Journal of Solid State Chemistry 182 (2009) 3155–3161

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis and characterization of copper 4-carboxyphenylphosphonates

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ARTICLE INFO

Article history:
Received 2 February 2009
Received in revised form
1 September 2009
Accepted 6 September 2009
Available online 11 September 2009

Keywords:
Copper
Carboxyphenylphosphonate
X-ray diffraction
Infrared spectroscopy

ABSTRACT

Three new copper 4-carboxyphenylphosphonates with formulae $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$, $Cu(HOOCC_6H_4PO_3)$ and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ were prepared and characterized by thermogravimetric analysis, X-ray diffraction analysis, energy-dispersive X-ray microanalysis and infrared spectroscopy. The preparation conditions of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ differ in the acidity of the reaction mixture, where $Cu(HOOCC_6H_4PO_3)$ was prepared under hydrothermal conditions. Copper 4-carboxyphenylphosphonate with formula $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ reacts with 4-carboxyphenylphosphonic acid to form $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$.

$Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ is orthorhombic, space group *Pbcn* (no. 60), $a=8.234(2)$ Å, $b=9.438(2)$ Å, $c=24.899(5)$ Å. $Cu(HOOCC_6H_4PO_3)$ crystallizes in the monoclinic space group $P2_1/c$ (no. 14), $a=19.0951(3)$, $b=8.0968(4)$, $c=5.2111(11)$ Å, $\beta=94.914(6)^\circ$, $Z=4$. Its layered structure is composed of distorted CuO_6 octahedra arranged hexagonally in a gibbsite-like manner around two phosphonate groups, which have their carboxyphenyl groups extending into the space above and below the copper–phosphonate layer. Infrared spectra indicate that for both $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ and $Cu(HOOCC_6H_4PO_3)$ the acid hydrogen is present at the carboxyl group and not at the phosphonic group.

1. Introduction

Metal organophosphonates are inorganic–organic hybrid compounds with many potential applications. These hybrid materials have potential applications in catalysis [1], proton conductivity [2,3], as sorbents [4,5], ion exchangers [5,6], or as hosts in intercalation reactions [3,7]. Great effort has been devoted to the preparation of porous metal phosphonates [8] and phosphonates with distinct magnetic [9] and optical properties [10]. Metal phosphonates can be also applied to biotechnology [11] and biology [12]. A large variety of such compounds can be prepared due to the large amount of metals which can be employed in the formation of the inorganic part. There is also a great variability in the organic part as this can be formed of various organic structures having attached various functional groups.

Very thoroughly studied metal organophosphonates were those of zirconium [13]. Regarding phenylphosphonates of divalent metals, the first systematic study dealing with a large range of metals appeared roughly three decades ago [14]. Since that time, there has been a perpetual and increasing interest in these compounds.

As far as copper is concerned, several alkyl- and arylphosphonates were prepared [15] and their intercalation behavior was studied [16]. Also copper organophosphonates, in which the organic part is functionalized, for instance with $-NH_2$ or $-COOH$ groups, were prepared [17]. Recently, several copper based materials containing organic ligands with phosphonic and carboxyl functional groups have been described [18].

Recently, we have focused on the synthesis, structure and chemical behavior of alkaline-earth phenylphosphonates [19–21] and 4-carboxyphenylphosphonates [19,22,23]. It was found that, depending on the acidity of the reaction mixture, compounds with different compositions can be prepared. Up to now, no such study has been made of transition metal carboxyphenylphosphonates. In this paper, we report on the synthesis and characterization of the first of these compounds, copper 4-carboxyphenylphosphonates.

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 [24].

Diffraction data (Cu*K*α, $\lambda=1.5418$ Å) were collected on a Bruker AXS D8 Advance diffractometer with a Bragg–Brentano θ–θ geometry, equipped with parallel (Soller) slits, a secondary beam

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doi:10.1016/j.jssc.2009.09.001

curved graphite monochromator, a Na(Tl)I scintillation detector and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. The following slits were used: divergence 0.5°, anti-scatter 0.5° and receiving 0.1 mm. The diffraction angles were measured at room temperature from 2° to 65° (2θ) in 0.02° steps with a counting time of 10 s per step.

The powder patterns were indexed, when possible, using a DicVOL method in a WinPLOTR program [25]. The space groups were determined by processing the data in the Checkcell program [26].

The copper and phosphorus contents were determined by an electron scanning microscope JEOL JSM-5500LV and energy-dispersive X-ray microanalyser IXRF systems equipped with GRESHAM Sirius 10 detector (EDX). The accelerating voltage of the primary electron beam was 20 kV.

The thermogravimetric analysis (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.

The X-ray data for blue–green crystal of Cu($HOOCC_6H_4PO_3$) were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with Mo$K\alpha$ radiation (λ=0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [27]. The absorption was corrected by integration methods [28]. Structures were solved by direct methods (Sir92) [29] and refined by full matrix least-square based on F^2 (SHELXL97) [30]. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{\mathrm{iso}}(H)=1.2\ U_{\mathrm{eq}}$(pivot atom) with C–H=0.93 Å for aromatic hydrogen atoms, and 0.82 Å for O–H bonds, respectively.

Crystallographic data for Cu($HOOCC_6H_4PO_3$): $C_7H_5CuO_5P$, M=263.62, monoclinic, $P2_1/c$, a=19.0951(3), b=8.0968(4), c=5.2111(11) Å, β=94.914(6)°, Z=4, V=802.72(17) Å^3, D_c=2.181 g cm^{-3}, μ=2.908 mm^{-1}, $T_{\min}/T_{\max}$=0.461/0.859; 8406 reflections measured ($\theta_{\max}$=27.5°), 1814 independent (R_{int}=0.0503), 1216 with $I>2\sigma(I)$, 127 parameters, S=1.049, $R1$(obs. data)=0.0405, w$R2$(all data)=0.0974; max., min. residual electron density=0.895–1.164 e Å^{-3}.

$R_{\mathrm{int}}=\Sigma|F_o^2-F_{o,\mathrm{mean}}^2|/\Sigma F_o^2$, $\mathrm{GOF}=[\Sigma(w(F_o^2-F_c^2)^2)/(N_{\mathrm{diffrs}}-N_{\mathrm{params}})]^{1/2}$ for all data, $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ for observed data, $wR(F^2)=[\Sigma(w(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 718642 for Cu($HOOCC_6H_4PO_3$). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

2.2. Preparation of Cu($HOOCC_6H_4PO_3$)·$2H_2O$

To 0.88 g of 4-carboxyphenylphosphonic acid monohydrate, $HOOCC_6H_4PO_3H_2\cdot H_2O$ (4 mmol), 20 mL of a mixture of water and ethanol (1/1 v/v) was added under stirring. After 20 min the mixture was filtered to remove any undissolved impurities. To this solution, 0.68 g of $CuCl_2\cdot 2H_2O$ (4 mmol) dissolved in 10 mL of water was added under stirring. A light blue precipitate was formed which was separated by filtration. The filtrate was left to stand at room temperature overnight and produced another part of the light blue precipitate which was added to the first part of the solid product. The product was washed with the water/ethanol (1/1 v/v) mixture, then twice with ethanol and dried in air at room temperature. The yield was 0.41 g (34%). Elemental analysis (%) for $C_7H_9CuO_7P$ (299.66) found: 29.12% C, 3.65% H; calcd.: 28.06% C, 3.03% H. The relative amounts of copper and phosphorus were 1/1, according to EDX.

2.3. Preparation of Cu($HOOCC_6H_4PO_3$)

A reaction mixture containing 0.319 g of CuO (4 mmol), 0.88 g of $HOOCC_6H_4PO_3H_2\cdot H_2O$ (4 mmol) and 8 mL of water was placed in a Teflon-lined 23-mL Parr acid digestion bomb and heated under autogenous pressure at 160 °C for 20 h. After cooling, the blue product was separated by filtration, washed twice with distilled water, ethanol and dried in air at room temperature. The relative atomic ratio of copper and phosphorus was 1/1, according to EDX. Elemental analysis calcd. (%) for $C_7H_5CuO_5P$ (263.63): C 31.89, H 1.91; found: C 31.71, H 2.61.

Preparation of Cu($HOOCC_6H_4PO_3$) suitable for single-crystal X-ray diffraction: 0.25 g of $CuSO_4\cdot 5H_2O$ (1 mmol) was mixed with 0.11 g of $HOOCC_6H_4PO_3H_2\cdot H_2O$ (0.5 mmol), 1 mL of hydrofluoric acid and 5 mL of water in a Teflon-lined 23-mL Parr acid digestion bomb, heated under autogenous pressure at 180 °C for 40 h and then cooled to room temperature within another 22 h. The hydrofluoric acid was chosen a mineralizing agent enabling better crystallization of the prepared compound. The product contained a blue powder together with blue–green prismatic crystals which were separated manually and used for structure determination.

2.4. Preparation of $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$

To a solution of $HOOCC_6H_4PO_3H_2\cdot H_2O$ (0.88 g, 4 mmol) in 50 mL of water an aqueous solution of ammonia (8 mmol) was added. This diammonium salt solution was mixed under stirring with a solution containing 1.02 g of $CuCl_2\cdot 2H_2O$ (6 mmol) in 25 mL of water. A blue solid immediately precipitated, which was isolated by filtration, washed twice with water, twice with ethanol, and dried over P_2O_5 in vacuo. The yield was 0.79 g (60%). The relative atomic ratio of copper and phosphorus was 3/2, according to EDX. Elemental analysis for the dehydrated $Cu_3(OOCC_6H_4PO_3)_2$: calcd. (%) for $C_{14}H_8Cu_3O_{10}P_2$ (588.79): C 28.53, H 1.36; found: C 27.79, H 2.61.

2.5. Reaction of $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ with 4-carboxyphenylphosphonic acid

The reaction was carried out at room temperature using a computer-controlled Schott Titronic 97 piston burette. Using this burette, an aqueous solution of 4-carboxyphenylphosphonic acid was added to an aqueous suspension of the copper 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 copper 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 $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (0.33 g; 0.513 mmol) in a mixture of ethanol (30 mL) and water (20 mL) was titrated with a 0.0465 M aqueous solution of 4-carboxyphenylphosphonic acid, which was added in 0.5-mL doses with 1800-s intervals between doses. The values of pH were measured in 1-min intervals during the reaction.

3. Results and discussion

According to the experimental conditions, three different compounds were obtained from the reaction of 4-carboxyphenylphosphonic acid with a Cu(II) compound.

A compound, in which the relative atomic ratio of copper and phosphorus is 1/1, can be prepared directly by mixing the solutions of Cu^{2+} salt and 4-carboxyphenylphosphonic acid at room temperature without a pH adjustment.

On heating, this compound loses weight in two steps (Fig. 1a). The first weight loss of 12% occurs in the temperature range 150–200 °C. The second weight loss begins at 350 °C. The total weight loss is 50% and the product of heating is $Cu_2P_2O_7$, as identified by powder X-ray diffraction (PDF no. 44-0182 [31]). Presuming that the formula of the prepared compound is $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$, the first weight loss corresponds to the release of two molecules of water per formula unit (theoretical weight loss of 11.8%), and the second weight loss corresponds to the decomposition of the organic part with the theoretical weight loss of 37.8% (i.e., total theoretical weight loss of 49.6%).

The diffractogram (Fig. 2a) shows a pattern typical for layered compounds with well pronounced (00*l*) reflections. The powder pattern was indexed in an orthorhombic system with cell parameters a=8.234(2) Å, b=9.438(2) Å, c=24.899(5) Å and space group *Pbcn* (no. 60). The parameter c is quite small, compared to copper phenylphosphonate with formula $CuC_6H_5PO_3\cdot H_2O$ which is orthorhombic with lattice parameters a=7.5547 Å, b=7.4478 Å, c=27.982 Å [15]. On the other hand, the a and b parameters are larger for $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ than for $CuC_6H_5PO_3\cdot H_2O$. We can presume that the structure of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ differs from that of $CuC_6H_5PO_3\cdot H_2O$. Most probably, one of the water molecules resides between the phenyl rings and is coordinated to the Cu atom of the layer by free electron pairs of the oxygen atom. The smaller parameter c indicates that the 4-carboxyphenyl groups are interdigitated. The carboxyl group points between the phenyl rings of the neighboring layer and forms a hydrogen bond with the coordinated water molecule.

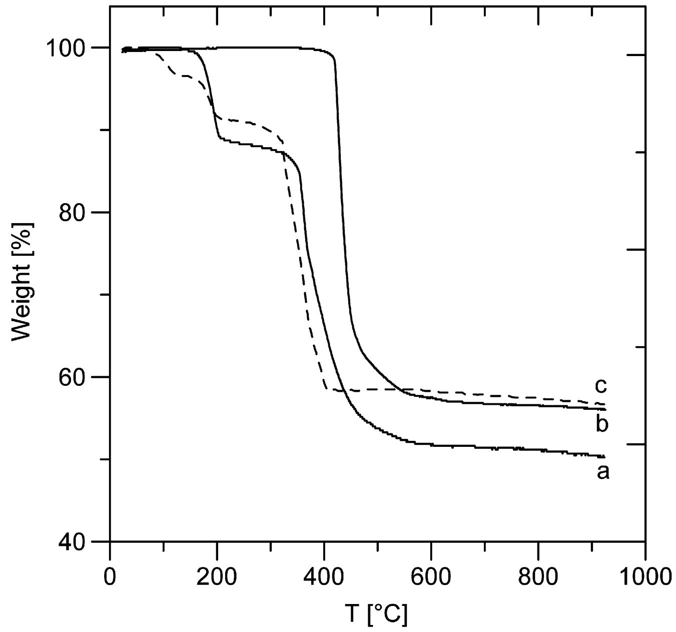

Fig. 1. Thermogravimetric curves of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (a), $Cu(HOOCC_6H_4PO_3)$ (b) and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (c).

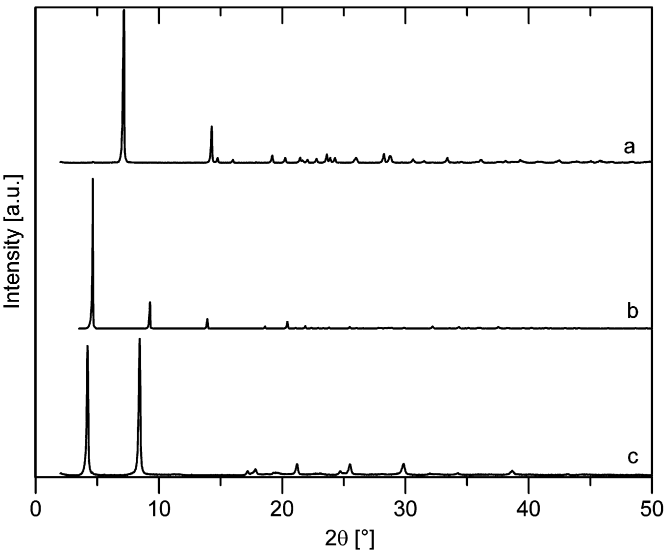

Fig. 2. X-ray powder diffractograms of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (a), $Cu(HOOCC_6H_4PO_3)$ (b) and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (c).

By dehydration at 200 °C, the X-ray diffraction powder pattern of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ changes and the basal spacing shifts to d=19.4 Å.

Under hydrothermal conditions, when a mixture of CuO and 4-carboxyphenylphosphonic acid is heated in water at 160 °C for several hours, a new compound is formed. As in the previous compound, also in this compound the relative atomic ratio copper to phosphorus is 1/1. The thermogravimetry (Fig. 1b) shows that heating causes a weight decrease in one step only. The decomposition begins at 400 °C and the total weight loss is 44%. The product of the heating to 950 °C is $Cu_2P_2O_7$, according to X-ray powder diffraction (PDF no. 44-0182 [31]). The TGA results are in agreement with the presumed formula $Cu(HOOCC_6H_4PO_3)$. The theoretical weight loss calculated according to the decomposition reaction

$$2Cu(HOOCC_6H_4PO_3)+15O_2 \rightarrow Cu_2P_2O_7+14CO_2+5H_2O \quad (1)$$

is 43%.

In the thermogravimetric curves for $Me(HOOCC_6H_4PO_3H)_2$ (Me=Ca [19], Sr [22], Ba [23]), a typical small decrease of weight starting below 400 °C was observed which was caused by a condensation of the phosphonate RPO_3H groups to pyrophosphonate $(RPO_2)_2O$ groups. No such decrease is observed in the thermogravimetric curve for $Cu(HOOCC_6H_4PO_3)$, which indicates that the phosphonate group is deprotonated.

This statement is in agreement with the results of the FTIR spectroscopic study of the molecular structure of the prepared samples. We used the analogy of their structure with the structure of the earlier studied strontium 4-carboxyphenylphosphonates [22]. We compared the spectra of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (Fig. 3a) and $Cu(HOOCC_6H_4PO_3)$ (Fig. 3b) with the spectrum of 4-carboxyphenylphosphonic acid (Fig. 3c) and with the spectra of the earlier studied samples of α-$Sr(HOOCC_6H_4PO_3H)_2$ (Fig. 3d), $SrH(OOCC_6H_4PO_3)\cdot H_2O$ (Fig. 3e) and $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f). The interpretation of the bands and the position of the acid hydrogen atom determined from the infrared spectra were done in [22].

We can see that the spectrum of $Cu(HOOCC_6H_4PO_3)$ (Fig. 3b) is very close to the spectrum of 4-carboxyphenylphosphonic acid

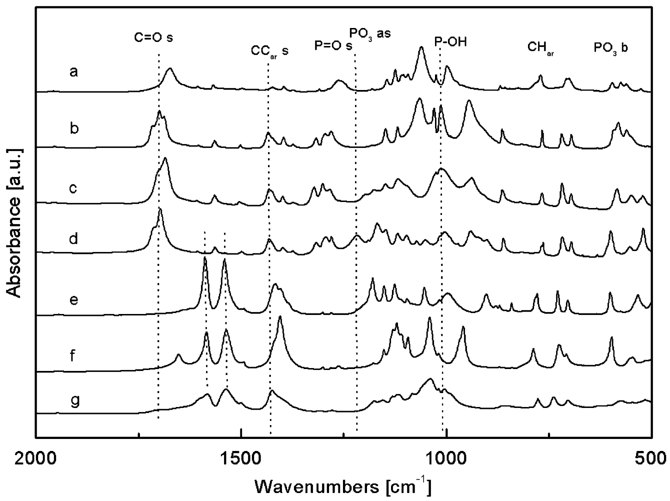

Fig. 3. The infrared spectra of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (a), $Cu(HOOCC_6H_4PO_3)$ (b), 4-carboxyphenylphosphonic acid (c), $Sr(HOOCC_6H_4PO_3H)_2$ (d), $SrH(OOCC_6H_4PO_3\cdot H_2O$ (e) and the spectra of $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (f) and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (g) (s=stretch, as=antisymmetric stretch, ss=symmetric stretch, b=bend).

(Fig. 3c) and α-$Sr(HOOCC_6H_4PO_3H)_2$ (Fig. 3d) in the region above 1250 cm^{-1}. In all these spectra we observe a strong stretching vibration of the carboxyl-group C=O bond at about 1690 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 [22]. This band is missing in the spectra of intermediate samples $SrH(OOCC_6H_4PO_3)\cdot H_2O$ (Fig. 3e) and $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f), where two bands (at about 1585 and 1400 cm^{-1}) characteristic of the carboxyl anion are observed [22]. Other bands corresponding to the carboxyl group [32]: the O–H stretching vibration at about 3000 cm^{-1}, the overtones bands at about 2678 and 2555 cm^{-1} (not shown in the spectrum figure), 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} are also detected in the spectra of our samples. These bands are also missing in the spectra of $SrH(OOCC_6H_4PO_3)_4\cdot H_2O$ (Fig. 3e) and $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f) supporting the presence of the carboxyl anion in their structure [22].

The $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ sample (Fig. 3a) differs from $Cu(HOOCC_6H_4PO_3)$ (Fig. 3b) only by the presence of water molecules, which is well documented by the corresponding small differences in their spectra. Besides the red shift of the stretching vibration of the C=O bond and of the C–O stretching vibration due to the interaction with the water molecules we observe a sharp and intense band at about 3400 cm^{-1} and a broad band with the maximum at 3200 cm^{-1} in the spectrum of $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (not shown in the figure), which correspond to the stretching OH vibrations of two differently bonded water molecules.

The absence of the $-PO_3H$ groups in $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ (Fig. 3a) and $Cu(HOOCC_6H_4PO_3)$ (Fig. 3b) is well documented by the comparison with the spectrum of $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f) in the region of the symmetric and antisymmetric modes relative to PO_3R tetrahedra situated in the spectral range 1300–850 cm^{-1}. The bands evident in the all spectra at about 1217 cm^{-1} can be assigned to the POO stretching vibration of the delocalized P=O double bond [22].

The X-ray powder diffraction pattern of $Cu(HOOCC_6H_4PO_3)$ shows a set of intensive (00*l*) lines, typical for layered structures alongside with less intensive (*hkl*) lines (Fig. 2b). The value of the basal spacing $d=19$ Å is about 0.25–0.6 Å lower than that found for alkaline-earth metal hydrogen 4-carboxyphenylphosphonates [19,22,23] and about 5 Å higher than that of $Cu(C_6H_5PO_3)\cdot H_2O$ [15]. Indexing showed that $Cu(HOOCC_6H_4PO_3)$ is monoclinic with the space group $P2_1/c$ (no. 14), lattice parameters: $a=19.1340(1)$ Å, $b=8.11880(1)$ Å, $c=5.23360(1)$ Å, $\beta=95.0187(2)^\circ$.

Under basic conditions, another copper 4-carboxyphenylphosphonate can be prepared from a Cu^{2+} salt and 4-carboxyphenylphosphonic acid. The relative atomic ratio copper to phosphorus was 3/2 in this compound, according to EDX.

By heating, the compound loses weight in three steps (Fig. 1c). The first one of 3% occurs at around 100 °C, the second one of 6% at around 180 °C. The last one, of 32.5%, occurs in the temperature range 300–400 °C. Considering the composition of this compound to be $Cu_3(OOCC_6H_4PO_3)_2\cdot yH_2O$, the first step corresponds to the release of one molecule of water, the second step is caused by the release of another two molecules of water and the last decrease is given by the decomposition of the organic part, according to the equation

$$Cu_3(OOCC_6H_4PO_3)_2+15O_2\rightarrow Cu_3(PO_4)_2+14CO_2+4H_2O \qquad (2)$$

The product of the heating was identified by X-ray powder diffraction to be $Cu_3(PO_4)_2$ (PDF No. 70-0494 [31]).

As in the previous cases, the X-ray powder diffraction pattern of $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ shows pronounced (001) and (002) lines, indicating a layered structure (Fig. 2c). The value of the basal spacing is $d=21$ Å. The other lines are largely suppressed, which did not allow us to determine lattice parameters for this compound.

The absence of the acid hydrogen atom and the composition of the product as $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ were confirmed by its infrared spectrum. In Fig. 3 the spectrum of this sample (Fig. 3g) has been compared with the spectrum of previously studied $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f) [22]. The bands corresponding to the PO_3H groups are indicated by strong peaks at about 939, 913, 902 and 880 cm^{-1}, assigned to P–OH stretching vibrations in the spectrum of $SrH(OOCC_6H_4PO_3)\cdot H_2O$ (Fig. 3e) [33]. These bands are missing in the spectra of the samples $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (Fig. 3g) and $Sr_3(OOCC_6H_4PO_3)_2\cdot 4H_2O$ (Fig. 3f), supporting the presence of the PO_3^{2-} group [20]. On the on the other hand, the two typical bands (at about 1585 and 1400 cm^{-1}) characteristic of the carboxyl anion are observed in the spectra of all samples $SrH(OOCC_6H_4PO_3)\cdot H_2O$ (Fig. 3e), $Sr_3(OOCC_6H_4PO_3)\cdot 4H_2O$ (Fig. 3f) and $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (Fig. 3g) [22].

Copper 4-carboxyphenylphosphonate prepared under basic conditions is able to react with 4-carboxyphenylphosphonic acid. The reaction was studied using a computer-controlled addition of the acid, as described in the Experimental part. At first, only a decrease of pH is observed with the additions of the acid to the aqueous suspension of $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ (Fig. 4). When pH reaches a value of around 3.3, the decrease of pH is stopped and almost a constant value indicates that the acid is consumed in the reaction. The pH value remains constant up to the point A when two moles of the acid per one mole of the phosphonate are added. Further additions of the acid cause only a decrease of pH, which indicates that the reaction is finished. The product of the reaction is $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$, according to powder X-ray diffraction, TGA and EDX, and thus the whole reaction can be described by the equation

$$Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O+HOOCC_6H_4PO_3H_2+H_2O\rightarrow 3Cu(HOOCC_6H_4PO_3)\cdot 2H_2O \qquad (3)$$

On the other hand, a reversible reaction, that is formation of $Cu_3(OOCC_6H_4PO_3)_2\cdot 3H_2O$ from $Cu(HOOCC_6H_4PO_3)\cdot 2H_2O$ or

$Cu(HOOCC_6H_4PO_3)$ in the presence of a moderate base, does not proceed. Strongly basic solutions, for instance a 0.05 M aqueous solution of sodium hydroxide, cause a decomposition of these copper phosphonates.

The crystallographic data of $Cu(HOOCC_6H_4PO_3)$ are given in Experimental. Fig. 5 shows the ORTEP drawing and the numbering of the atoms. Selected distances and angles are listed in the caption of Fig. 5.

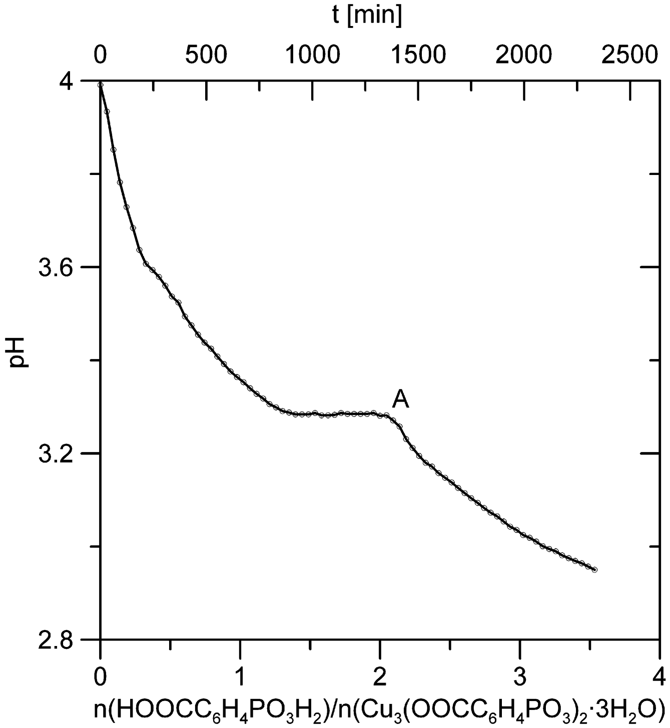

Fig. 4. Course of the reaction of the $Cu_3(OOCC_6H_4PO_3)_2 \cdot 3H_2O$ suspension with the 4-carboxyphenylphosphonic solution.

All oxygen atoms of the phosphonate group are of μ_3 type and each one bridges two copper atoms as shown in Fig. 6 depicting the inorganic fragment of $Cu(HOOCC_6H_4PO_3)$. The copper atoms lie in the *bc* plane and are six-coordinated by the oxygen atoms of the phosphonate groups forming an octahedron. The Cu–O bonds of the octahedron are considerably longer in the direction of the *c* axis (more than 2.5 Å) than the other Cu–O bonds (around 1.9 Å) indicating quite strong Jahn–Teller effect. These CuO_6 octahedra are edge shared in two ways: (i) through two O1 atoms in the *b* direction and (ii) through O2 and O3 atoms in the direction of the *bc* diagonal. Thus, every PO_3 group shares its oxygen atoms with six copper atoms. Consequently, two CPO_3 tetrahedra, lying above each other in the direction of the *a* axis and pointing into opposite directions through their P–C bonds, are surrounded by six CuO_6 octahedra as seen in Fig. 7 forming a hexagonal motif. The inorganic layers of $Cu(HOOCC_6H_4PO_3)$ are similar to those of the gibbsite modification of $Al(OH)_3$ [34], or dioctahedral sheets typical for clays containing trivalent metals [35]. To the best of our

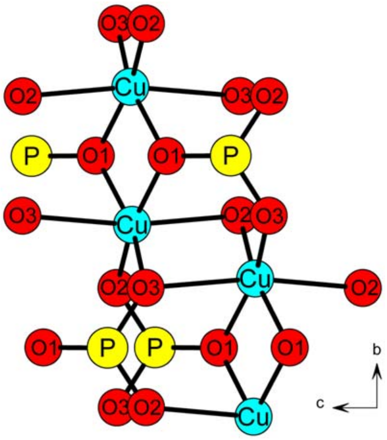

Fig. 6. Inorganic fragment of $Cu(HOOCC_6H_4PO_3)$ viewed down the *a* axis.

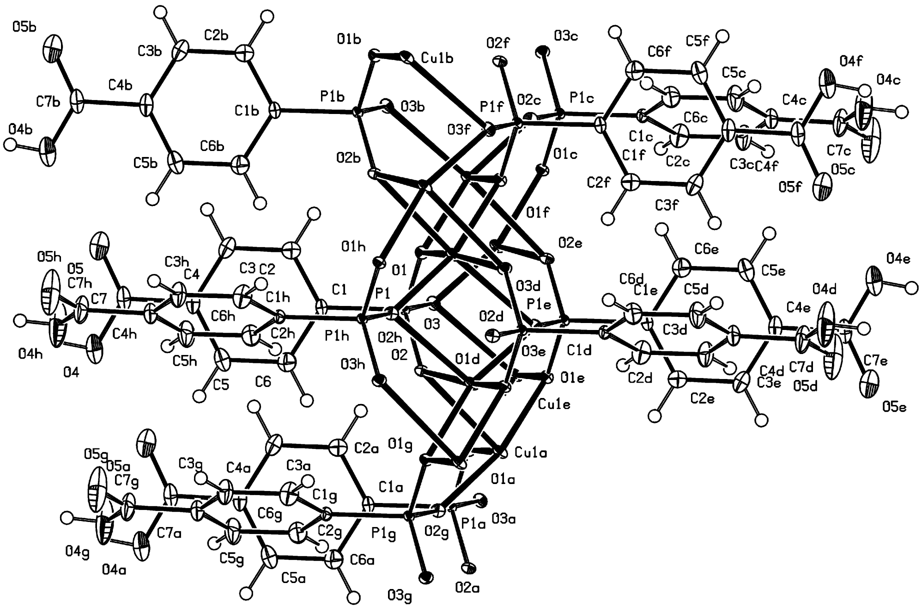

Fig. 5. ORTEP plot of $Cu(HOOCC_6H_4PO_3)$ fragment showing 40% probability displacement ellipsoid and the atom numbering scheme. The selected bonding lengths (Å) and angles (deg): Cu1–O2 1.927(3), Cu1–O3 1.932(3), Cu1–O1 1.967(3), Cu1–O1 1.974(3), P1–O2 1.519(3), P1–O3 1.526(3), P1–O1 1.560(2), P1–C1 1.790(3), C7–O5 1.247(7), C7–O4 1.256(7), O2–Cu1–O3 92.71(10), O2–Cu1–O1 165.80(11), O3–Cu1–O1 93.09(11), O2–Cu1–O1 93.46(11), O3–Cu1–O1 163.16(11), O1–Cu1–O1 84.60(10), O2–P1–O3 111.65(14), O2–P1–O1 111.72(15), O3–P1–O1 110.89(16), O2–P1–C1 108.19(18), O3–P1–C1 108.08(18), O1–P1–C1 106.04(15).

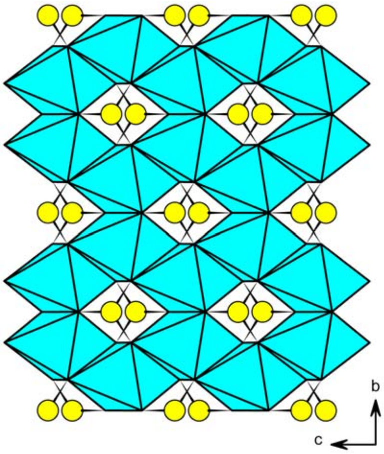

Fig. 7. Structure of $Cu(HOOCC_6H_4PO_3)$ layer viewed down the *a* axis showing CuO_6 octahedra and phosphorus atoms (open circles). Organic part is omitted.

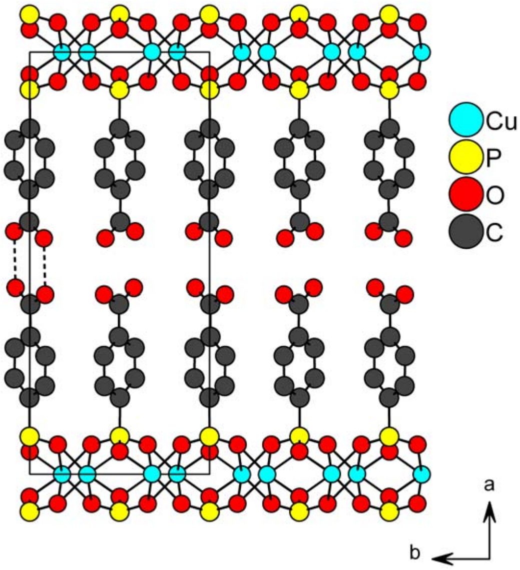

Fig. 8. Structure of $Cu(HOOCC_6H_4PO_3)$ viewed along the *c* axis. Dashed lines indicate the H bonds.

knowledge, this compound is the first example of a copper compound having this gibbsite–like structure.

The layers consisting of copper, phosphorus and phosphonate oxygen atoms are stacked perpendicular to the *a* axis with an interlayer distance of 19.067 Å (Fig. 8). The phenyl groups extend from the CPO_3 groups into the interlayer space above and below the copper–phosphonate layer. The plane of the benzene rings is tilted at an angle of about 85° to the plane of the layer. The benzene rings are arranged in an ordered fashion. One row of benzene rings, running in the *b* direction, has the planes of these rings parallel and oriented in the direction of the *bc* diagonal. The second row has the benzene-ring planes perpendicular to those in the first row. These two rows regularly alternate in the *c* direction.

Two organic carboxyphenyl groups lying above each other in one interlayer space have the same orientation of the benzene rings, which is given by an existence of hydrogen bonds between the oxygens of the carboxyl groups as indicated by dashed lines in Fig. 8. The existence of these H bonds is supported by the fact that the distance between the O4 and O5 atoms of these carboxyl groups is 2.7 Å.

The structure of $Cu(HOOCC_6H_4PO_3)$ differs from that described for $CuC_6H_5PO_3 \cdot H_2O$ [15] in the coordination environment of copper. In $CuC_6H_5PO_3 \cdot H_2O$, the Cu atom is five coordinate in a tetragonal pyramidal geometry. Thus, it has the sixth coordination site available, which can be complemented by an electron-donor guest molecule in an intercalation reaction. This vacant coordination site is not present in $Cu(HOOCC_6H_4PO_3)$, therefore an attempt to intercalate basic guests (for instance *n*-butylamine) into this compound was unsuccessful.

4. Conclusions

Three new copper 4-carboxyphenylphosphonates were prepared. Two of them, namely $Cu(HOOCC_6H_4PO_3) \cdot 2H_2O$ and $Cu_3(OOCC_6H_4PO_3)_2 \cdot 3H_2O$, were prepared under otherwise similar conditions, only the pH value was increased to about 7. Compound with formula $Cu(HOOCC_6H_4PO_3)$ was prepared under hydrothermal conditions, at 160 °C. All these compounds have well pronounced (00*l*) reflections in their X-ray powder patterns, which indicate their layered or pillared layered structure.

The position of the acid hydrogen atom in $Cu(HOOCC_6H_4PO_3) \cdot 2H_2O$ and $Cu(HOOCC_6H_4PO_3)$ was determined from the infrared spectra. The bands connected with the presence of variously hydrogenated PO_3 and CO_2 groups have been compared with the spectra of the analogous strontium 4-carboxyphenylphosphonates. It follows from the comparison of the spectra, that the acid hydrogen is present at the carboxyl group and not at the phosphonate group. Similarly, the existence of protonated carboxy groups was observed in polyfunctional phosphonocarboxylates as in the case of calcium 2-phosphonobutane-1,2,4-tricarboxylate [36]. On the other hand, the phosphonic group is protonated in copper compounds containing phosphonoacetic and hydroxyphosphonoacetic acids with formulae $Cu(HO_3PCH_2CO_2) \cdot H_2O$ and $Cu(R,S\text{–}HO_3PCH(OH)CO_2)(H_2O)_2] \cdot H_2O$ [18]. The structure of $Cu(HOOCC_6H_4PO_3)$ was determined by single-crystal X-ray diffraction. The copper atoms in this compound are six coordinated by oxygen atoms of the phosphonate groups. These CuO_6 octahedra are arranged around two phosphonate groups in a hexagonal motif, thus forming a layer composed of Cu, P and O atoms. The carboxyphenyl groups extend into the interlayer space above and below these layers. The arrangement of the benzene rings is similar to that found for $CuC_6H_5PO_3 \cdot H_2O$ but the structure of the layers is different.

Acknowledgments

We would like to acknowledge the Czech Science Foundation (Project no. GA 203/08/0208), the Academy of Sciences of the Czech Republic (AV0Z40500505) and the Ministry of Education, Youth and Sports of the Czech Republic (MSM 0021627501) for support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.09.001.

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