaporate from the solution. Small clear platelets crystallized out, which were collected after the bottom of the beaker was covered with these crystals. No elemental analysis was carried out, but the thermogravimetric weight loss curve showed that the crystals contained 6.6% H_2O as compared to a calculated value for $La(O_3P$-$CH_2C_6H_5)(HO_3PCH_2C_6H_5) \cdot 2H_2O$ of 6.98%.

Crystals of $La(O_3PC_6H_5)(HO_3PC_6H_5)$ were grown hydrothermally. About 0.2 g of the powder was sealed in a Pyrex tube with 10 mL of 0.4 M HCl. The tube was kept in an oven while cycling the oven temperature between 130 and 190 °C. After 10 days very small, clear platelets were obtained.

Reagents. $Ce(NO_3)_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ (Aldrich) were used as received. The phenylphosphonic acid was from Alfa and used as received. Distilled, deionized water was used throughout.

Crystallography. Lanthanum Phenylphosphonate. A colorless square platelet of approximate dimensions 0.2 × 0.2 × 0.01 mm³ was mounted on a hollow glass fiber with silicone cement. All measurements were carried out with a Rigaku AFC5 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12–kW rotating anode generator. Unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 25 carefully centered reflections in the range 10.0 < 2θ < 25°. The cell was found to be triclinic, and on the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$.

The data were collected[27] 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. ω scans of several

(27) TEXSAN, Texray Structural Analysis Package; Molecular Structure Corp: The Woodlands, Texas, 1987 (revised).

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intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a takeoff angle of 6.0°. Scans of $(1.21 + 0.30 \tan \theta)°$ were made at a speed of 8.0°/min (in ω). The weak reflections $(I < 10.0\sigma(I))$ were rescanned (maximum of two rescans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator 0.5 mm, and the crystal to detector distance was 285.0 mm. Of the 2652 reflections which were collected, 2465 were unique $(R_{int}\ 0.072)$. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction, using the program DIFABS,[28] was applied as were corrections for Lorentz and polarization effects. Crystallographic details are given in Table II.

Structure Solution and Refinement. The structure was solved by direct methods.[29] The non-hydrogen atoms were refined anisotropically except for the carbon atoms, which were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 1591 observed reflections $(I > 3.00\ \sigma(I))$ and 172 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.056$$

$$R_w = [(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)]^{1/2} = 0.062$$

The standard deviation of an observation of unit weight was 1.38. The weighting scheme was based on counting statistics and included a factor $(p = 0.03)$ to down-weight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.75 and -1.48 e$^-$/Å^3, respectively, about 2.5 Å from the La atom.

Neutral atom scattering factors were taken from Cromer and Waber.[30] Anomalous dispersion effects were included in F_{calc}, the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[31] All calculations were performed using the TEXSAN[27] crystallographic software package of Molecular Structure Corp.

Refinement of the data in the small unit cell shown in Table II led to disordered phenyl rings as shown in Figure 1. The same difficulty was experienced with the phenylphosphonates of zinc[8] and manganese.[7] We therefore examined several crystals along each of these three axes for evidence of a superlattice structure. The crystals showed evidence of disorder including streaking and reflections giving indications of higher multiples along the c axis. Therefore, the possible missing zone of reflections, was sought with the aid of a utility program ZONE.[27] The peak shapes were examined with program 2D SCAN to eliminate mistaking streaks or other disorder effects for spots. In this search only 25 weak reflections were found in a zone which required doubling of the c axis. A second data set was gathered in the larger unit cell in the ω-step scan mode and processed with the Lehmann–Larsen profile analysis algorithm to extract the intensities. In this manner 4859 unique reflections were collected of which only 1481 had $I > 3\sigma(I)$, an indication that this crystal was of slightly poorer quality than that used for the smaller cell data collection. The SHELXTL-PLUS[32] programs were used to do the initial least-squares refinement with constraints placed on the P–O and P–C bond
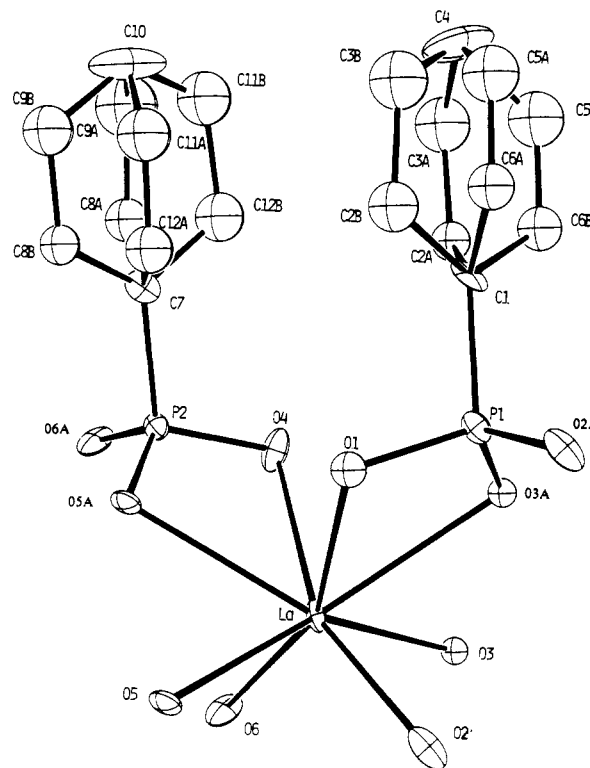
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(31) Cromer, D. T. Reference 30, Table 2.3.1.

(32) SHELXTL-PLUS, Siemans X-ray Corp., Madison, WI, 1987. (b) Sheldrick, G. M.; SHELX76; University of Cambridge, England, 1976.

Figure 1. ORTEP drawing of the coordination about the lanthanum atom in $La(O_3PC_6H_5)(HO_3PC_6H_5)$ including the numbering scheme used in the tables. The phenyl rings were included to show the disorder which arises from use of the small unit cell.

lengths. The results were then used as a starting set of parameters for unconstrained refinement in TEXSAN[27] with anisotropic thermal parameters for the La and P atoms. Isotropic thermal parameters were used for the oxygen and carbon atoms, with rigid refinement of the phenyl rings. Pertinent data are listed in Table II.

$La(O_3PCH_2C_6H_5)(HO_3CH_2C_6H_5)\cdot 2H_2O$. An irregularly shaped platelet of approximate dimensions $0.30 \times 0.20 \times 0.10$ mm^3 was selected for this study. Indexing and unit-cell parameters were derived from least-squares refinement of 25 high-angle reflections $(28 < 2\theta < 41°)$ in which the orthorhombic cell angles were constrained to be 90°. A total of 3730 reflections were collected and averaged to yield 1207 unique reflections with $I > 3\sigma(I)$. Crystallographic data are collected in Table I. The La and P atom positions were obtained by the deconvolution routine from a three dimensional Patterson map. The remaining non-hydrogen atoms were found in successive electron density maps calculated by using a direct method phase refinement technique DIRDIF[29b] and in difference Fourier electron density maps. Hydrogen atoms of the phenyl and methylene groups were placed in calculated positions and assigned fixed isotropic temperature factors. Both an initial ψ-scan absorption correction and later a more elaborate correction with the use of DIFABS[28] was applied. The final difference electron density map contained no chemically significant peaks, the highest peak being 1.4 e/Å^3 at a distance of 1.05 Å from the La atom.

Results

Table I contains the X-ray powder d spacings for the two types of cerium phenylphosphonates prepared in this study. The patterns do not contain many reflections because of severe preferred orientation; however, the diphosphonates always have interlayer spacings of ~ 15.9 Å, whereas the $Ln_2(O_3PC_6H_5)_3\cdot 3H_2O$ type have interlayer spacings of ~ 15.2 Å. As might be expected the acid phosphonates are formed below a pH of 3, whereas the $Ln_2(O_2PC_6H_5)\cdot 3H_2O$ type form at pH values of 8. At pH values between these two, mixtures of the two phases are obtained. The base-formed 2:3 compound readily converts

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Figure 2. Struplot representation of the La(O₃PC₆H₅)(HO₃P-C₆H₅) structure as viewed perpendicular to the *c* axis. The filled circles represent phosphorus atoms, and the largest open circles represent La atoms.

to the acid form but not the reverse. The following reactions are easily carried out under reflux conditions:

$$Ln_2(O_3PC_6H_5)_3 + C_6H_5PO_3H_2 \xrightarrow{H^+}$$
$$2Ln(O_3PC_6H_5)(HO_3PC_6H_5) \quad (1)$$

$$2Ln_2(O_3OC_6H_5)_3 + 3HCl \rightarrow$$
$$3Ln(O_3PC_6H_5)(HO_3PC_6H_5) + LnCl_3 \quad (2)$$

TGA weight loss curves yield a single weight loss for La-(O₃PC₆H₅)(HO₃PC₆H₅) which begins at ~400 °C and corresponds to a weight loss of 26.6%. However, the X-ray pattern indicates that LaPO₄ has formed which requires a weight loss of 48.3%. The residue contained a heavy carbon deposit and retreatment of the residue at 1000 °C in air was necessary to achieve the correct weight loss. A weight loss of 27% is just equal to the loss of the phenyl rings. Thus, conversion to LaPO₄ plus a phosphate glass must occur with volatilization of P₂O₅ at higher temperatures. La₂(O₃PC₆H₅)₃·3H₂O lost 6.56% of its mass up to about 200 °C and underwent a second weight loss of 20.4% from 410 to 700 °C. At 950 °C a third weight loss of 10.8% was observed. An X-ray pattern taken after the sample was heated to 750 °C showed the presence of a poorly crystalline LaPO₄ plus amorphous material. The initial weight loss is ascribed to the loss of 3 mol of water, while the second weight change represents the loss of organic matter. This change requires a weight loss of 22.8%, slightly more than observed, the deficiency probably resulting from incomplete combustion. The final weight loss must result from removal of the excess phosphate (11.9% calculated). Only under an oxygen atmosphere does all the carbon burn off to give the expected weight losses.

Structure of La(O₃PC₆H₅)(HO₃PC₆H₅). Although the true unit cell is that with four molecules, the refinement in the smaller cell yielded better bond distances and angles. Therefore, the tables will refer to this smaller cell with the information obtained in the true cell provided as supplementary material. The positional and isotropic thermal parameters are given in Table III. The structure is layered, as seen in Figure 2. Bond distances and angles are

Table III. Positional Parameters and *B*(eq) for La(O₃PC₆H₅)(HO₃PC₆H₅)

atom	*x*	*y*	*z*	*B*(eq)
La	0.2466 (1)	0.02261 (7)	0.2479 (2)	0.72 (3)
P1	0.0294 (5)	−0.1218 (3)	0.3887 (7)	0.9 (2)
P2	0.5088 (5)	−0.1224 (3)	0.1289 (7)	0.9 (2)
O1	0.212 (1)	−0.0957 (7)	0.531 (2)	1.4 (2)
O2	0.082 (1)	0.1082 (7)	−0.0091 (5)	2.6 (6)
O3	0.023 (1)	0.0674 (6)	−0.147 (2)	1.0 (2)
O4	0.320 (1)	−0.0990 (7)	−0.016 (2)	1.5 (5)
O5	0.459 (1)	0.0687 (6)	0.504 (7)	1.1 (4)
O6	0.385 (1)	0.1083 (7)	0.054 (8)	1.5 (4)
C1	0.045 (2)	−0.233 (1)	0.349 (9)	1.4 (6)
C2A	0.065 (4)	−0.261 (2)	0.246 (5)	1.8 (6)
C2B	0.163 (5)	−0.285 (3)	0.504 (7)	2.7 (7)
C3A	0.083 (6)	0.352 (3)	0.054 (8)	3.8 (9)
C3B	0.162 (6)	−0.378 (3)	0.459 (7)	3.7 (9)
C4	0.073 (3)	−0.408 (1)	0.246 (5)	4 (1)
C5A	0.033 (5)	−0.378 (3)	0.464 (8)	3.4 (8)
C5B	−0.055 (6)	−0.352 (3)	0.074 (8)	3.7 (9)
C6A	0.028 (5)	−0.296 (2)	0.495 (7)	2.3 (7)
C6B	−0.065 (5)	−0.267 (2)	0.107 (7)	2.3 (7)
C7	0.535 (2)	−0.2341 (1)	0.1527 (7)	1.2 (6)
C8A	0.573 (5)	−0.289 (2)	0.1309 (6)	2.5 (7)
C8B	0.657 (4)	−0.269 (2)	0.1645 (5)	1.9 (6)
C9A	0.578 (7)	−0.381 (3)	0.1861 (7)	5 (1)
C9B	0.678 (5)	−0.356 (3)	0.486 (7)	3.0 (8)
C10	0.569 (3)	−0.408 (1)	0.325 (4)	4 (1)
C11A	0.531 (5)	−0.348 (3)	0.493 (8)	3.3 (8)
C11B	0.454 (6)	−0.383 (3)	0.110 (9)	3.7 (9)
C12A	0.518 (5)	−0.262 (3)	0.444 (7)	2.6 (7)
C12B	0.423 (5)	−0.288 (3)	0.061 (8)	3.1 (8)

Table IV. Intramolecular Distances Involving the Non-Hydrogen Atoms[a] of La(O₃PC₆H₅)(HO₃PC₆H₅)

atom	atom	dist	ADC[a]
La1	O2	2.40 (1)	1
La1	O6	2.41 (1)	1
La1	O3	2.46 (1)	1
La1	O5	2.48 (1)	1
La1	O1	2.55 (1)	1
La1	O4	2.58 (1)	1
La1	O5A	2.65 (1)	2
La1	O3A	2.67 (1)	2
P1	O2A	1.50 (1)	2
P1	O3A	1.53 (1)	2
P1	O1	1.57 (1)	1
P1	C1	1.79 (2)	1
P2	O6A	1.50 (1)	2
P2	O5A	1.52 (1)	2
P2	O4	1.55 (1)	1
P2	C7	1.81 (2)	1
C1	C2A	1.36 (4)	1
C1	C2B	1.48 (4)	1
C1	C6B	1.41 (4)	1
C1	C6A	1.43 (4)	1
C2B	C3A	1.47 (5)	1
C3A	C(4)	1.43 (5)	1
C3B	C(4)	1.31 (5)	1
C4	C(5A)	1.44 (5)	1
C5A	C(6A)	1.30 (5)	1
C5B	C(6B)	1.34 (5)	1
C7	C(8A)	1.34 (4)	1
C7	C(8B)	1.35 (4)	1
C7	C(12B)	1.40 (4)	1
C7	C(12A)	1.40 (4)	1
C8A	C(9A)	1.46 (6)	1
C(8B)	C(9B)	1.40 (5)	1
C(9A)	C(10)	1.31 (6)	1
C(9B)	C(10)	1.38 (4)	1
C(10)	C(11B)	1.32 (5)	1
C(10)	C(11A)	1.43 (5)	1
C(11A)	C(12A)	1.37 (5)	1
C(11B)	C(12B)	1.51 (6)	1

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses. [b] Position 1 is *xyz*; position 2 is *x̄*, *ȳ,z̄*.

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Table V. Intramolecular Bond Angles (deg) Involving the Non-Hydrogen Atoms for La(O₃PC₆H₅)(HO₃PC₆H₅)

atom	atom	atom	angle
O2	La1	O6	112.3 (4)
O2	La1	O3	85.9 (3)
O2	La1	O5	76.0 (4)
O2	La1	O1	83.0 (3)
O2	La1	O4	158.2 (3)
O2	La1	O5A	139.3 (3)
O2	La1	O3A	80.1 (3)
O6	La1	O3	75.9 (3)
O6	La1	O5	85.2 (4)
O6	La1	O1	158.5 (3)
O6	La1	O4	84.0 (4)
O6	La1	O5A	80.8 (3)
O6	La1	O3A	139.6 (3)
O3	La1	O5	146.6 (3)
O3	La1	O1	121.8 (3)
O3	La1	O4	84.2 (3)
O3	La1	O5A	134.6 (3)
O3	La1	O3A	66.6 (4)
O5	La1	O1	84.0 (3)
O5	La1	O4	121.4 (3)
O5	La1	O5A	66.6 (4)
O5	La1	O3A	134.9 (3)
O1	La1	O4	85.8 (3)
O1	La1	O5A	77.8 (3)
O1	La1	O3A	55.3 (3)
O4	La1	O5A	54.8 (3)
O4	La1	O3A	78.2 (3)
O5	La1	O3	115.5 (3)
O2	P1	O3	115.4 (6)
O2	P1	O1	111.0 (6)
O2	P1	C1	108.3 (7)
O3	P1	O1	103.1 (6)
O3	P1	C1	111.1 (7)
O1	P1	C1	107.7 (7)
O6	P2	O5	116.3 (6)
O6	P2	O4	110.8 (6)
O6	P2	C7	108.2 (7)
O5	P2	O4	103.4 (6)
O5	P2	C7	109.5 (6)
O4	P2	C7	108.3 (7)

Figure 3. Struplot representation of the La(O₃PC₆H₅)(HO₃P-C₆H₅) structure as viewed down the *b* axis. The large filled circles are carbon atoms of the phenyl rings which are above the mean plane of the layer, while the carbon atoms below the mean plane are not filled. The smallest circles represent H, the next larger size P and the largest unfilled circles are La atoms.

given in Tables IV and V, respectively. Bond distances for the C–C bonds have high esd's because of the disorder. In the larger cell these values are quite regular. The lanthanum atoms are dodecahedrally coordinated by eight phosphonate oxygens as seen in Figure 1. Defining bond angles in the coordination sphere are O1–La–O4 85.3 (3)°, O3A–La–O5A 134.9°, O2–La–O6 112.3°, O3–La–O5 146.6°. Both phosphonate groups chelate the metal atom while the third oxygen of each group (O2A and O6A in Figure 1) bridge to an adjacent lanthanum atom along the [101] diagonal (Figure 3). The final two coordination sites are filled by one oxygen of each chelate ring (O3 and O5) also bonding to adjacent lanthanum atoms in directions at right angles to the directions of the chelate rings (parallel to the [101] diagonal). This arrangement creates additional four-membered rings as shown in Figures 2 and 3. The angles formed at the lanthanum atoms by the chelate rings are quite small (O1–La–O3A, 55.3 (3)°; O4–La–O5A 54.8°), leading to a highly distorted dodecahedron about the lanthanum. The bond distances are grouped in pairs. The shortest (La–O2, 2.40 (1) Å and La–O6, 2.41 (1) Å) are to those oxygens that are not members of a chelate ring. These oxygens are two coordinate, being bonded to phosphorus and La. Each chelate ring has one short and one longer La–O bond: La–O3A, 2.67 (1) Å; La–O1, 2.55 (1) Å; and La–O5A, 2.65 (1) Å; La–O4, 2.58 (1) Å, making them unsymmetrical. O3 and O5 are each three–coordinate, being bonded to two lanthanum atoms and phosphorus. In this bridging of lanthanum atoms to form four–membered rings, one La–O bond is considerably
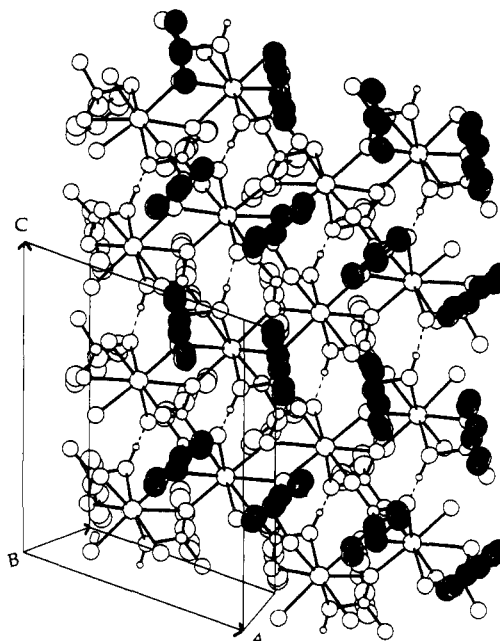
shorter, La–O3, 2.46 (1) Å, than the other, La–O3A, 2.67 (1) Å. The same situation holds for the La–O5 and –O5A bonds.

In the larger unit cell there is no disorder of the phenyl groups. As seen in Figure 3 all the phenyl rings in any one row parallel to the *a* axis are oriented parallel to each other. However, in adjacent rows the phenyl rings are inclined to those in an adjacent layer. The angle of inclination is 58°. In the smaller cell, where the *c* axis is halved, both orientations are present in equal weight.

The acid proton was not located in the Fourier difference maps. However, examination of the P–O bond lengths shows that P1–O1, 1.57 (1) Å and P2–O4, 1.55 (1) are slightly longer than the other P–O bonds. These oxygens are also two-coordinate and are separated by a distance of 2.41 (1) Å. Thus, it is possible for the proton to bond to either one of these oxygens or to be shared equally between them. To help decide, a ³¹P MAS NMR spectrum was obtained with the thought that the P–OH phosphorus would have a chemical shift somewhat different from that of the other phosphorus. However, only a single resonance peak was obtained at +9.6 ppm, indicative of the equality of the phosphorus atoms. Either the proton is randomly distributed between the two oxygen atoms or it is equidistant between them. In contrast, the solid-state ³¹P MAS spectrum of La₂(O₃PC₆H₅)₃·3H₂O showed two peaks at 8.6 and 2.3 ppm in a 1:2 ratio. Thus one of the three phosphonate groups must have a bonding mode different from the other two.

La(O₃PCH₂C₆H₅)(HO₃PCH₂C₆H₅)·2H₂O. Table VI gives the positional and isotropic thermal parameters for lanthanum benzylphosphonate. Bond distances and angles for the non-hydrogen atoms are given in Tables VII and VIII, respectively. The structure consists of layers of composition La(O₃P)(HO₃P)·2H₂O parallel to the *ab* plane with the benzyl groups occupying the interlamellar space. The basal spacing is just half the *c* axis, or 16.62 Å. The lanthanum atom is eight-coordinate as shown in Figure 4. The layer structure is schematically depicted in Figures

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**Table VI. Positional Parameters and B(eq) for the
Non-Hydrogen Atoms of
La(O$_3$PCH$_2$C$_6$H$_5$)(HO$_3$PCH$_2$C$_6$H$_5$)•2H$_2$O**

atom	x	y	z	B(eq)
La	0.1306 (1)	0.1505 (1)	0.01098 (4)	1.47 (4)
P1	−0.1388 (5)	0.1608 (6)	0.0530 (1)	1.7 (2)
P2	0.2278 (5)	0.4233 (6)	0.0818 (2)	1.8 (3)
O1	0.238 (1)	0.316 (1)	0.0507 (4)	1.7 (6)
O2	0.337 (1)	0.041 (1)	−0.0091 (5)	2.6 (6)
O3	0.196 (1)	0.040 (1)	0.0725 (4)	1.9 (3)
O4	0.237 (1)	0.295 (1)	−0.0388 (3)	1.3 (3)
O5	−0.083 (1)	0.054 (1)	0.0264 (3)	1.1 (2)
O6	−0.039 (1)	0.268 (1)	0.0537 (4)	1.5 (3)
O7	−0.018 (1)	0.245 (1)	−0.0422 (8)	3.2 (8)
O8	0.090 (1)	0.463 (1)	0.0859 (4)	2.2 (7)
C1	−0.156 (2)	0.097 (2)	0.1033 (6)	2 (1)
C2	−0.218 (2)	0.183 (2)	0.1329 (6)	1.8 (4)
C3	−0.342 (2)	0.179 (2)	0.1416 (7)	3 (1)
C4	−0.394 (3)	0.255 (3)	0.1696 (8)	5 (2)
C5	−0.323 (3)	0.348 (4)	0.1884 (8)	5 (2)
C6	−0.201 (3)	0.363 (4)	0.1816 (7)	4 (1)
C7	−0.149 (2)	0.276 (3)	0.1527 (7)	3 (1)
C8	0.273 (2)	0.358 (3)	0.1309 (6)	2.8 (5)
C9	0.268 (2)	0.452 (2)	0.1645 (5)	2 (1)
C10	0.165 (2)	0.482 (3)	0.1861 (7)	4 (1)
C11	0.168 (3)	0.570 (4)	0.2169 (8)	6 (2)
C12	0.279 (4)	0.625 (3)	0.2283 (8)	6 (2)
C13	0.377 (4)	0.602 (4)	0.2054 (8)	8 (2)
C14	0.375 (4)	0.519 (2)	0.1747 (6)	3 (1)

**Table VII. Bond Distances (Å) Involving the
Non-Hydrogen Atoms of
La(O$_3$PCH$_2$C$_6$H$_5$)(HO$_3$PCH$_2$C$_6$H$_5$)•2H$_2$O**

atom	atom	distance	atom	atom	distance
La1	O1	2.45 (1)	P2	C8	1.83 (2)
La1	O2	2.58 (1)	C1	C2	1.48 (3)
La1	O3	2.45 (1)	C2	C3	1.36 (3)
La1	O4	2.50 (1)	C2	C7]	1.39 (3)
La1	O5	2.56 (1)	C3	C4	1.34 (3)
La1	O5A^a	2.50 (1)	C4	C5	1.38 (4)
La1	O6	2.62 (1)	C5	C6	1.34 (3)
La1	O7	2.58 (2)	C6	C7	1.43 (4)
P1	O4	1.49 (1)	C8	C9	1.48 (3)
P1	C5	1.53 (1)	C9	C10	1.36 (3)
P1	O6	1.54 (1)	C9	C14	1.39 (3)
P1	C1	1.80 (2)	C10	C11	1.37 (4)
P2	O1	1.51 (1)	C11	C12	1.38 (4)
P2	O3A^a	1.49 (1)	C12	C13	1.33 (4)
P2	O8	1.55 (1)	C13	C14	1.33 (4)

^{a} Atom O5A is in symmetry position $(\bar{x}, \bar{y}, \bar{z})$. Atom O3A is in
symmetry position $(^1/_2 - x, ^1/_2 + y, z)$.

5 and 6. There are six phosphonate oxygen atoms and
two water oxygens in the lanthanum coordination sphere,
which has a distorted dodecahedral arrangement. Bond
distances range from 2.45 (1) to 2.62 (1) Å. These distances
are in accord with expected values based upon the sum of
the ionic radii and geometrical considerations. There are
two different kinds of phosphonate groups. The first type
chelates the La atom through O5 and O6 forming a four-
membered ring. The third oxygen of this phosphate group,
O4, then bridges to another lanthanum atom. O5 also
bridges across to another lanthanum atom making it a
three–coordinate oxygen, but O6 does not. The four-
membered chelate ring has bond angles of 104.1 (7)° for
O5–P1–O6 and 56° for O5–La–O6. The second type of
phosphonate group has two oxygens, O1 and O3, which
bridge to different adjacent La atoms, creating the layer
framework, and a third oxygen O8, which does not bond
to metal atoms. Therefore, the proton is placed on this
oxygen. These bridging oxygens form the shortest La–O
bonds at 2.45 (1) Å.

The chelate group is more symmetrical than those in
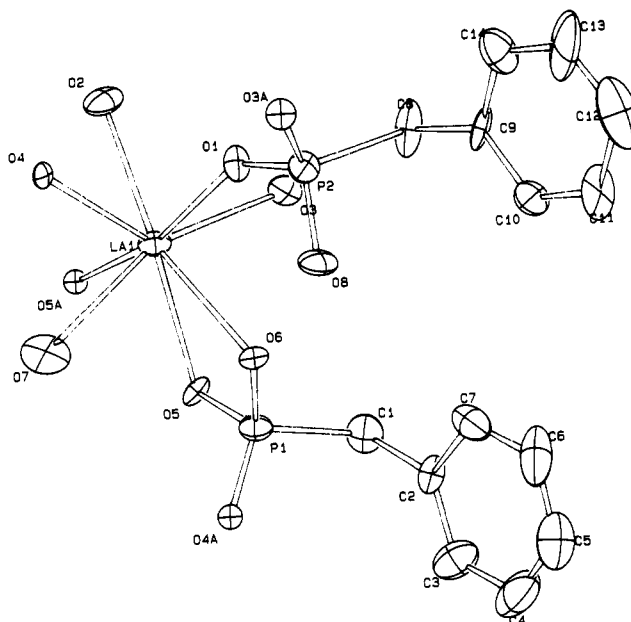lanthanum phenylphosphonate. La–O5 is 2.56 (1) Å, while

Figure 4. ORTEP drawing of a portion of the lanthanum ben-
zylphosphonate structure showing the coordination about the La
atom, the numbering scheme used in the tables and the thermal
ellipsoids (50% probability level). O7 and O2 are the water
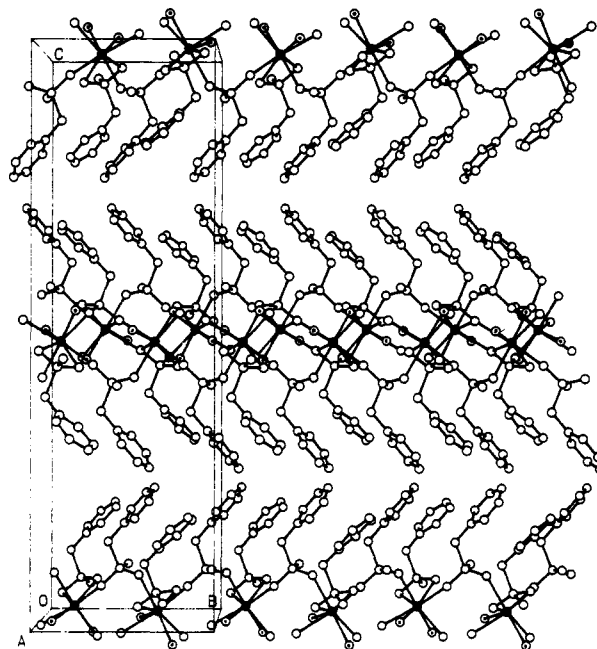molecule oxygen atoms.

Figure 5. Struplot representation of the layer structure of lan-
thanum benzylphosphonate dihydrate as viewed down the a axis.
Dark circles are the lanthanum atoms and dotted circles are the
water molecule oxygens.

La–O6 is 2.62 (1) Å. O5 in bridging to an adjacent La
forms a four-membered ring, and this ring is slightly more
symmetrical than in lanthanum phenylphosphonate, La–
O5 being 2.56 (1) Å and La–O5 Å, 2.50 (1) Å. The water
molecules, O2 and O7, coordinated to La, have identical
bond lengths of 2.58 Å.

The lanthanum atoms which are directly bridged
through O5 are 4.26 Å apart, almost in the ab face diagonal
direction, while two other adjacent lanthanum atoms are
5.76 and 5.82 Å, both in the directions almost parallel with
the ab plane. The P–C–C ring angles, at 116°, are not
much larger than the expected tetrahedral angle. The
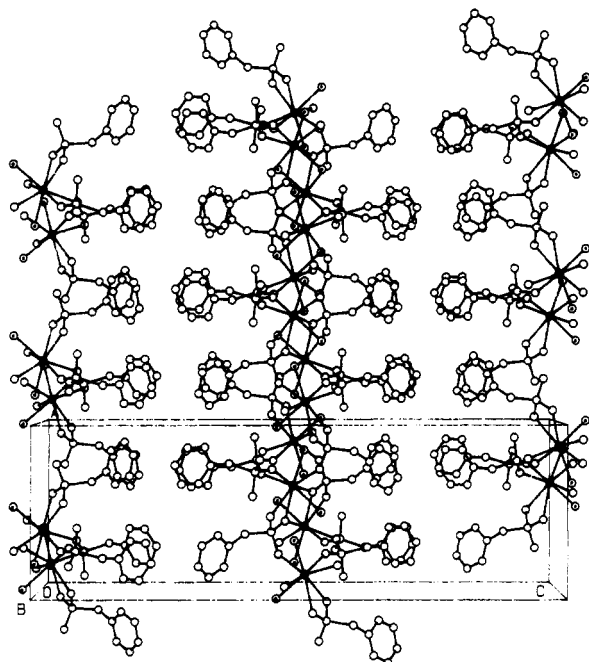benzyl group forming part of the bridging (monohydrogen)

Figure 6. Struplot representation of lanthanum benzylphosphonate as viewed down the *c* axis.

phosphonate group protrudes into the interlamellar space to a greater extent than the one forming part of the chelating phosphonate. This dissimilarity arises because the chelating phosphonate group is positioned so that the phosphorus atom is only slightly above or below the lanthanum atom it chelates. In contrast the P2 phosphorus is well above or below the mean layer plane so that its benzyl group protrudes deeper into the interlameller space than does the P1 benzyl group. This difference produces voids which makes the lanthanum benzylphosphonate less dense than the phenylphosphonate compound. Furthermore the symmetry of the space group *Pbcn* requires that the benzyl groups on either side of the same layer point in opposite directions thereby requiring a repeat distance every two layers.

Within each layer there is a significant network of hydrogen bonds. The PO–H acid group forms a strong hydrogen bond with O6 in which the O6–O8 distance is 2.67 (2) Å. If the P2–O8–H5 angle is assumed to be tetrahedral, then the hydrogen atom lies very nearly on the O--O line. These hydrogen bonds run roughly along the body diagonal of the unit cell. The water molecule represented by O2 forms two hydrogen bonds, O2--O6, 2.81 (2) Å approximately along the body diagonal and O2--O4, 2.84 Å almost parallel to the *b*-axis direction. Finally, there is a hydrogen bond O7–H···O₁ with O–O distance 2.73 (2) Å formed by the second water molecule in the *a*-axis direction.

Discussion

Sufficient work has now been completed to show that many di- and trivalent elements form extensive series of aryl and alkylphosphonates.[6-10] The bonding modes of the phosphonate groups in these compounds is now becoming clear. The divalent ions prefer six coordination of the metal atoms. This is achieved in compounds of composition $M^{II}(O_3PR)\cdot H_2O$ by having the phosphonate group chelate the metal atom and at the same time both oxygens forming the chelate ring bridge to adjacent metal atoms. The third oxygen then bonds to a metal atom in a different row to form the layer and the sixth coordination site is occupied by a water molecule. In this way, the phosphonate bonds to four different metal atoms. Copper phos-

Table VIII. Selected Intramolecular Bond Angles (deg) Involving the Non-Hydrogen Atoms for $La(O_3PCH_2C_6H_5)(HO_3PCH_2C_6H_5)\cdot 2H_2O$

atom	atom	atom	angle
O1	La1	O2	92.1 (4)
O1	La1	O3	74.8 (4)
O1	La1	O4	74.1 (4)
O1	La1	O5	126.0 (4)
O1	La1	O5A^a	162.4 (4)
O1	La1	O6	73.5 (5)
O1	La1	O7	113.7 (4)
O2	La1	O3	76.3 (5)
O2	La1	O4	72.1 (5)
O2	La1	O5	131.1 (4)
O2	La1	O5A^a	71.5 (4)
O2	La1	O6	161.1 (4)
O2	La1	O7	121.6 (5)
O3	La1	O4	134.2 (4)
O3	La1	O5A^a	84.9 (4)
O3	La1	O5	94.7 (4)
O3	La1	O6	88.0 (4)
O3	La1	O7	158.3 (4)
O4	La1	O5	140.8 (4)
O4	La1	O5A^a	105.5 (4)
O4	La1	O6	114.0 (4)
O4	La1	O7	67.0 (4)
O5	La1	O5A^a	65.5 (4)
O5	La1	O6	56.0 (4)
O5	La1	O7	73.9 (4)
O5A^a	La1	O6	121.0 (4)
O5A^a	La1	O7	81.34 (4)
O6	La1	O7	76.2 (5)
O4A^b	P1	O5	113.2 (7)
O4A^b	P1	O6	114.2 (8)
O4A^b	P1	C1	108.2 (8)
O5	P1	O6	104.3 (7)
O5	P1	C1	108.3 (9)
O6	P1	C1	108.3 (9)
O1	P2	O3A^c	113.8 (8)
O1	P2	O8	108.8 (8)
O1	P2	C8	109 (1)
O3A^c	P2	O8	109.8 (9)
O3A^c	P2	C8	109 (1)
O8	P2	C8	106.0 (9)
La1	O1	P2	147.2 (9)
La1	O3	P2A^d	135.2 (8)
La1	O4	P1A^e	143.4 (8)
La1	O5	La1A^a	114.5 (4)
La1	O5	P1	101.2 (6)
La1	O5A^a	P1B^a	143.8 (7)
La1	O6	P1	98.4 (6)
P1	C1	C2	117 (2)
P2	C8	C9	115 (2)

^{a}Symmetry position $(-x,-y,-z)$. ^{b}Symmetry position $(x - 1/2, 1/2 - y, -z)$. ^{c}Symmetry position $(1/2 - x, 1/2 + y, z)$. ^{d}Symmetry position $(1/2 - x, y - 1/2, z)$. ^{e}Symmetry position $(1/2 + x, 1/2 - y, z)$.

phonates,[33] $Cu(O_3PR)\cdot H_2O$, are unusual in that the copper atoms are five-coordinate, being bonded to oxygens arranged in a distorted tetragonal pyramid. The base of the pyramid consists of three phosphonate oxygens and one water molecule. No chelation of copper takes place. Instead two phosphonate groups bridge the same two copper atoms to form an eight-membered ring:
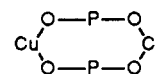
The third oxygen then bridges two coppers in an adjacent row. These copper atoms are also doubly bridged forming four-membered rings. One of the oxygens of the four-membered ring is part of the pyramid base, while the other forms the pyramid apex.

(33) Zhang, Y.-P.; Clearfield, A. Submitted to *Inorg. Chem.*

The structure of calcium methyl phosphonate, $Ca(O_3P-CH_3)\cdot H_2O$, is unusual.[10] While the structure is a layered one, it differs from that of either $Zn(O_3PCH_3)\cdot H_2O$ or $Cu(O_3PCH_3)\cdot H_2O$ is that the calcium is seven coordinate in a distorted pentagonal bipyramidal arrangement. To accomplish this high coordination number with only four oxygens, one of the phosphate oxygens is bonded to three calcium ions. This oxygen chelates a calcium atom together with another phosphonate oxygen and at the same time bridges to an adjacent calcium in a manner described for the $Zn(O_3PC_6H_5)\cdot H_2O$ structure. However, this oxygen atom then forms a long bond (2.707 (2) Å) with a third calcium atom. By bonding to three Ca atoms, a single phosphonate group plus one water molecule is able to achieve 7-fold coordination of the metal atom.

A contrasting structure is that of the acid phosphonate,[10] $Ca(HO_3PO_6H_{13})_2$. Only two of the three phosphonate oxygens bond to calcium atoms, the third being bonded to the proton. The layers are parallel to the *ab* plane. Running parallel to the *b* axis the calcium atoms are bridged by O–P–O groups above and below the plane of metal atoms, forming eight-membered rings. The hydrocarbon groups then protrude into the interlamellar space. At the same time one of the oxygens participates in the now familiar M–O–M type bridging forming four-membered rings running parallel to the *b* axis. Cao et al.[10] point out that the bonding in this calcium compound is similar to that in α-zirconium phosphate[34] and zirconium phenylphosphonate. In these compounds three of the phosphate (phosphonate) oxygens bridge to three different metal atoms in an almost equilateral triangle arrangement. In the calcium compound only two oxygens accomplish this bridge bonding to three metal atoms, causing a shortening of one side of the triangle.

The only trivalent layered metal phosphonates that have been reported prior to this study are those of $HFe(O_3P-C_6H_5)_2$[35] and $LaH(O_3PR)_2$.[10] The structures were not de-

termined, but it was considered that the layers resembled those of zirconium phenylphosphonate. However, the structure of a nonlayered phosphonate, $HFe(HO_3PC_6H_5)_4$, was determined.[35] This compound consists of linear chains in which the iron atoms are six-coordinate. Six different phosphonate groups bond to the metal atoms, four of which bridge two iron atoms through O–P–O bridges and two others bond to only one Fe atom. In this structure there is a short P–O–H–O–P hydrogen bond (2.48 Å) in which it was assumed that the H atom is equidistant from the two oxygens.

In $La(O_3PC_6H_5)(HO_3PC_6H_5)$ there are only six oxygens to satisfy the 8-fold coordination of the rare-earth metal. This coordination is accomplished by three types of bonding. Both phosphonate groups chelate the metal atom and half the chelating oxygens then bridge to another metal atom. The third oxygen of each phosphonate group then bonds to only one metal atom. In the hydrated benzylphosphonate, two water molecules coordinate the metal atom. Thus, only one phosphonate group chelates the metal atom and coordinates to an adjacent La while the other phosphonate uses only two of its oxygens to bridge two adjacent metal atoms. In the phenylphosphonate the phenyl rings must take a zigzag arrangement in adjacent rows to avoid severe H–H repulsions which would otherwise occur. The same is true for the divalent phenylphosphonates.

We have also prepared metal phosphonates of di- and trivalent metals which contain functional groups attached. This functionalization allows novel interlayer chemistry to be carried out, which will be described in a future publication.

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