Mechanochemical synthesis of cerium(IV)-phosphonates

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Abstract

The syntheses and crystal structures of two cerium(IV) phosphonates are presented. Cerium(IV) bis(phenylphosphonate) $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** can be formed from precipitation and mechanochemical reaction, whereas cerium(IV) bis(carboxymethylphosphonate) monohydrate $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2** is only accessible via ball milling. All reactions proceed very fast and are completed within a short time span. *In situ* measurements for the syntheses of **1** show that the product occurs within seconds or a few minutes, respectively. The structures were solved from powder X-ray diffraction (PXRD) data.

Keywords

Mechanochemistry, in situ, PXRD, cerium(IV), metal phosphonate

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Introduction

The synthesis and characterization of metal phosphonates has gained increasing interest because of their promising properties for applications like gas adsorption [1-3], catalysis [3-5], proton conduction [6-10], corrosion protection [11], or magnetic cooling [12, 13]. The phosphonate ligand offers a wide range of possible coordination modes, therefore metal phosphonates exhibit variable structure motifs, from molecular compounds (0D) to 3D frameworks [12, 14, 15]. This structural variety makes metal phosphonates promising candidates for application-tuned materials. New synthesis methods like high-throughput hydrothermal methods [16, 17] or ultrasonic synthesis [18] were developed. Recently, we could show that divalent metal phosphonates of different dimensionality can easily be synthesized mechanochemically [19-22]. The mechanisms of mechanochemical reactions are not completely understood yet. Therefore, several methods have been developed enabling in situ monitoring of the milling process [23-25]. Although tetravalent metal phosphonates are widely studied [26-29], only a few cerium(IV) phosphonates are known so far [30-32]. One reason is the high potential of cerium(IV) to act as oxidizing agent. Since Ce(IV) is able to oxidize water, the formation of Ce(III) phosphonates is typically observed in hydrothermal reactions [33].

Here, we present the synthesis of two cerium(IV) phosphonates, namely cerium(IV) bis(phenylphosphonate) $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** and cerium(IV) bis(carboxymethylphosphonate) monohydrate $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2** (**Fig. 1**). Compound **1** was synthesized from solution at room temperature and from mechanochemical synthesis using ceric ammonium nitrate (CAN, diammonium cerium(IV) nitrate) and phenylphosphonic acid. Compound **2** was synthesized via a liquid assisted grinding (LAG) reaction with CAN and phosphonoacetic acid. The structures were solved from PXRD (powder X-ray diffraction) data. Both syntheses of **1** were investigated *in situ* using synchrotron PXRD.

Figure 1 Reaction schemes for the synthesis of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** and $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2**.

Materials and Methods

Chemicals

The following chemicals were used without further purification: Ceric ammonium nitrate ($\geq 98\%$, reinst, Roth, Germany) phenylphosphonic acid (98%, Acros Organics, USA), phosphonoacetic acid (98%, abcr, Germany), methanol (99.8+%, Acros Organics, USA), glacial acetic acid (100%, p. a., Roth, Germany), and MilliQ water (18.2 M Ω , ultrapure water system seralpur Pro 90 CN, Seral, Germany).

Synthesis of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1**

Synthesis from solution: 1097.0 mg (2.00 mmol) of ceric ammonium nitrate and 632.0 mg (4.00 mmol) of phenylphosphonic acid were dissolved in 30 mL of water, respectively. The clear solutions were mixed and an immediate precipitation could be observed. The reaction mixture was stirred at room temperature for 5 min. The precipitate was separated by filtration, washed with water and dried in air. 820 mg (1.8 mmol) of a pale yellow powder was obtained (yield = 91%).

Mechanochemical synthesis: For the mechanochemical synthesis a vibration ball mill Pulverisette 23 (Fritsch GmbH, Germany) was used. Ceric ammonium nitrate and phenylphosphonic acid were added in a 10 mL steel jar with a total load of 1 g and a molar ratio of 1:2. Two stainless steel balls (diameter = 10 mm, weight = 4 g) were added. This mixture was ground at 50 Hz for 15 min. A yellow powder was obtained, washed with methanol and dried in air. 339.7 mg (0.75 mmol) of a pale yellow powder were obtained (yield = 65%). The synthesis was repeated with an addition of 400 μL of water which results in a slightly more crystalline product.

Synthesis of $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2**

The synthesis procedure was similar to the mechanochemical synthesis of **1** except that phosphonoacetic acid was used and that the ratio of ceric ammonium nitrate to phosphonoacetic acid was 1:4. To obtain a product with a good crystallinity, the addition of 400 μL acetic acid was necessary. The wet product was washed with methanol and dried in air. 264.6 mg (0.61 mmol) of a pale yellow powder were obtained (yield = 68%).

Analytical techniques

PXRD patterns were collected on a D8 Discover diffractometer (Bruker AXS, Germany) with Cu $K_{\alpha 1}$ radiation ($\lambda = 0.154056$ nm). The diffractometer is equipped with a Lynxeye detector and a Johansson monochromator in the incident beam. Measurements were performed in transmission geometry in a 2θ range from 4° to 60° . For structure solution a step size of 0.009° with a measured time per step of 25 s was chosen. The structure solutions of all compounds were conducted from PXRD data. The crystal data of **1** and **2** were indexed using the indexing routine in Topas (version 5, Bruker AXS, 2014). The crystal structures were determined using the simulated annealing routine implemented in DASH [34]. For **1** the Ce atom was fixed at the Wyckoff position 2a (0,y,0). Rietveld refinements were conducted with Topas. CCDC-1824013 and CCDC-1824014 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.cdc.cam.ac.uk/data_request/cif.

The *in situ* PXRD measurements were performed at the μSpot beamline (Bessy II, Helmholtz-Zentrum Berlin, Germany) [34]. For data collection, a MarMosaic CCD detector (pixel size: 3072 x 3072, point spread function width: 73 μm) was used. The exposure time was 30 s, with a delay time of 3-4 s between two measurements. For the direct comparison with the laboratory PXRD data, the

scattering vector q was transformed to the diffraction angle 2θ for Cu $K_{\alpha 1}$ radiation using FIT2D [35]. All given times are rounded to the nearest 15 s.

The setup used for the investigation of the precipitation reaction was described in detail elsewhere [36]. In brief, the stopped-flow-module SFM-3000 (Bio-Logic SAS, France) equipped with a capillary head and a custom-made extension was used. The starting solutions were loaded to two inner syringes. For the measurements, the starting solutions were mixed and the reaction solution was pushed through the capillary head and the custom-made extension. By varying the flow rate and the position of the measurement (capillary head or extension), different points in time could be investigated. Every point in time was measured three times and the resulting patterns were accumulated.

The *in situ* investigation of mechanochemical reactions with synchrotron radiation was described elsewhere [20]. The reactions were conducted as described above, except that the steel jar was replaced with a Perspex jar.

Results

Synthesis and structure

The final Rietveld and difference plots of **1** and **2** (Fig. 2) proof the purity of the obtained compounds. The crystal data and figure of merits of both compounds are shown in Table 1. Selected bond lengths and angles of all new compounds are given in Table S1 and S2.

Table 1: Crystal data and structure refinement parameters for $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** and $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2**. R values refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, as defined by Langford and Louer [35].

	1	2
Empirical formula	$\text{CeC}_{12}\text{H}_{10}\text{O}_6\text{P}_2$	$\text{CeC}_4\text{H}_8\text{O}_{11}\text{P}_2$
Formula weight/g mol ⁻¹	452.27	434.16
Crystal system	monoclinic	monoclinic
Space group	C2 (No. 5)	P2 ₁ /a (No. 11)
a/Å	9.4040(3)	21.3543(5)
b/Å	5.6454(2)	9.8053(3)
c/Å	14.9146(5)	5.1358(2)
$\beta/^\circ$	83.352(4)	90.731(3)
V/Å ³	786.48(4)	1075.27(5)
Z	2	4
D _{calc} /g cm ⁻³	1.910	2.682
R _{wp}	1.71	3.59
R _{Bragg}	0.88	1.89
GOF	1.56	2.19

Figure 2 Scattered intensity of **a)** $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** and **b)** $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2** 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 the observed and calculated profiles are shown. The wavelength is $\lambda = 0.154056$ nm (Cu $\text{K}\alpha_1$).

The structure of **1** is depicted in **Fig. 3**. The Ce^{4+} -ion is coordinated by six oxygen atoms, from six different phenylphosphonate ligands, in a slightly distorted octahedron. The Ce-O bond lengths range from 2.105(6) Å to 2.223(1) Å and the O-Ce-O angles from 84.8(4)° to 94.2(4)°. Each oxygen atom of each phosphonate group is coordinating to one Ce^{4+} -ion. The CeO_6 -octahedra are connected via the phosphonate group, leading to the typical layered structure motif for metal phosphonates: The Ce^{4+} -ion and the coordinating phosphonate groups are forming an inorganic layer while the phenyl rings point into the interlayer space. The layers are connected via van der Waals forces between the phenyl rings.

Figure 3 a) Molecular structure of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** with coordination polyhedron for the Ce^{4+} -ion and **b)** crystal structure of **1** shown along the b-axis. Pale yellow: cerium, orange: phosphorus, red: oxygen, grey: carbon, light grey: hydrogen.

The structure of **2** is shown in **Fig. 4**. The Ce^{4+} -ion is coordinated by seven oxygen atoms in a capped octahedron. The oxygen atoms stem from six different carboxymethylphosphonate ligands and one water molecule. The Ce-O bond lengths differ from 2.08(1) Å to 2.34(1) Å. All oxygen atoms of the phosphonate groups and the water molecule are coordinating to one Ce^{4+} -ion. The CeO_7 -units are connected via the phosphonate group. A layered structure as in **1** is formed, except that the layers are connected via hydrogen bonds between the carboxylic groups ($d_{\text{O4-O5}} = 2.63(2)$ Å).

Figure 4: a) Molecular structure of $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2** with coordination polyhedron for the Ce^{4+} -ion in and b) crystal structure of **2** shown along the b-axis. Pale yellow: cerium, orange: phosphorus, red: oxygen, grey: carbon, light grey: hydrogen.

Mechanistic studies

The syntheses of **1** from solution and as mechanochemical reaction were studied *in situ*. **Fig. 5** shows the powder patterns of the *in situ* investigation of the precipitation reaction. Already in the first pattern after 0.33 s, a reflection at 5.9° is proving the formation of the final product **1**. Additional reflections at 8.0° and 11.1° cannot be assigned to any starting material or the product. An intermediate is formed. After 0.66 s, only the reflection for **1** remains. Its intensity increases during the next ten seconds, but no other reflections appear.

Figure 5: Powder patterns of the *in situ* studies of the synthesis from solution of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1**: a) for the measurements of the reaction points in time 0.33 s and 0.66 s and b) for the measurements of the reaction points in time 1 s to 10 s.

The 2D plots of the *in situ* investigations of the mechanochemical syntheses of **1** are depicted in **Fig. 6**. The results for the neat grinding synthesis are shown in **Fig. 6a**. At the beginning only reflections for the starting materials are present (step 1). After 3.30 min, a reflection at 5.9° shows the formation of the final product **1** (step 2). The intensity of the reflections of the starting materials is decreasing but they remain until the end. After 10.30 min, additional reflections at 17.9°, 22.4° and 28.9° prove the formation of ammonium nitrate as side product (step 3). With the addition of water to the grinding material the reaction pathway changes massively. The respective 2D plot is shown in **Figure 6b**. At the beginning, no reflections, not even of the starting materials, can be detected. After 30 s, two reflections at 7.7° and 8.9° show the formation of an unknown intermediate (step 2). After 1.15 min, the formation of **1** is evident by the reflection at 5.9°. The product and the intermediate remain side by side until after 3.30 min the reflections of the intermediate are vanished (step 3). For the next minutes, only reflections of **1** can be detected (step 4). After 7.00 min, additional reflections show again the formation of ammonium nitrate as side product (step 5). The synthesis of $\text{Ce}(\text{O}_3\text{PCH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$ **2** could not be investigated *in situ* since the perspex jar was not stable against the used chemicals.

Figure 6: Powder patterns of the *in situ* studies of the mechanochemical syntheses of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1**: **a)** neat at 50 Hz and **b)** as LAG synthesis with water at 50 Hz.

Discussion

Compound **1** was synthesized from precipitation reaction and mechanochemical reaction. The first product shows a slightly higher crystallinity (see **Fig. S1**). The syntheses can be described as follows:

(R = C_6H_5 for **1**).

Ammonium nitrate and nitric acid are formed as side products. To get the pure product in the mechanochemical synthesis, the product was washed with methanol.

For **2**, the reaction equation is basically the same (with $R = \text{CH}_2\text{COOH}$) except for the following changes: For the hydrated compound, water is required. No water was added in the synthesis. Most probably, there is already surface water present or the hygroscopic side product ammonium nitrate attracts water from the environment. The use of an excess of phosphonoacetic acid and the addition of glacial acetic acid is necessary for a higher crystallinity. The addition of a strong acid increases the protonation degree of the phosphonic acid, which results in a slower reaction progress and in a prolonged crystallization time. The glacial acetic acid also ensures a protonated carboxyl group. Neat grinding or the LAG synthesis with water as well as precipitation reaction lead to an amorphous product. The amorphous products have been characterized by IR- and Raman-spectroscopy (Fig. S2, S3)

The synthesis of a cerium(IV) bis(carboxymethylphosphonate) monohydrate from solution under ambient conditions, like the synthesis of **1**, was not successful. Adding a phosphonoacetic acid solution to a CAN solution results in an immediate precipitation, but the separated and dried product shows no reflections in the PXRD analysis.

The *in situ* investigation of the precipitation reaction of **1** shows that the product is formed rapidly, but a complete crystallization needs more time. The life time of the detected intermediate is too short for an isolation. Based on the data, no suggestion of the nature of this compound can be made.

The *in situ* investigations of the mechanochemical reactions indicate that the addition of water increases the reaction speed drastically and also leads to a complete conversion. Only in the LAG synthesis the formation of an intermediate is observed. The reflections of this intermediate are not at the same positions as the reflections of the intermediate in the precipitation reaction, but they are in good agreement with the reflection positions of an unknown intermediate found earlier for the mechanochemical synthesis of metal phenylphosphonates with Cu [33], Co [19, 20] and Ni [22]. Since the use of phenylphosphonic acid is the only common aspect in these reactions, the intermediate is probably a polymorphic form of this reactant.

In both syntheses compound **1** is formed very quickly, in the precipitation reaction even within the first second. In both reactions an unknown intermediate is formed. Because of the different reflection positions their nature is different, therefore the two syntheses have different pathways. The fast synthesis under mild conditions also ensure that the cerium(IV) remains in its oxidation state.

Conclusion

Two cerium(IV) phosphonates were synthesized in fast and facile procedures. Both compounds have layered structures with coordinating phosphonate groups and the organic part between the layers. The *in situ* investigations of the syntheses of $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ **1** reveal that the product is formed within the first seconds from solution and the first two minutes in the mechanochemical synthesis. In both pathways an unknown intermediate could be obtained. In the mechanochemical synthesis the intermediate is most probably a polymorphic phase of phenylphosphonic acid. The results show that the use of fast syntheses under mild conditions can easily lead to metal phosphonates containing cerium(IV).

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Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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