

# Supramolecular arrangement of 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid and its complex with calcium



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## HIGHLIGHTS

- 3,5-Bis[methylene(dihydroxyphosphoryl)]benzoic acid and its supramolecular network (**1a**) and calcium complex (**1b**) are reported.
- **1a** and **1b** crystals are acetone solvate and methanol disolvate, respectively.
- The solvate acetone or methanol molecules are disordered.
- **1a** and **1b** exhibit layered arrangement with different interaction between the layers.

## ARTICLE INFO

### Article history:

Received 8 March 2013

Received in revised form 22 May 2013

Accepted 22 May 2013

Available online 30 May 2013

### Keywords:

Phosphonic acid  
Supramolecular assembly  
Metal–organic framework  
Coordinating polymer  
Calcium  
Hydrogen bonds

## ABSTRACT

3,5-Bis[methylene(dihydroxyphosphoryl)]benzoic acid and its complex with calcium in the crystalline form were obtained. The 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid crystallises as acetone monosolvate (**1a**) while its calcium complex as methanol disolvate (**1b**). The solvent molecules in the crystals are disordered. The 3,5-bis[methylene(dihydroxy-phosphoryl)]benzoic acid molecules in crystal **1a** are interconnected via O–H...O hydrogen bonds forming two-dimensional layers parallel to (100) plane. Within the layers there are present holes that occupied disordered acetone molecules. In **1b** the calcium cation is surrounded by six singly deprotonated 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid forming distorted octahedral environment. Each singly deprotonated 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid links three calcium cations forming two-dimensional coordinating polymers parallel to (010) plane. The O–H...O hydrogen bonds between the singly deprotonated 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid ligands stabilize the two-dimensional polymers. Statistically disordered methanol molecules are located in the holes between the two-dimensional coordinating polymers and interact with them via O–H...O hydrogen bonds.

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## 1. Introduction

Phosphonic acids have received much attention in the field of supramolecular assemblies [1,2] and also in a synthesis of metal–organic frameworks (MOFs) [3,4] or more generally – coordination polymers [5]. The biggest group of coordination polymers, which was obtained in last several years is based on polytopic carboxylic acids [6,7] but phosphonic acids are also often examined to obtain new structures [8]. The interest in metal phosphonates and MOFs is determined by a large number of potential applications, like ion exchange [9,10], catalysis [11], luminescence [12], corrosion inhibition [13], gas storage [14] and separation [15] and drugs carriers [16].

Crucial differences between carboxylates and phosphonates are connected with the functional groups of them. Tetrahedral

phosphonic group offers richer coordination chemistry than a planar carboxylic group. Coordination modes possible for single phosphonic group is from 1.100 to 7.322 [3,17]. Preferred mode is also depend on protonation state of the phosphonic group because while deprotonated oxygen atom is good donor of coordinate bond, then hydroxyl group take part in hydrogen bond formation preferably.

Most of already synthesized metal phosphonates form layered-pillared networks [18,19]. It is not desirable property, especially in case of MOFs design, which from definition require 3-dimensionally propagated strong, directed interaction [5]. One of the possible opportunity to break this tendency is insertion of additional electron donor group to the structure, like carboxylic, hydroxyl or amine groups [20]. In the case of aromatic-based phosphonic acid, insertion of methylene bridge between aromatic ring and phosphonic group make the ligand conformation more flexible which is able to adjust its conformation during formation of coordination frameworks [21].

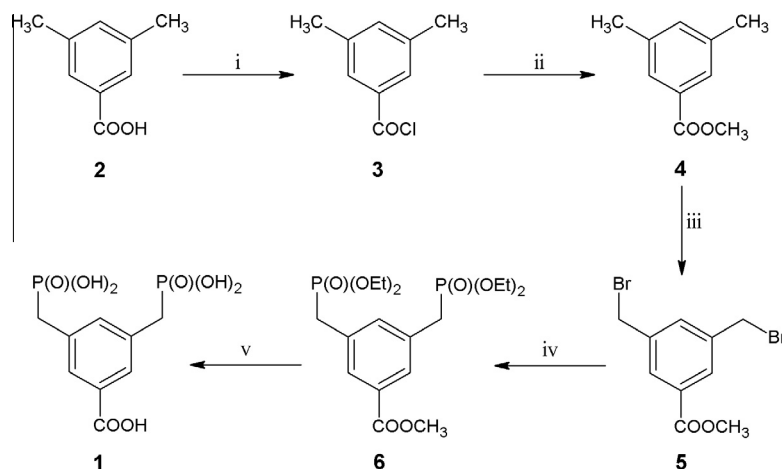
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**Table 1**  
Crystallographic data for **1a** and **1b**.

|  | <b>1a</b>   | <b>1b</b>   |
|--|---|---|
| Empirical formula  | C <sub>9</sub> H <sub>12</sub> O <sub>8</sub> P <sub>2</sub> ·C <sub>3</sub> H <sub>6</sub> O | C <sub>18</sub> H <sub>22</sub> CaO <sub>16</sub> P <sub>4</sub> ·2(CH <sub>3</sub> OH) |
| Formula weight (g mol <sup>-1</sup> )                                    | 368.20  | 722.40  |
| Crystal system, space group  | Triclinic, P-1 (No. 2)  | Triclinic, P-1 (No. 2)  |
| <i>a</i> (Å)   | 7.9610(16)  | 8.6630(10)  |
| <i>b</i> (Å)   | 10.680(2)   | 10.069(2)   |
| <i>c</i> (Å)   | 11.340(2)   | 10.389(2)   |
| α (°)  | 67.73(2)  | 66.830(10)  |
| β (°)  | 88.21(1)  | 69.770(10)  |
| γ (°)  | 68.75(1)  | 69.308(6)   |
| <i>V</i> (Å <sup>3</sup> )   | 825.3(3)  | 756.5(2)  |
| <i>Z</i>   | 2   | 1   |
| <i>D</i> <sub>calc</sub> / <i>D</i> <sub>obs</sub> (g cm <sup>-3</sup> ) | 1.482/1.48  | 1.586/1.58  |
| μ (mm <sup>-1</sup> )  | 0.306   | 0.498   |
| <i>F</i> (000)   | 324   | 374   |
| Crystal size (mm)  | 0.19 × 0.15 × 0.12  | 0.35 × 0.28 × 0.24  |
| Radiation type, wavelength, λ (Å)  | Mo Kα, 0.71073  | Mo Kα, 0.71073  |
| Temperature (K)  | 295(2)  | 295(2)  |
| θ range (°)  | 3.11–26.35  | 2.97–28.00  |
| Absorption correction  | Numerical, CrysAlis Red   | Numerical, CrysAlis Red   |
| <i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>                        | 0.9467/0.9681   | 0.8512/0.8922   |
| Reflections collected/unique/observed                                    | 8189/4032/2100  | 8221/3621/2974  |
| <i>R</i> <sub>int</sub>  | 0.0520  | 0.0142  |
| Refinement on  | <i>F</i> <sup>2</sup>   | <i>F</i> <sup>2</sup>   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]          | 0.0594  | 0.0286  |
| <i>wR</i> ( <i>F</i> <sup>2</sup> all reflections)                       | 0.1282  | 0.0629  |
| Goodness-of-fit, <i>S</i>  | 1.001   | 1.020   |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )               | +0.349, -0.355  | +0.242, -0.213  |

$wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum wF_o^4} \right\}^{1/2}$ ;  $w^{-1} = (\sigma^2(F_o^2) + (aP)^2 + bP)$  where  $a = 0.0469$  and  $b = 0.4022$  for **1a** and  $a = 0.0280$  and  $b = 0.2463$  for **1b**, and  $P = (F_o^2 + F_c^2)/3$ .



**Scheme 1.** Synthesis route of compound **1**. Reagents: (i) SOCl<sub>2</sub>; (ii) MeOH; (iii) NBS, CCl<sub>4</sub>, (PhCOO)<sub>2</sub>; (iv) P(OEt)<sub>3</sub>; and (v) HCl, H<sub>2</sub>O.

In this paper we report synthesis of multifunctional phosphonic acid 3,5-bis[methylene-(dihydroxyphosphoryl)]benzoic acid (**1**) and structural studies of its supramolecular structure (**1a**) and also its coordination polymer with calcium (**1b**). According to CSD database (17.12.2012) there are only two structures of calcium phosphonates containing benzylophosphonate ligand [22].

## 2. Experimental part

### 2.1. Materials and methods

Thionyl chloride was purified by distillation (79–80 °C boiling fraction was collected). Carbon tetrachloride was dried with the P<sub>2</sub>O<sub>5</sub> under the reflux conditions, then distilled (77–78 °C). Other materials and solvents were used as received. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P

NMR spectra were recorded on a Bruker Avance DRX300 instrument operating at 300.13 MHz, 121.50 MHz and 75.46 MHz respectively. For samples dissolved in CDCl<sub>3</sub> the reference signal was CHCl<sub>3</sub>; whereas for measurements in DMSO-d<sub>6</sub> it was the DMSO. Melting points of the compounds were determined using a Boëtius PHMK 05 apparatus.

### 2.2. Synthesis

#### 2.2.1. (i) 3,5-Dimethylbenzoyl chloride (**3**)

3,5-Dimethylbenzoic acid (**2**, 5.00 g, 0.033 mol) and thionyl chloride (4.0 ml, 0.059 mol) were placed in 50 ml round-bottom flask. The flask was heated under the reflux conditions for 70 min. Then the excess of the thionyl chloride was evaporated in vacuo and obtained crude product was used in the next reaction.

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