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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.

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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 $O-H\cdots O$ 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 (100) plane. The $O-H\cdots O$ 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 $O-H\cdots O$ 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 metalorganic 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

* Corresponding author. E-mail address: j.janczak@int.pan.wroc.pl (J. Janczak). 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 layeredpillared 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				
Crysta	llograph	ic da	ta for	1a	and

1b.

	1a	1b
Empirical formula	$C_9H_{12}O_8P_2 \cdot C_3H_6O$	$C_{18}H_{22}CaO_{16}P_{4} \cdot 2(CH_{3}OH)$
Formula weight (g mol ⁻¹)	368.20	722.40
Crystal system, space group	Triclinic, P-1 (No. 2)	Triclinic, P-1 (No. 2)
a (Å)	7.9610(16)	8.6630(10)
b (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)
$V(Å^3)$	825.3(3)	756.5(2)
Z	2	1
$D_{\rm calc}/D_{\rm obs}~({\rm g~cm^{-3}})$	1.482/1.48	1.586/1.58
$\mu (\mathrm{mm}^{-1})$	0.306	0.498
F(000)	324	374
Crystal size (mm)	$0.19 \times 0.15 \times 0.12$	$0.35\times0.28\times0.24$
Radiation type, wavelength, λ (Å)	Μο Κα, 0.71073	Μο Κα, 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
T_{\min}/T_{\max}	0.9467/0.9681	0.8512/0.8922
Reflections collected/unique/observed	8189/4032/2100	8221/3621/2974
R _{int}	0.0520	0.0142
Refinement on	F^2	F^2
$R[F^2 \ge 2\sigma(F^2)]$	0.0594	0.0286
wR(F ² all reflections)	0.1282	0.0629
Goodness-of-fit, S	1.001	1.020
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e Å ⁻³)	+0.349, -0.355	+0.242, -0.213

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



Scheme 1. Synthesis route of compound 1. Reagents: (i) SOCl₂; (ii) MeOH; (iii) NBS, CCl₄, (PhCOO)₂; (iv) P(OEt)₃; and (v) HCl, H₂O.

In this paper we report synthesis of multifunctional phosponic 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 phoshponates containing benzylphosphonate 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_2O_5 under the reflux conditions, then distilled (77–78 °C). Other materials and solvents were used as received. The ¹H, ¹³C and ³¹P

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 $CDCl_3$ the reference signal was $CHCl_3$; whereas for measurements in DMSO-d₆ 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.

2.2.2. (ii) Methyl-3,5-dimethylbenzoate (4)

To the crude acid chloride (**3**), methanol (25.0 ml) was added, and heated under the reflux conditions for 2 h. The excess methanol was evaporated in vacuo. The ester (**4**) was crystallized from hexane yielding 2.98 g (55%), mp. = 26-29 °C.

2.2.3. (iii) Methyl-3,5-bis(bromometylene)benzoate (5)

The ester (**4**, 2.76 g, 0.0168 mol), *N*-bromosuccinimide (6.07 g, 0.0341 mol) and benzoyl peroxide (85 mg, 0.35 mmol) were placed in 100 ml round-bottom flask. Then dried carbon tetrachloride (25 ml) was added and heated under the reflux conditions for 3 h. After cooling to room temperature, the mixture was filtered and the solvent was evaporated in vacuo to obtain the crude product as residue (5.39 g). The crude product was crystallized from hexane to yield the dibromide (**5**): 1.37 g (25%), mp. 94–98 °C.

¹H NMR (300 MHz, CDCl₃) *δ*: 8.00 (s, 2H, arom. H); 7.61 (s, 1H, arom. H); 4.50 (s, 4H, CH₂Br); 3.93 ppm (s, 3H, COOCH₃).

2.2.4. (iv) Methyl-3,5-bis[(diethoxyphosphoryl)methyl]benzoate (6)

The compound **5** (1.35 g, 4.19 mmol) and triethyl phosphite (1.9 ml, 0.011 mol) were placed in 20 ml round-bottom flask of micro-distillation set and heated at 140 °C for 2 h. The reaction mixture was chromatographed on silica gel column using ethyl acetate as an eluent and the pure product **6** was obtained: 1.27 g (70%), Rf = 0.06 (AcOEt, UV lamp for visualisation) mp. 71–74 °C.

¹H NMR (300 MHz, CDCl₃) δ : 7.86 (s, 2H, arom. H); 7.48 (s, 1H, arom. H); 4.03 (q, 8H, ³*J*_{HH} 7.2 Hz, O–CH₂–CH₃); 3.91 (s, 3H, O–CH₃); 3.19 (d, 4H, ²*J*_{PH} 21.9 Hz, CH₂P); 1.26 ppm (t, 12H, ³*J*_{HH} 7.2 Hz, O–CH₂–CH₃). ³¹P{¹H} NMR (121.5 MHz, CDCl₃) δ : 24.33 (s).

2.2.5. (v) 3,5-Bis[(dihydroxyphosphoryl)methyl]benzoic acid (1)

The compound **6** (1.24 g, 2.84 mmol), deionized water (5.0 ml) and 36% hydrochloric acid (5.0 ml) were placed in 50 ml roundbottom flask and heated at 130 °C for 20 h. After cooling, the solvent was evaporated in vacuo to dryness; obtained white solid was dissolved in 5 ml of deionized water, which was evaporated in vacuo again. 3,5-Bis[(dihydroxyphosphoryl)methyl]benzoic acid (**1**) was obtained as white powder (0.854 g, 97%), mp. 245–250 °C.

¹H NMR (300 MHz, d₆-DMSO) δ : 7.71 (s, 2H, arom. H); 7.33 (s, 1H, arom. H); 2.98 (d, 4H, ²*J*_{PH} 21 Hz, CH₂P); 2.49 (s, 4H, POH). ³¹P{¹H} NMR (121.5 MHz, d₆-DMSO): δ 21.32 (s). ¹³C{¹H} NMR (75.46 MHz, d₆-DMSO): δ 167.88 (s, COOH); 136.08–135.92(m), 134.93–134.79 (m), 130.88, 128.94 (aromatic); 35.51 (d, CH₂—P, ¹*J*_{PC} = 132 Hz).

2.2.6. Crystallization of $C_9H_{12}O_8P_2 \cdot C_3H_6O$ (1a)

3,5-Bis[(dihydroxyphosphoryl)methyl]benzoic acid (1, 30 mg, 0.097 mmol) was placed in 10 ml glass vial and dissolved in 0.3 ml of deionized water. Then 6 ml of acetone was added, the vial was closed and placed in a refrigerator for 3 days. Next the glass vial was left in room temperature and after 1 day colourless single crystals of **1a** have been isolated.

2.2.7. Crystallization of $C_{18}H_{22}O_{16}P_4Ca \cdot 2CH_3OH$ (1b)

3,5-Bis[(dihydroxyphosphoryl)methyl]benzoic acid (1, 30 mg, 0.097 mmol) was placed in 10 ml glass vial and dissolved in 2.0 ml of deionized water and 5.0 ml of 0.020 mol/dm³ solution of CaCl₂ and 6 drops of methanol were added. The partially open vial was left in room temperature. Colourless, longitudinal single crystals suitable to X-ray measurements were obtained by slow evaporation of the solvent, almost to dryness, at room temperature (about 1 month).

2.3. X-ray single crystal measurements and crystal structure analysis

Single crystal X-ray diffraction measurements of **1a** and **1b** were carried out at 295 K on a four-circle KUMA KM4 diffractometer equipped with two-dimensional CCD area detector. Graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) and ω -scan technique ($\Delta \omega = 1^{\circ}$) were used for data collection. Data collection and reduction along with absorption correction were performed using *CrysAlis* software package [23]. The structures were solved by direct methods using *SHELXS-97* [24], which revealed the positions of almost all non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The



Fig. 1. Asymmetric unit of **1a** showing the disordered acetone molecule, the occupation factors of O11 and C11 as well as of O12 and C12 are equal to 0.5.

Table 2Selected geometrical parameters (Å, °) of 1a and 1b.

	1b
$Ca-O4^{i}$	2.2944(11)
Ca—O4	2.2944(11)
Ca—O2 ⁱⁱ	2.3150(10)
Ca—O2 ⁱⁱⁱ	2.3150(10)
Ca—07 ^{iv}	2.3960(10)
Ca—07 ^v	2.3960(10)
P1-O1 1.449(2)	1.5117(11)
P1-O2 1.547(2)	1.5070(10)
P1-O3 1.550(2)	1.5693(11)
P2-04 1.495(2)	1.4911(11)
P2-O5 1.549(2)	1.5454(11)
P2-06 1.555(2)	1.5540(11)
P1-C7 1.778(3)	1.8009(15)
P2-C8 1.782(3)	1.7954(14)
C9–O7 1.214(4)	1.2142(17)
C9–O8 1.319(4)	1.3138(18)
04 ⁱ —Ca—O2 ⁱⁱ	89.91(4)
04–Ca–O2 ^{<i>ii</i>}	90.09(4)
04^{i} —Ca— $07^{i\nu}$	85.68(4)
$04-Ca-07^{iv}$	94.32(4)
02^{ii} —Ca— 07^{iv}	83.85(4)
02^{iii} —Ca— 07^{iv}	96.15(4)
02–P1–O1 112.57(13)	115.07(6)
02–P1–O3 105.60(13)	106.52(6)
01–P1–O3 113.60(14)	110.76(6)
O4—P2—O5 112.20(14)	115.07(6)
04–P2–06 113.63(13)	113.44(6)
05–P2–O6 105.11(14)	101.46(6)
C3–C8–P2 111.9(2)	111.60(9)
C1–C7–P1 111.8(2)	112.58(9)
07–C9–08 123.4(3)	122.32(13)
C6–C1–C7–P1 –97.35(30)	93.49(16)
C4–C3–C8–P2 87.27(31)	82.82(14)
C4–C5–C9–O7 –163.49(31)	-175.52(15)

Symmetry codes: (i) -x + 1, -y, -z; (ii) -x, -y + 1, -z + 1; (iii) x + 1, y, z - 1; (iv) -x, -y + 1, -z; (v) x + 1, y, z.



Fig. 2. Single layer of **1a** showing the voids of disordered acetone molecules viewed along *a*-axis (a) and arrangement of layers viewed along *c*-axis (b). In (b) the acetone molecules are omitted for clarify. Dashed lines represent the $O-H \cdots O$ hydrogen bonds.

structure was refined using *SHELXL-97* [24] with the anisotropic thermal displacement parameters. Visualisation of the structures was made with the Diamond 3.0 program [25]. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1.

into powder form. Then they were measured on a X'PERT PANalytical diffractometer [26] using Cu K α_1 radiation (λ = 1.54060 Å) at room temperature.

3. Results and discussion

2.4. X-ray powder diffraction measurements

The **1a** and **1b** crystals at room temperature after several days loss the solvated acetone or methanol molecules and transform

3,5-Bis[methylene(dihydroxyphosphoryl)]benzoic acid (1) was synthesized from 3,5-dimethylenebenzoic acid (2) in 5-steps procedure shown on Scheme 1 and described in details the Experimental part. Thus, the starting compound – 3,5-dimethylbenzoic

Geometry of hydrogen-bonds (Å, °) of **1a**.

D—H···A	D—H (Å)	H⊷∙A (Å)	D· · ·A (Å)	D—H···A (°)
02−H2O····O1 ⁱ	0.91(4)	1.68(4)	2.586(3)	171(4)
03—H30…07 ⁱⁱ	0.78(4)	1.89(4)	2.637(3)	160(4)
05–H50···01 ⁱ	0.83(4)	1.79(4)	2.607(3)	171(4)
06—H60…04 ⁱⁱⁱ	0.72(4)	1.95(4)	2.668(3)	175(5)
08—H80…04 ^{iv}	0.86(4)	1.79(4)	2.654(3)	176(4)

Symmetry codes: (i) -x + 1, -y, -z; (ii) x, y - 1, z; (iii) -x + 1, -y + 1, -z - 1; (iv) -x + 1, -y + 1, -z.



Fig. 3. Asymmetric unit of 1b showing statistically disordered methanol molecule.

acid (2) was transformed into methyl ester (4) through acid chloride intermediate (3). Methyl groups were brominated by *N*-bromosuccimide (NBS) in presence of benzoyl peroxide in carbon tetrachloride (CCl₄) under reflux conditions. The dibromide (5) was used as a substrate in the Michaelis–Arbuzov reaction [27,28] with triethyl phosphite at 140 °C giving the phosphonate (6) that after acidic hydrolysis was transformed into title compound.

Single crystals of acid **(1a)** and its calcium complex **(1b)**, suitable for X-ray measurements, were obtained by recrystallization in water/acetone (\sim 1:20, V/V) and in water/methanol (\sim 1:20, V/V) solutions, respectively. Both compounds, i.e. acid and Ca-complex,

crystallize in centrosymmetric space group of the triclinic system as a monosolvate of acetone and disolvate of methanol, respectively.

The asymmetric unit of **1a** contains one molecule of the acid and one molecule of acetone, which takes two orientations, statistically (Fig. 1).

Lengths of all C—O and P—O bonds (Table 2) are typical for protonated carboxylic and phosphonate groups, respectively [3,29]. Both phosphonic groups lie on the same side of aromatic ring. The plane, determined by carboxylic group is twisted in relation to plane of aromatic ring by a torsion angle of 15.9(3)°.

The hydrogen bonds O2—H2O···O1 and O5—H5O···O1, formed between phosphonic groups, as also O8—H8O···O4 and O3—H3O···O7 derived from phosphonic and carboxylic groups, create zig-zag type polymeric chains along crystallographic *b*-axis (see Fig. 2a). These chains are interconnected by the O6—H6O···O4 and its symmetrically equivalents hydrogen bonds propagated along *c*-axis (geometrical parameters of all H-bonds of **1a** are contained in Table 3). Described hydrogen bonds scaffolding form 2-dimensional supramolecular layers that interact between each other by stacking of aromatic rings (distance between them, derived from different layers, is 3.46(2) Å) (Fig. 2b). In structure of **1a** formation of 1-dimensional channels is observed (along *a*-direction, see Fig. 2a), which are filled by disordered acetone molecules.

Single crystals of the complex (**1b**) was obtained by dissolution of **1** and CaCl₂ in water with addition of methanol (~5% (V/V)). It crystallized in P-1 space group as a methanol disolvate. Asymmetric unit contains one molecule of the acid, half of Ca²⁺ cation that occupies special position and one disordered molecule of methanol, which takes two positions, statistically (see Fig. 3). Conformation of the acid molecule is very similar to this in structure of **1a**, but there are some differences in lengths of several bonds. Length of P1–O2 bond was decreased because of deprotonation, while P1–O1 and P1–O3 were slightly increased. Bonds lengths P–O in the second phosphonic group are without changes, but slight elongation of C7–P1 and C8–P2 is observed (see Table 2).

Coordination sphere of calcium cation exhibits a distorted octahedral and centrosymmetric environment consisting of six O atoms (Fig. 4) with three different Ca—O bond lengths. The longest Ca—O bond links the carbonyl oxygen atom of COOH group (Ca—O7 = 2.396(1)Å), whereas the shorter Ca—O bonds link the oxygen atoms (Ca—O4 = 2.294(1)Å, Ca—O2 = 2.315(1)Å) from dissociated and non-dissociated phosphonic groups. Consequently each ligand of the singly deprotonated acid bridges three calcium cations (coordination mode is 3.111 according to mentioned



Fig. 4. Coordination sphere of calcium cation.

Table 3



Fig. 5. Single layer of 1b, viewed along *b*-axis (a) and arrangement of the layers viewed along *a*-axis (b). In (a) the solvated and disordered methanol molecules are omitted for clarity. Dashed lines represent the O–H···O hydrogen bonds.

notation [17]) forming two-dimensional layers that are parallel to (010) plane (Fig. 5a). Three different O–H···O hydrogen bonds stabilise these layers. The O–H···O hydrogen bonds formed between the dissociated phosphonic groups of two anions related by an inversion (O3···O1 = 2.579 Å and O5···O1 = 2.535 Å) are propa-

gated in the [-101] direction (Fig. 5a). In turn, the next hydrogen bond completes six-membered rings Ca-O7-C9-O8-H8···O2^{*ii*} (Table 4.) These interactions, i.e. Ca-O and O-H···O, determine layered structure of the polymer. The solvated methanol molecules are located in the voids between the layers. Refinement of the

Geometry of hydrogen-bonds (Å, °) of 1b.

D—H···A	D—H (Å)	H· · ·A (Å)	$D{\cdots}A~({\rm \AA})$	D–H···A (°)
03–H3…01 ⁱ	0.79(2)	1.80(2)	2.5787(15)	175(2)
05—H5…01' 06—H61…09	0.85(2) 0.82(1)	1.70(2) 1.65(1)	2.5354(15)	166(2) 165(2)
08—H8…02 ⁱⁱ	0.78(3)	1.84(3)	2.6192(15)	177(3)
09—H91…03 ⁱⁱⁱ	0.82	2.05	2.831(4)	159
09—H91…08 ^{iv}	0.82	2.54	2.961(3)	113
010—H10· · · 04	0.84(2)	2.08(2)	2.913(4)	172(7)

Symmetry codes: (i) -x, -y + 1, -z + 1; (ii) x, y, z - 1; (iii) -x + 1, -y, -z + 1; (iv) -x + 1, -y, -z.

crystal structure established two possible positions for location of methanol molecule that are not structurally equivalent. In the first positions the molecule forms three H-bonds: one with a distance of 2.453(3) Å (D···A) and two bifurcated hydrogen bonds with distances of 2.831(4) and 2.960(3) Å (D···A). In the second position, the hydroxyl group of methanol act as a donor only into one O–H···O hydrogen bond (O10–H10···O4 = 2.914(3) Å). Methanol molecules from the first positions interconnect the layers and stabilise the structure (see Fig. 5b).

Crystals of 1a and 1b have limited stability on air in room temperature and undergo decomposition after several days. Powder diffraction diagrams (Figs. S1 and S2) showed that both samples saved crystallinity. In the case of 1a decomposition of single crystals lead to powder form those diagram contains less number of peaks than theoretical one, generated with Diamond 3.0 program (Fig. S1 and Table S1). It allow to conclude that this process, connected with the loss of solvated acetone molecules (experimental weight loss \sim 16%, and calculated 15.8%) lead to the higher symmetry structure. Although, unequivocal indexing of peaks on the diagram was unsuccessful and any concluding about the structure would not be reliable. In the case of **1b** the weight loss of \sim 9.0% (calculated of 8.9%) is connected with the loss of solvated methanol molecules. In addition, after loss of solvated methanol molecules, the triclinic system is maintained (Fig. S2 and Table S2) with the lattice parameters of unit cell a = 8.827(7) Å c, b = 9.41(2) Å, c = 10.24(2) Å, $\alpha = 72.41(7)^{\circ}$, $\beta = 68.9(1)^{\circ}$, $\gamma = 59.60(7)^{\circ}$ and volume 677(1) Å³. Decrease of unit cell volume (\sim 79 Å³), relative to the value determined for single crystal (756 Å³) correlate well with the loss of solvated methanol molecules. As can be seen from Fig. 5b, the crystals of **1b** consist of 2-dimensional polymeric layers that are interconnected by solvated methanol molecules. Releasing of solvated molecules from **1b** leads to decreasing of *b* parameter (~1.28 Å) caused by reduction of the distance between 2-dimensional polymeric layers of the complex (see Fig. 5b).

4. Conclusions

Synthesis of 3,5-bis[methylene(dihydroxyphosphoryl)]benzoic acid (1) and its supramolecular network (1a) and calcium complex (1b) were reported. Structure 1a occur as monosolvate of acetone and structure 1b as methanol disolvate, and both of them manifest layered arrangement with different interaction between the layers. In the case of 1a this is stacking interactions between aromatic rings; in 1b disordered methanol molecules play role of the bridge between the layers, which are connected *via* hydrogen bonds. Moreover, structure **1a** contains 1-dimensional channels filled with acetone molecules interacted with walls of the channels by van der Waals forces. Coordination sphere of calcium cations is fully saturated by ligand molecules. Conformation of the ligand has small differences in some geometrical parameters, but general conformation is very similar in both cases. Both crystals (**1a** and **1b**) have limited stability at room temperature.

Appendix A. Supplementary material

Details on data collection and refinement, fractional atomic coordinates, anisotropic displacement parameters and full list of bond lengths and angles in CIF format has been deposited at the Cambridge Crystallographic Data Centre, No. CCDC 927207 and 927208 for **1a** and **1b**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.05.045.

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