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Assembly of benzene-1,3,5-tris(methylenephosphonic acid) and guanidinium salt: Single crystal-X-ray characterisation and ^{31}P solid state NMR investigations†

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The co-crystallisation of benzene-1,3,5-tris(methylenephosphonic acid) [$C_9H_{15}O_9P_3$] **1** with guanidinium chloride [CH_6N_3]Cl, yields compound **2** that possesses the following composition [CH_6N_3]$_3$ [$C_9H_{13}O_9P_3$] [$C_9H_{14}O_9P_3$]. The crystal structure of this supramolecular material, which possesses six crystallographically inequivalent phosphorus atoms, is reported. The packing of this 3D-supramolecular arrangement reveals the presence of 33 hydrogen bonds engaging the couples phosphonic acid-guanidinium and phosphonic acid-phosphonic acid. Solid-State MAS NMR of the sensitive ^{31}P nucleus in this supramolecular arrangement is used in order to develop alternative analytical method to get information on supra-molecular assemblies. ^{31}P through-space single quantum – double quantum correlation experiments have been performed leading to two possible assignments of the 6 crystallographic P sites to the corresponding resonances in the 1D ^{31}P MAS NMR spectrum.

Introduction

The design of new materials based on supramolecular assemblies has received considerable interest due to their potential application as NLO materials,[1] magnetic materials[2] or as sensors.[3] Supramolecular assemblies can be the result of weak links (hydrogen bonds, π–π interactions, electrostatic interactions…) between organic molecules only or on the contrary between organic and metallic substrates.[4] The knowledge of the supramolecular interactions is also essential to understand the kinetic or the mechanism of action of enzymes. In this field the interaction of guanidine function (arginine, creatine…) with molecules possessing a phosphate moiety (*e.g.*: ADP) plays a central role in the course of reactions catalysed by enzymes (*e.g.* Arginine Kinase,[5] creatine kinase[6]). Organogels or hydrogels chemistry is another dynamic field of research where macroscopic properties are coming from the supramolecular assembly of small molecules.[7,8] Noteworthy, much of the attention has been focused on the interaction *via* hydrogen bonds of functions possessing nitrogen (amine, amide, nitrile) and oxygenated functions[9] like ketone, carboxylic acid, nitro, amide or sulfonic acid.[10]

Phosphonates and phosphonic acids that are close to phosphate functions present in biological systems form attractive building blocks that may be useful to design materials based on hydrogen bonding. These substrates have been widely used to form coordination materials based on the interaction with a metal to produce metal-phosphonate hybrid bulk materials[11] or immobilised materials.[12] A second possibility to design materials formed by phosphonic acids as building blocks consists in engaging these substrates into a hydrogen bond network. This approach which is as yet less developed than the metal-phosphonate approach, may be achieved by the generation of hydrogen bonds between two phosphonic acid functions or between phosphonic acids and another partner. According to the first strategy, Clearfield *et al.* synthesised a macrocyclic leaflet[13] based on hydrogen bonding between phosphonic acid functions. The second strategy was employed by Schrader *et al.* to design spheroidal molecular assemblies based on the interaction of a symmetrical tris-(phosphonic acid monomethyl ester) and symmetrical tris-ammonium or tris-amidinium compounds.[14] According to molecular modelling the authors indicate that the assemblies are based on both hydrogen bonding and electrostatic interactions. Glidewell and Ferguson report several crystal structures obtained by crystallisation of a phosphonic acid with a diamine[15] or a di-phosphonic acid with di-amine[16] derivatives. In the first case they report 1D, 2D or 3D structures while according to the second approach 3D structure were obtained. In all these structures

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† Electronic supplementary information: tables of relevant intermolecular hydrogen bonding parameters, PO bond lengths and OPO angles in crystalline complex **2**. See http://www.rsc.org/suppdata/nj/b4/b406938b/

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one proton is transferred from the phosphonic acid to the amine. Finally Clearfield *et al.*[17] have recently reported the synthesis of three dimensional materials based on hydrogen bonds between a tris(phosphonic acid) and different amine or pyridine derivatives.

The structure elucidation of a supramolecular assembly at the solid state is usually resolved from single crystal X-ray diffraction data. Powder diffraction has been used with success in a few cases to describe supramolecular assembly.[18] Nevertheless for complex structures this approach is not suitable so far. In this case, high-resolution solid-state NMR can provide complementary structural information.[19,20] For example, 2D ^{31}P through-space or through-bond homonuclear correlation methods have been used to evidence the number of crystallographically inequivalent P sites in crystalline pyrophosphate allowing to discriminate between the possible space group symmetries.[21,22]

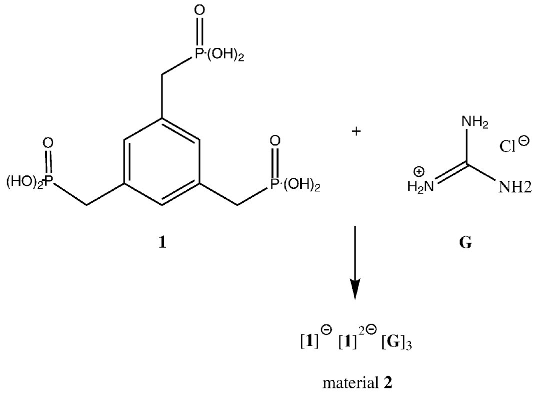
We report herein the X-ray structure of an original supramolecular assembly obtained by crystallisation of tris-phosphonic **1** with guanidinium chloride leading to material **2**. In order to develop alternative analytical techniques to get information about the structure of supramolecular assembly engaging phosphorus atom (phosphonic acid . . .), two-dimensional ^{31}P through-space single quantum – double quantum (SQ–DQ) MAS NMR correlation experiment has been performed. According to this experiment we report the attribution of the resonances of the 1D ^{31}P MAS NMR spectrum to their crystallographic locations.

Results and discussion

Synthesis and X-ray characterization

Compound **1** (benzene-1,3,5-tris(methylenephosphonic acid) [$C_9H_{15}O_9P_3$]) was synthesised by the hydrolysis of the ester functions of the corresponding tris-phosphonate[23] and its crystal structure was previously reported.[24] The co-crystallisation of compound **1** with guanidinium chloride [CH_6N_3]Cl (Scheme 1) by slow evaporation of water yields compound **2** (Scheme 1) as colourless crystals of different sizes (from small mono-crystal to a microcrystalline powder).

The elemental analysis of these crystals is in agreement with the following composition for compound **2**: [CH_6N_3]$_3$ [$C_9H_{13}O_9P_3$] [$C_9H_{14}O_9P_3$]. This result indicates that chlorine anions are excluded from the crystal in the course of the crystallisation. Therefore the positive charges hold by the guanidinium cations are balanced by the presence of phosphonic anions moieties. The DSC analysis of material **2** reveals an exothermic transition (fusion) starting at 260 °C and with a maximum at 288 °C. The structure of material **2** was obtained from X-ray diffraction on single crystal (Table 1). The asymmetric unit is composed as expected from elemental analysis, by three guanidinium cations and two molecules **1** (Fig. 1).



Scheme 1 Synthesis of material **2**.

Table 1 Crystal data and details of measurements for material **2**

	2
Formula	$C_{42}H_{90}O_{36}P_{12}N_{18}$
Molecular weight (g · mol^{-1})	897.48
T (K)	293(2)
Crystal size (mm)	0.7 × 0.5 × 0.2
System	Triclinic
Space group	$P\bar{1}$
a (Å)	8.0657(5)
b (Å)	9.7732(7)
c (Å)	23.7540(10)
α (°)	84.167(6)
β (°)	90.429(7)
γ (°)	82.825(7)
Cell volume (Å^3)	1847.81(19)
D_x (mg m^{-3})	1.613
θ range (°)	2 to 27
No of reflections used for cell refinement	25
Maximum indices: h, k, l	−10 to10, −12 to12, 0–30
μ (mm^{-1})	0.378
Measured reflections	8231
Unique reflections	8033
Unique reflections with $I > 2\sigma$(I)	7386
R_{int}[a]	0.0136
R (all data)[b]	0.0422
$wR2$ (on F^2, all data)[b]	0.1233 ($A = 0.0686$, $B = 1.8746$)
Goodness of fit on F^{2c}	1.098
Number of refined parameters	664
Max., Min. electron density/eÅ^{-3}	0.531, −0.438

[a] $R_{int} = \Sigma|F_0^2 - F_0^2\,(mean)| \,/\, \Sigma[F_0^2]$ $R = \Sigma||F_0| - |F_c|| \,/\, \Sigma[F_0]$ $wR2 = \{\Sigma[w(F_0^2 - F_C^2)^2] \,/\, \Sigma[w(F_0^2)^2]\}^{1/2}$, where [b] $w = 1 \,/\, [\sigma^2(F_0^2) + (AP)^2 + BP]$ $P = (F_0^2 + 2F_c^2) \,/\, 3$. [c] $S = \{\Sigma[w(F_0^2 - F_c^2)]/\,(no.\ reflection-total\ no.\ of\ parameters\ refined)\}^{1/2}$.

Molecule **1** has a different conformation in material **2** than it adopts when it crystallises alone.[24] Indeed, in material **2**, the phosphonic functions placed in the three benzylic positions are not located on the same side of the benzene ring (two phosphonic functions on one side and the third one (Phosphorus atom P2A for molecule A and phosphorus atom P2B for molecule B) on the other side). The positions of the hydrogen atoms, which were determined by Fourier difference maps, indicate that the phosphorus atoms P1A and P1B are bearing a negative charge on the oxygen atoms O11A and O11B (Fig. 2). According to X-ray diffraction the third negative charge, that

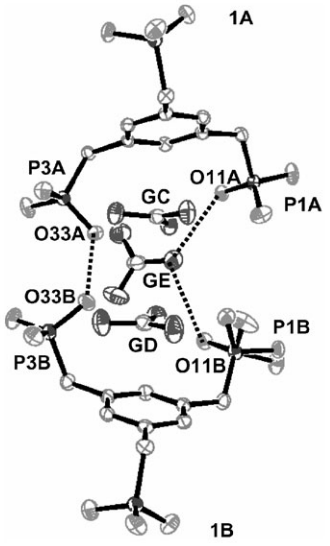


Fig. 1 Asymmetric unit of material **2**.

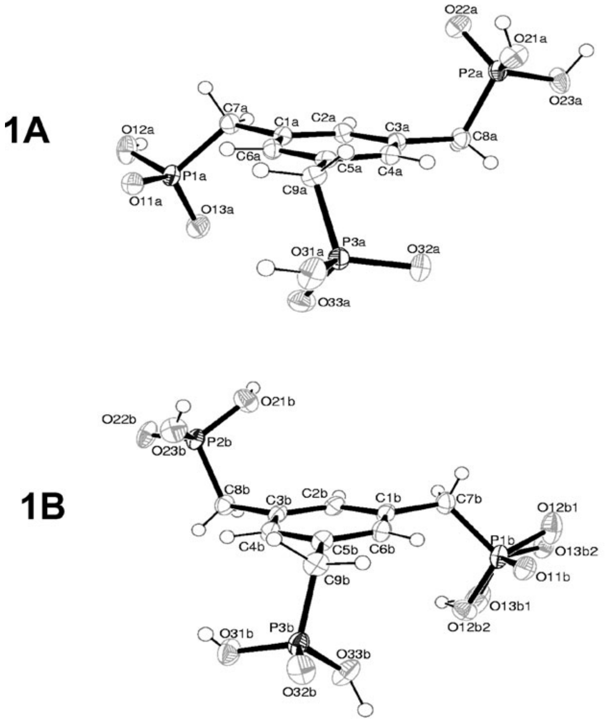


Fig. 2 Molecules 1A and 1B present in material **2**.

balance the three positive charges due to the guanidinium cations, is hold by the oxygen atom O33A which is bonded to the phosphorus P3A. The other phosphonic functions (P2A, P2B and P3B), are neutral. It should be mentioned that two crystallographic positions are suitable for the oxygen atoms O12B and O13B. Two guanidinium cations are placed parallel to the *ab* plane while the third guanidinium is parallel to the *ac* plane.

The study of the packing (Fig. 3) reveals a complex network of hydrogen bonds (33 hydrogen bonds, see supporting information-Table 3) that can be classified in two categories: (1) hydrogen bonds between the phosphonic acid functions acting as acceptor (A) and the guanidinium cations as donor (D); (2) hydrogen bonds between phosphonic acid functions. The guanidinium cations engaged 22 hydrogen bonds with the phosphonic acid for a total of 18 hydrogen atoms borne by the nitrogen of the guanidinium. This observation indicates that some hydrogen atoms are engaged in bifurcated hydrogen bonds. Indeed the hydrogen atoms H21C, H21D, H22D, H32D and H31E are in contact with two acceptors. Noteworthy the D...A length engaging the bifurcated hydrogen bonds correspond to the longest distances (2.976 to 3.477 Å) indicating the weakness of these bonds. Another characteristic of the hydrogen bonds between the oxygen atoms from the phosphonic acid functions and the nitrogen atoms of the guanidinium cations is their length. Indeed, the shortest distance D...A is 2.86 Å for an average distance of 3.024 Å. These values, which are certainly due to the weak acidity of the guanidinium ion (pK_a=13.5),[25] are consistent with the hydrogen bond lengths observed when a guanidinium cation and a phosphate are in contact.[26] Furthermore the positive charge is distributed on the three nitrogen atoms of the guanidinium ion leading to a weak electrostatic interaction between the guanidinium (D) and the negatively charged oxygen atoms of the phosphonic acid.

The second type of hydrogen bond is observed between phosphonic functions leading to ten O...H–O interactions across the structure. These bonds are stronger than the N–H...O hydrogen bonds according to the d(O...O) distances

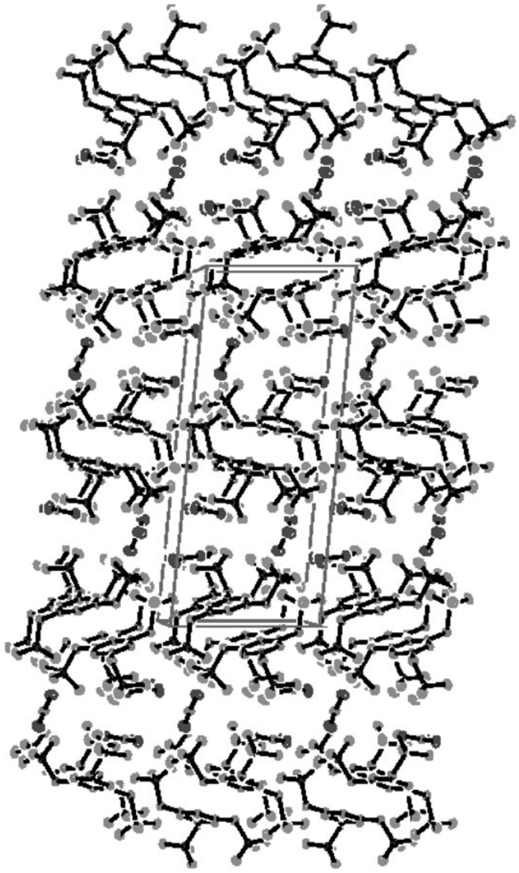


Fig. 3 Packing of material **2**.

(from 2.477 to 2.531 Å; average: 2.507 Å) and can be classified[27] as very strong (<2.50 Å) and strong hydrogen bonds (2.50–2.65 Å). This observation can be explained by the presence of homonuclear hydrogen bonds engaging two functions possessing similar electronic behaviours.[28] The P–O bond length (see supporting information-Table 4) is also in agreement with the position of the H atoms on the phosphonic acid. Indeed the P–O distances are around 2.50 Å for a double bond, around 2.55 Å for single bond when the oxygen is bearing a hydrogen (P–OH) and around 2.51 Å for a single bond when the oxygen is negatively charged ($P–O^-$). Nevertheless two P–O bonds that are connected *via* a hydrogen bond, have an intermediate length (P3B–O33B–H and P3A–O33A respectively 1.529 and 1.526 Å). This hydrogen bond, characterized by a short O...O distance (2.48 Å), corresponds to a very strong hydrogen bond ($d_{O...O}$ <2.50 Å) that can be explained by the existence of a negative charge assisted hydrogen bonding.[29] This type of strong interaction is usually observed when two partners, possessing a similar electronic repartition, are involved.

These hydrogen bonds yield a 3D structure (Fig. 3) formed by layers (parallel to the *ab* plane) of dimer of molecule **1**. These dimers are connected together through hydrogen bonds between different phosphonic acid groups and between phosphonic acid functions and the guanidinium cations GC and GD, placed parallel to the *ab* plane. The guanidinium cation GE and four O–H...O bonds link together these planes. In view of the packing, very small tunnels, delimited by the guanidinium cations, are formed along the *a* axis, but the size of these channels are not sufficient to expect some porosity in the material.

NMR

The ^{31}P MAS NMR spectra (proton decoupled) of a mixture of single crystals and microcrystals of material **2** are depicted in

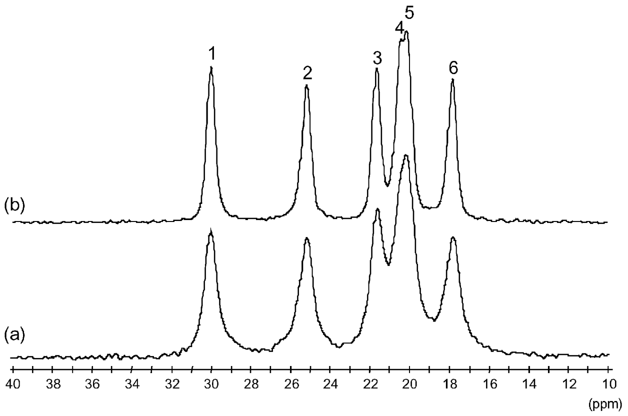


Fig. 4 ^{1}H decoupled ^{31}P MAS spectra of mixture of single crystals and microcrystal of compound **2**. The decoupling sequences were (a) continuous wave decoupling (CW) and (b) SPINAL-64 and the decoupling power was 100 kHz.

Fig. 4. Different schemes of broadband proton decoupling have been used in order to increase the resolution of the 1D ^{31} P MAS NMR spectrum (high power continuous wave irradiation CW, TPPM decoupling[30] and SPINAL-64 decoupling[31]). As illustrated in Fig. 4(b), the best spectral resolution was achieved using the new SPINAL-64 decoupling sequence. While 5 resonances with relative intensity in the ratio 1:1:1:2:1 and individual line widths of about 140 Hz (obtained by deconvolution[32]) are observed in the CW decoupled spectrum (Fig. 4(a)), the spectrum acquired with the SPINAL decoupling sequence exhibits 6 peaks with the same intensity and line widths of 80 Hz. In addition, ^{31}P proton mediated spin diffusion MAS experiment[33] (not shown) indicates that all these resonances belong to the same phase. Therefore, these six resolved peaks, located at 30.0, 25.2, 21.7, 20.5, 20.1 and 17.8 ppm respectively (labelled from 1 to 6 in Fig. 4(b)), are related to the 6 crystallographically inequivalent phosphorus sites characterized by X-ray diffraction on material **2**. Nevertheless, the attribution of these resonances to the crystallographic P sites is not obvious by considering only empirical trends between ^{31}P isotropic chemical shift values and structure in solids.

To provide additional constraints required for the spectral assignment, we have used ^{31}P double quantum homonuclear dipolar recoupling experiment under MAS conditions. In this experiment, the coherence transfer between coupled nuclei is driven by the ^{31}P–^{31}P through-space dipolar interactions giving rise to the observation of P–P nearest-neighbour spatial proximities in a two-dimensional (2D) single-quantum (SQ) double-quantum (DQ) correlation spectrum. This method has already been applied with success for resonance assignment in crystalline orthophosphates[34] and pyrophosphates.[35] Dealing with strong heteronuclear dipolar interactions in the sample, it is necessary to apply high power ^{1}H heteronuclear decoupling at the same time as double quantum homonuclear recoupling. Moreover, it has been shown that the ^{1}H decoupling rf-field strength should be three times the ^{31}P rf-field strength used for double quantum recoupling.[36] In this context, we have used the C14 double quantum recoupling[37] sequence which requires moderate ^{31}P rf-field strength ($\nu_{rf} = 3.5{*}\nu_R$) even at relatively high spinning frequency ($\nu_R = 10$ to 15 kHz) allowing efficient ^{1}H decoupling. Moreover, as our supramolecular assembly should be considered as a multispin system, we have used relatively short excitation and reconversion times, preventing from relaxation effects and/or relayed transfer processes.

The result of the double quantum ^{31}P dipolar coupling experiment is reported in Fig. 5. The spectrum is shown as a single-quantum – single-quantum (SQ–SQ) correlation spectrum obtained by a shearing transformation of the experimental SQ–DQ spectrum.[38] It allows to evidence two distinct autocorrelation peaks located on the diagonal of the 2D spectrum which reflect the through-space proximity between two crystallographically equivalent P sites. According to the internuclear P–P distances (Table 2), these two resonances could be attributed to the P2B and P2A sites which have the shortest P–P distances with other crystallographically equivalent sites. Therefore two hypotheses can be formulated.

The hypothesis 1 corresponds to the attribution of the resonances 1 and 2 (at 30.0 and 25.2 ppm) to the phosphorus atoms P2A and P2B, respectively. In the 2D spectrum, the

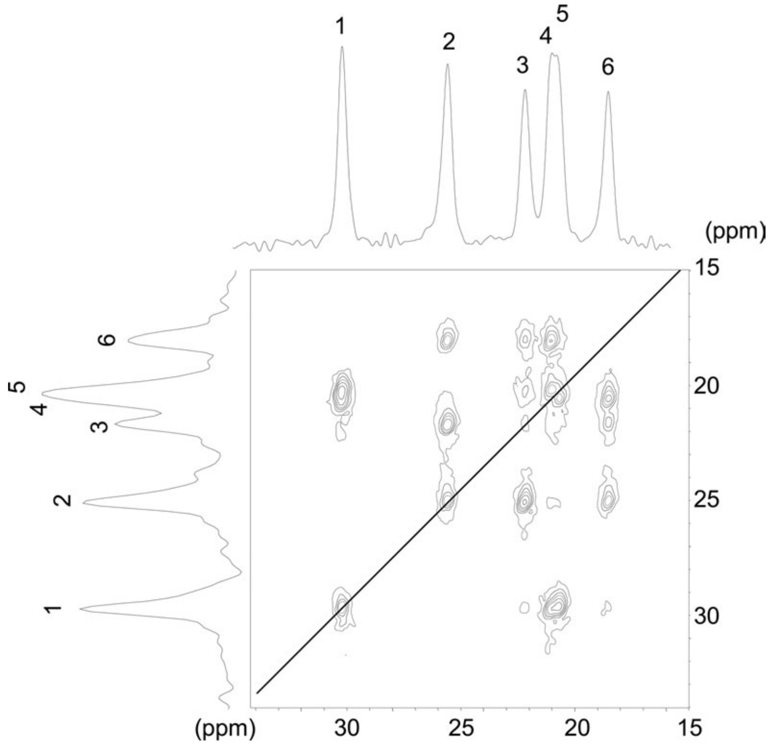


Fig. 5 ^{1}H decoupled ^{31}P 2D through space SQ–SQ spectrum of mixture of single crystals and microcrystal of compound **2**.

Table 2 Through-space distances (up to 8.6 Å) between the phosphorus atoms in materials **2**

	P1A	P2A	P3A	P1B	P2B	P3B
P1A	8.066	4.762 4.81 5.530 7.538	4.703 6.470 7.261 7.265	5.801	8.553	7.615 7.981 8.110
P2A	4.762 4.81 5.530 7.538	4.908 5.12 8.066	4.862 6.761 6.221 6.879			7.449
P3A	4.703 6.470 7.261 7.265	4.862 6.761 6.221 6.879	8.066	6.103 7.519		4.470
P1B	5.801		6.103 7.519	8.066	4.857 5.849 7.499	4.616 6.202 7.346 7.516
P2B	8.553			4.857 5.849 7.499	5.147 8.066	4.878 6.884 6.936
P3B	7.615 7.981 8.110	7.449	4.470	4.616 6.202 7.346 7.516	4.878 6.884 6.936	8.066

resonance 2 shows two main cross-correlation peaks with the resonances 3 and 6. In addition, the correlation peak between resonances 2 and 3 is of higher intensity. According to the structure, the nearest neighbouring P sites of the phosphorus atom P2B are two phosphorus atoms P1B and one phosphorus atom P3B. Therefore, the resonances 3 and 6 are assigned to the phosphorus sites P1B and P3B, respectively. This is also compatible with the observation of a cross-peak between the resonances 3 (P1B) and 6 (P3B) for which the internuclear P–P distance is 4.61 Å. Similarly, the resonance 1 (P2A) exhibits two partly overlapping cross-correlation peaks with resonances 4 and 5, the correlation between 1 and 5 being of highest intensity. According to the X-ray structure, this leads to the attribution of the resonances 4 and 5 to the crystallographic sites P3A and P1A, respectively. This is supported by the observed cross-correlation between resonances 4 (P3A) and 5 (P1A) for a P–P distance of 4.70 Å. The proposed assignment, for which the resonances 2, 3, 6 are attributed to the 3 inequivalent P sites of the molecule **1B** and the resonances 1, 4, 5 to the molecule **1A**, is also in agreement with the remaining intense correlation peak (4–6) and those of weaker intensities corresponding to longer range dipolar interactions (d(P–P) $>$ 6 Å).

The second hypothesis corresponds to the attribution of the resonances 1 and 2 to the crystallographic sites P2B and P2A, respectively. A similar analysis based on the observed cross-peak intensities leads to the assignment of the resonances 3, 4, 5, 6 to the sites P1A, P3B, P1B, and P3A. It should be noted that, in this case, the resonances 2, 3, 6 are attributed to the 3 inequivalent P sites of the molecule **1A** and the resonances 1, 4, 5 to the molecule **1B**. Nevertheless, the presence of a cross-correlation between the P1A and P3B sites, for which the internuclear distance is of 7.61 Å, makes this second possibility more unlikely.

Conclusion

The auto-assembly of triphosphonic acid **1** with guanidinium cation produces supramolecular materials **2** in which the cationic charged, borne by the guanidinium moieties, are balanced by the equivalent number of deprotonated phosphonic acid. Compound **2** is formed by hydrogen bonds between phosphonic acid and guanidinium cations but also by several hydrogen bonds between phosphonic acid functions. This observation illustrates the ability of the phosphonic acid to assemble to itself and to form very strong hydrogen bonds, leading to the formation of small channels running along the *a* axe. Further works, dealing with the use of more rigid triphosphonic acids to design porous supramolecular assemblies based on their interactions with guanidinium cation, are presently investigated. The characterisation of material **2** by using ^{31}P MAS NMR is also reported. The 1D ^{31}P MAS spectra with SPINAL-64 proton decoupling reveals the presence of 6 distinct ^{31}P resonances in agreement with the six inequivalent crystallographic P sites in compound **2** according to the X-ray structure. 2D ^{31}P through-space single quantum – quantum MAS NMR correlation experiment has been used to probe the through-space connectivities between the different ^{31}P sites. On the basis of a qualitative analysis of the correlation peak intensities, an attribution of the ^{31}P resonances to the distinct crystallographic phosphorus locations in the structure is proposed.

Experimental

General methods

^{1}H, ^{13}C and ^{31}P NMR spectra (liquid-state) were recorded on a Bruker AC 250 spectrometer. The ^{31}P solid-state magic angle spinning (MAS) NMR experiments (number of scan: 4; recycling delay: 60 s; pulse angle: 45°) were performed at RT (it must be noted that due to the Magic Angle Spinning, the temperature inside the rotor is estimated to be close to 30 C) with a spinning frequency of 10 kH, using a 2.5 mm MAS probehead on a Bruker Avance 400 spectrometer operating at a resonance frequency of $\nu_0 = 162$ MHz. The one-dimensional ^{31}P MAS spectra were acquired using a single pulse followed by a broadband ^{1}H decoupling during the acquisition (^{1}H νrf = 100 kHz). The two-dimensional ^{31}P through-space single quantum – double quantum (SQ–DQ) MAS NMR correlation – spectrum (contact time: 1 ms; number of scan: 16; recycling delay: 1s) was acquired using the C14 recoupling sequence[37] to achieve an efficient broadband excitation and reconversion of double quantum coherence (νrf = 35 kHz =3.5*νrot). Short excitation and reconversion periods of 980 μs were used. The excitation was preceded by a cross-polarization sequence to reduce the experiment time, and a ^{1}H SPINAL-64 decoupling[24] was applied during all the sequence. The ^{31}P chemical shifts were referenced relative to 85% H_3PO_4 aqueous solution.

Elemental analyse was recorded on a CE Instrument NA 2500.

Syntheses

Benzene-1,3,5-*tris*(*methylenephosphonic acid*) **1**. Benzene-1,3,5-tris(diethoxyphosphoryl-methyl)[23] (5.71 g; 10.8 mmol) and 37% aqueous HCl (150 ml) was heated at reflux for 24 h. The excess of HCl and water was removed *in vacuo* to afford compound **1** as a white powder (3.58 g, 92%). Single crystals were isolated by recrystallisation in methanol/water (7/1) with a slow diffusion of diethylether. m.p.(DSC, 40 °C/min) = 294 °C; ^{1}H($D_2O + K_2CO_3$): 2.90 (d, ^{2}J = 21.4 Hz, CH_2–P), 6.89 (m, ^{4}J = 1.67 Hz, C–H_{Ar}); ^{31}P($D_2O + K_2CO_3$): 24.3 (s); ^{13}C ($D_2O + K_2CO_3$): 34.72 (d, $^1J_{CP}$ = 129.9 Hz, CH_2), 129.36 (m, CH_{Ar}), 133.97 (m, C_{Ar}).

$[C_9H_{14}O_9P_3]^- \cdot [C_9H_{13}O_9P_3]^{2-} \cdot [C(NH_2)_3]^+{}_3$ **2**. A solution of benzene-1,3,5-tris(methylenephosphonic acid) **1** (300 mg; 0.833 mmol) in methanol/water (10 ml/5 ml) was added to a solution of guanidinium chloride (238 mg; 2.49 mmol) in water (10 ml). This solution was left at 18 °C for 24 h to produce a white powder (150 mg). The filtrate was left to evaporate further at 18 °C for 6 weeks, filtered and dried at room temperature to produce complex **2** (130 mg). Suitable crystals were found for a single crystal X-ray structure analysis (Found: C, 28.19; H, 5.26; N, 14.14. Calc. For $C_{21}H_{45}N_9O_{18}P_6$:C, 28.10; H, 5.05; N, 14.05%; m.p. (DSC, 40 °C/min.), 288 °C. ^{31}P MAS NMR (see Fig. 4).

Crystallography

Intensity data for compound **1** and complex **2** were collected on an Enraf-Nonius – CAD4 diffractometer with Mo K_α radiation (λ = 0.71073 Å) at room temperature. The crystal structures were solved by direct methods using SHELX97 package.[39] All non-hydrogen atoms were refined anisotropically. The positions of H atoms were determined *via* difference Fourier maps and refined with isotropic atomic displacement parameters, with exception of two hydrogen atoms of N_{1E} (H_{11E}, H_{12E}) and two hydrogen atoms of N_{3E} (H_{31E}, H_{32E}) of the guanidine cation GE which were calculated and fixed on the N-atoms in the ideal geometry. The temperature factors of fixed H-atoms were refined isotropically. One of the phosphonic groups (P_{1B}) of one molecule (**1B**) in structure of complex **2** is disordered, and the occupancy factors of disordered positions were refined. Crystal data and data collection parameters are summarised in Table 1. CCDC reference number 151632. See http://www.rsc.org/suppdata/nj/b4/b406938b/ for crystallographic data in .cif or other electronic format.

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