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New multifunctional phosphonic acid for metal phosphonate synthesis

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HIGHLIGHTS

- A new multifunctional phosphonic acid, 3-amino-5-(dihydroxyphosphoryl)benzoic acid, has been synthesized and characterized.
- It crystallizes in *P*–1 space group and forms a three dimensional supramolecular structure using seven hydrogen bonds.
- Molecular structure makes it potentially interesting for synthesis of open framework metal phosphonates.

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ABSTRACT

A new heterotopic phosphonic acid, 3-amino-5-(dihydroxyphosphoryl)benzoic acid (**1**) has been synthesized and obtained in the crystalline form. Second multifunctional phosphonic acid – namely 3-(dihydroxyphosphoryl)-5-nitrobenzoic acid (**2**) has also been obtained, following a different synthetic route than previously reported. Compound **1** crystallizes in a centrosymmetric space group of the triclinic system as monohydrate, $-C_6H_3(NH_2)(COOH)PO_3H_2{\cdot}H_2O$ – **1a**. The molecule in the crystal exists in a zwitterionic form, in which one of the proton of the phosphonic group is transferred to the amine group. The zwitterionic molecules interact to each other and with water molecules via N—H···O and O—H···O hydrogen bonds forming a three-dimensional network.

1. Introduction

Metal organic frameworks (MOFs) have received much attention from many research groups around the world in the last ten years [1,2]. This fact is not surprising as MOF materials form a new class of hybrid compounds – often porous – that posses numerous potential industrial and social applications. Gas storage [3] and separation [4], catalysis [5], drug delivery [6] and non-linear optics [7] are just some of them. The most promising feature of MOF materials is the potential ability to fine-tune the size and shape of its pores as well as their functionality.

The most popular O-donor organic species used in metal–organic framework synthesis are carboxylic acids. There are several known carboxylic ligands and some of them like 1,4-benzenedicarboxylic acids are already considered substrates for industrial-scale MOF synthesis [8]. Along with them, there is another important group of O-donor, which are phosphonic acids [9]. These compounds, although not so popular in MOF synthesis as carboxylic acids and having some drawbacks, still pose an interesting research field. First phosphonate based hybrid materials were synthesized by Alberti et al. [10].

Most of already used phosphonic acids formed layered-pillared networks when reacting with metal ion species. It is a matter of concern for researchers to obtain metal phosphonate porous materials, that do not have the layer-pillared architecture. Layer-pillared metal phosphonates are already well studied by Clearfield and co-workers [11,12]. Although materials of such topology can posses some porosity they also have some disadvantages. As porosity is mostly achieved by using a phosphate or small monophosphonate as a co-ligand – so called spacers – pores tend to have wide size distribution owning to the random distribution of spacers. On the other hand non-layered metal-phosphonates tend to form open frameworks. Synthesis of MP's that not posses such topology can be achieved by using two different approaches [2]. The first one is to use organic ligands that are not linear. Change of angle between binding phosphonate groups interacting with metal moieties can usually let one to acquire metal organic phosphonate framework of non-layered topology. One example of such ligand is methylenediphosphonic acid [13]. The second approach concerns using ligands with additional functional groups that have the ability to chelate metal ions thus braking the tendency to form layered structure. Such groups are: carboxylic [14], hydroxyl, and

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amine. One can also use a pyridine moiety with its nitrogen atom acting as a binding group.

In this paper we report the syntheses of two multifunctional phopsphonic acids potentially interesting in hybrid materials science: 3-amino-5-(dihydroxyphosphoryl)benzoic acid – **1** and 3-(dihydroxyphosphoryl)-5-nitrobenzoic acid – **2,** as well as crystal structure of the former compound. The synthesis of the latter compound has been conducted in a different way to previously described [15].

2. Experimental

2.1. Materials and methods

All starting materials and solvents were used as received. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRX300 instrument operating at 300.13 MHz (^{1}H), 121.50 (^{31}P) and 75.46 (^{13}C). Chemical shifts are in ppm. IR spectra were measured on a Perkin–Elmer 1600 spectrometer as KBr discs. Elemental analysis was performed on a Elementar vario EL III apparatus.

2.2. Synthesis

Methyl 3-bromo-5-nitrobenzoate (**4**). **4** was synthesized using previously reported procedure [16]. Yield: 2.22 g (31%), mp. = 71–74 °C (lit. 70–71 °C. [16])

Methyl 3-(diisopropyloxyphosphoryl)-5-nitrobenzoate **(5).** To a 50 ml round-bottomed flask containing **4** (2.18 g, 8.36 mmol), acetonitrile (15 ml), diisopropyl phosphite (1.67 g, 10.03 mmol), diisopropylethylamine (1.41 g, 1087 mmol), palladium acetate (0.019 g; 0.084 mmol) and dppf (0.051 g, 0092 mmol) were added. The flask was put under reflux condenser and was flushed with argon (15 min.). Then it was put in an oil bath heated to 85 °C and kept there for 20 h under argon. After that the mixture was cooled to room temperature and the solvent was evaporated *in vacuo*. The residue was separated between water (10 ml) and ethyl acetate (10 ml). Water phase was extracted with ethyl acetate (10 ml), and the mixed organic phases were washed with brine (10 ml) and dried over anhydrous magnesium sulfate. Afterwards drying agent was filtered off and ethyl acetate was evaporated in vacuum to give 2.62 g of crude product. Column chromatography on silica gel using ethyl acetate as eluent gave pure **5** (0.826 g, 28%). ^{1}H NMR ($CDCl_3$) δ: 9.00 (s, 2H, arom. H), 8.78 (t, J = 10.9 Hz, 2H, arom. H), 4.78 (m, 2H, CH), 4.01 (s, 3H, CH_3), 1.42 (d, J = 6.1, 6H, CH_3), 1.27 (d, J = 6.2, 6H, CH_3); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 11.85.

3-(dihydroxyphosphoryl)-5-nitrobenzoic acid (**2**)**.** A 25 ml round-bottomed flask was charged with methyl 3-(diisopropyloxyphosphoryl)-5-nitrobenzoate (0.773 g, 2.24 mmol). Concentrated hydrochloric acid (3 ml) and water (3 ml) were added and the mixture was heated in reflux for 12 h. After cooling it was diluted with water (5 ml), and charcoal was added. Mixture was heated to reflux and charcoal was filtered off. Filtrate was evaporated to dryness and the residue was dissolved in small amount of water and again water was evaporated. This action were repeated with ethanol. Finally 0.469 g (85%) of **2** were obtained (mp. 217–220 °C). ^{1}H NMR (d_6-DMSO) δ: 8.66 (s, 1H, arom. H), 8.53 (m, 2H, arom. H); ^{13}C NMR (d_6-DMSO) δ: 165.53, 148.24, 138.08, 136.97, 133.14, 128.88, 126.18 $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 8.40; IR (KBr) 3383, 3106, 3081, 2880, 2671, 1698, 1542, 1352, 1193, 1028 cm^{-1}; MS: m/z = 245.9837, calc for $C_7H_5NO_7P$ $[M-H]^-$ = 245.9809;

Methyl 3-amino-5-bromobenzoate (6). A 50 ml round bottomed flask was charged with a solution of **4** (0.626 g, 2.4 mmol) in ethyl acetate (10 ml). Then tin (II) chloride (2.27 g, 12 mmol) and water (0.432 g, 24 mmol) were added and the reaction mixture was refluxed for 30 min. After cooling to room temperature ethyl acetate (10 ml) and water (10 ml) were added. pH was adjusted to nine using 3 M sodium hydroxide solution. Next additional ethyl acetate (10 ml) and water (10 ml) were added and phase were separated. Organic phase was washed with brine (10 ml) and dried over anhydrous magnesium sulfate. Drying agent was filtered and solvent was evaporated to afford **6** (0.323 g, 59%) mp. 93–96 °C. ^{1}H NMR ($CDCl_3$) δ: 7.97 (s, 1H arom. H); 7.52 (s, 1H, arom. H); 7.02 (s, 1H, arom. H); 3.88 (s. 3H, CH_3);

Methyl 3-amino-5-(diethoxyphosphoryl)benzoate **(7).** A 50 ml round bottomed flask was charged with **6** (1.00 g, 4.34 mmol), acetonitryl (10 ml), diethyl phosphite (0.718 g, 5.20 mmol) and ethyldiisopropylamine (0.729 g, 5.64 mmol). The flask was flushed with argon for 15 min. and palladium acetate (0.009 g, 0.0434 mmol) and dppf (0.026 g, 0.047 mmol) were added. Reaction mixture was heated to 90 °C and this temperature was maintained for 20 h. After that the mixture was cooled to room temperature and solvent was evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate as eluent to afford **7** (1.77 g, 94%). ^{1}H NMR ($CDCl_3$) δ: 7.82 (d, J = 15.0 Hz, 1H, arom. H); 7.57 (s, 1H, arom. H); 7.42 (d, J = 15.0 Hz, 1H, arom. H); 4.13 (m, 4H, CH_2); 3.90 (s, 3H, CH_3); 1.32 (m, 6H, CH_3); ^{31}P NMR ($CDCl_3$) δ: 17.92;

3-amino-5-(dihydroxyphosphoryl)benzoic acid **(1). 6** (0.868 g, 2.75 mmol) was placed in a 25 ml round-bottomed flask, concentrated hydrochloric acid (6 ml) and water (6 ml) were added. The mixture was refluxed for 10 h and then cooled to room temperature. Solvent was evaporated in vacuum, residue was dissolved in small amount of water. Evaporation and dissolution was repeated. Finally product was filtered off and dried to give 0.475 g (80%) of **1** (mp. >360 °C).^{1}H NMR (d_6-DMSO) δ: 7.42 (d, J = 13.2 Hz, 1H, arom. H), 7.26 (s, 1H, arom. H), 7.13 (d, J = 13.6 Hz, 1H, arom. H); ^{13}C NMR (d_6-DMSO) δ: 167.87, 148.74, 135.19, 131.17, 120.44, 119.50, 117.229; $^{31}P\{^{1}H\}$ NMR (d_6-DMSO) δ: 13.70; $C_7H_8NO_5P{*}H_2O$ (235,13) calc. C 35.76; H 4.29; N 5.96; found C 35.71; H 4.19; N 5.88; IR (KBr) 3222, 3041, 2800, 2578, 1884, 1686, 1531, 1297, 1127 cm^{-1}; MS: m/z = 218.0214, calc for $C_7H_9NO_5P$ $[M+H]^+$ = 218.0213;

2.3. Single crystal X-ray data collection and structure determination

A colorless single crystal of **1a** was used for data collection on a four-circle KUMA KM4 diffractometer equipped with a two-dimensional CCD area detector. The graphite monochromatized Mo Kα radiation and the ω-scan technique ($\Delta\omega$ = 1°) were used for data collection. The data collection and reduction along with absorption correction were performed using *CrysAlis* software package [17]. The structure was solved by direct methods using *SHELXS-97* [18] that revealed positions of almost all non-hydrogen atoms. The remaining atoms were located from subsequent difference Fourier syntheses. The structure was refined using *SHELXL-97* [18] with the anisotropic thermal displacement parameters. The hydrogen atoms joined to the aromatic ring were refined with the riding model, the H atoms involved in the hydrogen bonds were refined. Visualization of the structure was made with the Diamond 3.0 program [19]. Refinement detail and crystallographic data for **1a** are listed in Table 1.

3. Results and discussion

3-amino-5-(dihydroxyphosphoryl)benzoic acid (**1**) was synthesized from methyl 3-nitrobenzoate (**3**) in a four-step procedure as shown in Scheme 1. Firstly the compound **3** was brominated using bromine in concentrated sulfuric acid in 90 °C over a period of 2 h. The resulting bromonitrocompound (**4**) was reduced with tin (II) chloride in ethyl acetate in the presence of water. Following was

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

Empirical formula	$C_7H_8NO_5P{\cdot}H_2O$
Formula weight (g mol^{-1})	235.13
Crystal system, space group	Triclinic, $P\bar{1}$ (No. 2)
a (Å)	6.7086(13)
b (Å)	8.4972(17)
c (Å)	8.7745(18)
α (°)	107.83(2)
β (°)	92.73(1)
γ (°)	95.18(1)
V (Å^3)	472.72(16)
Z	2
D_{calc}/D_{obs} (g cm^{-3})	1.652 / 1.65
μ (mm^{-1})	0.301
$F(000)$	244
Crystal size (mm)	0.27 × 0.21 × 0.15
Radiation type, wavelength, λ (Å)	Mo Kα, 0.71073
Temperature (K)	295(2)
θ range (°)	2.92–29.41
Absorption correction	Numerical, CrysAlis Red
T_{min}/T_{max}	0.9272/0.9581
Reflections collected/unique/observed	6551/2384/1496
R_{int}	0.0404
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0478
$wR(F^2$ all reflections)	0.1265
Goodness-of-fit, S	1.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.563, −0.325

$wR = \{\Sigma\ [w(F_o^2 - F_c^2)^2]/\Sigma wF_{o^4}^{1/2}$; $w^{-1} = (\sigma^2(F_o^2) + (0.068P)^2)$ where $P = (F_o^2 + 2F_c^2)/3$.

catalytic phosphonylation of **4** using palladium catalyst. Phosphonate ester was purified with column chromathography. The last step was acidic hydrolysis of the ester which yielded compound **1**. Synthesis of 3-(dihydroxyphosphoryl)-5-nitrobenzoic acid (**2**) was achieved in three steps. The first step was the same as in the synthesis of **1**. In the next step bromide was phosphonylated using palladium catalyst. Phosponate (**5**) was then hydrolyzed using hydrochloric acid to afford **2**.

Single crystals suitable for X-ray measurements were obtained by recrystalization of **1** from water. Despite numerous trails using different solvents recrystalization of **2** was not achieved. Compound **1** crystallizes in the centrosymmetric space group of the triclinic system as monohydrate (**1a**). The asymmetric unit of **1a** consists of one molecule of 3-amino-5-(dihydroxyphosphoryl)-benzoic acid and one molecule of water (Fig. 1a).

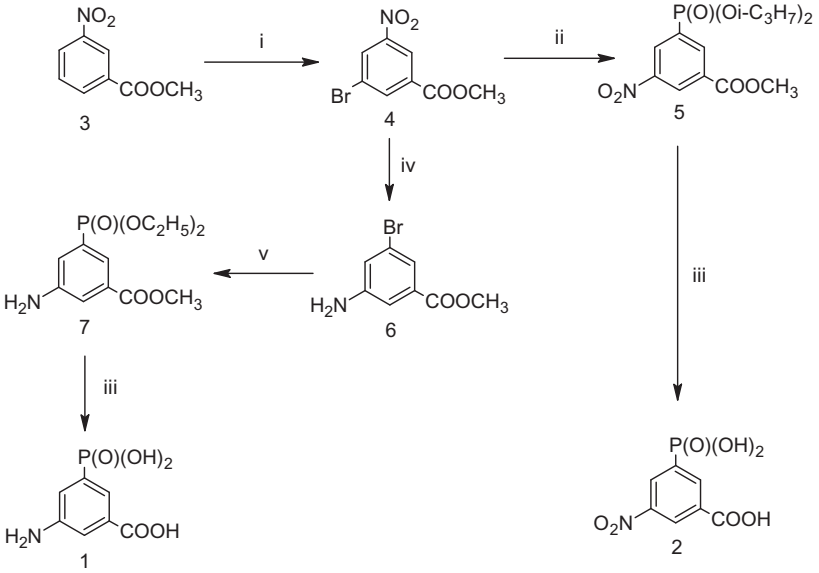
Molecule of **1** exists in the crystal in a zwitterionic form in which the proton from the phosphonic group as a stronger acidic group than carboxyl is transferred to the amino group forming the NH_3^+. Due to deprotonation of the dihydroxyphosphoryl group two of three P—O bonds are almost equal and shorter than the third P—O bond (Table 2).

The C—O bond lengths of the carboxyl group are typical for the non-dissociated group (C=O, 1.219(3) and C—OH, 1.308(3)). The conformation of the molecule of **1** can be defined by the orientation of the carboxyl, phosphoryl and ammonium groups in relation to the planar aromatic ring. The carboxyl group of **1** is almost coplanar with the aromatic ring (3.3(2)°), while the orientation of the PO_3H^- can be given by a torsion – angle of C6—C1—P1—O2 (−28.0(2)). One of the hydrogen atom of the NH_3^+ group is almost coplanar with the ring (the torsion angle of C4—C5—N1—H13 is equal to 4(2)°), which is not an uncommon feature in structures containing a protonated aromatic amine.

The zwitterionic molecules of **1** in the crystal of **1a** interact via relatively short O—H···O hydrogen bonds (O5···O2 = 2.559(3) Å, Table 3) between the carboxyl group of one molecule and the oxygen atom (O2) the of phosphonate group of the other forming one dimensional chains along the [001] direction (Fig. 1b).

The chains are interconnected by the water molecules that serve as a donor and as an acceptor of the hydrogen bonds, and by the N—H···O hydrogen bonds between the ammonium group and one oxygen atom (O2) of the phosphonate group forming a double chain (Fig. 1b). The zwitterionic 3-amino-5-(dihydroxyphosphoryl)-benzoic acid molecules within the chain related by an inversion center interact by a pair of N—H···O hydrogen bonds forming centrosymmetric dimers with a graph of $R_2^2(14)$. Repetitive translational occurrence of such dimers forms a three-dimensional hydrogen bonding supramolecular network (Fig. 1c).

All H atoms of the ammonium group (—NH_3^+) and H atom of carboxyl (COOH) and phosphonate (PO_3H^-) groups are involved as donors in hydrogen bonds. Thus each zwitterionic molecule of **1** in the crystal of **1a** forms as the donor five hydrogen bonds, three N—H···O and two O—H···O. In addition each zwitterionic molecule is an acceptor of three hydrogen bonds. The water molecules interconnect the one-dimensional chains via three O—H···O hydrogen bonds, in two of them the water molecules act as the donor and



Scheme 1. Synthesis of **1** and **2**. Reagents: (i) Br_2, Ag_2SO_4, conc. H_2SO_4; (ii) H(O)P(Oi—Pr)$_2$, Pr_2NEt, Pd(OAc)$_2$, dppf; (iii) conc. HCl, H_2O; (iv) $SnCl_2$, H_2O, AcOEt; (v) H(O)P(OEt)$_2$, Pr_2NEt, Pd(OAc)$_2$, dppf.

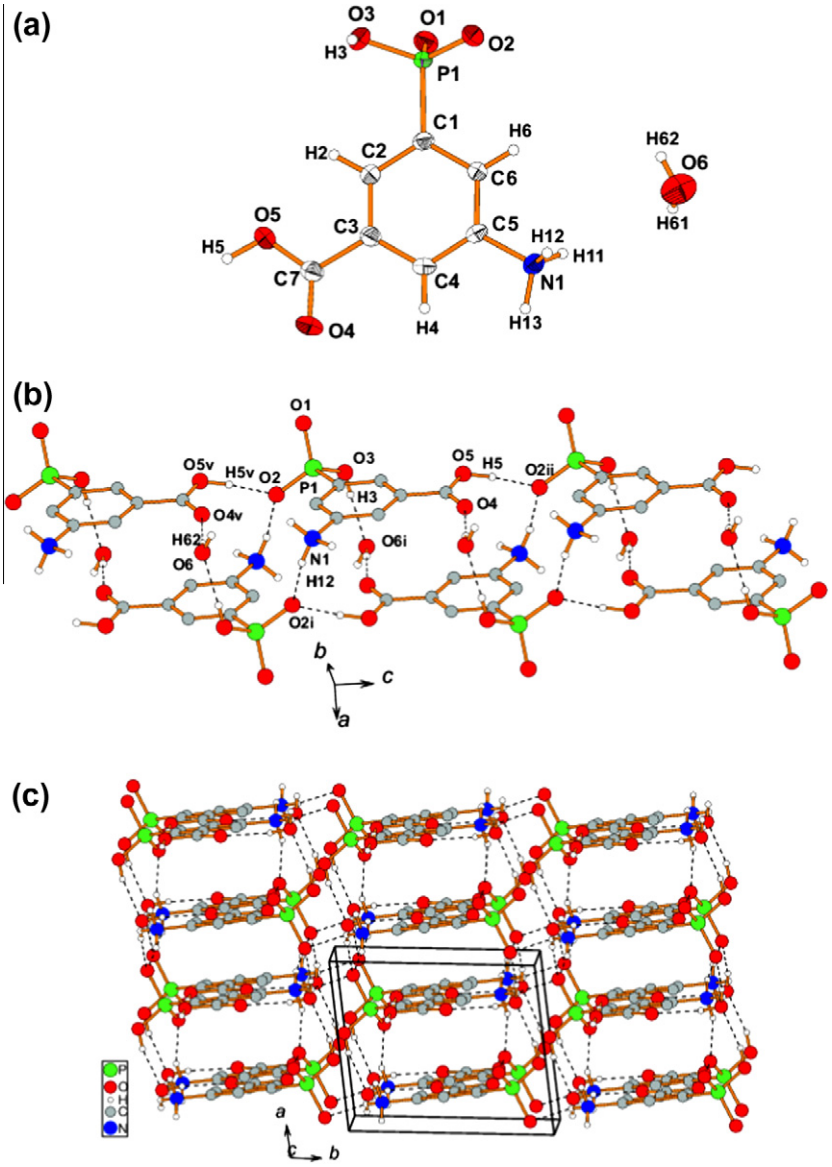


Fig. 1. (a) View of the molecular structure of **1a**. Displacement ellipsoids are shown at the 50% probability level; (b) view of the O—H···O hydrogen bonded chains of zwitterionic 3-amino-5-(dihydroxyphosphoryl)-benzoic acid molecules. H atoms joined to the ring are omitted for clarity. (Symmetry codes as in Table 3); (c) molecular packing of **1** showing the layered structure. H atoms joined to the ring are omitted for clarity. Dashed lines represent the O—H···O and N—H···O hydrogen bonds.

Table 2
Selected geometrical parameters (Å, °).

P1—O1	1.5029(19)	P1—O2	1.5006(18)
P1—O3	1.559(2)	C1—P1	1.802(3)
C3—C7	1.496(3)	C5—N1	1.467(3)
C7—O4	1.219(3)	C7—O5	1.308(3)
O1—P1—O2	114.71(11)	O1—P1—O3	106.17(11)
O2—P1—O3	111.57(11)	O4—C7—O5	123.5(2)
C2—C3—C7—O5	3.3(3)	C6—C1—P1—O1	97.7(2)
C6—C1—P1—O2	−28.0(2)	C6—C1—P1—O3	−147.8(2)

Table 3
Geometry of the hydrogen bonds (Å, °).

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
O3—H3···O6^{i}	0.79(3)	1.83(3)	2.599(3)	165(3)
O5—H5···O2^{ii}	0.95(3)	1.62(3)	2.559(3)	167(3)
N1—H11···O1^{iii}	0.91(3)	1.88(3)	2.761(3)	163(3)
N1—H12···O2^{i}	0.92(3)	1.85(3)	2.761(3)	159(3)
N1—H13···O1^{iv}	1.01(3)	1.89(3)	2.727(3)	154(2)
O6—H61···O1^{iii}	0.81(3)	2.03(3)	2.810(3)	160(4)
O6—H62···O4^{v}	0.82(3)	1.97(3)	2.786(3)	173(4)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, *y*, *z*+1; (iii) −*x*, −*y*+1, −*z*+1; (iv) *z*, *y*−1, *z*; (v) *x*, *y*, *z*−1.

in one as the acceptor. Thus the water molecule interacts with three neighboring molecules of **1**

Hydrogen bonds observed in the structure of **1** result in the organization of molecules in the layered structure. One can notice that the layers stacked along the *a* axis are shifted against each other along the *c* axis. Moreover molecules of the adjacent layers are 'facing' in the opposite direction. This is due to formation of hydrogen bonds between phosphonic and amino groups. Two 'types' of layers can be therefore distinguished, designated A and B, formed in a ABABAB... mode along the *a* axis. Formation of zig–zag sheets stretching in the direction of *a* axis and connected with adjacent sheets along *b* and *c* axes is also visible.

4. Conclusion

One new multifunctional aromatic phosphonic acid has been synthesized and characterized. Additionally another multifunctional phosphonic acid has been obtained following a different reaction pathway than previously reported. In the crystal the zwitterionic molecules of **1** interact via hydrogen bonds and with water molecules forming a 3D supramolecular network. Both acids are potentially interesting in metal-phosphonate chemistry. This is due to their distinctive features. Firstly, both compound posses two different binding groups – phosphonate and carboxylate. Moreover the position of binding groups may lead to formation of non-layered products when **1** is reacted with metal ions, even thought structure of **1a** is layered. Conducted search of CDS database (version 5.33, November 2011) revealed nine non-layered structures of metal carboxyphosphonates based on a ligand similar to the one presented in this paper [20–26]. One must notice thought that in case of six of those structures the ligand contained an additional binding group – a carboxylate – in the same position in which compound **1** bears an amino group. This amino group is prone to post-synthetic modification as well as can act as a catalytic site.

Supplementary materials

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 817610 for **1a**. 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).

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