

Synthesis and characterization of new strontium 4-carboxyphenylphosphonates

Vítězslav Zima^{a,*}, Jan Svoboda^a, Ludvík Beneš^a, Klára Melánová^a,
Miroslava Trchová^b, Jiří Dybal^b

^aJoint Laboratory of Solid State Chemistry of the Institute of Macromolecular Chemistry of Academy of Sciences, University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic

^bInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

Received 25 August 2006; received in revised form 5 December 2006; accepted 14 December 2006

Available online 29 December 2006

Abstract

Several new strontium 4-carboxyphenylphosphonates, i.e., two modifications of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$, $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$, $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ were prepared and characterized by elemental analysis, thermogravimetry, X-ray powder diffraction and infrared spectroscopy. It was found that the compositions of these compounds depend on the acidity of the reaction medium. In addition, the presented compounds are interconvertible in dependence on pH. The position of the acid hydrogen atom in $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ was determined from the IR spectra of the studied compounds.

The structure of the β modification of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ was solved from its X-ray powder diffraction pattern using an ab initio method (the FOX program) with subsequent Rietveld refinement in the FULLPROF program. The compound is monoclinic, with the space group $P2_1/c$ (No. 14), $a = 49.88(2)$, $b = 7.867(2)$, $c = 5.602(3)$ Å, $\beta = 128.68(2)^\circ$, and $Z = 4$. It has a one-dimensional structure with an inorganic part built of SrO_8 distorted tetragonal antiprisms.

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Keywords: Metal phosphonates; Strontium; Carboxyphenylphosphonic acid; Inorganic–organic hybrid compounds; Chain compounds; Layered compounds

1. Introduction

The study of inorganic–organic hybrid materials based on metal organophosphonates has recently become widely developing area of solid state chemistry. The possibility to attach various functional groups to the organic moiety to confer specific properties to these materials make them especially interesting. These phosphonates are investigated from the point of their potential applications as catalysts, proton conductors, ion exchangers, sensors, optically and photochemically active materials, and hosts in intercalation chemistry [1,2].

Compounds, in which a carboxylic group is attached to the organic part of the phosphonate, represent one such class of metal organophosphonates. Probably, most

extensively studied organophosphonates containing the carboxylic group were zirconium phosphonates [1]. In the last decade, phosphonates derived from simple carboxyethylphosphonic acid, $\text{H}_2\text{O}_3\text{PCH}_2\text{CH}_2\text{COOH}$, with nickel [3], titanium and zinc [4], manganese [5,6], aluminum and chromium [6] were prepared and characterized. Phosphonic acids prepared by a Mannich-type reaction, containing the carboxylic group, were employed in a preparation of titanium [7], lead and nickel [8], zinc and lead [9], samarium and calcium [10]. Ability to intercalate amines [4,7,8], magnetic properties [4–6], and proton conductivity [7] were studied for these compounds.

In our previous work, we have studied synthesis and properties of calcium phenylphosphonates and 4-carboxyphenylphosphonates [11], and strontium phenylphosphonate [12]. We have found that compounds with various *Me/P* ratios (*Me* = Ca, Sr) are formed in dependence on the acidity of the reaction medium, nevertheless, there is difference in

*Corresponding author. Fax: +420 46 603 6011.

E-mail address: vitezslav.zima@upce.cz (V. Zima).

chemical behavior between calcium and strontium phenylphosphonate. In this paper, we report on behavior of strontium 4-carboxyphenylphosphonates under conditions similar to those described in the previous papers.

2. Experimental

2.1. Materials and methods

All starting materials were purchased from Aldrich Chemical Co. and were used as received. 4-Carboxyphenylphosphonic acid monohydrate was prepared according to a previously described procedure [13].

The TGA was done using a home-made apparatus constructed of a computer-controlled oven and a Sartorius BP210 S balance. The measurements were carried out in air between 30 and 960 °C at a heating rate of 5 °C min⁻¹.

Infrared spectra in the range of 400–4000 cm⁻¹ were recorded at 64 scans per spectrum at 2 cm⁻¹ resolution using a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer equipped with a DTGS TEC detector. Measurements of the powdered samples were performed *ex situ* in the transmission mode in KBr pellets. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path.

Powder X-ray diffraction (XRD) data were obtained by means of a D8-Advance diffractometer (Bruker AXS, Germany) with Bragg–Brentano θ – θ geometry (40 kV, 40 mA) using CuK α radiation with secondary graphite monochromator and with a dynamic scintillation counter as a detector. The diffraction angles were measured at room temperature from 2° to 65° (2θ) in 0.02° steps with a counting time of 10 s step⁻¹. Indexing of the powder pattern was carried out with a DICVOL91 computer program [14] embedded in a CRYSFIRE computer program package [15]. The space groups were determined by processing the data in the Checkcell program [16].

The *ab initio* model calculations were carried out at the density functional theory (DFT, B3LYP functional) level of theory employing the Gaussian 03 program package [17,18]. Geometries have been fully optimized with the 6-31G(d) basis set. The calculated vibrational frequencies were uniformly scaled by a factor of 0.9603.

The structure of β -Sr(HOCC₆H₄PO₃H)₂ was solved using an FOX program [19]. The geometry of 4-carboxyphenylphosphonic acid was first optimized using a PM3 semiempirical quantum mechanical calculation implemented in the HYPERCHEM software package [20]. The obtained data were transformed using the BABELWIN program [21] into the form of a Fenske–Hall Z-matrix. Two these matrices were imported into the FOX program as crystal scatterers; all hydrogen atoms data were removed. One strontium atom was added as another crystal scatterer. The initial positions and orientations of the organic fragments were randomized before optimization. The coordinates of the Sr atom were fixed to a position (x , y , 1/4) for the first 10⁶ of iterations and then unfixed. A

parallel tempering algorithm was used to fit the calculated diffraction profile with the observed pattern. The obtained atomic coordinates were used for a Rietveld refinement using the FullProf program incorporated in the WinPLOT software package [22]. In this program, the profile parameters in the pseudo-Voigt profile type were optimized. Number of observed reflections was 62, number of calculated reflections was 647.

2.2. Separations of the products

In all cases, unless otherwise noted, the solid products were separated by filtration, washed with an ethanol-water 1:1 (v/v) mixture and with ethanol and dried in air at room temperature. All the products were white.

2.3. Preparation of Sr(HOCC₆H₄PO₃H)₂, α -phase

To 60 mL of a mixture of water and ethanol (1/1 v/v) was added 0.44 g (2×10^{-3} mol) of 4-carboxyphenylphosphonic acid monohydrate, HOCC₆H₄PO₃H₂ · H₂O. The mixture was heated under stirring until the acid dissolved. To this solution, cooled to room temperature, 0.42 g of Sr(NO₃)₂ (2×10^{-3} mol) dissolved in 10 mL of water was added. Immediately after mixing a precipitate was formed. The reaction mixture was stirred for additional 10 min. The product was obtained in a 63% yield (0.308 g). Elemental analysis (%) for C₁₄H₁₂O₁₀P₂Sr (489.8): calcd C 34.30, H 2.45; found C 34.82, H 2.28.

2.4. Preparation of Sr₃(OCC₆H₄PO₃)₂ · 5.7H₂O

Using an automated burette, 65.9 mL of 0.315 M NH₄OH solution was added to 1.32 g (6×10^{-3} mol) of 4-carboxyphenylphosphonic acid monohydrate in 20 mL of water and 20 mL of ethanol to adjust pH to 9. To this solution, 1.902 g of Sr(NO₃)₂ (9×10^{-3} mol) in 20 mL of water was added. Slowly formed precipitate was dried over P₂O₅ in a dessicator. The yield of the product was 1.47 g (67%). Elemental analysis calcd (%) for C₁₄H_{19.4}O_{15.7}P₂Sr₃ (763.6): C 22.00, H 2.54; found C 21.27, H 2.54.

2.5. Preparation of Sr₃(OCC₆H₄PO₃)₂ · 4H₂O

About 0.1386 g of Sr₃(OCC₆H₄PO₃)₂ · 5.7H₂O (1.8×10^{-4} mol) prepared according to the above given procedure was dissolved in 8 mL of water. The reaction mixture was placed in a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogeneous pressure at 180 °C for 48 h. The yield was 0.076 g (57%). The same compound, but in a distinctly lower yield, can be obtained by heating an aqueous solution of the starting compound until precipitation. Elemental analysis calcd (%) for C₁₄H₁₆O₁₄P₂Sr₃ (733.1): C 22.92, H 2.18; found C 21.12, H 1.95.

2.6. Reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid

The reaction was carried out at room temperature using a computer-controlled Schott Titronic 97 piston burette. Using the burette, an aqueous solution of 4-carboxyphenylphosphonic acid was added to an aqueous suspension of the strontium compound. The intervals between additions of the acid were chosen to be sufficiently long to ensure that practically all added acid would be consumed in the reaction with the strontium compound. The acidity of the solutions during the reaction was checked with a glass pH electrode. The value of pH at the end of the intervals (just before another addition of the acid) as a function of the amount of the added acid was then evaluated.

A suspension of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (0.147 g; 1.92×10^{-4} mol) in a mixture of ethanol/water (1/1 v/v; 75 mL) was stirred with a 0.043 M aqueous solution of 4-carboxyphenylphosphonic acid, which was added in 0.2-mL doses with 1500-s intervals between doses. The values of pH were measured in 65-s intervals during the reaction.

2.7. Reactions of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid at constant pH

A 0.0442 M aqueous solution of 4-carboxyphenylphosphonic acid was added to a stirred suspension of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (0.095 g; 1.25×10^{-4} mol) in an ethanol/water mixture (1/1 v/v; 60 mL) or in ethanol (60 mL) so that the pH value of the reaction mixture was maintained at 5.00 ± 0.05 or 3 ± 0.05 . The additions of 4-carboxyphenylphosphonic acid were accomplished using a computer-controlled Schott Titronic 97 piston burette. The products of the reactions were determined by TGA and powder XRD. The yields of the solid products based on the starting $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ were about 90%.

2.8. Reaction of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ with ammonia

This reaction was done under the same experimental arrangement as the reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid. In this case, aqueous ammonia was added using the computer-controlled burette into the reaction mixture.

Finely ground $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (0.245 g; 5×10^{-4} mol) was added to a solution of $\text{Sr}(\text{NO}_3)_2$ (0.529 g; 2.5×10^{-3} mol) in a mixture of water (25 mL) and ethanol (35 mL). The suspension was reacted with an aqueous solution of NH_4OH ($c = 0.335 \text{ mol L}^{-1}$), which was added in 0.1-mL doses with 1800-s intervals between doses. The values of pH during the reaction were measured in 50-s intervals. The solid product was obtained in a quantitative yield. The same experiment was repeated with $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (see below).

2.9. Reactions of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ with ammonia in the presence of Sr^{2+} salt at constant pH

A 0.787 M aqueous solution of ammonia was added to a stirred reaction mixture which contained 0.245 g of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (5×10^{-4} mol) and 0.528 g of $\text{Sr}(\text{NO}_3)_2$ (2.5×10^{-3} mol) in a mixture of water (25 mL) and ethanol (35 mL) so that the pH value of the reaction mixture was maintained at 8.00 ± 0.05 or 6.00 ± 0.05 at room temperature. The additions of ammonia were accomplished using a computer-controlled Schott Titronic 97 piston burette. The yields of the solid products were 97% and 87% for pH 8.00 and 6.00, respectively.

3. Results and discussion

3.1. Synthesis, characterization and reactions of strontium 4-carboxyphenylphosphonates

4-Carboxyphenylphosphonic acid can form mono- to trivalent anions in its compounds depending on the acidity of the reaction medium. Consequently, three different strontium 4-carboxyphenylphosphonates can theoretically be formed with the Sr/P atomic ratio of 1/2, 1/1, and 3/2.

The first of them is formed in the reaction mixture without pH adjustment simply by mixing aqueous solutions of $\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$. The compound is stable up to 350°C as follows from the TGA (Fig. 1, solid line). The first small weight loss between 350 and 450°C is due to the condensation of hydrogen phosphonate groups to pyrophosphonate groups analogously to that observed for $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3)_2$ by Mahmoudkhani et al. [23]. This weight loss is not well resolved

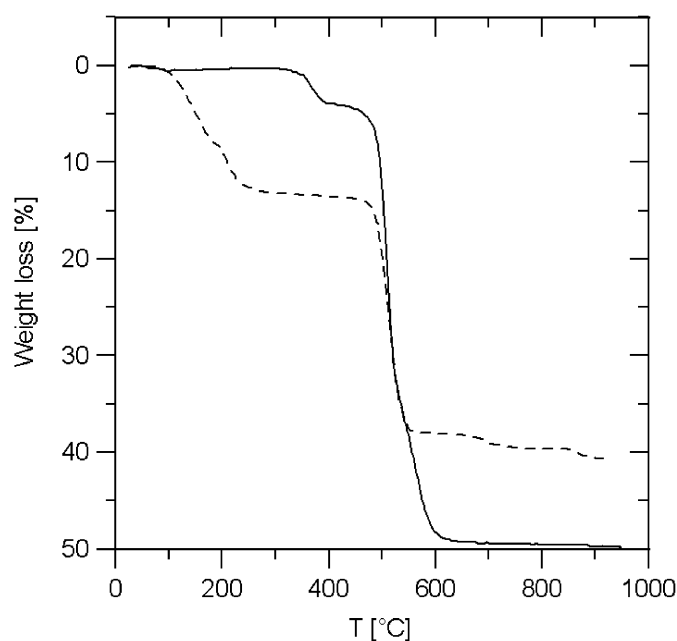


Fig. 1. TGA curves of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (solid line) and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (dashed line).

Table 1
Cell parameters of strontium 4-carboxyphenylphosphonates ($P'' = \text{OOC}_6\text{H}_4\text{PO}_3$)

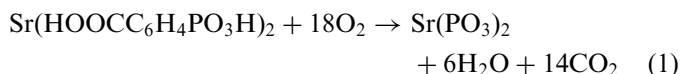
	$\alpha\text{-Sr}(\text{H}_2\text{P}'')_2$	$\beta\text{-Sr}(\text{H}_2\text{P}'')_2$	$\text{Sr}_3\text{P}''_2 \cdot 5.7\text{H}_2\text{O}$	$\text{Sr}_3\text{P}''_2 \cdot 4\text{H}_2\text{O}$	$\text{SrH}(P'') \cdot \text{H}_2\text{O}$	$\text{SrH}(P'')$
$a, \text{\AA}$	38.736(9)	46.58(2)	21.59(1)	13.640(3)	24.480(4)	19.902(9)
$b, \text{\AA}$	5.834(2)	7.868(2)	3.294(3)	5.864(2)	8.166(1)	5.629(3)
$c, \text{\AA}$	7.808(2)	5.603(3)	12.34(1)	13.466(3)	5.689(1)	7.743(4)
$\beta, ^\circ$	95.94(3)	123.30(2)	114.40(6)	99.02(2)	125.670(3)	96.090(6)
SG ^a	$P2_1/a$ (14)	$P2_1/c$ (14)	$P2_1/m$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$C2/c$ (15)
$M(n)^b$	7.3	17.2	8.7	15.1	29.0	9.3
$F(n)^b$	19.4 (0.0090, 202)	37.8 (0.0071, 93)	4.9 (0.0165, 211)	29.2 (0.0073, 141)	50.1 (0.0058, 69)	12.4 (0.0144, 112)
n^c	35	25	17	30	30	20

^aSpace group; the number of the group is in parentheses.

^b $M(n)$ and $F(n)$ are figures of merit according to [25] and [26], respectively.

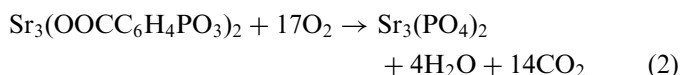
^c n is the number of the indexed lines.

nevertheless its estimated value of 4% roughly corresponds to the release of one molecule of water from two PO_3H groups. The next weight loss at 500 °C is typical of the decomposition of the organic part of metal phosphonates [11]. The product of the heating above 900 °C is $\text{Sr}(\text{PO}_3)_2$, as confirmed by powder XRD (PDF No. 12-0366) [24]. The observed total mass loss of 50.0% corresponds to the presumed mass loss (49.9%) calculated according to the equation



The cell parameters of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ obtained by powder XRD are given in Table 1 and differs distinctly from that XRD found for an analogous $\text{Ca}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ [11].

Another strontium 4-carboxyphenylphosphonate was prepared by the reaction of a strontium salt solution with a solution of 4-carboxyphenylphosphonic acid, which pH was adjusted to 9. A thermogravimetric curve of the sample kept over P_2O_5 is depicted in Fig. 1 as a dashed line. The first two-step mass loss observed at temperatures below 200 °C indicates a release of water from the structure of the product. The weight decrease by 13.5% corresponds to 5.7 molecules of water per formula unit. We found that the amount of water varied strongly with drying conditions (the sample dried only in air at room temperature contained about 8 molecules of water per formula unit). Another mass loss at 500 °C is due to the decomposition of the organic part of the compound. The weight decrease between 400 and 900 °C is 27.3% of the starting compound that is 31.6% of the dehydrated compound ($\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$). This value is identical with that calculated according to the equation



The formation of $\text{Sr}_3(\text{PO}_4)_2$ as a product of the heating to 900 °C was confirmed by powder XRD (PDF No. 24-1008) [24]. Thus, the formula of this strontium carboxyphenylphosphonate can be written as $\text{Sr}_3(\text{OOC}_6\text{H}_4$

$\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$. As this compound contains less organic components than $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$, a presence of cavities in the structure of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ can be presumed which are filled with weakly bonded water molecules. This can explain the fact that the amount of crystalline water in this compound is variable.

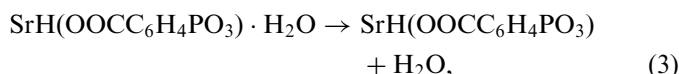
The cell parameters of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (see Table 1) shows that the compound is monoclinic. The basal spacing $d = 19.55 \text{\AA}$ is close to that found for $\text{Ca}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($d = 19.27 \text{\AA}$) [11].

As in the case of calcium arylphosphonates [11] and strontium phenylphosphonates [12], a possibility of the formation of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ from $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ by its treatment with an acid was investigated. It was accomplished by additions of small doses of 4-carboxyphenylphosphonic acid to a suspension of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ using a computer-controlled burette. At first, only a decrease of pH is observed (Fig. 2). When pH reaches a value about 5, the decrease stops (point A in Fig. 2) and is followed by a small increase of pH. At this point, the reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid starts which is indicated by an increase of pH between the additions of the acid (see inset in Fig. 2). This process continues up to the addition of more than 1 mol of the acid per 1 mol of the strontium compound (point B in Fig. 2). Then pH starts to decrease to about 4 (point C). Further addition of the acid causes another small increase of pH followed by a plateau (with constant pH) up to about 4 mol of 4-carboxyphenylphosphonic acid per 1 mol of strontium compound (point D).

The thermogravimetric and elemental analyses suggest that the final product should be $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$. The shape of the TGA curve is similar to that of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ prepared by the synthesis, only the condensation step is less pronounced and is shifted to higher temperatures (440–500 °C). The total weight loss (51%) corresponds to that found for the synthesized $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$. Nevertheless, the powder XRD pattern is different from the pattern of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ obtained by the synthesis as described in Experimental. The compound prepared by the reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with the acid can be there-

fore considered as another modification of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and is thereafter denoted as $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$. Its cell parameters are given in Table 1 and its structure is described below.

The shape of the curve in Fig. 2 indicates that there is a formation of an intermediate between points A and C. To obtain this intermediate, we reacted $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid to point C only. The product of the heating of this intermediate to 950°C is $\text{Sr}_2\text{P}_2\text{O}_7$, as follows from powder diffraction pattern (PDF No. 24-1011) [24]. It means that the Sr/P atomic ratio is 1/1 in the intermediate corresponding to the formula $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \gamma\text{H}_2\text{O}$. The TGA (solid line in Fig. 3) showed one-step weight loss of 5.7% at 200°C which could correspond to a release of 1 molecule of water per formula unit according to the equation



for which the theoretical weight loss is 5.9%. The second weight loss between 300 and 500°C is caused most probably by a condensation of the hydrogen phenylphosphonate groups analogously to the same condensation observed for $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (see above). The mass loss above 500°C is due to the decomposition of the organic part of the compound. The total observed weight loss of 42% is in a good agreement with the theoretical one (42.9%) calculated according to the equation

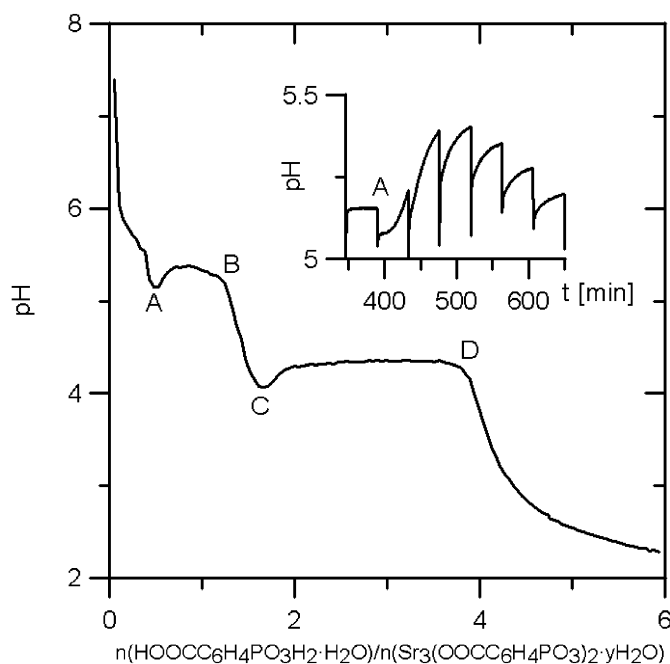
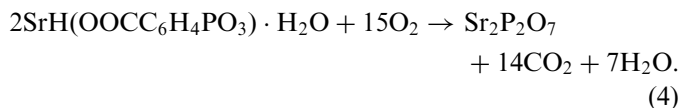
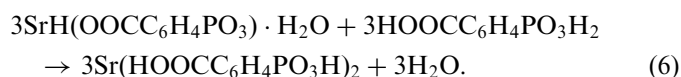
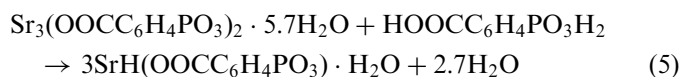


Fig. 2. Course of the reaction of the $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ suspension with 4-carboxyphenylphosphonic acid solution. The inset represents a time dependence of pH near point A.

The cell parameters of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (Table 1) indicate that its structure is different from those of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ as well. The structure probably changes during the dehydration to $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3)$ according to Eq. (3), as can be deduced from the change of the cell parameters (see Table 1).

The reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ with 4-carboxyphenylphosphonic acid can be then summarized in these two equations



About 1 mol of 4-carboxyphenylphosphonic acid is needed per one mole of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ to complete the first reaction (point B in Fig. 2) during which the intermediate, $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$, is formed. This intermediate then reacts with 3 mol of the acid according to Eq. (6) to produce $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (point D).

Based on Fig. 2, it can be expected that the reaction of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ with 4-carboxyphenylphosphonic acid carried out at constant pH produces $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ at $\text{pH} = 3$ and $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (the intermediate) at $\text{pH} = 5$. We therefore repeated reactions (5) and (6) in a pH stat mode, i.e., we kept constant pH of the suspension of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ at $\text{pH} = 3$ and 5 by adding 4-carboxyphenylphosphonic acid. When the reaction at $\text{pH} = 3$ in carried out in an ethanol/water mixture, addition of a small amount of the acid to the reaction mixture causes dissolution of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ before

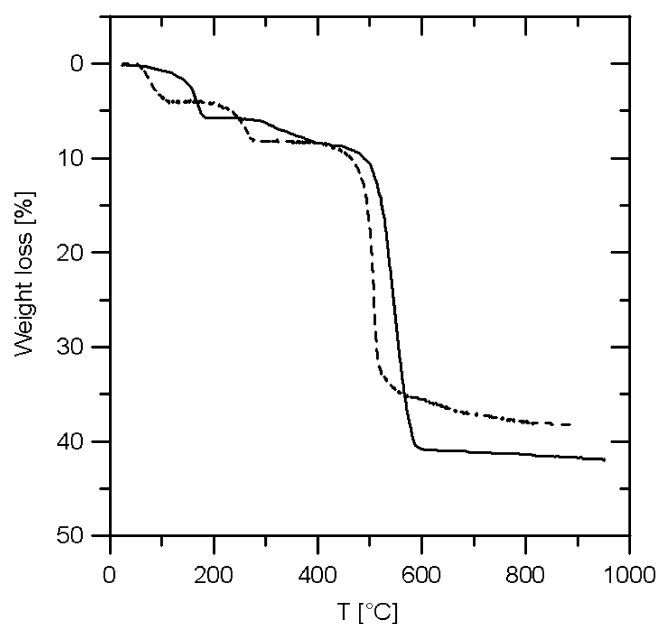
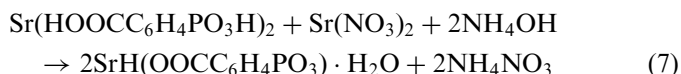


Fig. 3. TGA curves of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (solid line) and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ (dashed line).

pH = 3 is reached. Dissolved $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ reacts very fast with the added acid and a precipitation of the product occurs within several minutes. The powder X-ray pattern of the formed solid corresponds to that of $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$. When the same reaction is carried out in 96% ethanol, it is much slower and no dissolution of starting $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2$ occurs. The dependence of the amount of the added acid on time has an exponential shape. $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ is formed at both pH = 3 and 5, as confirmed by powder XRD. No formation of the intermediate was observed at pH = 5. We presume that the excess of the acid in the reaction mixture, which is needed to keep constant pH, causes a rapid formation of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ from the intermediate.

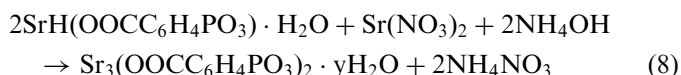
A reverse interconversion was also investigated, that is a formation of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot y\text{H}_2\text{O}$ in a reaction of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ with Sr^{2+} ions in a moderately basic medium. This reaction was accomplished by a computer-controlled addition of an ammonia solution to an aqueous suspension of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ in the presence of a strontium salt solution. As the starting compounds, both α - and $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ were tested and it was found that they behave in the same way.

The value of pH decreases exponentially between the additions of ammonia indicating an uptake of OH^- ions due to their reaction with $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ as seen in the inset in Fig. 4. The course of the reaction as a dependence of pH on the molar amount of added ammonia per 1 mol of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ is depicted in Fig. 4. The values of pH are those reached just before an addition of another dose of ammonia. The pH value is around 5 up to $n(\text{NH}_4\text{OH})/n(\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2) = 2$ (point A). At this point, the formation of the intermediate can be expected according to the equation



The compound obtained in the reaction carried out only to point A was characterized by powder XRD and TGA. It was found to be identical with the intermediate formed in reaction (5).

Further addition of ammonia causes a steep increase of pH to more than 7 (point B). Then, a decrease of pH occurs which is followed by a plateau at around pH = 6.5. Another steep increase of pH is observed at $n(\text{NH}_4\text{OH})/n(\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2) = 4$ (from point C) which indicates a formation of the product from the intermediate according to the equation



The TGA of the product (Fig. 3, dashed line) differs from that obtained for $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (cf. Fig. 1, dashed line). A weight loss of 10% between 70 and 300 °C with two clearly distinguished steps is smaller than that for $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ and the calculated

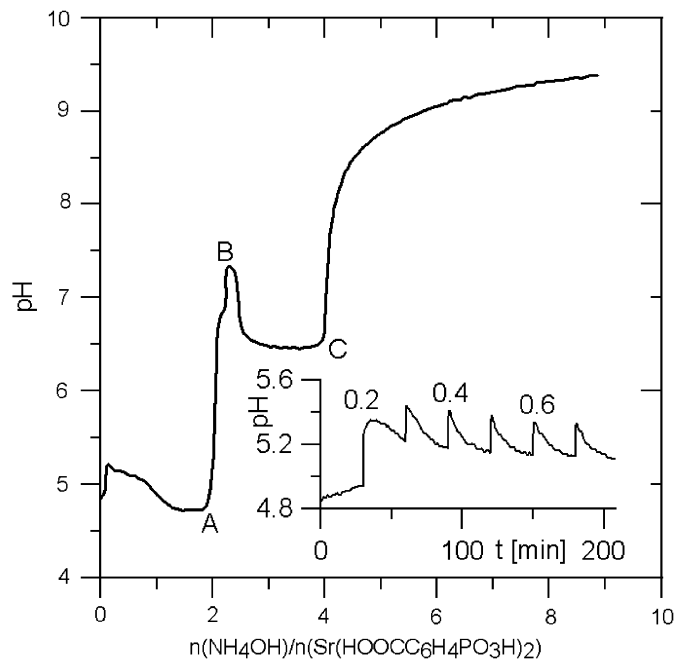


Fig. 4. Course of the reaction of the $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ suspension with ammonia in the presence of $\text{Sr}(\text{NO}_3)_2$. The inset represents a time dependence of pH at the beginning of the reaction; the numbers in the inset represent the amount of added NH_4OH in millilitres.

content of water is $y = 4$. The product of heating to 900 °C is $\text{Sr}_3(\text{PO}_4)_2$ as was confirmed by powder XRD (PDF No. 24-1008) [24]. Also, elemental analysis confirmed that the formula of the product can be written as $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$. The powder XRD pattern differs from that of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$. The basal spacing of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ is $d = 10.3 \text{ \AA}$ and the cell parameters are given in Table 1. This tetrahydrate undergoes the same reverse reaction—interconversion—with 4-carboxyphenylphosphonic acid to $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ as $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$.

Reactions (7) and (8) were also carried out at constant pH. The reaction mixture consisting of $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3)_2$ suspended in $\text{Sr}(\text{NO}_3)_2$ solution was kept at pH = 6 or 8 by adding an aqueous ammonia solution. At pH = 8, the reaction was almost finished after about 40 min and the product was a mixture of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$, as confirmed by powder XRD. At pH = 6, the product was $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ with some traces of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$. No formation of the intermediate was observed in both cases. The reaction at pH = 6 was about four times slower than that at pH = 8. It seems therefore, that the kinetically favored $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ is formed first and changes to thermodynamically more stable $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ with prolonged time of the reaction.

3.2. Infrared spectroscopic study of the prepared compounds

All studied strontium 4-carboxyphenylphosphonates were characterized by FTIR spectroscopy and their spectra

are shown in Fig. 5. It was found that the spectra of both modifications of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ are identical; therefore, only the spectrum of the α modification is included in Fig. 5. The spectrum of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ was practically the same as the spectrum of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ and therefore it is not included in Fig. 5.

The spectra of the presented compounds are compared with the spectra of phenylphosphonic acid ($\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$), strontium hydrogen phenylphosphonate ($\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$) and strontium phenylphosphonate dihydrate ($\text{SrC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$) described in our previous paper [12] to determine the bands connected with the presence of variously hydrogenated PO_3 groups. In addition, the spectra of the presented compounds are compared with the spectrum of 4-carboxyphenylphosphonic acid monohydrate ($\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$) to explain the bands connected with the carboxylic anion. To support the interpretation of the infrared spectra, the theoretical spectra of all discussed compounds were calculated at the B3LYP/6-31G(d) level of theory. The assignment of the vibrational modes in the theoretical spectra presented in Fig. 6 is based on the elucidation of the vibration motions of the atoms in the studied molecules using an animation of normal modes in the graphics of the GaussView program [27].

The interpretation of the infrared spectrum of phenylphosphonic acid was summarized by Bujoli [28]. The symmetric and antisymmetric modes relative to PO_3R tetrahedra are situated in the spectral range $1300\text{--}850\text{ cm}^{-1}$ (Fig. 5). The strong band centered at 1220 cm^{-1} corre-

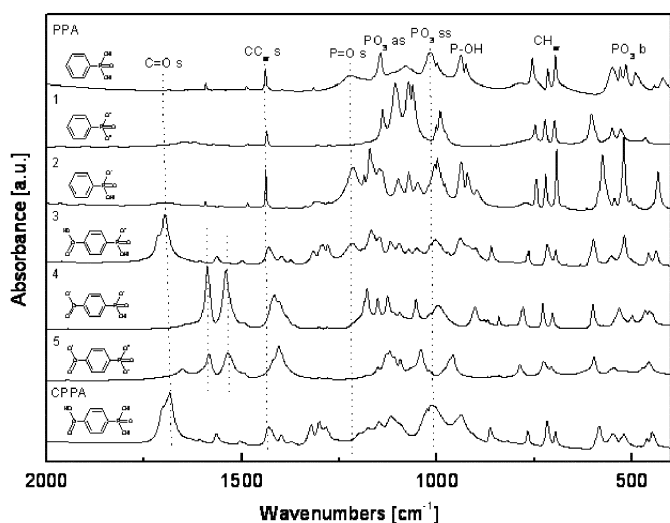


Fig. 5. The infrared spectra of phenylphosphonic acid ($\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$, marked as **PPA**), strontium phenylphosphonate dihydrate ($\text{SrC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$, **1**), strontium hydrogen phenylphosphonate ($\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$, **2**) and the infrared spectra of newly prepared α - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ (marked as **3**, both modifications, i.e., α and β , have identical spectra), the spectrum of the intermediate $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (**4**), $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ (**5**, the spectrum of which was the same as that of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$) and the spectrum of 4-carboxyphenylphosphonic acid (**CPPA**) (s = stretch, as = antisymmetric stretch, ss = symmetric stretch, b = bend).

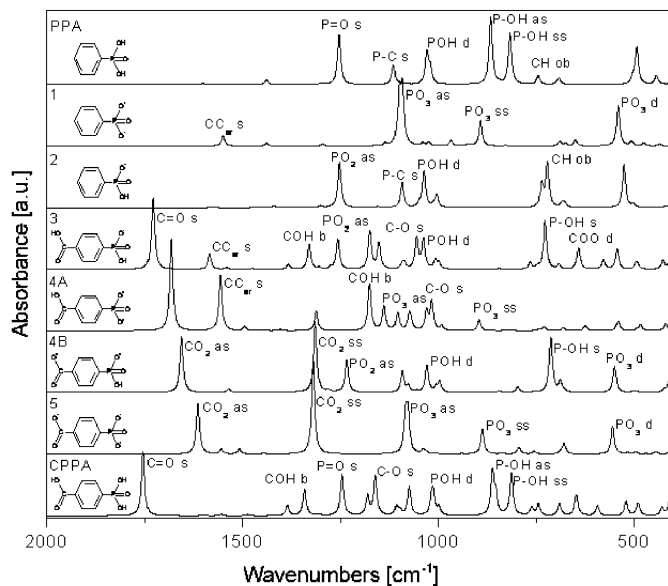


Fig. 6. Infrared spectra of strontium phenylphosphonates and 4-carboxyphenylphosphonates calculated at the B3LYP/6-31G(d) level (marking of the compounds is the same as in Figs. 5, **4A** and **4B** represent two possible positions of the hydrogen atom in the organic fragment of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (s = stretch, as = antisymmetric stretch, ss = symmetric stretch, b = bend, d = deformation, ob = out-of-plane bend).

sponds to a $\text{P}=\text{O}$ stretching vibration. The bands evident in the spectra of $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$ and α - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ at 1215 and 1217 cm^{-1} , respectively, can be assigned to the POO^- stretching as supported by the calculations (Fig. 6), which means that the $\text{P}=\text{O}$ double bond is delocalized. Such band is missing in the spectra of $\text{SrC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$. The doublet situated at 938 and 926 cm^{-1} corresponds to the $\text{P}(\text{OH})$ antisymmetric and symmetric stretching vibrations. The spectra of $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$, α - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ are very similar in this region indicating clearly the presence of the PO_3H groups [12]. The strong doublet observed at 1061 and 1072 cm^{-1} in the spectrum of $\text{SrC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$ and the strong peak situated at 1040 cm^{-1} in the spectrum of $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ should be assigned to an antisymmetric vibration mode of the CPO_3^{2-} group [29]. The peaks at 551 , 530 and 515 cm^{-1} and the peak at 491 cm^{-1} in the spectrum of phenylphosphonic acid correspond to the PO_3 symmetric and PO_3 antisymmetric bending modes, respectively.

In the spectra of all samples, several absorptions can be assigned to the phenyl ring: the $\text{C}-\text{H}$ stretching vibrations in the region of $3090\text{--}3000\text{ cm}^{-1}$ and the aromatic $\text{C}=\text{C}$ stretching vibrations observed at about 1438 cm^{-1} . The CH and $\text{C}-\text{C}$ out-of plane bending vibration appears as three absorptions at 756 , 716 and 696 cm^{-1} and two peaks of the stretching mode of $\text{P}-\text{C}_6\text{H}_5$ are situated at 443 and 420 cm^{-1} in the spectrum of phenylphosphonic acid. All these vibrations are found very close to these positions in the spectra of all other samples.

In the spectra of $\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$ and $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$, we observed a strong band of the stretching vibration of the $\text{C}=\text{O}$ bond of the carboxylic group at 1684 and 1696 cm^{-1} , with a shoulder at the higher-wavelength side of the spectrum due to the transition dipole coupling (TDC) of the carbonyl groups in the crystalline cell. This band is missing in the spectra of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$, where two bands (a strong one at $1660\text{--}1590\text{ cm}^{-1}$ and a weak one at 1400 cm^{-1}) characteristic of the carboxylic anion are observed. Other bands corresponding to the carboxylic group are: the O-H stretching vibration at about 3000 cm^{-1} , the overtones bands at about 2678 and 2555 cm^{-1} , the O-H in-plane bending vibration at 1430 cm^{-1} , the C-O stretching vibration at 1295 cm^{-1} and the O-H out-of-plane deformation vibration at 938 cm^{-1} [29]. These bands are present in the spectra of $\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$ and $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and missing in the spectra of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$.

In the region of the characteristic absorptions of the OH moieties, a drastic difference appears between the spectra of phenylphosphonic acid, $\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$, $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$ and the spectra of $\text{SrC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$, $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$, which contain coordinated water molecules in their structure. Typical frequency patterns specific of strong hydrogen bonds, with broad absorptions centered at 2800 , 2730 and 2240 cm^{-1} are seen in the spectra of phenylphosphonic acid and $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$. The broadband of the O-H stretching vibration at about 3000 cm^{-1} corresponding to the carboxylic group in the spectra of $\text{HOOC}_6\text{H}_4\text{PO}_3\text{H}_2 \cdot \text{H}_2\text{O}$ and $\alpha\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ is overlapped by the stretching vibration of the OH entities bonded to the P atoms. The broadbands at about 2281 and 2794 cm^{-1} in the infrared spectra of phenylphosphonic acid and $\text{Sr}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$ correspond to the presence of the $(\text{P})\text{-O-H}\cdots\text{O-P}$ hydrogen bonds [12]. The presence of sharp and intense bands observed at about 3600 cm^{-1} in the spectra of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ indicates an occurrence of a single well-defined kind of a water molecule most probably coordinated to a metal [30]. These bands disappear after dehydration, as confirmed for $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3)$.

In the quantum chemical calculations of the infrared spectra of all discussed compounds (Fig. 6), the water molecules were not taken into the consideration. We concentrated our attention to the positions of the bands connected with the presence of variously hydrogenated PO_3 and CO_2 groups. The spectra 4A and 4B in Fig. 6 represent two possible positions of the hydrogen atom in the organic fragment of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ (spectrum 4 in Fig. 5). Comparison of calculated and experimental spectra supports the assignment of the spectrum 4 to the structure with the acid hydrogen atom located at the phosphonate group. The doublet of two strong bands in the COO^- asymmetric stretching region ($1600\text{--}1500\text{ cm}^{-1}$) is due to

the presence of the water molecule in the fragment of $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$.

3.3. Structure of $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$

The structure of $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ was solved from its powder X-ray pattern using the FOX program. The crystallographic data are given in Table 2. The cell parameters were refined using the FullProf program and the plotted output from the Rietveld refinement is shown in Fig. 7. The selected distances and angles are given in Table 3.

In the structure of $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$, the strontium atom is eight coordinated by the O15, O16, and O17 oxygen atoms of the phosphonate groups as depicted in Fig. 8 (viewed approximately in the direction of the *ac* diagonal), forming a distorted tetragonal antiprism. Two neighboring Sr atoms share the O15 and O17 oxygen atoms, which are both μ_3 -atoms. The third coordination of these oxygens is complemented by the P atom of the phosphonate group, with the organic rests directed in the opposite directions from the inorganic part of the structure. The remaining O16 atom of the phosphonate group is connected to one Sr atom only. The Sr, P, and O atoms thus form a one-dimensional ribbon running in the direction of the *c*-axis, in which the Sr atoms are arranged in a zigzag pattern. The aryl groups jut out alternatively above and below this ribbon as depicted in Fig. 9 viewed in the direction of the *c*-axis. The distance between the COOH groups of two carboxyphenylphosphonate fragments neighboring in the direction of the *a*-axis indicates that a hydrogen bond is formed between them (the O13–O14 distance between these two neighboring groups is 2.721 \AA). All the $[\text{Sr}_2(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_4]_\infty$ ribbons are connected

Table 2
Crystallographic data for $\beta\text{-Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$

Formula	$\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$
Formula weight, g mol^{-1}	489.81
Calculated density, g cm^{-3}	1.897
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
<i>a</i> , \AA	46.545(2)
<i>b</i> , \AA	7.8669(3)
<i>c</i> , \AA	5.5988(2)
β , $^\circ$	123.283(2)
<i>V</i> , \AA^3	1714.6(1)
<i>Z</i>	4
2θ range, $^\circ$	2–65
<i>T</i> , $^\circ\text{C}$	25
λ , \AA	1.5418
R_p^a	12.8
R_{wp}^a	17.8
R_B^a	5.97
R_F^a	5.46

^aThe definitions of R_p , R_{wp} , R_B , R_F are described in [31]. The values are given in %.

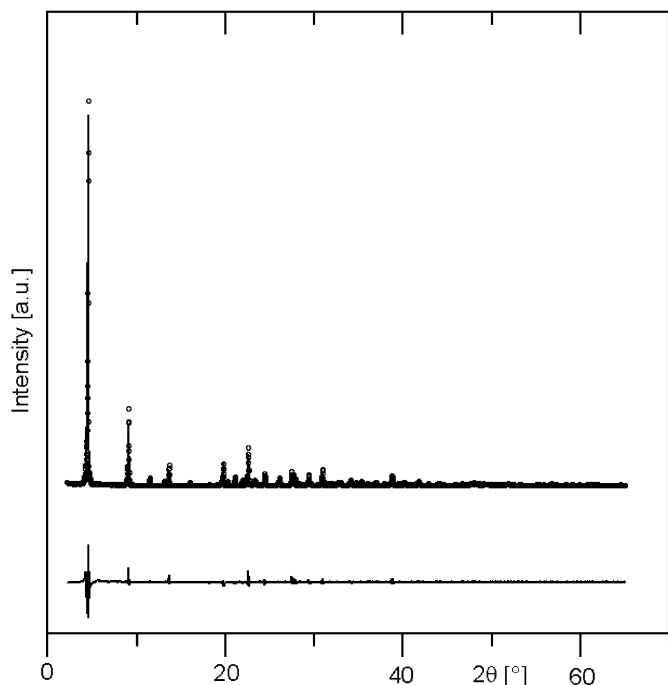


Fig. 7. The Rietveld plot: observed (circles), calculated (line) and difference (bottom line) X-ray powder diffraction patterns for β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$.

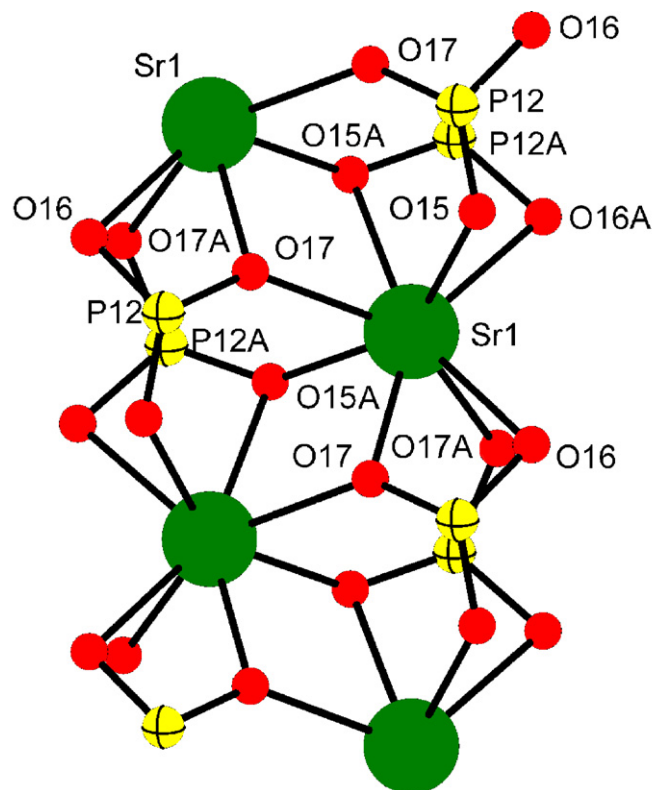


Fig. 8. The inorganic fragment of β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$.

Table 3

Selected bond lengths and angles (\AA , $^\circ$) for β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2^a$

Sr1–O15	2.509(1)	Sr1–O15A	2.51(1)
Sr1–O16	2.587(1)	Sr1–O16A	2.708(1)
Sr1–O17	2.299(9)	Sr1–O17A	2.618(1)
P12–O15	1.486(1)	P12–O16	1.582(1)
P12–O17	1.631(9)	P12A–O15A	1.525(1)
P12A–O16A	1.681(1)	P12A–O17A	1.524(1)
O15–P12–O16	114.46(7)	O16–P12–O17	88.50(6)
O17–P12–O15	109.13(5)	O15A–P12A–O16A	112.26(6)
O16A–P12A–O17A	107.08(7)	O17A–P12A–O15A	129.63(6)
O15–Sr1–O15A	147.43(3)	O15–Sr1–O16	79.39(3)
O15–Sr1–O16A	73.95(3)	O15–Sr1–O17	110.41(3)
O15–Sr1–O17A	132.83(4)	O15A–Sr1–O16	128.34(3)
O15A–Sr1–O16A	111.26(3)	O15A–Sr1–O17	81.24(3)
O15A–Sr1–O17A	103.8(3)	O16–Sr1–O17	121.39(3)
O16–Sr1–O17A	73.02(3)	O16A–Sr1–O17	150.48(3)
O16A–Sr1–O17A	74.25(3)		

^aSee Fig. 8 for the atom marks.

together by these hydrogen bonds in such a way that the strontium atoms are positioned in a plane parallel to the bc plane. The structure of β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ is very similar to that of $\text{Ca}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ published previously [11]. The only difference is in the orientation of the phenyl rings, which results in a lower symmetry for the Sr compound.

4. Conclusion

Depending on the acidity of the reaction medium, two strontium 4-carboxyphenylphosphonates with formulae

$\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ were prepared. Using computer-controlled additions of the reagents, it was found that $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 5.7\text{H}_2\text{O}$ reacts with 4-carboxyphenylphosphonic acid in a two-step reaction with $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ as an intermediate and $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ as a final product. The powder X-ray pattern of this product differs from that of the synthesized $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ and is therefore denoted as a beta modification. Both modifications of $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ can be converted to $\text{Sr}_3(\text{OOC}_6\text{H}_4\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ by a treatment with ammonia in the presence of a strontium salt. This conversion is again a two-step process with the same intermediate as in the reverse conversion. In summary, the interconversions of strontium 4-carboxyphenylphosphonates can be expressed by a flow diagram depicted in Fig. 10. These interconversions differ from those of strontium phenylphosphonates, where no analogous intermediate was obtained [12]. The behavior of strontium phenylphosphonates and 4-carboxyphenylphosphonates is quite opposite to that observed for analogous calcium compounds [11]. No intermediate was obtained for calcium 4-carboxyphenylphosphonates. On the other hand, a formation of an intermediate with formula $\text{Ca}_3(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$ was observed in the interconversions of calcium phenylphosphonates with formulae $\text{Ca}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2$ and $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$. All studied compounds were further characterized by the FTIR spectroscopy and the theoretically calculated spectra. The IR bands given by the presence of the hydrogen atoms in

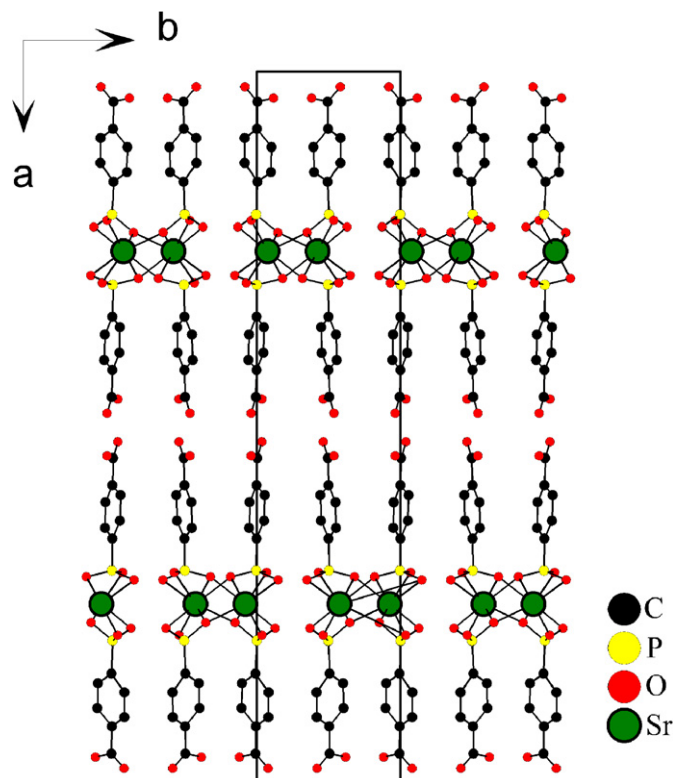


Fig. 9. The structure of β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ viewed in the direction of the c -axis.

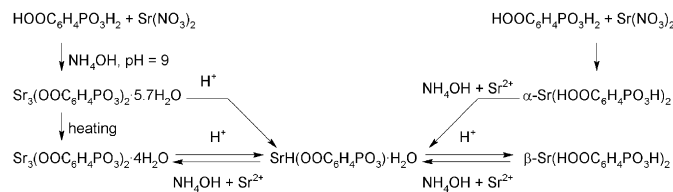


Fig. 10. Reactions of strontium 4-carboxyphenylphosphonates in acid and basic media. 4-Carboxylic acid was used as a source of H^+ ions.

the COOH and PO_3H groups were determined. From the comparison of the spectra of strontium 4-carboxyphenylphosphonates and phenylphosphonates it was concluded that the acid hydrogen atom in $\text{SrH}(\text{OOC}_6\text{H}_4\text{PO}_3) \cdot \text{H}_2\text{O}$ is present at the phosphonate group and not at the carboxylic group. The structure solution carried out for β - $\text{Sr}(\text{HOOC}_6\text{H}_4\text{PO}_3\text{H})_2$ showed that its inorganic part, composed of dimers of SrO_8 tetragonal antiprisms, forms one-dimensional ribbons running parallel with the bc plane. To these ribbons, the arylphosphonic fragments are attached jutting out below and above their bc plane.

Acknowledgments

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

Appendix A. Supporting information

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 618000. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Appendix B. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.12.021.

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