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Synthesis and Characterization of New Calcium Phenylphosphonates and 4-Carboxyphenylphosphonates

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Three new calcium phenylphosphonates, $CaC_6H_5PO_3{\cdot}2H_2O$, $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$, and $CaC_6H_5PO_3{\cdot}H_2O$, and two calcium 4-carboxyphenylphosphonates, $Ca(HOOCC_6H_4PO_3H)_2$ and $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$, were prepared. It was found that $CaC_6H_5PO_3{\cdot}2H_2O$ transformed into previously known $Ca(C_6H_5PO_3H)_2$ via $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ in the presence of phenylphosphonic acid, and vice versa, $Ca(C_6H_5PO_3H)_2$ turned into $CaC_6H_5PO_3{\cdot}2H_2O$ in a weak basic medium. A similar relationship was found between $Ca(HOOCC_6H_4PO_3H)_2$ and $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$; i.e., $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ transformed into $Ca(HOOCC_6H_4PO_3H)_2$ in the presence of 4-carboxyphenylphosphonic acid. On the contrary, $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ is formed from $Ca(HOOCC_6H_4PO_3H)_2$ in the presence of ammonium as a weak base. The structure of $Ca(HOOCC_6H_4PO_3H)_2$ was solved from X-ray powder diffraction data by an ab initio method using a FOX program. The compound is monoclinic, space group $C2/c$ (No. 15), $a = 49.218(3)$ Å, $b = 7.7609(4)$ Å, $c = 5.4452(3)$ Å, $\beta = 128.119(3)°$, and $Z = 4$. Its structure is one-dimensional with $[Ca_2(HOOCC_6H_4PO_3H)_4]_\infty$ ribbons forming basic building blocks. The ribbons are held together by hydrogen bonds between carboxylic groups.

Introduction

Metal organophosphonates belong to a group of inorganic–organic hybrid compounds which have received much attention with the aim to obtain novel materials with interesting properties. Due to their stability, metal(IV) phosphonates, especially zirconium phosphonates, were the most thoroughly investigated.[1] Phosphonates of divalent metals, on the other hand, have been studied to a much less extent, and the stress was put on their structure determination. For instance, a group of metal(II) alkylphosphonates and phenylphosphonates was structurally characterized.[2] Among phosphonates of the alkaline-earth metals, structures of hydrogen phenylphosphonates with a general formula of $Me(C_6H_5PO_3H)_2$ (Me = Ca,[3] Sr,[4] or Ba[5]), were described. Calcium hydrogen phenylphosphonate, $Ca(C_6H_5PO_3H)_2$, was also synthesized and characterized, and its ability to intercalate alkylamines was investigated.[6] Regarding compounds in which phenylphosphonate is in the form of a dianion, $C_6H_5PO_3^{2-}$, only magnesium phenylphosphonate hydrate, $MgC_6H_5PO_3{\cdot}H_2O$, was prepared and characterized by TGA and IR, and its unit cell dimensions were determined from powder X-ray diffraction data.[7] To the best of our knowledge, no phenylphosphonate of other alkaline-earth metals, has been described. The acidity of the reaction mixture plays an important role in the controlling of the resulting metal/phosphonate ratio in the products.[8]

In an attempt to prepare $Ca(C_6H_5PO_3H)_2$ according to a previously described procedure,[3] we found that another calcium phenylphosphonate with a Ca/P molar ratio of 1 was formed at higher pH. Furthermore, we studied the possibility of the formation of this compound from $Ca(C_6H_5PO_3H)_2$ by a treatment in a basic medium, and we also studied a reverse

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process, that is the formation of $Ca(C_6H_5PO_3H)_2$ from calcium phenylphosphonate with Ca/P = 1/1 in an acidic medium. In addition, two new functionalized phenylphosphonates, calcium 4-carboxyphenylphosphonates, were also synthesized and characterized, and their behavior in media with different acidities was investigated.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical Co. and were used as received. The calcium and phosphorus contents were determined by an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray microanalyzer IXRF Systems (detector GRESHAM Sirius 10). The accelerating voltage of the primary electron beam was 20 kV. The thermogravimetric analysis was done using a homemade apparatus constructed of a computer-controlled oven and a Sartorius BP210S balance. The measurements were carried out in air between 30 and 960 °C at a heating rate of 5 °C min^{-1}.

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) with Bragg−Brentano $\theta-\theta$ geometry (40 kV, 40 mA) using Cu Kα radiation with a secondary graphite monochromator. The diffraction angles were measured at room temperature from 2 to 65° (2θ) in 0.02° steps with a counting time of 10 s per step, except for $Ca(HOOCC_6H_4PO_3H)_2$ where the counting time was 20 s per step. The powder patterns were indexed, when possible, using a DicVOL method in a WinPLOTR program.[9] The space groups were determined by processing the data in the Checkcell program.[10]

The structure of $Ca(HOOCC_6H_4PO_3H)_2$ was solved using a FOX program.[11] The geometry of 4-carboxyphenylphosphonic acid was first optimized using a PM3 semiempirical quantum chemical calculation implemented in the HYPERCHEM software package.[12] The hydrogen atoms at the phosphonate group were removed, and the remaining organic fragment was imported into the FOX program in the form of a Fenske−Hall *Z*-matrix as a crystal scatterer. One calcium atom was added as another crystal scatterer. The initial position and orientation of the organic fragment and the position of the calcium atom were randomized before optimization. A parallel tempering algorithm was used to fit the calculated diffraction profile with the observed pattern. The coordinates of the Ca atom were found to be close to a special position (0, y, $^1/_4$) and were therefore fixed to this special position. The obtained atomic coordinates (excluding the H atoms) were used for a Rietveld refinement using the FullProf program incorporated in the WinPLOTR software package.[9] In this program, the profile parameters in the pseudo-Voigt profile type were optimized. The number of observed reflections was 70, and the number of calculated reflections was 310.

Preparation of $Ca(C_6H_5PO_3H)_2$. A solution of $CaCl_2$ (2.75 g; 2.5×10^{-2} mol) in water (100 mL) was added under stirring to a solution of phenylphosphonic acid (7.9 g; 5×10^{-2} mol) in hot water (150 mL). The reaction mixture was further stirred for 1 h, and the product slowly precipitated during this time. The pH of the reaction mixture was from 0 to 0.4 during the reaction. The white product was obtained in a 37% yield (3.3 g). The relative amount of calcium and phosphorus was 67 atom % of P and 33 atom % of Ca, according to energy-dispersive X-ray analysis (EDX). The powder X-ray diffraction pattern of the product fully corresponded to the diffraction pattern calculated using a PowderCell program[13] from coordinates determined by a single-crystal X-ray diffraction for this compound.[3]

Preparation of $CaC_6H_5PO_3{\cdot}2H_2O$. A concentrated solution of ammonia was added to phenylphosphonic acid (7.9 g; 5×10^{-2} mol) in hot water (100 mL) to adjust the pH to 9. A solution of $CaCl_2$ (5.5 g; 5×10^{-2} mol) in water (50 mL) was added under stirring to the solution of phenylphosphonic acid. The reaction mixture was further stirred for about 30 min. The final pH of the reaction mixture was 8.5. The voluminous precipitate was separated by filtration and washed twice with boiling water and then with ethanol. The white product was dried in air at room temperature. The yield was 10.5 g (90%). Elemental analysis calcd (%) for $C_6H_9CaO_5P$ (232.2): C 31.04, H, 3.91; found: C 31.39, H 4.27. The relative amounts of calcium and phosphorus were 49.7 atom % of P and 50.3 atom % of Ca, according to EDX.

Preparation of $CaC_6H_5PO_3{\cdot}H_2O$. A reaction mixture containing $CaC_6H_5PO_3{\cdot}2H_2O$ (0.232 g; 10^{-3} mol), aqueous NH_4OH (c = 0.391 mol L^{-1}; 5.1 mL; 2×10^{-3} mol), and water (4 mL) was placed in a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 180 °C for 48 h. After cooling, the white product was separated by filtration, washed twice with distilled water and ethanol, and dried in air at room temperature. The relative atomic ratio of calcium and phosphorus was 1/1, according to EDX. Elemental analysis calcd (%) for $C_6H_7CaO_4P$ (214.2): C 33.65, H 3.29; found: C 33.32, H, 3.07.

Preparation of $Ca(HOOCC_6H_4PO_3H)_2$. 4-Carboxyphenylphosphonic acid was prepared according to a previously described procedure.[14] It was found by TGA that this acid is a monohydrate, $HOOCC_6H_4PO_3H_2{\cdot}H_2O$, releasing water at 270 °C. The acid (4.4 g; 0.02 mol) was dissolved in a boiling ethanol−water 1:1 vol. mixture (80 mL) and added to a solution of $CaCl_2$ (1.11 g; 0.01 mol) in water (10 mL). The reaction mixture was slowly cooled to room temperature and kept at this temperature overnight under stirring. The white precipitate was separated by filtration, washed with water and ethanol, and dried in air at room temperature. The yield was 2.285 g (52%). Elemental analysis calcd (%) for $C_{14}H_{12}CaO_{10}P_2$ (442.3): C 38.02, H 2.73; found: C 38.18, H, 2.80. The relative atomic ratio of calcium and phosphorus was 65.6 atom % of P and 34.4 atom % of Ca, according to EDX.

Preparation of $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$. The acidity of a solution of 4-carboxyphenylphosphonic acid monohydrate[14] (1.52 g; 6.9×10^{-3} mol) in water (50 mL) was adjusted to pH = 9.5 with a concentrated aqueous solution of NH_4OH. A solution of $CaCl_2$ (1.26 g; 1.13×10^{-2} mol) in water (20 mL) was then added under stirring. The reaction mixture was stirred overnight at room temperature. The precipitate formed was separated by filtration, washed with water and ethanol, and dried in air at room temperature. The dried white solid was ground and washed twice with boiling water and again dried at the same conditions. The yield was 1.5 g (69%). Elemental analysis calcd (%) for $C_{14}H_{20}Ca_3O_{16}P_2$ (626.5): C 26.84, H 3.22; found: C 25.75, H 3.07. The relative atomic

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Table 1. Most Intense X-ray Powder Diffraction Peaks of the Prepared Compounds

$CaC_6H_5PO_3\cdot 2H_2O$		$CaC_6H_5PO_3$		$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2\cdot 4H_2O$		$CaC_6H_5PO_3\cdot H_2O$		$Ca_3(OOCC_6H_4PO_3)_2\cdot 6H_2O$	
d, Å	I^a	*d*, Å	I^a	*d*, Å	I^a	*d*, Å	I^a	*d*, Å	I^a
15.05	36279	14.91	24719	15.20	6023	14.46	28517	19.27	2489
8.896	140	7.452	1533	7.595	545	7.232	5187	10.57	261
7.522	696	4.971	764	5.066	638	5.498	1108	9.633	3347
6.420	70	4.704	205	4.646	192	4.898	432	6.427	95
5.511	169	4.113	84	3.961	175	4.820	483	5.495	88
4.848	135	3.724	125	3.801	294	3.744	201	4.954	189
4.773	142	3.439	94	3.040	180	3.615	1380	4.814	223

[a] Intensities are given in counts.

amounts of Ca and P were 59.8 and 40.2%, respectively, according to EDX.

Reactions of $Ca(C_6H_5PO_3H)_2$ and $Ca(HOOCC_6H_4PO_3H)_2$ with Ammonia. The reactions were carried out at room temperature using a computer-controlled Schott Titronic 97 piston buret. Using the buret, an aqueous solution of ammonia was added to an aqueous suspension of the calcium compound. The intervals between additions of ammonia were chosen to be sufficiently long to ensure that practically all added base would be consumed in the reaction with the calcium compound. The acidity of the solutions during the reactions was checked with a glass pH electrode. The value of pH at the end of the intervals (just before another addition) depending on the amount of added ammonia was then evaluated.

At first the reaction was done in the presence of $CaCl_2$. $Ca(C_6H_5PO_3H)_2$ (0.4 g; 1.13×10^{-3} mol) was added to a solution of $CaCl_2$ (0.251 g; 2.26×10^{-3} mol) in a mixture of water (25 mL) and ethanol (35 mL). The suspension was reacted with an aqueous solution of NH_4OH ($c = 0.405$ mol L^{-1}), which was added in 0.25-mL doses with 3240-s intervals between doses. The values of pH during the reaction were measured in 120-s intervals. The solid white product was obtained in a 96% yield (calculated on $Ca(C_6H_5PO_3H)_2$).

Similarly, $Ca(HOOCC_6H_4PO_3H)_2$ (0.4 g; 9×10^{-4} mol) was suspended in a solution of $CaCl_2$ (0.251 g; 2.26×10^{-3} mol) in a mixture of water (25 mL) and ethanol (35 mL). The suspension was reacted with the aqueous ammonia solution ($c = 0.405$ mol L^{-1}), which was added in 0.1-mL doses with 1150-s intervals between doses and 25-s intervals between measurements of pH. An analogous reaction was also carried out under the same conditions in the absence of $CaCl_2$.

Reaction of $CaC_6H_5PO_3\cdot 2H_2O$ with Phenylphosphonic Acid. This reaction was conducted using the same experimental arrangement as $Ca(C_6H_5PO_3H)_2$ with ammonia.

A suspension of $CaC_6H_5PO_3\cdot 2H_2O$ (0.4 g; 1.723×10^{-3} mol) in a mixture of water (25 mL) and ethanol (35 mL) was titrated with a 0.1 M aqueous solution of phenylphosphonic acid, which was added in 0.2-mL doses with 1800-s intervals between doses. An analogous reaction was carried out using a 0.5 M aqueous solution of acetic acid instead of phenylphosphonic acid.

Reactions of $CaC_6H_5PO_3\cdot 2H_2O$ with Phenylphosphonic Acid at Constant pH. A 0.0482 M aqueous solution of phenylphosphonic acid was added to a stirred suspension of $CaC_6H_5PO_3\cdot 2H_2O$ (0.15 g; 6.46×10^{-4} mol) in a mixture of water (25 mL) and ethanol (35 mL) so that the pH value of the reaction mixture was maintained at 4 ± 0.05 or 3 ± 0.05 at room temperature. The additions of phenylphosphonic acid were accomplished using a computer-controlled Schott Titronic 97 piston buret. The products of the reactions were determined by EDX, TGA, and powder XRD. The yields of the solid products based on the starting $CaC_6H_5PO_3\cdot 2H_2O$ were about 60 and 40% for the reactions at pH = 4 and 3, respectively.

Reaction of $Ca_3(OOCC_6H_4PO_3)_2\cdot 6H_2O$ with 4-Carboxyphenylphosphonic Acid. This reaction was done under the same experimental arrangement as the reaction of $CaC_6H_5PO_3\cdot 2H_2O$ with phenylphosphonic acid. A suspension of $Ca_3(OOCC_6H_4PO_3)_2\cdot 6H_2O$ (0.272 g; 4.34×10^{-4} mol) in a mixture of ethanol/water (1/1 v/v; 75 mL) was stirred with a 0.665 M aqueous solution of 4-carboxyphenylphosphonic acid, which was added in 0.5-mL doses with 2000-s intervals between doses.

Results and Discussion

Calcium phenylphosphonate with a Ca/P molar ratio of 1 is formed by the addition of a $CaCl_2$ solution to a phenylphosphonic acid solution, the acidity of which was adjusted to pH = 9. The diffraction pattern of this compound contains a series of sharp (00*l*) reflections, giving evidence of a layered structure, and also contains some (*hkl*) diffraction lines with low intensity. The basal spacing ($d = 15.05$ Å) (see Table 1) of this compound is lower than that of $Ca(C_6H_5PO_3H)_2$ ($d = 15.4$ Å). The lower interlayer distance inferred from the basal spacing is consistent with a lower density of phenylphosphonic groups present on the inorganic layer.

The weight decrease of 15.6% found by thermogravimetric analysis in the temperature range 25−200 °C corresponds to a dehydration of $CaC_6H_5PO_3\cdot 2H_2O$ (calculated weight decrease is 15.6%) and comprises two poorly resolved steps (Figure 1). This dehydrated $CaC_6H_5PO_3$ exists in a quite-large temperature range from 200 to 500 °C. Heating above 500 °C causes a further loss of weight due to the decomposition of the organic part of the compound and formation of $Ca_2P_2O_7$ (weight loss: found 29.7%, calculated 29.8%). The product of heating to 960 °C is pure $Ca_2P_2O_7$, as confirmed by powder X-ray diffraction (PDF No. 09-0345).[15]

The loss of water causes a decrease of the basal spacing to $d = 14.91$ Å (Table 1) for $CaC_6H_5PO_3$. Some (*hkl*) diffraction lines observed in the diffraction pattern of $CaC_6H_5PO_3\cdot 2H_2O$ disappear, indicating that the dehydration causes a disorder in the layer arrangement.

This dehydrated sample can be reversibly hydrated, as was found by TGA for the dehydrated sample put over the saturated solution of $Mg(NO_3)_2$ (53% relative humidity) for 20 days.

The relationship between $CaC_6H_5PO_3\cdot 2H_2O$ and previously described $Ca(C_6H_5PO_3H)_2$ was investigated by the reaction of a suspension of $CaC_6H_5PO_3\cdot 2H_2O$ with phen-

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(15) Joint Committee on Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, PA.

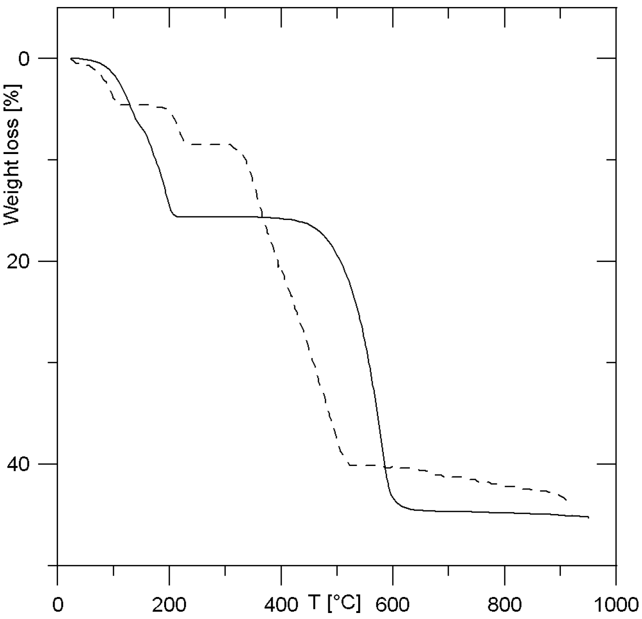

Figure 1. TGA curves of $CaC_6H_5PO_3{\cdot}2H_2O$ (solid line) and $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ (dashed line).

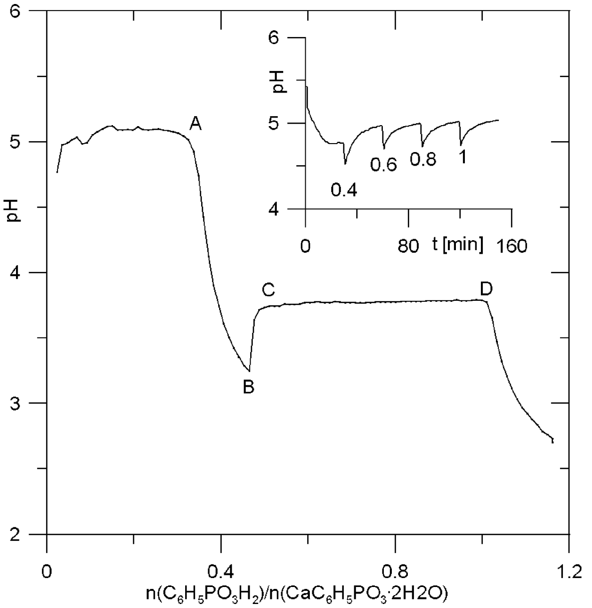

Figure 2. Course of the reaction of the $CaC_6H_5PO_3{\cdot}2H_2O$ suspension with the phosphonic acid solution. (Inset) Time dependence of pH at the beginning of the reaction; the numbers indicate the milliliters of the added acid.

ylphosphonic acid added in small doses using a computer-controlled buret (Figure 2). At the beginning of the additions, no reaction occurs and the pH of the reaction mixture decreases due to the added acid. When the pH of the reaction mixture decreases below 5, the reaction of $CaC_6H_5PO_3{\cdot}2H_2O$ with phenylphosphonic acid starts, which is indicated by an increase of pH between the additions of acid (see inset in Figure 2), and the pH reaches a value of around 5.1 before another addition of the acid. After the addition of 0.33 mol of phenylphosphonic acid per 1 mol of $CaC_6H_5PO_3{\cdot}2H_2O$ (point A in Figure 2), the pH starts to decrease down to about 3.2 (point B). Then there is another steep increase of pH to 3.7, and this pH is maintained constant (from point C) during further additions of the acid. Another decrease of pH follows after the addition of about 1 mol of phenylphosphonic acid per 1 mol of $CaC_6H_5PO_3{\cdot}2H_2O$ (point D). The product of the reaction was identified by powder XRD, TGA, and EDX to be $Ca(C_6H_5PO_3H)_2$.

The shape of the curve in Figure 2 indicates that there is a formation of an intermediate during the reaction. To obtain this intermediate, we reacted $CaC_6H_5PO_3{\cdot}2H_2O$ with phenylphosphonic acid to point B only. The product of this reaction has a relative Ca/P molar ratio of $0.745 \approx 3/4$ as found by EDX. Its formula can therefore be estimated as $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}yH_2O$. Thermogravimetric analysis (Figure 1) shows a two-step release of water at 100 and 200 °C and a decomposition of the organic part at 400 °C. The product of the decomposition is a mixture of $Ca_2P_2O_7$ (PDF No. 09-0346) and $Ca(PO_3)_2$ (PDF No. 11-0039).[15] The first two-step weight decrease of 8.7% to 250 °C corresponds to a release of 4 molecules of water per formula unit (calculated weight decrease: 8.8%).

$$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O \rightarrow Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 + 4H_2O \quad (1)$$

The decomposition of the organic part of the intermediate in the temperature range 300−550 °C, according to the equation,

$$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 + 30O_2 \rightarrow Ca_2P_2O_7 + Ca(PO_3)_2 + 24CO_2 + 11H_2O \quad (2)$$

causes a weight decrease of 35.1% (calculated: 36.0%). Powder X-ray diffraction data confirm that $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ is a new compound, with $d = 15.197$ Å (Table 1), and not a mixture of the starting compound and the product of the reaction. The proposed formula of $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ was also confirmed by elemental analysis. Calculated (%) for $C_{24}H_{30}Ca_3O_{16}P_4$ (818.6): C 35.20, H 3.69; found: C 34.95, H, 3.44.

The course of the reaction of $CaC_6H_5PO_3{\cdot}2H_2O$ with phenylphosphonic acid can be then described by the following equations

$$3CaC_6H_5PO_3{\cdot}2H_2O + C_6H_5PO_3H_2 \rightarrow Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O + 2H_2O \quad (3)$$

$$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O + 2C_6H_5PO_3H_2 \rightarrow 3Ca(C_6H_5PO_3H)_2 + 4H_2O \quad (4)$$

One mole of phenylphosphonic acid is needed per three moles of $CaC_6H_5PO_3{\cdot}2H_2O$ to complete the first reaction. The intermediate is, therefore, formed at point A in Figure 2, and a further addition of phenylphosphonic acid causes a decrease of pH only. To start the second reaction, a pH close to 3.2 must be achieved. All added phenylphosphonic acid is then consumed in the following reaction and pH remains constant. The second reaction is finished when the molar amount of phenylphosphonic acid is the same as the amount

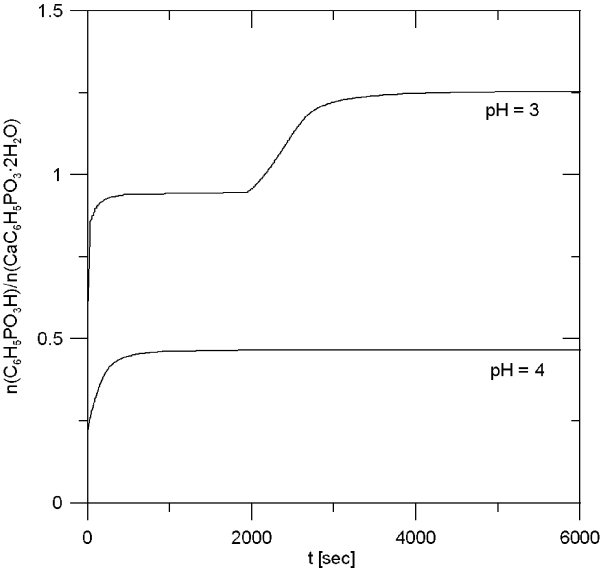

Figure 3. Amount of consumed phenylphosphonic acid as a function of time in the reaction with $CaC_6H_5PO_3{\cdot}2H_2O$ at pH = 3 and 4.

of original $CaC_6H_5PO_3{\cdot}2H_2O$ (point D in Figure 2). Further addition of phenylphosphonic acid causes only a decrease of pH.

A similar reaction of the $CaC_6H_5PO_3{\cdot}2H_2O$ suspension was done with acetic acid. At first, the value of pH decreases to less than 3.5 after the addition of 0.15 mol of acetic acid per 1 mol of $CaC_6H_5PO_3{\cdot}2H_2O$. This decrease is followed by an increase of pH up to about 4.2, indicating that the reaction proceeds. After the addition of about 1.5 mol of CH_3COOH per 1 mol of $CaC_6H_5PO_3{\cdot}2H_2O$, this trend slows down and gradually turns into a decrease of pH. The product has the Ca/P molar ratio ≈ 3/4, according to EDX; also, powder XRD (d = 15.20 Å) and TGA indicate that the product is $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$. The final product corresponding to reaction 4, that is $Ca(C_6H_5PO_3H)_2$, is not formed in this case. The addition of HCl to the $CaC_6H_5PO_3{\cdot}2H_2O$ suspension leads to a dissolution of the calcium compound.

Employing the results depicted in Figure 2, we determined that the reaction of $CaC_6H_5PO_3{\cdot}2H_2O$ with phenylphosphonic acid proceeds to $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ at pH = 4 and to $Ca(C_6H_5PO_3H)_2$ at pH = 3. Therefore, we repeated this reaction in a pHstat mode; i.e., we kept a constant pH by adding phenylphosphonic acid to a stirred suspension of $CaC_6H_5PO_3{\cdot}2H_2O$. The amount of added phenylphosphonic acid (expressed as a molar ratio of $n(C_6H_5PO_3H_2)/n(CaC_6H_5PO_3{\cdot}2H_2O)$) is given in Figure 3 as a function of time. It is obvious from the figure that at pH = 4, only $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ is formed, and the course of the reaction follows a typical kinetic curve. At pH = 3, the same course is followed at first. After the formation of $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$, however, another reaction takes place, and the final product, $Ca(C_6H_5PO_3H)_2$, is formed. The amount of phenylphosphonic acid consumed in both cases is higher than that expected, according to reactions 3 and 4. We found that under the given reaction conditions, the reaction products are partially soluble and form a sort of buffer in the reaction mixture. The effect of this buffer must be compensated by an increase of the amount of acid needed to achieve the desired pH, which explains why the amount of consumed acid is higher than the theoretical one.

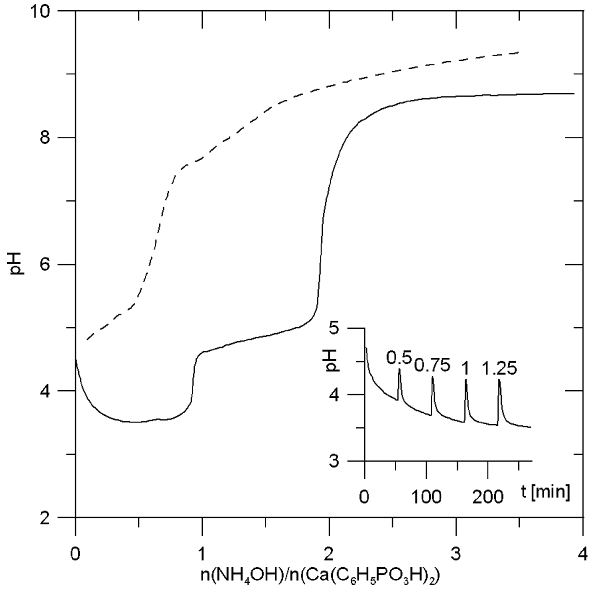

Figure 4. Course of the reaction of the $Ca(C_6H_5PO_3H)_2$ suspension with ammonia in the presence (solid line) and in the absence (dashed line) of $CaCl_2$. (Inset) Time dependence of pH at the beginning of the reaction; the numbers represent the milliliters of added NH_4OH.

A reverse reaction was also investigated, that is a formation of $CaC_6H_5PO_3{\cdot}2H_2O$ in a reaction of $Ca(C_6H_5PO_3H)_2$ with Ca^{2+} ions in a moderately basic medium. This reaction was accomplished by a computer-controlled addition of an ammonia solution to an aqueous suspension of $Ca(C_6H_5PO_3H)_2$ in the presence of $CaCl_2$. The value of the pH decreased exponentially between the additions of ammonia, indicating an uptake of OH^- ions due to its reaction with $Ca(C_6H_5PO_3H)_2$, as seen in the inset in Figure 4. The product of the reaction was found to be $CaC_6H_5PO_3{\cdot}2H_2O$ by powder XRD, TGA, and EDX. The course of the reaction as a dependence of pH on the molar amount of added ammonia per one mole of $Ca(C_6H_5PO_3H)_2$ is depicted in Figure 4 as a solid curve. The values of pH are those reached just before the addition of another dose of ammonia. Two equivalence points observed at $n(NH_4OH)/n(Ca(C_6H_5PO_3H)_2)$ = 1 and 2 indicate an existence of an intermediate during the reaction. This intermediate was prepared from a suspension of $Ca(C_6H_5PO_3H)_2$ in a $CaCl_2$ solution by adding ammonia up to $n(NH_4OH)/n(Ca(C_6H_5PO_3H)_2)$ = 1. The product was identified to be $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O$ by powder XRD, TGA, and EDX. Therefore, the reaction can be written as

$$2Ca(C_6H_5PO_3H)_2 + CaCl_2 + 2NH_4OH + 2H_2O \rightarrow Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O + 2NH_4Cl \quad (5)$$

followed by

$$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2{\cdot}4H_2O + CaCl_2 + 2NH_4OH + 2H_2O \rightarrow 4CaC_6H_5PO_3{\cdot}2H_2O + 2NH_4Cl \quad (6)$$

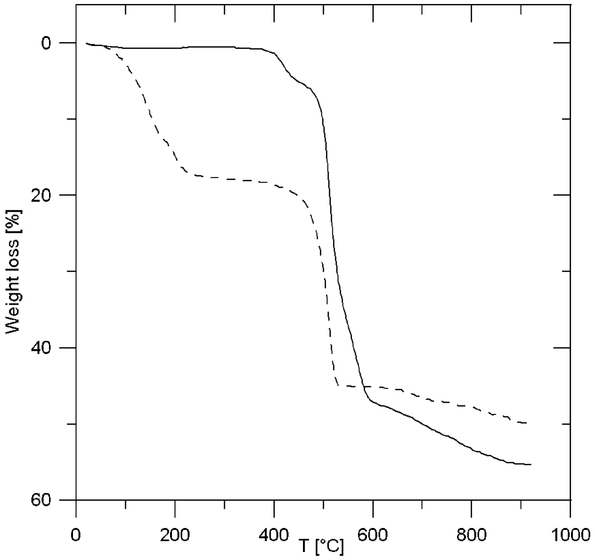

Figure 5. TGA curves of $Ca(HOOCC_6H_4PO_3H)_2$ (solid line) and $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ (dashed line).

This reaction was also carried out under the same conditions without $CaCl_2$. In this case, no distinct two-step increase of pH was observed (Figure 4, dashed line), and the product of the reaction was found to be $CaC_6H_5PO_3{\cdot}2H_2O$ by powder XRD, TGA, and EDX.

By heating $CaC_6H_5PO_3{\cdot}2H_2O$ for 2 days at 180 °C, a new compound was formed which, by elemental analysis, TGA, and EDX, was identified to be calcium phenylphosphonate monohydrate, $CaC_6H_5PO_3{\cdot}H_2O$. The powder pattern (Table 1) was indexed in a monoclinic system with cell parameters $a = 5.9435(3)$ Å, $b = 14.4622(3)$ Å, $c = 5.2069(3)$ Å, $\beta = 90.664(5)°$ with a space group $P2/m$. The basal spacing ($d = 14.46$ Å) found for this compound is even lower that that observed for dehydrated $CaC_6H_5PO_3$. This indicates that the structure of $CaC_6H_5PO_3{\cdot}H_2O$ is different from those of $CaC_6H_5PO_3{\cdot}2H_2O$ and $CaC_6H_5PO_3$ and belong most probably to the group of the $M(II)C_6H_5PO_3{\cdot}H_2O$ (M = Mg, Zn, Co, Ni, Mn, or Cu) layered compounds.[1]

A new functionalized calcium phosphonate was prepared by the reaction of $HOOCC_6H_4PO_3H_2{\cdot}H_2O$ with an aqueous solution of $CaCl_2$. The Ca/P molar ratio was 1/2 in the product. This means that its formula can be written as $Ca(HOOCC_6H_4PO_3H)_2$. The compound is stable up to 400 °C, as follows from the thermogravimetric analysis (Figure 5). The temperature at which the weight loss occurs is typical for the decomposition of the organic part of metal phosphonates. The product of TGA is $Ca(PO_3)_2$, as confirmed by powder XRD (PDF No. 79-0700).[15] The observed weight loss is 55.4%, which is in very good agreement with the calculated one (55.2%), according to the equation

$$Ca(HOOCC_6H_4PO_3H)_2 + 15O_2 \rightarrow Ca(PO_3)_2 + 6H_2O + 14CO_2 \quad (7)$$

Table 2. Crystallographic Data for $Ca(HOOCC_6H_4PO_3H)_2$

formula	$Ca(HOOCC_6H_4PO_3H)_2$
fw, g mol^{-1}	442.27
calculated density, g cm^{-3}	1.79
cryst syst	monoclinic
space group	$C2/c$ (No. 15)
a, Å	49.218(3)
b, Å	7.7609(4)
c, Å	5.4452(3)
β, deg	128.119(3)
V, Å^{-3}	1636.3(2)
Z	4
2θ range, deg	2−65
T, °C	25
λ, Å	1.5418
$R_p{}^a$	0.163
$R_{wp}{}^b$	0.221

[a]
$$R_p = \frac{\sum_{i=1,n} |y_i - y_{c,i}|}{\sum_{i=1,n} y_i}$$

[b]
$$R_{wp} = \left[\frac{\sum_{i=1,n} w_i |y_i - y_{c,i}|^2}{\sum_{i=1,n} w_i y_i^2}\right]^{1/2}$$

where y_i and $y_{c,i}$ are observed and calculated profile intensities, respectively, and w_i is defined as $w_i = 1/\sigma_i^2$ with σ_i^2 being the variance of y_i.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Ca(HOOCC_6H_4PO_3H)_2$

P12−O16	1.543(20)
P12−O17	1.600(16)
Ca−O15	2.575(27)
Ca−O16	2.343(31)
Ca−O17	2.290(14)
P12−O15	1.601(25)
O15−P12−O16	104.32(78)
O16−P12−O17	119.75(94)
O15−P12−O17	112.59(98)
O15−Ca−O16	117.46(51)
O15−Ca−O17	76.84(74)
O16−Ca−O17	74.77(56)

The powder pattern of $Ca(HOOCC_6H_4PO_3H)_2$ allowed us to solve the structure using a combination of FOX and FullProf programs. The crystallographic data are given in Table 2, and the selected bond lengths and angles, in Table 3. In the structure of $Ca(HOOCC_6H_4PO_3H)_2$, the calcium atoms are eight coordinated by O15, O16, and O17 oxygen atoms of the phenylphosphonate groups, similar to that of $Ca(C_6H_5PO_3H)_2$.[3] In contrast with $Ca(C_6H_5PO_3H)_2$, the $Ca(HOOCC_6H_4PO_3H)_2$ compound is not layered but forms a one-dimensional structure. Each calcium atom is surrounded by two phosphonate groups to which it is connected through O15 and O16 atoms. Every such structure unit shares two O17 atoms with two neighboring structure units forming a chain running along the c axis. Two such chains are connected via O16 atoms, as depicted in Figure 6, forming a $[Ca_2(HOOCC_6H_4PO_3H)_4]_\infty$ ribbon. The distance between the carboxylic groups of two carboxyphenylphosphonate fragments neighboring in the direction of the a axis indicates that a hydrogen bond is formed between them (the distance O13−O14 between these two neighboring groups is 2.689

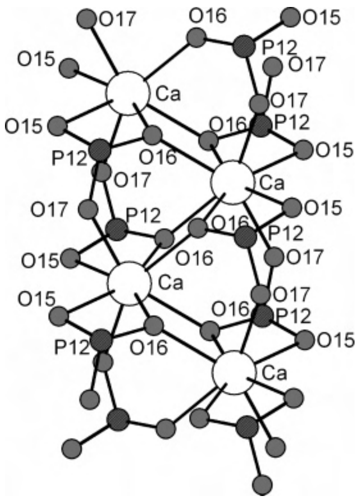

Figure 6. Structural unit of $Ca(HOOCC_6H_4PO_3H)_2$ showing an arrangement of CaO_8 polyhedra and phosphonate groups. The phenyl groups are omitted for clarity. Open circles − calcium, light gray circles − oxygen, dark gray circles − phosphorus.

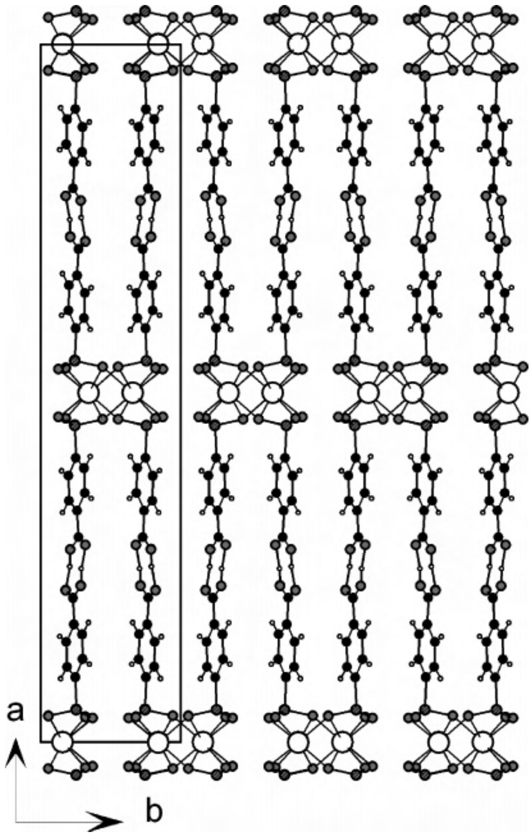

Figure 7. Structure of $Ca(HOOCC_6H_4PO_3H)_2$ viewed along the *c* axis. The hydrogen bonds between carboxylic groups are shown with small open circles representing hydrogen atoms.

Å). This hydrogen bond is shown in Figure 7, obtained from the FOX computation which included hydrogen atoms on the carboxylic group. All of the $[Ca_2(HOOCC_6H_4PO_3H)_4]_\infty$ ribbons are connected together by these hydrogen bonds in such a way that the calcium atoms are positioned in a plane coplanar to the *bc* plane (Figure 8).

Another calcium 4-carboxyphenylphosphonate with a Ca/P molar ratio of 3/2 was prepared by the reaction of the $CaCl_2$ solution with an ammonium 4-carboxyphenylphosphonate solution. The powder XRD pattern of $Ca_3(OOCC_6H_4PO_3)_2 \cdot 6H_2O$ shows an interlayer distance of 19.27 Å (Table 1), which is slightly lower than that found for $Ca(HOOCC_6H_4PO_3H)_2$. The thermogravimetric analysis in Figure 5 shows a weight loss of 17.2% at around 200 °C, with two poorly resolved steps, followed by another steep weight decrease at 500 °C. The first weight loss indicates a presence of water. Presuming that the compound has a formula $Ca_3(OOCC_6H_4PO_3)_2 \cdot yH_2O$, the content of water was calculated to be $y = 6$ (theoretical weight loss 17.3%). The second weight loss is a decomposition of the organic part. The product of TGA is $Ca_3(PO_4)_2$, as confirmed by powder XRD (PDF No. 01-0169).[15] The total weight loss was 50.1%; the weight loss calculated, according to the equation,

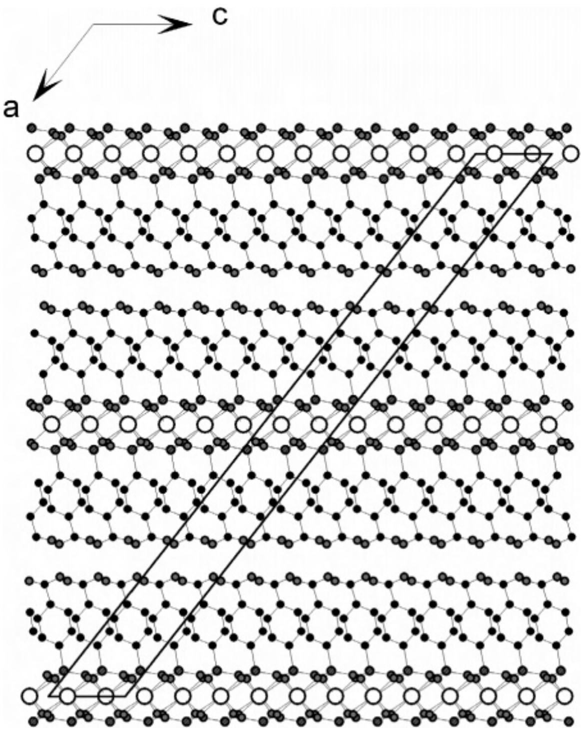

Figure 8. Structure of $Ca(HOOCC_6H_4PO_3H)_2$ viewed along the *b* axis.

$$Ca_3(OOCC_6H_4PO_3)_2 \cdot 6H_2O + 16O_2 \rightarrow Ca_3(PO_4)_2 + 12H_2O + 14CO_2 \quad (8)$$

was 50.5%.

The release of water is reversible, and dehydrated $Ca_3(OOCC_6H_4PO_3)_2$ can be hydrated back to the hexahydrate by contact with water for 10 days. The water in the interlayer space can also be replaced with, for instance, ethylenediamine by suspending the dehydrated sample in pure ethylenediamine and keeping the mixture in a closed vessel for 3 days at room temperature.

Analogously to the preparation of $CaC_6H_5PO_3 \cdot 2H_2O$ from $Ca(C_6H_5PO_3H)_2$, $Ca_3(OOCC_6H_4PO_3)_2 \cdot 6H_2O$ was prepared by the computer-controlled addition of aqueous ammonia to a suspension of $Ca(HOOCC_6H_4PO_3H)_2$ in the presence of the $CaCl_2$ solution. In contrast with the reaction of $CaC_6H_5PO_3 \cdot 2H_2O$, the reaction of $Ca(HOOCC_6H_4PO_3H)_2$ shows only one

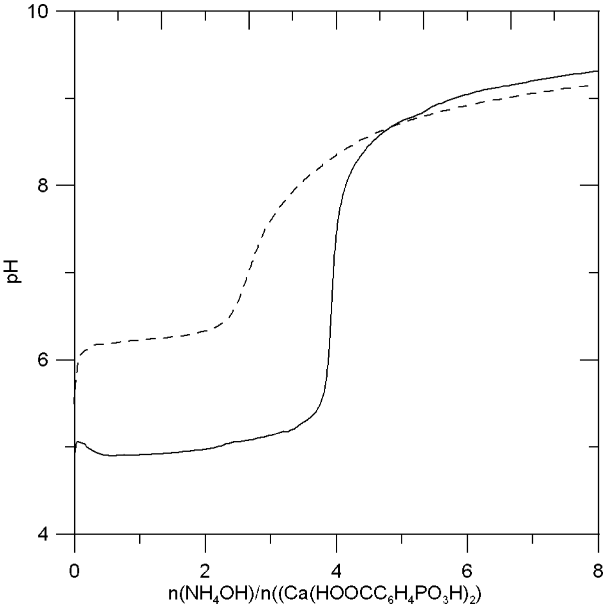

Figure 9. Course of the reaction of the $Ca(HOOCC_6H_4PO_3H)_2$ suspension with ammonia in the presence (solid line) and in the absence (dashed line) of $CaCl_2$.

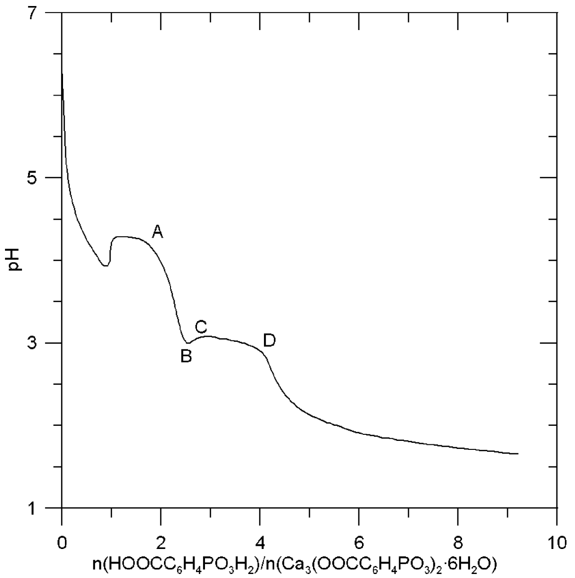

Figure 10. Course of the reaction of the $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ suspension with the solution of 4-carboxyphenylphosphonic acid.

equivalence point at $n(NH_4OH)/n(Ca(HOOCC_6H_4PO_3H)_2) = 4$ (Figure 9, solid line). This means that no intermediate is formed in this case, and $Ca(HOOCC_6H_4PO_3H)_2$ turns into $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ according to the equation

$$Ca(HOOCC_6H_4PO_3H)_2 + 2CaCl_2 + 4NH_4OH + 2H_2O \rightarrow Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O + 4NH_4Cl \quad (9)$$

When the same reaction is carried out in the absence of $CaCl_2$ (Figure 9, dashed line), the equivalence point is reached at $n(NH_4OH)/n(Ca(HOOCC_6H_4PO_3H)_2) = 2.7$, that is 8 mol of ammonia is consumed per 3 mol of $Ca(HOOCC_6H_4PO_3H)_2$. Such a reaction could then be described by the equation

$$3Ca(HOOCC_6H_4PO_3H)_2 + 8NH_4OH \rightarrow Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O + 4(NH_4)_2H(OOCC_6H_4PO_3) + 2H_2O \quad (10)$$

The formation of $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ in both cases was confirmed by powder XRD, EDX, and TGA. The yields were 100 and 94% in the presence and in the absence of $CaCl_2$, respectively. The formation of the diammonium salt, $(NH_4)_2H(OOCC_6H_4PO_3)$, in reaction 10 was confirmed by a titration of 4-carboxyphenylphosphonic acid with ammonia. This titration proceeds to the second degree only; that is, the triammonium salt of 4-carboxyphenylphosphonic acid is not formed in the solution at such pH values.

The course of the reverse reaction, i.e., the formation of $Ca(HOOCC_6H_4PO_3H)_2$ from $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ and 4-carboxyphenylphosphonic acid, is similar to that observed for the formation of $Ca(C_6H_5PO_3H)_2$ from $CaC_6H_5PO_3{\cdot}2H_2O$ and phenylphosphonic acid (Figure 10). The explanation of points A−D in Figure 10 is analogous to that given for Figure 2. In this case, point A in Figure 10 occurs at $n(HOOCC_6H_4PO_3H_2)/n(Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O) = 2$, which means that the formation of an intermediate could be presumed at this point. Point D, corresponding to the formation of the product, lies at $n(HOOCC_6H_4PO_3H_2)/n(Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O) = 4$, and the total reaction can be then described by the equation

$$Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O + 4HOOCC_6H_4PO_3H_2 \rightarrow 3Ca(HOOCC_6H_4PO_3H)_2 + 6H_2O \quad (11)$$

The small difference in pH between points B and C indicates that the intermediate is less stable and changes to the product more easily than in the case of the reaction of $CaC_6H_5PO_3{\cdot}2H_2O$ with phenylphosphonic acid. This was

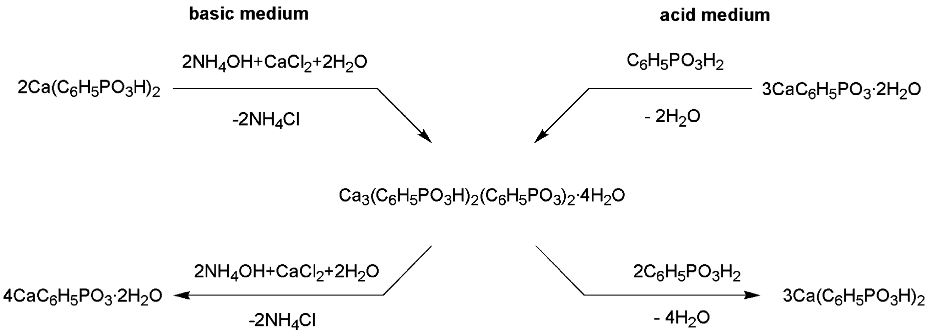

Figure 11. Interconversion of calcium phenylphosphonates.

confirmed by the fact that the formation of the intermediate was not observed in an experiment in which the interval between doses of 4-carboxyphenylphosphonic acid was 3 times longer. The fast addition of 2 mol of 4-carboxyphenylphosphonic acid to 1 mol of $Ca_3(OOCC_6H_4PO_3)_2{\cdot}6H_2O$ results in the formation of a mixture of $Ca(HOOCC_6H_4PO_3H)_2$ and an unknown compound (most probably the intermediate), as proved by powder XRD.

In summary, we have found that calcium phenylphosphonates could be interconverted depending on the acidity of the reaction medium according to the flow diagram depicted in Figure 11. Calcium 4-carboxyphenylphosphonates reacted in an analogous way except that the intermediate could not be isolated. We successfully solved the structure of $Ca(HOOCC_6H_4PO_3H)_2$ from X-ray powder diffraction data. The described computer-controlled additions of the reagents proved to be a useful method not only for the study of the stability of the prepared compounds but also as a tool for the synthesis of new materials under defined conditions.

Acknowledgment. This study was supported by the Grant Agency of the Czech Republic (GA 203/05/2306).

Supporting Information Available: X-ray crystallographic file for $Ca(HOOCC_6H_4PO_3H)_2$, in CIF format, list of bond lengths and angles for $Ca(HOOCC_6H_4PO_3H)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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