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Cadmium phenylphosphonates: preparation, characterisation and *in situ* investigation[†]

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The crystalline cadmium phenylphosphonates $\text{Cd}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$ (**1**), $\text{Cd}(\text{HO}_3\text{PPh})_2$ (**2**), and $\text{Cd}(\text{HO}_3\text{PPh})_2(\text{H}_2\text{O}_3\text{PPh})$ (**3**) can be synthesized in solid state reactions by grinding together cadmium acetate with respective equivalents of phenylphosphonic acid. The phosphonates (**2**) and (**3**) were not obtained by any other synthesis method so far. The determination of the crystal structure of the new compounds (**2**) and (**3**) based on the powder X-ray diffraction (PXRD) data is reported. The milling reactions were investigated using *in situ* synchrotron PXRD. Based on these data, an identification of intermediates and a detailed analysis of the underlying mechanisms was possible.

Introduction

Metal phosphonates are of great interest with respect to their high potential for applications in gas storage,^{1,2} catalysis,³ proton conductors,^{4–6} and the modification of surfaces.^{7,8} The phosphonates implemented in the coordination polymer differ in the number of phosphonate groups and in the nature of the organic part. Different divalent metal phenylphosphonates with a 1:1 metal:phenylphosphonate composition are known, including the fully deprotonated phenylphosphonate.⁹ These compounds are isomorphous. Furthermore, several functionalised metal phosphonates were described.^{10,11} Typically, the synthesis is carried out in aqueous solutions. Hydrothermal methods are used to achieve highly crystalline products and a high-throughput synthesis was developed.¹² *In situ* investigations of the formation of metal phosphates under solvothermal conditions with synchrotron XRD were described.^{13,14} *In situ* investigations of the crystallisation of metal aminophosphonates, phosphonosulfates and -carboxylates under hydrothermal and ultrasonic conditions were carried out, recently.^{15–17}

Unlike for the related class of metal organic frameworks (MOFs) the use of alternative synthetic routes like mechanochemistry is scarce.^{18–20} Recently, *in situ* methods were developed to investigate milling syntheses to provide the necessary data for a thorough mechanistic study.^{21–24}

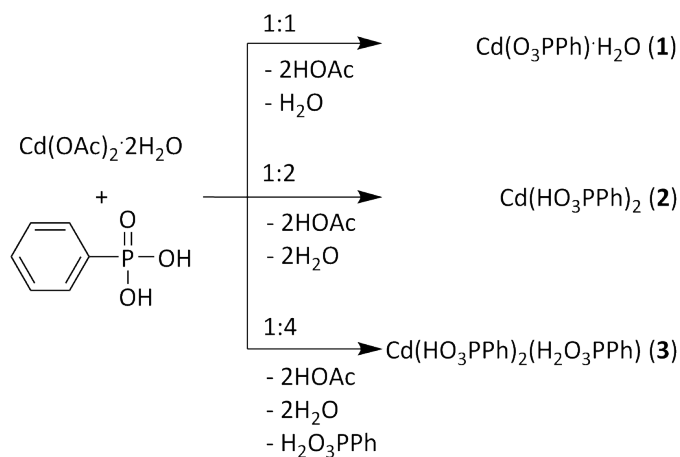


Fig. 1 Reaction scheme for the syntheses of the products (**1**), (**2**) and (**3**); OAc = $(\text{O}_2\text{CCH}_3)^-$.

Here, we present the mechanochemical synthesis of three cadmium phenylphosphonates; the cadmium monophenylphosphonate $\text{Cd}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$ (**1**) ($\text{Ph} = \text{C}_6\text{H}_5$)²⁵ and two novel structures (1:2 and 1:3) (Figure 1). The structures of the new compounds $\text{Cd}(\text{HO}_3\text{PPh})_2$ (**2**) and $\text{Cd}(\text{HO}_3\text{PPh})_2(\text{H}_2\text{O}_3\text{PPh})$ (**3**) were determined from powder X-ray diffraction (PXRD) data. Compound (**2**) contains two monodeprotonated phenylphosphonate ligands. The compound (**3**) contains a further neutral

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[†] Electronic Supplementary Information (ESI) available: Crystallographic information files, Tables with selected bond length of compound (**2**) and (**3**), PXRD patterns of the starting materials, compounds (**1**), (**2**), (**3**) (before and after the cleaning step), and of the product mixture of the mechanochemical synthesis with an 1:3 ratio of the starting materials, enlarged 2D plots of the *in situ* investigations of the syntheses of compound (**1**)-(3), PXRD patterns of the products of the mechanochemical syntheses with compound (**1**) and (**3**) as starting materials, and PXRD patterns of the products of the slurry experiments. See DOI: 10.1039/b000000x/

phenylphosphonic acid ligand. The synthesis of the three compounds was analysed *in situ* using time resolved synchrotron PXRD. Based on these results, a formation mechanism is proposed.

Experimental Section

Chemicals

The following chemicals were used: Cadmium acetate dihydrate (purum p.a., Fluka, Switzerland), phenylphosphonic acid (98%, Acros Organics, USA), and diethyl ether (analytical reagent grade, Fisher Chemical, USA). All chemicals were used without further purification.

Synthesis of $\text{Cd}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$ (1)

The synthesis was performed in a vibration ball mill (Pulverisette 23, Fritsch, Germany). Cadmium acetate dihydrate and phenylphosphonic acid were added together in a stainless steel vessel in a molar ratio of 1:1 and a total load of 1 g. Two stainless steel balls (\varnothing 10 mm, 4 g) were added and the mixture was ground at 50 Hz for 15 min. A damp white powder was obtained and dried in air.

Synthesis of $\text{Cd}(\text{HO}_3\text{PPh})_2$ (2)

The synthesis was performed similar to the synthesis of compound (1). Here, the molar ratio of cadmium acetate dihydrate and phenylphosphonic acid was 1:2.

Synthesis of $\text{Cd}(\text{HO}_3\text{PPh})_2(\text{H}_2\text{O}_3\text{PPh})$ (3)

The synthesis was performed following the synthesis procedure described for compound (1). Here, the molar ratio of cadmium acetate dihydrate and phenylphosphonic acid was 1:4. The obtained powder was stirred strongly in diethyl ether to remove excess phenylphosphonic acid, filtrated and dried in air.

With respect to the metal atom, the yields of the reactions are 100%. One has to keep in mind that during the removal of the samples, small amounts remain in the grinding jar. About 95% yield is a realistic estimation. For compound (3) 87% yield was obtained with respect to the metal atom after the cleaning step.

Slurry experiments

Slurry experiments were performed to determine the relative stability of the compounds. Each compound (250 mg) was stirred for 24 h in water (25 mL) under ambient conditions. The solid phase was gained by filtration and analyzed by powder X-ray diffraction (PXRD), see Figure S8.

Analytical Techniques

PXRD measurements were performed in transmission geometry mode in a 2θ range from 4° to 60° , with a step size of 0.009° , using $\text{Cu } K_{\alpha 1}$ ($\lambda = 1.54056 \text{ \AA}$) radiation. The patterns were collected on a diffractometer (D8 Discover, Bruker AXS, Germany) equipped with a Lynxeye detector and a Johansson monochromator in the incident beam. For structure solution, the measured time per step was 20 s for (2) and 33 s for (3). The PXRD data

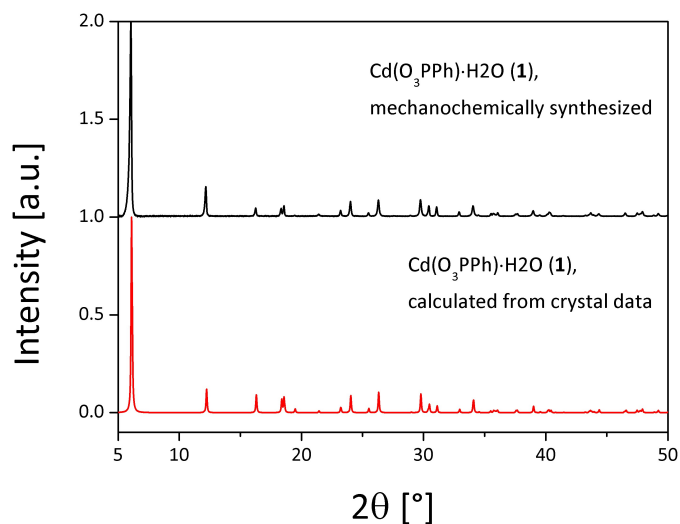


Fig. 2 Comparison of the measured PXRD pattern of (1) (black) and the calculated (red) PXRD pattern for $\text{Cd}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$.²⁵

were indexed using the program DICVOL, implemented in the DASH software.²⁶ The structures were solved using the simulated annealing routine implemented in DASH. For (2) the position of the Cd atom was fixed at (0.5/0.5/0). For (3) the missing hydrogen atoms H3A, H5A, H8A, and H9A were added using PowderCell.²⁷ The final Rietveld refinements were conducted using TOPAS.²⁸ CCDC-1402479 and CCDC-1402480 contain the supplementary crystallographic data for this structure. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

The reactions were investigated *in situ* using synchrotron XRD. The experiments were performed at the μSpot beamline (Bessy II, Helmholtz Centre Berlin for Materials and Energy, Germany).²⁹ The setup was reported in detail previously.²³ A specially adapted vibration ball mill was used. The compounds were synthesized in a 10 mL custom-made Perspex vessel. The starting materials were ground together with two stainless steel balls (10 mm, 4 g). The experimental conditions were similar to those described before, except for a lower frequency (30 Hz) applied. The XRD patterns were collected using a two dimensional MarMosaic CCD detector (3072x3072 pixels and a point spread function width of about $100 \mu\text{m}$). The exposure time was 30 s per measurement, with a delay time of 3-4 s between two measurements. For processing the scattering images, an algorithm of the computer program FIT2D was used.³⁰ The transformation of the scattering vector (q) to the diffraction angle 2θ for $\text{Cu } K_{\alpha 1}$ radiation allows a direct comparison to the results of the laboratory PXRD measurements.

Results and Discussion

Syntheses and Structure Characterization

The compounds (1)-(3) were synthesized by neat grinding (see Experimental Section). The PXRD patterns of (1) and (2) show no reflection of the starting materials, indicating a complete reaction (Figure S1). The successful mechanochemical synthesis of (1) was confirmed by comparing the PXRD pattern with the calcu-

lated pattern from the known structure (Figure 2).²⁵ The crystal structures of (2) and (3) were solved from the PXRD patterns. For both compounds (2) and (3) the final Rietveld and difference plots are shown in Figure 3. Table 1 summarizes the crystallographic data. In the PXRD pattern of (2) a weak reflection at 6.1° indicates the formation of (1) as a side product. A Rietveld refinement with both structures results in an amount of (1) close to 1%.²⁸ The synthesis of (3) comprises a cleaning step to remove excess phosphonic acid. The PXRD pattern of (3) before the cleaning step shows reflections of phenylphosphonic acid, which is reasonable because the acid is used in excess (Figure S2). After stirring in diethyl ether, the corresponding PXRD pattern shows no reflections of the starting materials (Figure S2). The diffraction patterns of all three compounds are characterized by a strong reflection in the low 2θ range ((1): 6.1°, (2): 5.7° and (3): 7.1°). These characteristic reflections can be used for an unambiguous phase identification.

Structure Description

The structure of (1) is shown in Figure 4d along the *c*-axis. The structure is isomorphic to a group of divalent metal phenylphosphonate monohydrates and was described in detail by Cao *et al.*²⁵ The Cd²⁺-ion is six-fold coordinated in a distorted octahedron. The coordination environment consists of six oxygen atoms from four different phenylphosphonate ligands and one water molecule. These [CdO₆] octahedrons are directly corner connected (see Figure 4a). An additional connection is formed by the phosphonate groups. The inorganic part of the phenylphosphonate ligands and the Cd²⁺-ion form a layer structure. The organic part points into the interlayer space, as often is observed for metal phosphonates. The position of the phenyl rings is disordered. The two possible positions are oriented orthogonal to each other along the C1-C2 axis.

The structure of (2) is depicted in Figure 4e along the *c*-axis. Selected bond lengths and angles are given in Table S1. The Cd²⁺-ion is coordinated by six oxygen atoms from six different phenylphosphonate ligands in a distorted octahedron (Figure 4b). The oxygen atoms of the phenylphosphonate ligands are involved in the coordination of three different Cd²⁺-ions. Four longer bonds (2.5319(3) Å and 2.5762(3) Å) and two shorter bonds (2.2262(2) Å) can be distinguished. The O-Cd-O angles range from 72.59(1)° to 107.41(1)°. Since all oxygen atoms coordinate to only one Cd²⁺-ion, there is no direct connection between the octahedrons. Here, the connection is established by the phosphonate groups (see Figure 4b), resulting in a typical layer structure for the inorganic part of the compound including the isolated CdO₆-octahedrons. The phenyl rings point into the interlayer space. They are ordered alternating above and below the layer, slightly tilted with respect to the layer plane. The asymmetric unit contains only monodeprotonated phenylphosphonate ligands. The position of the acidic hydrogen atom could not be determined directly. Based on the values of the P-O-bonds (1.4196(1) Å (O2), 1.5388(1) Å (O3) and 1.5796(1) Å (O1)), O2 can be identified as the double bonded oxygen atom. A strong hydrogen bond connects the oxygen atom O1 with another

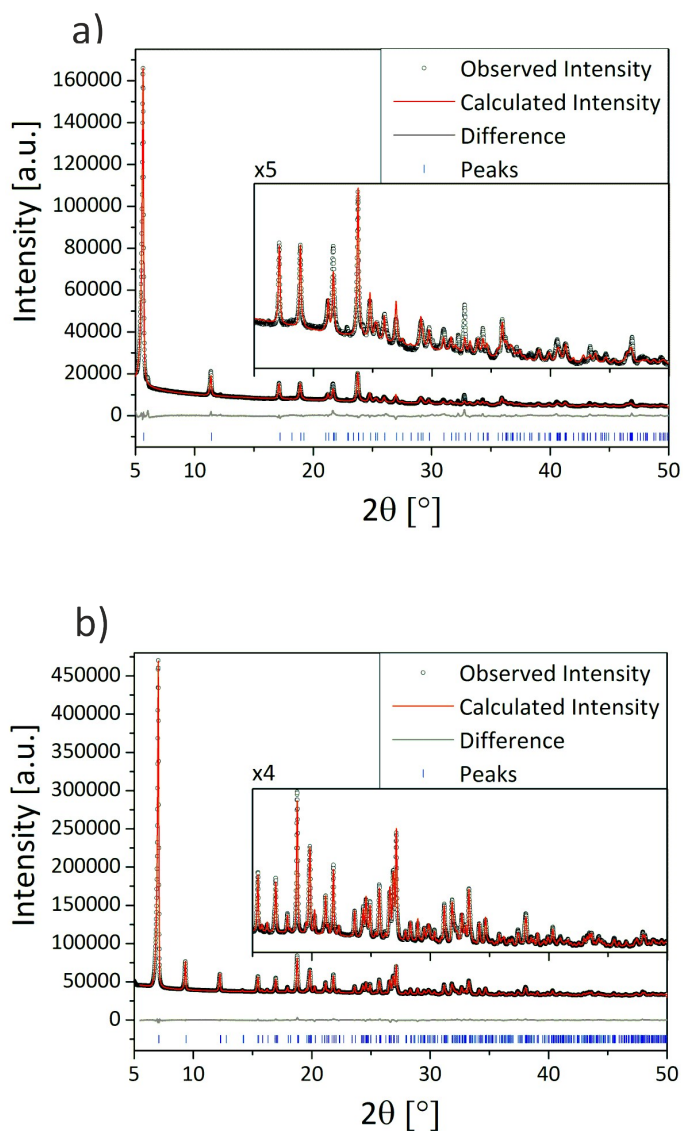


Fig. 3 Scattered X-ray intensity of **a)** (2) and **b)** (3) under ambient conditions as a function of the diffraction angle 2θ . The observed pattern (circles), the best Rietveld fit profile (red line), the reflection positions (blue tick marks), and the difference curve (grey line) between observed and calculated profiles are shown. The wavelength is $\lambda = 1.54056 \text{ \AA}$ (Cu $K_{\alpha 1}$).

phenylphosphonate molecule (O2), which additionally stabilizes the structure ($d_{\text{O-O}} = 2.5569(2) \text{ \AA}$).

The structure of (3) is shown in Figure 4f along the *a*-axis. Selected bond lengths and angles are given in Table S2. The Cd²⁺-ion is also coordinated by six oxygen atoms from six different phenylphosphonates in a distorted octahedron (Figure 4c). The six Cd-O-bonds range from 2.2439(7) Å to 2.5202(5) Å and the O-Cd-O-angle from 72.681(16)° to 108.637(26)°. The three phenylphosphonate ligands coordinate differently. The neutral phenylphosphonic acid coordinates monodentately to one Cd²⁺-ion. The P-O-bond length for the coordinating oxygen atom (O7) is 1.5525(6) Å and for non-coordinating oxygen atoms 1.5299(7) Å (O9) and 1.5422(4) Å (O8). The second ligand coordinates with two oxygen atoms to two different Cd²⁺-ions. The third oxy-

Table 1 Crystal data and structure refinement parameters for the cadmium phenylphosphonates Cd(O₃PPh) · H₂O (**1**),²⁵ Cd(HO₃PPh)₂ (**2**), and (Cd(HO₃PPh)₂(H₂O₃PPh) (**3**). R_p and R_{wp} refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, as defined by Langford and Louer.³¹

	1 ²⁵	2	3
Empirical formula	CdC ₆ H ₇ O ₄ P	CdC ₁₂ H ₁₂ O ₆ P ₂	CdC ₁₈ H ₁₉ O ₉ P ₃
Formula weight/g mol ⁻¹	286.49	426.58	584.67
Crystal system	orthorhombic	triclinic	monoclinic
Space group	Pmn2 ₁	P $\bar{1}$	P2 ₁ /c
a/Å	5.860(4)	16.1586(16)	5.732864(91)
b/Å	14.459(14)	5.60337(54)	24.84899(42)
c/Å	5.054(3)	4.46652(33)	14.40494(22)
α /°	90	119.6039(72)	90
β /°	90	94.4432(77)	91.1232(15)
γ /°	90	101.7890(80)	90
V/Å ³	428.2(6)	336.556(62)	2051.674(57)
Z	2	1	4
D _{calc} /g cm ⁻³	2.22	2.09479(39)	1.892851(51)
R _{wp}		0.0697	0.0416
R _{Bragg}		0.02694	0.02084
GOF		5.08	4.00

gen atom (O5) is non-coordinating and carries the acidic hydrogen atom. The P-O5-bond length amounts to 1.5609(4) Å. For the coordinating oxygen atoms the P-O-bond lengths are 1.5220(4) Å (O4) and 1.5708(5) Å (O6). This phenylphosphonate ligand is monodeprotonated. The third phenylphosphonate ligand is also monodeprotonated. Two oxygen atoms are coordinating to three different Cd²⁺-ions. The oxygen atom O2 is bridging two of them. The P-O2-bond length is 1.5337(4) Å. The non-coordinating oxygen atom (O3) is protonated. The P-O3-bond length is 1.5271(6) Å. The P-O-bond length for the non-bridging coordinating oxygen atom (O1) is 1.5333(4) Å. As a result of this coordination, pairs of edge connected CdO₆-octahedrons are formed (see Figure 4c). These pairs are connected to two other pairs in opposite directions via four phosphonate groups, respectively. Two neutral phenylphosphonic acid units are located adjacent to this pair. The arrangement results in a double chain built by pairs of CdO₆-octahedrons and the inorganic part of the phenylphosphonate. The phenyl rings point into the interchain space. The neutral ligands are located at the smaller edges of the chain and the protonated ligands above and below the chain. The chains are connected via π - π -stacking of parallel orientated phenyl rings and build a layered superstructure. The two orientations for the CdO₆-octahedron pairs lead to two orientations in the resulting chain and layered structure. The layers are stacked in an alternating manner. Here, the acidic hydrogen atoms are located at the non-coordinating oxygen atoms. The orientation of the hydrogen atoms was estimated based on the direction of the hydrogen bonds. Two strong hydrogen bonds ($d_{O9-O5} = 2.5554(5)$ Å and $d_{O5-O8} = 2.4135(6)$ Å) stabilise the structure. The latter value is short, but was also observed for other phosphoric acids.³² Additionally, moderate ($d_{O3-O7} = 2.8242(6)$ Å) and weak ($d_{O8-O3} = 3.2504(8)$ Å) hydrogen bonds are formed.

Mechanistic studies

All syntheses were investigated by *in situ* synchrotron XRD. The milling reactions were performed at 30 Hz. Under these conditions, the same products are formed during an increased reaction

time, which facilitates the detection of intermediates that can be detected more clearly under these conditions. The data at $t = 0$ s represent the XRD pattern of the mixture without any milling. All synthesis pathways can be divided into five phases.

The 2D plot of the XRD data for the synthesis of (**1**) is shown in Figure 5a. The data collected at $t = 0$ s represent the reflections of the starting materials (phase 1). After 30 s a peak at $2\theta = 7.1^\circ$ appears, which can be assigned to (**3**) (phase 2). 30 s later a reflection at 6.1° indicates the formation of (**1**) (phase 3). During the next few minutes the intensity of the reflections of the starting materials decreases and vanishes after 4.30 min (start of phase 4). The intensities of the reflections for (**3**) also start to decrease, while the number and intensity of the product reflections increase. After 14 min only the reflections of the final product can be detected (phase 5).

The 2D plot of the XRD data of the synthesis of (**2**) is depicted in Figure 5b. In the first phase only the starting materials can be detected. After 1 min of milling, different reflections indicate the formation of (**1**) and (**3**) (phase 2). The strongest reflections are at 6.1° and 7.1° , respectively. The reflections for (**3**) are more pronounced. During this phase, the reflection intensities of the starting materials decrease. After 2.15 min the reflections of the starting materials vanish and only peaks for both intermediates can be detected (phase 3). In phase 4 a reflection at 5.7° indicates the formation of the final product. The intensity is very weak compared to the intensity of the reflections at 6.1° and 7.1° . After 6 min of milling, the reflection intensities of the intermediates start to decrease, while at the same time those of the product increase. With increasing milling time, only the strongest reflections of the intermediates can be detected. After 9 min of further milling all reflections of (**3**) disappear. Reflections of the final product and a very low contribution of (**1**) at 6.1° can be detected (phase 5). This additional peak remains unchanged during the observed synthesis. The same phenomenon could be observed in the final PXRD pattern of the product of the laboratory synthesis (see Figure S1).

The 2D plot of the XRD data of the synthesis of (**3**) is shown

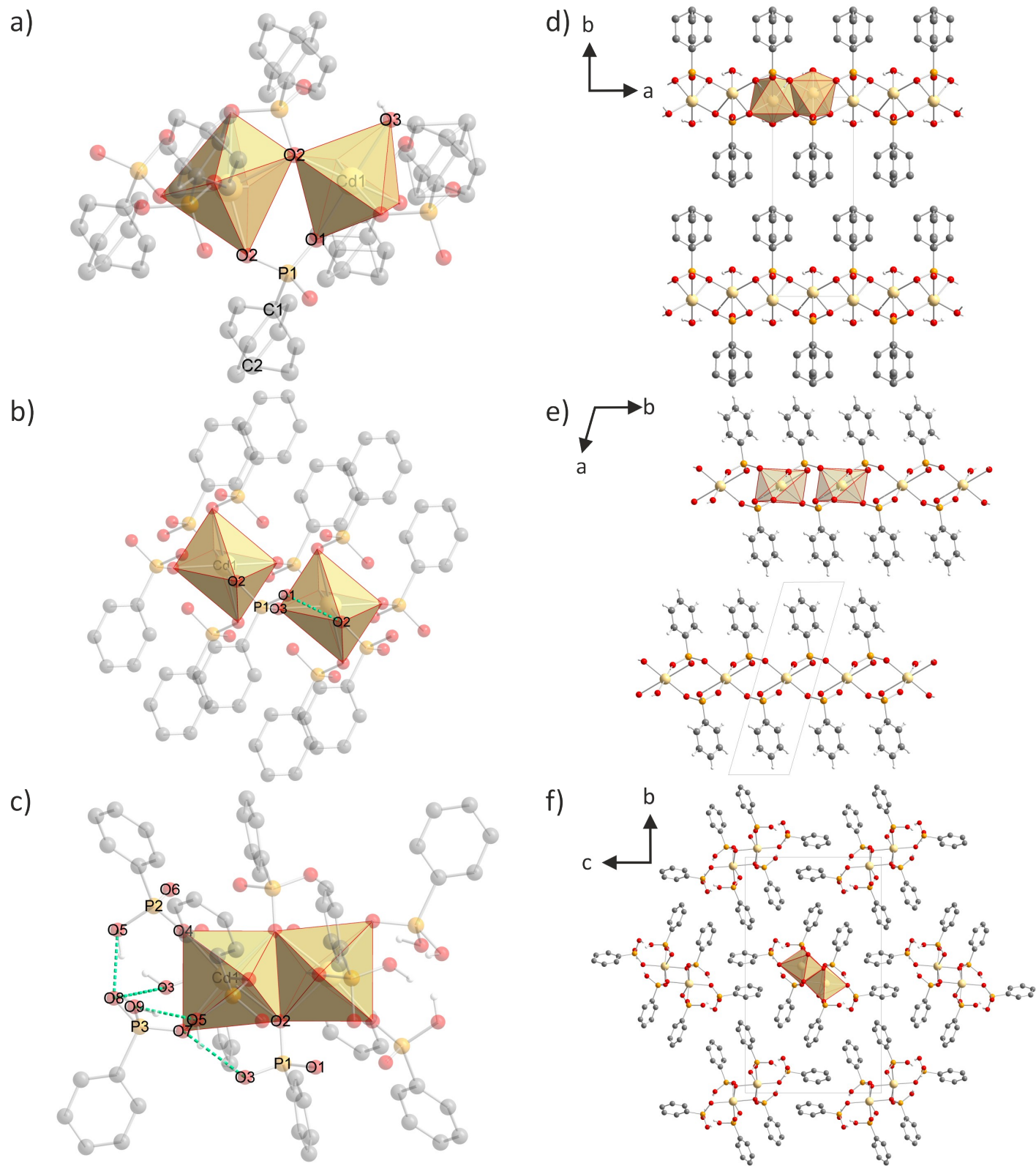


Fig. 4 Molecular structure and coordination polyhedra for the Cd²⁺-ions and hydrogen bonds (green dashed lines) of **a**) (1), **b**) (2) and **c**) (3) and crystal structures of **d**) (1) shown along the c-axis, **e**) (2) shown along the c-axis and **f**) (3) shown along the a-axis. Hydrogen atoms of the phenyl rings were omitted for clarity. Yellow: cadmium, orange: phosphorus, red: oxygen, gray: carbon, light gray: hydrogen.

in Figure 5c. At the beginning, only the starting materials can be detected. After 1 min of milling a peak at 7.1° indicates the formation of the final product. In the next minute the reflections of cadmium acetate dihydrate disappear (e.g. 12.6°). The ones belonging to phenylphosphonic acid (e.g. 20.4°) persist since the acid is used in excess (phase 3). After 4.30 min a reflection at 6.1° can be detected (phase 4). This reflection indicates the intermediate formation of (1). The peak remains observable until 6.45 min. At 5.30 min a reflection at 5.7° indicates the formation of (2). The reflection can be detected for the next two minutes. In the fifth phase, reflections of the final product and phenylphosphonic acid can be detected. During the last eleven minutes of the reaction, the intensities of the reflections changes. These non-systematic changes are an artifact of the measurement and stem from different amounts of powder in the beam path. A close inspection of Figure 5c shows that the reflections disappear at a certain time (12 minutes) and reappear again after 4 minutes. Two aspects are important: i) three reflections of compound (3) persist during this period in a weaker form and ii) no change in the crystallite size (the widths of the reflections stay the same) was observed before or after this period. We would expect a decrease in the crystallite size before an amorphous product is observed.

In situ measurements of mechanochemical reactions are a new field. Based on recent publications, mechanochemical reactions proceed either directly from the starting materials to the final product or are characterized by the formation of an intermediate phase.^{21,23,33,34} Beldon et al. also found indications for an Ostwald ripening process for the synthesis of ZIF.³⁵ Summarizing, for all three investigated compounds, a synthesis process involving different intermediate steps could be observed. The formation of (1) and (3) under milling conditions are much faster than the formation of (2). Compound (3) seems kinetically favored. Using a 1:1 and 1:4 starting stoichiometry, reflections of (3) can be detected after 30 s and one minute, respectively. Reflections of (1) can be detected after one minute using the 1:1 starting stoichiometry. Reflections of both compounds can be detected as well after one minute using a 1:2 starting stoichiometry, which finally leads to (2). The reflections of the starting materials vanish prior to the formation of (2). This indicates that (2) is directly formed from the intermediates (1) and (3). The same behavior could be observed for the synthesis of (3). Here, the final product is built first and (1) is formed intermediately. Shortly thereafter, reflections of (2) can be detected and those of (1) start to decrease. Further experiments showed that it is also possible to synthesize (2) by milling (1) and (3) in a molar ratio of 1:1. Acetic acid and water were added to meet the original synthesis conditions. The synthesis is successful but a higher energy is needed (see Figure S7). 15 min of milling at 50 Hz results in a mixture of all three compounds. 60 min of milling at the same frequency leads to the pure compound (2).

All compounds involved in the synthesis can be identified as one of the cadmium phenylphosphonates or as starting materials. There are no other intermediates, such as mixed salts or amorphous phases. All reactions can be described with the following equation (with $x = 1, 2, 3$, and $y = 0, 1$):

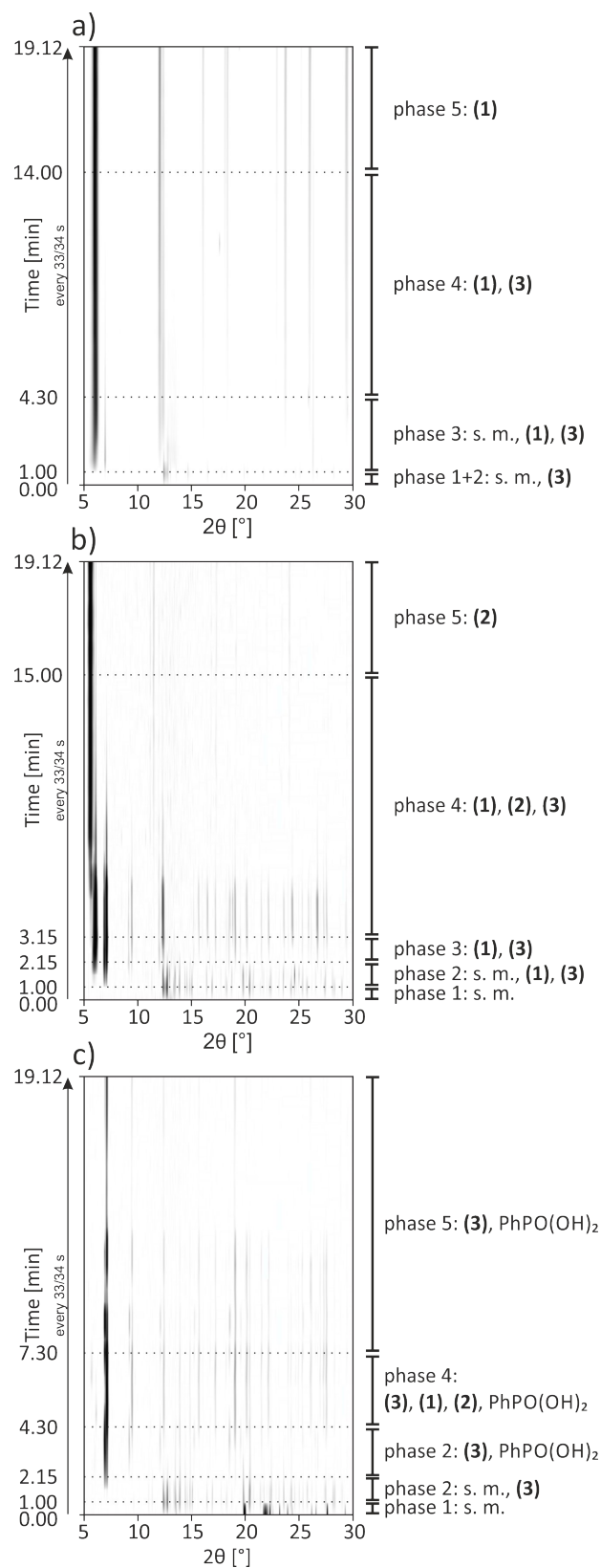


Fig. 5 2D plots of synchrotron XRD data for the synthesis of **a) (1)**, **b) (2)** and **c) (3)** with a description of the detected compounds; s.m. = starting materials.

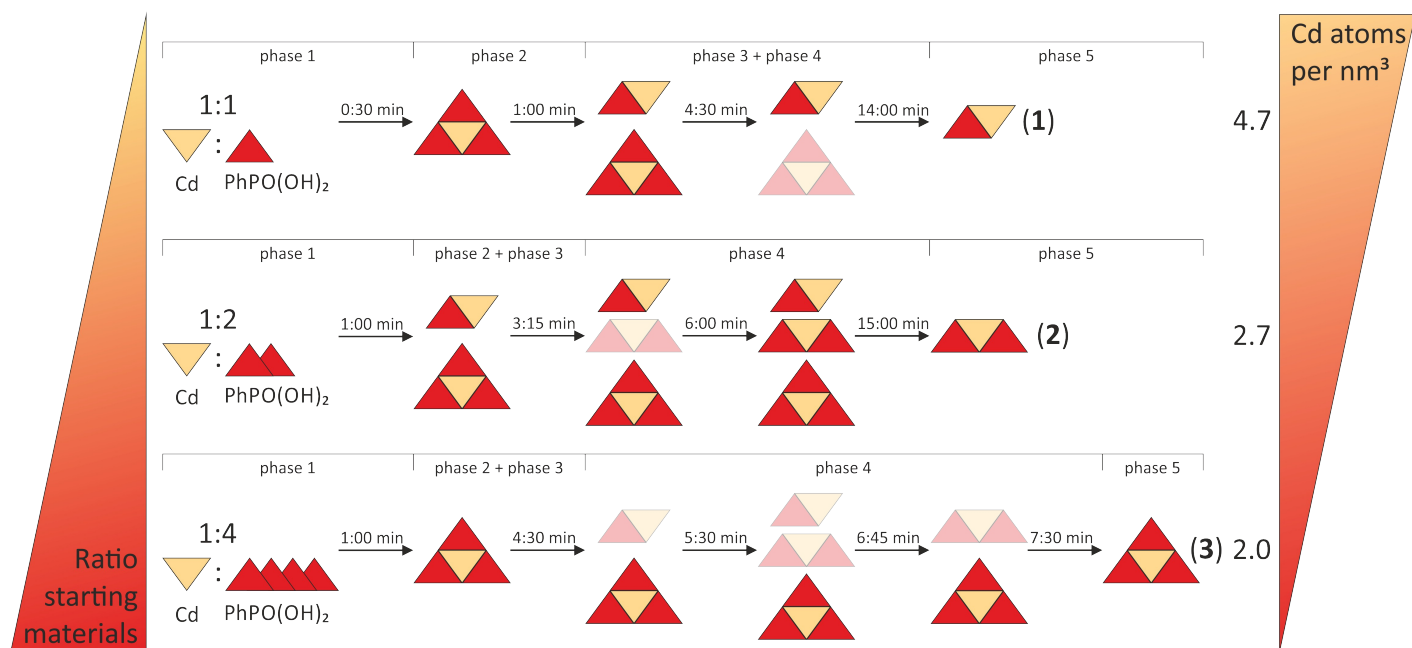
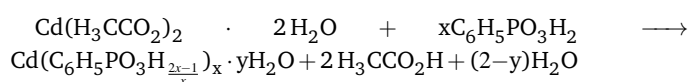


Fig. 6 Schematic overview of the reaction pathways for the formation of (1), (2) and (3). For clarity the starting materials are not mentioned after the beginning of the reaction. Yellow triangles represent the Cd²⁺-ions. Red triangles represent the phosphonate ligands. The combined triangles represent the compounds (1)-(3) indicating the Cd²⁺:phenylphosphonate ligand ratio. The pale symbols indicate small contributions of the respective compound.



This equation clearly shows that during the reaction acetic acid and water are released. Therefore, the dry milling synthesis is liquid assisted by its side products. Indeed, all products were wet after milling. Based on these results, a reaction mechanism like the classic hot-spot-theory and the magma-plasma model³⁶ can be ruled out.³⁷ Within the magma-plasma model and the expected high energies, more fragmental intermediates and distinctly amorphous phases would be expected. Ma *et al.* recently described a milling reaction mechanism based on thorough stirring of very small solid particles.³⁸ We have observed in agreement with the literature that the reaction speed could be easily increased by increasing the applied frequency. Furthermore, the diffusion rate in liquid assisted grinding reactions is higher than in dry ones. It has been shown that acetic acid as side product acts as an assisting liquid in self-sustaining reactions after a short initial activation.³⁹ The decreasing intensity of reflections of the starting materials and intermediates, together with the increasing reflections of the products, show that the described diffusion mechanism can be used to explain the formation mechanism of cadmium phenylphosphonates.

Figure 6 provides a schematic overview of the reaction pathways. The influence of the two directing factors, thermodynamic stability and stoichiometric ratio of the starting materials, which were identified for the nature of the product, are illustrated. The slurry experiments showed that compound (1) is the most stable one (see Figure S8). The thermodynamic stability of metal organic compounds is connected with the density of the framework.

For frameworks with the same composition it was shown that a more dense structure (expressed by the metal atom per nm³ ratio) also has a lower total energy.^{40,41} Beldon *et al.* showed that the mechanochemical formation of metal organic frameworks can follow Ostwald's rule of stages. The first types with a lower density of central atoms are formed intermediately.³⁵ The final product is the one with the highest density. This trend is not that clear for compounds with different composition. Compound (3) has the lowest density, with 2.0 Cd atoms per nm³. Consistently, (3) is formed first in all three reactions. Compound (1) shows the highest value with 4.7 Cd atoms per nm³. This could be the reason why the compound remains stable in a small amount for the whole milling time during the synthesis of (2). This reaction also shows the influence of the second directing factor, the composition of the starting materials. The 1:1 (cadmium acetate monohydrate : phenylphosphonic acid) and the 1:2 synthesis results mainly in the stoichiometric product, respectively. The influence of both directing factors can be seen in the PXRD pattern (see Figure S3) of the 1:3 synthesis where (2) (with 2.7 Cd atoms per nm³) and (3) are formed at the same time. Only with an excess of phenylphosphonic acid can (3) be obtained as the final product.

The comparison of the results of the *in situ* investigations of the mechanochemical syntheses of cadmium phenylphosphonates with the previously reported *in situ* investigations under hydrothermal and ultrasonic conditions is difficult. In all three investigated systems, the phosphonates carry functionalised organic groups which can also coordinate to the metal ion. The syntheses were carried out from aqueous solutions with addition of inorganic bases. Nevertheless, in the investigations of the crystallisation of calcium aminoethylphosphonate and copper(II) phospho-

noethanesulfonate crystalline intermediates were also observed. They are not based on the metal:phosphonate ligand ratio but on the presence of small molecules like water or hydroxide ions in the crystal structure.^{15,16} A correlation of the crystal density and the thermodynamic stability of the compounds was estimated.

Conclusions

The successful mechanochemical syntheses of three cadmium phenylphosphonates indicates that mechanochemistry is ideally suited for synthesizing metal phosphonates. With this powerful synthesis tool it is possible to synthesize rapidly and efficiently both known and novel phosphonates. The crystal structures of the two new compounds (**2**) and (**3**) were solved from PXRD data. They contain monodeprotonated phenylphosphonate and neutral phenylphosphonic acid ligands. The synthesis pathways of all three compounds were investigated *in situ*. A diffusion mechanism is corroborated by our findings. Intermediates could be detected and identified. The kinetically favored product (**3**) could always be detected during the syntheses. The thermodynamic stability of the compounds and the stoichiometric ratio of the starting materials are the two directing factors for the synthesis of the final products.

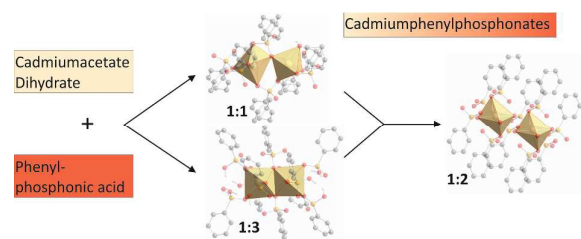
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New and known cadmium phenylphosphonates were prepared mechanochemically and their synthesis mechanism was determined in situ.