

Phosphonopropionic acid as a building block in supramolecular chemistry: salts with organic diamines

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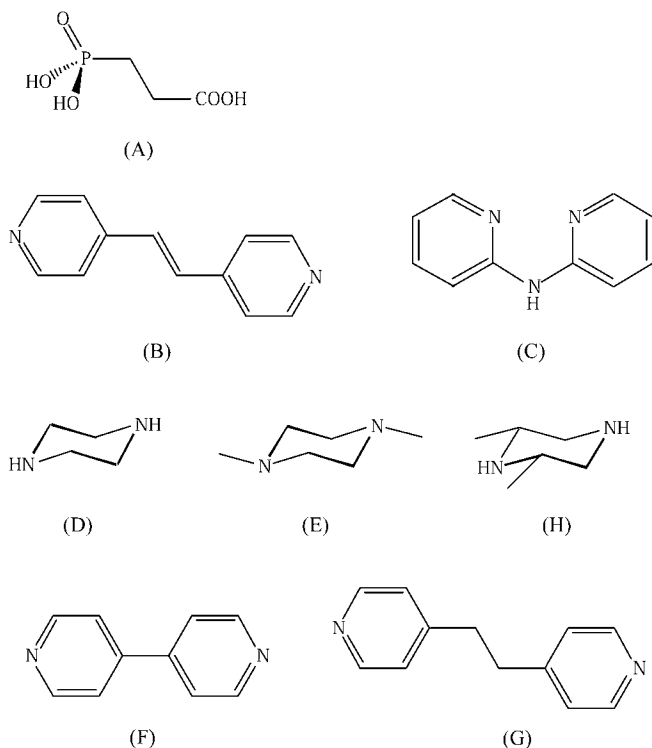
The structures of seven salts formed by phosphonopropionic acid with organic diamines are reported; in these salts, the hydrogen-bonded substructures formed by the anions can be zero-, one- or two-dimensional, while the overall hydrogen-bonded supramolecular structures are three-dimensional. The 1:1 adduct, compound (1), formed between 1,2-bis(4'-pyridyl)ethane and phosphonopropionic acid is a salt, $[\{(C_{12}H_{10}N_2)H_2\}^{2+}] \cdot [(C_{12}H_{10}N_2)] \cdot [(C_3H_6O_5P)^-]_2$, in which both diamine components lie across centres of inversion in space group $P2_1/c$. The anions form hydrogen-bonded head-to-head dimers, and these are linked by the two diamine units into sheets, which are themselves linked by C—H...O hydrogen bonds. With 2,2'-dipyridylamine the acid forms the hydrated salt $[\{(C_{10}H_9N_3)H\}^+] \cdot [(C_3H_6O_5P)^-] \cdot H_2O$ (2), in which all components are disordered with occupancy 0.5 in space group $Fmm2$. The anions form head-to-tail dimers, which are linked into sheets by the cations, and the sheets are linked into a three-dimensional framework by the water molecules. The piperazine salt $[\{(C_4H_{10}N_2)H_2\}^{2+}] \cdot [(C_3H_5O_5P)^{2-}]$ (3) contains simple anion chains linked into a three-dimensional framework by the two independent cations, both of which are centrosymmetric. In the hydrated salt formed by *N,N'*-dimethylpiperazine, $[\{(MeNC_4H_8NMe)H_2\}^{2+}] \cdot [(C_3H_6O_5P)^-]_2 \cdot (H_2O)_2$ (4), head-to-tail anion chains combine with the water molecules to form a three-dimensional framework, which encloses voids that contain the cations. In the 4,4'-bipyridyl adduct $[\{(C_{10}H_8N_2)H_{0.72}\}^{0.72+}] \cdot \{(H_{0.5}O)_3PCH_2CH_2COOH_{0.78}\}^{0.72-}$ (5), there is extensive disorder of the H atoms that are bonded to N and O atoms, and the anion chains are linked by the cations into sheets, which are themselves linked by C—H...O hydrogen bonds. In the 1:2 adduct formed with 1,2-bis(4'-pyridyl)ethane, $[\{(C_{12}H_{12}N_2)H_2\}^{2+}] \cdot [(C_3H_6O_5P)^-]_2$ (6), where the cation lies across an inversion centre, the anions form molecular ladders. These ladders are linked into sheets by the cations, which are themselves linked by C—H...O hydrogen bonds. In the methanol-solvated salt formed with 2,6-dimethylpiperazine, $[\{(C_6H_{14}N_2)H_2\}^{2+}] \cdot [(C_3H_6O_5P)^-]_2 \cdot (CH_4O)_{0.34}$ (7), the anions form sheets that are linked into a three-dimensional framework by the cations. The supramolecular structures are compared with those of analogous salts formed by phosphonoacetic acid.

1. Introduction

We have recently investigated a representative series of salt-type adducts formed between phosphonoacetic acid, $(HO)_2P(O)CH_2COOH$, and organic amines (Bowes *et al.*, 2003). Our interest in this acid was prompted both by the

structure of the acid itself and by the behaviour of its anions in simple metal salts (Lis, 1997). In the neutral acid, the three-dimensional structure is built from $C(4)$ and $C(6)$ spiral chains in space group $P2_12_12_1$, so that small rings are completely absent (Lis, 1997). In this respect, the behaviour of phosphonoacetic acid differs markedly from that of phenylphosphonic acid, PhP(O)(OH)_2 (Weakley, 1976), where it is possible to identify both $R_2^2(8)$ rings and $C(4)$ chains, motifs that dominate the aggregation patterns found in salts of the anion $[\text{PhP(O)}_2\text{OH}]^-$ (Ferguson *et al.*, 1998). In the lithium salt of phosphonoacetic acid [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcode TERMOS (Lis, 1997)], anions $[(\text{HO})\text{P(O)}_2\text{CH}_2\text{COOH}]^-$ are linked into chains that contain alternating $R_2^2(8)$ rings, which are formed by the phosphonate units, and $R_2^2(12)$ rings, which are formed by carboxyl donors and phosphonate acceptors. In these chains the $R_2^2(8)$ and $R_2^2(12)$ rings are linked in spiro fashion at the P atoms; despite the presence of un-ionized carboxyl groups, the characteristic $R_2^2(8)$ carboxyl dimer motif is absent. In salts with organic amines, phosphonoacetic acid forms hydrogen-bonded anion substructures that can be simple $C(4)$ chains, chains of spiro-fused $R_2^2(8)$ and $R_2^2(12)$ rings analogous to those found in the Li salt, molecular ladders [*i.e.* chains of edge-fused $R_2^2(8)$ and $R_4^4(20)$ rings], or sheets of alternating $R_2^2(12)$ and $R_6^6(28)$ rings. These substructures in combination with the organic cations generate a variety of supramolecular arrays that are hydrogen bonded in two or three dimensions.

Fascinated by the structural variety of the phosphonoacetate salts, we have now extended our study to encompass the homologous phosphonopropionic acid [carboxyethylphosphonic acid, $(\text{HO})_2\text{P(O)CH}_2\text{CH}_2\text{COOH}$, (A), see below],



and we present here the synthesis and structural character-

ization of the adducts formed by this acid with 1,2-bis(4'-pyridyl)ethene (B), 2,2'-dipyridylamine (C), piperazine (D), *N,N'*-dimethylpiperazine (E), 4,4'-bipyridyl (F), 1,2-bis(4'-pyridyl)ethane (G) and 2,6-dimethylpiperazine (H). The resulting adducts have the compositions $(\text{C}_{12}\text{H}_{10}\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})$ (1), $(\text{C}_{10}\text{H}_9\text{N}_3) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P}) \cdot (\text{H}_2\text{O})$ (2), $(\text{C}_4\text{H}_{10}\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})$ (3), $(\text{C}_6\text{H}_{14}\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})_2 \cdot (\text{H}_2\text{O})_2$ (4), $(\text{C}_{10}\text{H}_8\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})$ (5), $(\text{C}_{12}\text{H}_{12}\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})_2$ (6) and $(\text{C}_6\text{H}_{14}\text{N}_2) \cdot (\text{C}_3\text{H}_7\text{O}_5\text{P})_2 \cdot (\text{CH}_4\text{O})_{0.34}$ (7). Of these compounds, all but (5) and (7) are simple salts characterized by the transfer of integral numbers of protons from acid to base, and (7) is a solvated salt of this type, but in (5) there has been only partial transfer of protons (see below, §3.1).

The structure of phosphonopropionic acid itself does not appear to have been investigated. To date, all our attempts to grow single crystals of this material have been unsuccessful.

2. Experimental

2.1. Syntheses

Equimolar quantities of the appropriate amine and the acid were separately dissolved in methanol. The solutions were mixed, and the mixtures were set aside to crystallize, thus yielding (1)–(7). Analyses: (1) found C 53.5, H 4.9, N 8.3; $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_5\text{P}$ requires C 53.6, H 5.1, N 8.3%; (2) found C 45.3, H 5.6, N 12.3; $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_6\text{P}$ requires C 45.5, H 5.3, N 12.2%; (3) found C 35.2, H 6.3, N 11.8; $\text{C}_7\text{H}_{17}\text{N}_2\text{O}_5\text{P}$ requires C 35.3, H 7.0, N 11.8%; (4) found C 31.1, H 6.8, N 6.0; $\text{C}_{12}\text{H}_{32}\text{N}_2\text{O}_{12}\text{P}_2$ requires C 31.4, H 7.0, N 6.1%; (5) found C 50.3, H 4.7, N 8.9; $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5\text{P}$ requires C 50.3, H 4.9, N 9.0%; (6) found C 44.2, H 5.5, N 5.7; $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_{10}\text{P}_2$ requires C 43.9, H 5.3, N 5.7%; (7) consistent analysis was not obtained; $\text{C}_{12.34}\text{H}_{29.36}\text{N}_2\text{O}_{10.34}\text{P}_2$ requires C 34.2, H 6.8, N 6.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Diffraction data for (1)–(7) were collected at 150 (1) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a,b*). For (1), (3) and (4) the space group $P2_1/c$ was uniquely assigned from the systematic absences. The space group $P2_1/n$ was similarly assigned for (5). For (2) the systematic absences permitted $F222$, $Fmm2$ and $Fmmm$ as possible space groups. $Fmm2$ was selected and confirmed by the analysis: the Flack parameter (Flack, 1983) was -0.2 (2). Compound (6) is triclinic: the space group $P\bar{1}$ was chosen and confirmed by the successful structure analysis. For (7) the systematic absences permitted $Pca2_1$ and $Pcam$ ($= Pbcm$, No. 57) as possible space groups. $Pca2_1$ was selected and confirmed by the successful analysis: the Flack parameter was 0.07 (15).

Table 1
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$C_{12}H_{12}N_2^{2+} \cdot C_{12}H_{10}N_2 \cdot 2C_3H_6O_5P^-$	$C_{10}H_{10}N_3^+ \cdot C_3H_6O_5P^- \cdot H_2O$	$C_4H_{12}N_2^{2+} \cdot C_3H_5O_5P^{2-}$	$C_6H_{16}N_2^{2+} \cdot 2C_3H_6O_5P^- \cdot 2H_2O$
Chemical formula weight	672.55	343.27	240.2	458.34
Cell setting, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Fmm2$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a, b, c (Å)	10.1600 (3), 10.4061 (3), 14.5441 (5)	18.7267 (11), 22.6805 (11), 7.0893 (4)	10.6065 (3), 7.9214 (2), 12.8892 (4)	6.9270 (2), 20.6027 (5), 8.0115 (2)
β (°)	96.2880 (12)	90	94.0540 (12)	111.4092 (10)
V (Å ³)	1528.44 (8)	3011.0 (3)	1080.22 (5)	1064.47 (5)
Z	2	8	4	2
D_x (Mg m ⁻³)	1.461	1.514	1.477	1.43
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3496	1703	2230	2415
θ range (°)	2.8–27.5	3.2–27.5	3–27.5	2.9–27.5
μ (mm ⁻¹)	0.21	0.22	0.26	0.26
Temperature (K)	150 (1)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Block, colourless	Needle, colourless	Plate, colourless	Block, colourless
Crystal size (mm)	0.22 × 0.16 × 0.14	0.34 × 0.08 × 0.08	0.30 × 0.28 × 0.15	0.32 × 0.22 × 0.16
Data collection				
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	None	None	Multi-scan	None
T_{min}	–	–	0.904	–
T_{max}	–	–	0.971	–
No. of measured, independent and observed parameters	13 452, 3496, 2880	8696, 1703, 1445	6785, 2447, 2048	6838, 2415, 1990
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.042	0.085	0.028	0.035
θ_{max}	27.5	27.5	27.5	27.5
Range of h, k, l	–13 \Rightarrow h \Rightarrow 13 –13 \Rightarrow k \Rightarrow 13 –18 \Rightarrow l \Rightarrow 18	–21 \Rightarrow h \Rightarrow 24 –29 \Rightarrow k \Rightarrow 28 –9 \Rightarrow l \Rightarrow 9	–13 \Rightarrow h \Rightarrow 13 –10 \Rightarrow k \Rightarrow 9 –16 \Rightarrow l \Rightarrow 16	–8 \Rightarrow h \Rightarrow 8 –26 \Rightarrow k \Rightarrow 26 –10 \Rightarrow l \Rightarrow 10
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.097, 1.04	0.045, 0.111, 1.03	0.034, 0.091, 1.04	0.036, 0.092, 1.05
No. of reflections and parameters used in refinement	3496, 210	1703, 216	2447, 137	2415, 135
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.6401P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0134P)^2 + 1.5818P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 0.5908P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.3605P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	< 0.001	0.001	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.29, –0.42	0.19, –0.26	0.29, –0.39	0.34, –0.48
Extinction method	None	SHELXL	None	None
Extinction coefficient	–	0.0030 (7)	–	–
Absolute structure	–	Flack (1983); 708 Friedel pairs	–	–
Flack parameter	–	–0.2 (2)	–	–
<hr/>				
	(5)	(6)	(7)	
Crystal data				
Chemical formula	$C_{10}H_{8.82}N_2^{0.72+} \cdot C_3H_6O_{5.28}P^{0.72-}$	$C_{12}H_{14}N_2^{2+} \cdot 2C_3H_6O_5P^-$	$C_6H_{16}N_2^{2+} \cdot 2C_3H_6O_5P^- \cdot 0.34CH_4O$	
Chemical formula weight	1240.98	492.35	429.31	
Cell setting, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Orthorhombic, $Pca2_1$	
a, b, c (Å)	11.3482 (5), 6.7178 (3), 17.7354 (7)	7.5651 (3), 8.6472 (3), 9.0077 (4)	20.2229 (17), 8.6162 (6), 11.8812 (9)	
α, β, γ (°)	90, 97.4980 (18), 90	72.6340 (14), 73.1760 (15), 87.386 (2)	90, 90, 90	
V (Å ³)	1340.50 (10)	537.79 (4)	2070.2 (3)	
Z	1	1	4	
D_x (Mg m ⁻³)	1.537	1.520	1.377	
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	
No. of reflections for cell parameters	3059	5037	4652	

Table 1 (continued)

	(5)	(6)	(7)
θ range ($^{\circ}$)	3.3–27.5	2.8–27.6	3.8–27.5
μ (mm^{-1})	0.23	0.26	0.26
Temperature (K)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Plate, colourless	Plate, colourless	Plate, colourless
Crystal size (mm)	$0.22 \times 0.2 \times 0.08$	$0.30 \times 0.14 \times 0.12$	$0.24 \times 0.10 \times 0.04$
Data collection			
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	None	Multi-scan	None
T_{\min}	–	0.930	–
T_{\max}	–	0.973	–
No. of measured, independent and observed parameters	13 381, 3059, 2113	6047, 2457, 2163	15 150, 4652, 3521
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.060	0.035	0.125
θ_{\max}	27.5	27.6	27.5
Range of h, k, l	$-14 \Rightarrow h \Rightarrow 14$ $-8 \Rightarrow k \Rightarrow 8$ $-22 \Rightarrow l \Rightarrow 23$	$-9 \Rightarrow h \Rightarrow 9$ $-11 \Rightarrow k \Rightarrow 11$ $-11 \Rightarrow l \Rightarrow 11$	$-26 \Rightarrow h \Rightarrow 25$ $-11 \Rightarrow k \Rightarrow 11$ $-15 \Rightarrow l \Rightarrow 15$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.120, 1.03	0.032, 0.085, 1.06	0.064, 0.168, 1.03
No. of reflections and parameters used in refinement	3059, 194	2457, 148	4652, 250
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.2557P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.2452P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 2.3804P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	< 0.001	< 0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($\text{e } \text{\AA}^{-3}$)	0.27, –0.40	0.32, –0.36	0.56, –0.30
Extinction method	None	SHELXL	SHELXL
Extinction coefficient	–	0.022 (7)	0.019 (3)
Absolute structure	–	–	Flack (1983), 2161 Friedel pairs
Flack parameter	–	–	0.07 (15)

Computer programs: *Kappa-CCD server software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 1997b), *SHELXL97* (Sheldrick, 1997a), *PLATON* (Spek, 2003), *PRPKAPPA* (Ferguson, 1999).

The structures were solved by direct methods and refined with all data on F^2 . A weighting scheme based on $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). Compound (3) contains two independent cations, each located across a centre of inversion; the single cation in (5) also lies across an inversion centre; and in (1) there are two independent diamine units, one doubly protonated and one neutral, which both lie across inversion centres. In (2) all the independent molecular components lie in general positions with occupancy 0.5: the site occupancies are heavily correlated to avoid impossibly short inter-atom contacts (see §3.3.1). In (4) the water O atom is split over two closely adjacent sites [with refined site-occupation factors 0.928 (6) and 0.072 (6)], but the water H-atom sites, which are common to the two partial O components, are fully ordered. All H atoms were located from difference maps and included in the refinements as riding atoms with distances O–H 0.82–0.84, N–H 0.88–0.93 and C–H 0.92–1.00 Å.

Supramolecular analyses were performed and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Details of hydrogen-bond dimensions and molecular conformations are given in Tables 2 and 3. Figs. 1–20 show the molecular

components, with the atom-labelling schemes, and aspects of the supramolecular structures; further figures S1–S6 are available as part of the supplementary material.¹

3. Results and discussion

3.1. Compositions and molecular constitutions

Compounds (1), (3) and (5) all have 1:1 stoichiometry, while in (6) the ratio of amine to acid components is 1:2. In (7) the 1:2 ratio is accompanied by a partial methanol of solvation, while the 1:1 compound (2) and the 1:2 compound (4) are both stoichiometric hydrates.

Most of the compounds discussed here are simple salts in which one or, in the case of (3) only, two protons have been completely transferred from the phosphonic acid to the amine. However, in (1) the monoanion is accompanied not by a simple cation $[(\text{diamine})\text{H}]^+$ but by an equal number of dicationic $[(\text{diamine})\text{H}_2]^{2+}$ and neutral diamines, all of which

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0061). Services for accessing these data are described at the back of the journal.

Table 2
Hydrogen bond parameters (Å, °).

	D—H...A	H...A	D...A	D—H...A
(1)	O1—H1...N11	1.78	2.617 (2)	176
	O3—H3...O5 ⁱ	1.66	2.501 (2)	176
	N21—H21...O4	1.70	2.580 (2)	177
	C13—H13...O5 ⁱⁱ	2.55	3.489 (2)	170
	C17—H17...O5 ⁱⁱⁱ	2.25	3.185 (2)	169
	C22—H22...O3 ^{iv}	2.42	3.292 (2)	153
	C23—H23...O2 ^v	2.59	3.361 (2)	138
(2)	O1—H11...O5 ^{vi}	1.79	2.580 (4)	156
	O3—H3...O6	1.76	2.579 (5)	165
	O3—H3...O6 ^{vii}	2.60	3.308 (5)	143
	O6—H61...O5 ^{viii}	1.92	2.755 (6)	177
	O6—H61...O4 ^{ix}	1.91	2.744 (4)	172
	N1—H1...O4	1.88	2.755 (4)	173
	N12—H12...N22	1.90	2.589 (5)	134 [†]
	N12—H12...O2 ^x	2.27	2.961 (4)	135 [†]
	(3)	O3—H3...O4 ^{xi}	1.74	2.535 (2)
N11—H11A...O1		1.78	2.686 (2)	167
N11—H11B...O5 ^{xii}		1.72	2.640 (2)	176
N21—H21A...O4 ^{xiii}		1.82	2.738 (2)	172
N21—H21B...O1		2.43	2.992 (2)	119 [‡]
N21—H21B...O2		1.79	2.690 (2)	165 [‡]
C13—H13B...O2 ^{xiv}		2.41	3.243 (2)	142
C22—H22A...O5 ^{xv}		2.47	3.349 (2)	148
C22—H22B...O3 ^{xvi}		2.34	3.227 (2)	149
(4)	O3—H3...O6	1.72	2.562 (2)	174
	O1—H1...O5 ^{xvii}	1.74	2.562 (2)	167
	O6—H61...O4 ^{xviii}	1.88	2.717 (2)	176
	O6—H62...O5 ^{xviiii}	1.88	2.707 (2)	174
	N11—H11...O4	1.71	2.622 (2)	167
(5)	O3—H3...O3 ⁱ	1.67	2.475 (2)	160
	O5—H5...O5 ^{six}	1.24	2.473 (2)	180
	O1—H1...N11	1.77	2.585 (2)	164
	N11—H11...O1	1.71	2.585 (2)	173
	O4—H4...N21 ^{xx}	1.77	2.558 (2)	156
	N21—H21...O4 ^{xxi}	1.68	2.558 (2)	177
	(6)	O1—H1...O5 ^{xxii}	1.73	2.542 (2)
O3—H3...O4 ⁱ		1.79	2.619 (2)	168
N11—H11...O4		1.85	2.692 (2)	161
C12—H12...O2 ^{xxiii}		2.29	3.224 (2)	167
C13—H13...O5 ^{xxiv}		2.41	3.196 (2)	139
(7)	O11—H11...O15 ^{xxv}	1.76	2.587 (5)	166
	O13—H13...O24	1.72	2.534 (5)	164
	O21—H21...O25 ^{xxv}	1.83	2.624 (4)	157
	O23—H23...O15 ^{xxvi}	1.77	2.533 (5)	149
	N1—H1A...O23 ^{xxvii}	2.58	3.084 (5)	116 [§]
	N1—H1A...O24 ^{xxviii}	1.88	2.798 (5)	175 [§]
	N1—H1B...O14 ^{xxix}	1.82	2.731 (5)	170
	N4—H4A...O14 ^{xxx}	1.85	2.752 (6)	165
	N4—H4B...O25	1.88	2.792 (5)	171

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; (vi) $-x, -y, z$; (vii) $x, -y, z$; (viii) $x, y, -1 + z$; (ix) $\frac{1}{2} - x, -y, -\frac{1}{2} + z$; (x) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (xi) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (xii) $-x, 1 - y, 1 - z$; (xiii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (xiv) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (xv) $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (xvi) $-x, 1 - y, -z$; (xvii) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (xviii) $1 - x, 1 - y, -z$; (xix) $1 - x, -y, 1 - z$; (xx) $\frac{3}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (xxi) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (xxii) $x, 1 + y, z$; (xxiii) $-x, 1 - y, 2 - z$; (xxiv) $-x, -y, 2 - z$; (xxv) $x, -1 + y, z$; (xxvi) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (xxvii) $\frac{1}{2} - x, y, -\frac{1}{2} + z$; (xxviii) $\frac{1}{2} + x, 1 - y, z$. † Three-centre N—H... (N,O) system: sum of angles at H12, 360°. ‡ Three-centre N—H... (O)₂ system: sum of angles at H21B, 345°. § Three-centre N—H... (O)₂ system: sum of angles at H1A, 355°.

lie across centres of inversion. Compound (7) is a partially solvated salt with the formula $[(\text{H}_2\text{N}(\text{CHME-CH}_2)_2\text{NH}_2)]^{2+} \cdot [(\text{HO})\text{PO}_2\text{CH}_2\text{CH}_2\text{COOH}]^-]_2 \cdot (\text{CH}_3\text{OH})_{0.34}$.

In (5) the constitution is more complex. Each of the phosphoric O atoms (O3, O4 and O5) is associated with an H-atom site that has 0.5 occupancy. The H-atom sites associated with O3 and O4 are at the normal distance for O—H bonds, but the site associated with O5 is longer, 1.237 Å, as the corresponding H atom is located at a centre of inversion, *i.e.* mid-way between two O atoms. Between carboxyl O1 and pyridine N11 within the asymmetric unit (Fig. 16) there is an H atom disordered over two sites that have unequal occupancy: that adjacent to O1 has occupancy 0.78 (4) and that adjacent to N11 has occupancy 0.22 (4). Finally there is an H-atom site of occupancy 0.5 adjacent to N21. Hence the appropriate chemical formulation for (5) is $[(\text{C}_{10}\text{H}_8\text{N}_2)\text{-H}_{0.72}]^{0.72+} \cdot [(\text{H}_{0.5}\text{O})_3\text{PCH}_2\text{CH}_2\text{COOH}_{0.78}]^{0.72-}$. Where simple monoanions are present, these always contain an unionized carboxyl group, whereas in (3) the residual hydroxyl H is part of the phosphonic acid unit. The $\text{p}K_a$ values of acids in aqueous solution do not necessarily provide a reliable guide to the ionization status of acidic components in crystalline solids. Nonetheless, the order of the ionization events that is inferred from the observed anions in (1)–(7), provided that the H atoms are fully ordered, corresponds to the order of the $\text{p}K_a$ values of simple acids in aqueous solution, where the $\text{p}K$ values for carboxylic acids generally lie between the $\text{p}K_1$ and $\text{p}K_2$ values for phosphoric acid and for alkanephosphonic acids.

3.2. Molecular conformations

3.2.1. Amine components. Both diamine components in (1) are essentially planar, as judged by the leading torsional angles (Table 3), whereas the interplanar angle in (5) is indicative of a modest twist away from planarity, and the C13—C14—C17—C17ⁱⁱⁱ [(iii) $1 - x, 1 - y, 1 - z$] torsional angle in (6) indicates a conformation very far from planarity. The markedly different conformations in (1) and (6) may be strongly influenced by the orientation of the C—H...O hydrogen bonds. The cation in (2) is almost planar and this conformation is doubtless influenced by the intramolecular N—H...N hydrogen bond (Table 2). The piperazine cations in (3), (4) and (7) all adopt the usual chair conformation; equatorial methyl substituents are present in (4) and (7).

3.2.2. Phosphonate components. In each of (1)–(7) the phosphonate component adopts an extended conformation, with the P—C—C torsional angle close to 180° in each case and with the carboxyl or carboxylate group almost normal to the mean plane defined by the backbone chain. However, the orientation of the P—OH bond can vary, as in the analogous salts of phosphonoacetic acid (Bowes *et al.*, 2003). In general, this bond is synclinal to the backbone chain, but in (3) the bond is antiperiplanar.

3.3. Supramolecular structures

In all of the salts described in this paper, the ionic components are linked by an extensive series of hydrogen bonds (Table 2). This series encompasses hard (Braga *et al.*, 1995) hydrogen bonds, mainly of O—H...O and N—H...O types;

Table 3
Selected torsional and dihedral angles (°).

<i>(a) Amine components</i>				
(1)	C13—C14—C17—C17 ⁱ	-1.0 (3)	C23—C24—C27—C27 ⁱⁱ	3.8 (3)
(2)	C11—N1—C21—N22	-4.9 (9)	C21—N1—C11—N12	3.9 (7)
(4)	C14—N11—C12—C13	177.9 (2)		
(5)	(N11, C12—C16) [^] (N21, C22—C26)	18.6 (2)		
(6)	C13—C14—C17—C17 ⁱⁱⁱ	-124.4 (2)		
(7)	C7—C2—C3—N4	-178.3 (4)	C8—C6—C5—N4	-174.2 (4)
<i>(b) Acid components[†]</i>				
(1)	O3—P1—C3—C2	-53.7 (2)	P1—C3—C2—C1	-160.8 (2)
	O4—P1—C3—C2	-171.4 (2)	C3—C2—C1—O1	-169.3 (2)
	O5—P1—C3—C2	64.1 (2)	C3—C2—C1—O2	12.9 (2)
(2)	O3—P1—C3—C2	-62.0 (8)	P1—C3—C2—C1	175.7 (6)
	O4—P1—C3—C2	179.2 (5)	C3—C2—C1—O1	178.5 (7)
	O5—P1—C3—C2	52.4 (9)	C3—C2—C1—O2	-0.9 (11)
(3)	O3—P1—C3—C2	-174.2 (2)	P1—C3—C2—C1	171.3 (2)
	O4—P1—C3—C2	-60.4 (2)	C3—C2—C1—O1	163.1 (2)
	O5—P1—C3—C2	65.1 (2)	C3—C2—C1—O2	-20.5 (2)
(4)	O3—P1—C3—C2	-56.5 (2)	P1—C3—C2—C1	-170.4 (2)
	O4—P1—C3—C2	60.8 (2)	C3—C2—C1—O1	-154.9 (2)
	O5—P1—C3—C2	-175.5 (2)	C3—C2—C1—O2	25.9 (2)
(5)	O3—P1—C3—C2	55.0 (2)	P1—C3—C2—C1	-178.8 (2)
	O4—P1—C3—C2	176.0 (2)	C3—C2—C1—O1	176.7 (2)
	O5—P1—C3—C2	-63.6 (2)	C3—C2—C1—O2	3.8 (3)
(6)	O3—P1—C3—C2	-42.3 (2)	P1—C3—C2—C1	-169.4 (2)
	O4—P1—C3—C2	74.9 (2)	C3—C2—C1—O1	-174.9 (2)
	O5—P1—C3—C2	-159.3 (2)	C3—C2—C1—O2	6.2 (2)
(7)	O13—P1—C13—C12	-61.6 (5)	P1—C13—C12—C11	-175.7 (5)
	O14—P1—C13—C12	53.2 (5)	C13—C12—C11—O11	165.1 (7)
	O15—P1—C13—C12	178.2 (4)	C13—C12—C11—O12	-14.0 (11)
	O23—P2—C23—C22	60.9 (5)	P2—C23—C22—C21	-169.4 (4)
	O24—P2—C23—C22	-50.8 (5)	C23—C22—C21—O21	-163.0 (4)
	O25—P2—C23—C22	-179.3 (4)	C23—C22—C21—O22	20.7 (8)

Symmetry codes: (i) $-1-x, 1-y, -z$; (ii) $2-x, 1-y, 2-z$; (iii) $1-x, -1-y, 2-z$. [†] Phosphonate O3 carries H in all of (1)–(7); carboxyl O1 carries H in all except (3).

those of O—H...N type occur only in *A* and those of N—H...N type occur only within the macrocyclic cation in *C*. These hard hydrogen bonds are augmented in most compounds by soft hydrogen bonds, which are exclusively of the C—H...O type.

Analysis of the resulting supramolecular structures is greatly eased, in every case, by the use of the substructure approach (Gregson *et al.*, 2000). In each of (1)–(7), it is

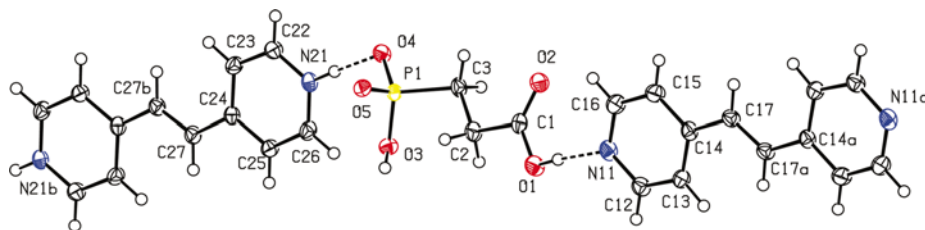


Figure 1

The molecular components of (1) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

possible to identify a low-dimensional substructure that is formed by the phosphonic acid components alone, whether neutral or charged. These substructures are mostly one-dimensional and take the form of simple chains in (3), (4) and (5), and molecular ladders, alternatively described as chains of edge-fused rings, in (6). However, in (1) and (2) the anion substructure is zero-dimensional and in (7) it is two-dimensional. Consequently, the structure descriptions below are based firstly on the formation of the phosphonic substructures and secondly on the manner in which these are linked by the cationic components by means of the hard hydrogen bonds. Finally the effects of the soft C—H...O hydrogen bonds are analysed.

3.3.1. The anions form a finite (zero-dimensional) unit. *Hard hydrogen bonds generate a two-dimensional structure.* In (1) (Fig. 1) the anion substructure consists of an isolated and finite (zero-dimensional) dimer unit. Phosphonate O3 in the anion at (x, y, z) acts as a hydrogen-bond donor to phosphonate O5 in the anion at $(1-x, 1-y, 1-z)$, so generating a centrosymmetric $R_2^2(8)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). Each of these dimer units is linked to four different diamines: two cations act as donors *via* N—H...O hydrogen bonds, while two neutral diamines are acceptors of O—H...N hydrogen bonds (Table 2). Within the asymmetric unit (Fig. 1) pyridinium N21 acts as a donor to phosphonate O4, and carboxyl O1 acts as a donor to N11 in the neutral diamine. As the anion dimer is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the cationic dimer is centred at $(1, \frac{1}{2}, 1)$ and the neutral diamine is centred at $(-\frac{1}{2}, \frac{1}{2}, 0)$. In addition, the anion dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ also acts as a hydrogen-bond donor, *via* carboxyl O1 at $(1-x, 1-y, 1-z)$, to N11 in the neutral diamine centred at $(\frac{3}{2}, \frac{1}{2}, 1)$ and as an acceptor, *via* O4 at $(1-x, 1-y, 1-z)$, from N21 in the cation centred at $(0, \frac{1}{2}, 0)$. Propagation of the hydrogen bonds thus generates a sheet parallel to (010) in which the $R_2^2(8)$ rings generated by the anions alternate with long thin $R_{10}^{10}(80)$ rings built from all the independent components (Fig. 2).

Two (010) sheets pass through each unit cell: the non-H atoms in the

reference sheet centred at $y = \frac{1}{2}$ lie in the domain $0.32 < y < 0.68$, and a second sheet, which is related to the first by the translation operators, is centred at $y = 0$ in the domain

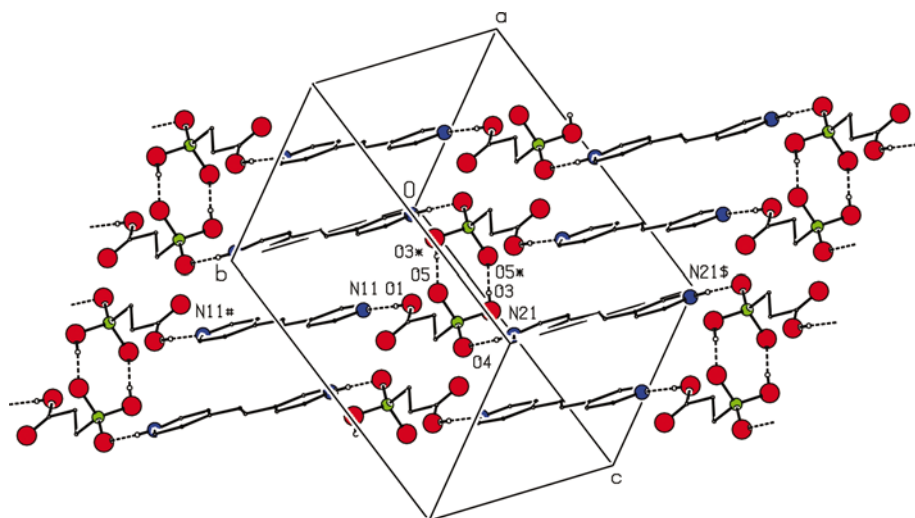


Figure 2

Part of the crystal structure of (1) showing the formation of a (010) sheet built from $R_2^2(8)$ and $R_{10}^{10}(80)$ rings. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(-1-x, 1-y, -z)$ and $(2-x, 1-y, 2-z)$, respectively.

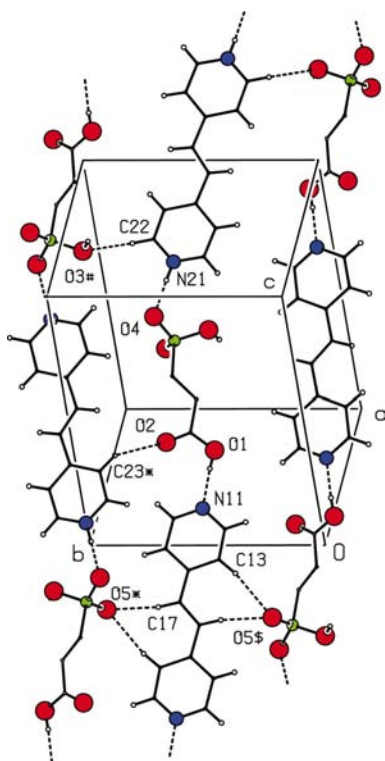


Figure 3

Part of the crystal structure of (1) showing the linking of the (010) sheets by means of C—H...O hydrogen bonds. For the sake of clarity, H atoms bonded to C are omitted from the anions. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(-1+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

$-0.18 < y < 0.18$. Each sheet is linked to its two immediate neighbours by two rather short C—H...O hydrogen bonds (Table 2). Atom C17 at (x, y, z) , which is part of the alkene spacer unit of the neutral diamine, acts as a hydrogen-bond donor to phosphonate O5 in the anion at $(-1+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, while atom C22 at (x, y, z) , which lies in the cationic diamine, acts as a donor to O3 in the anion at $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$. Both these anions lie in the (010) sheet centred at $y = 1.0$ (Fig. 3). The symmetry-related C17 at $(-1-x, 1-y, -z)$ and C22 at $(2-x, 1-y, 1-z)$ likewise act as hydrogen-bond donors to anions at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively, which both lie in the sheet centred at $y = 0$. These two hydrogen bonds are reinforced by two weaker interactions that involve C13 and C23 (Table 2; Fig. 3). In this way, all the (010) sheets are robustly linked into a single framework. There are, however, no aromatic $\pi \cdots \pi$ stacking interactions in this structure.

Hard hydrogen bonds generate a three-dimensional structure. The 1:1 adduct formed by 2,2'-dipyridylamine with phosphonopropionic acid crystallizes from methanol as a hydrated salt, $[(C_{10}H_9N_3)H]^+[(C_3H_6O_5P)^-](H_2O)$, in the rather uncommon space group $Fmm2$ (No. 42). The April 2002 release of the CSD (Allen & Kennard, 1993) shows only 26 molecular compounds in this space group, most of them

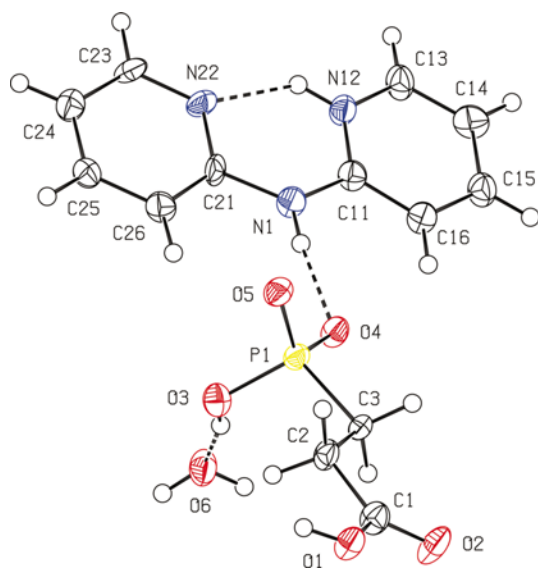


Figure 4

The molecular components of (2) and the atom-labelling scheme: all atom sites have 0.5 occupancy (see text). Displacement ellipsoids are drawn at the 30% probability level.

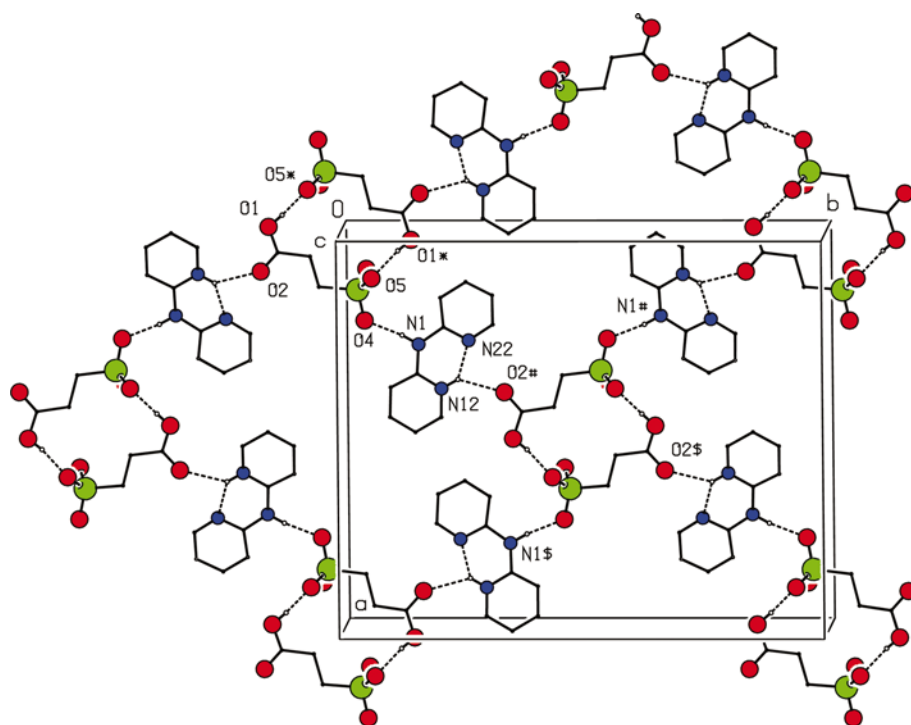


Figure 5

Part of the crystal structure of (2) showing the formation of a (001) sheet of cations and anions built from $R_2^2(14)$ and $R_{10}^{10}(46)$ rings. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(-x, -y, z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, respectively.

organometallics. Each of the independent components (Fig. 4) lies in a general position with 0.5 occupancy. The site occupancy is not random but must be strongly correlated among the different sites to avoid the occurrence of impossibly short intermolecular contacts and, in some cases, atom overlap. Subject to these considerations, the components are linked by a combination of O—H...O and N—H...O hydrogen bonds into a single three-dimensional framework, but analysis using the substructure approach (Gregson *et al.*, 2000) reveals not only a finite (zero-dimensional) substructural fragment comprising only anions but also two distinct two-component two-dimensional substructures, which are built, respectively, from anions and cations and from anions and water molecules.

The anion sites form groups of four around the twofold axes, such that if the anion site at (x, y, z) is occupied then those at $(-x, y, z)$ and $(x, -y, z)$ cannot be occupied, because of atom overlap, while the site at $(-x, -y, z)$ must be occupied to preserve the stoichiometry. A pair of anions that are related in this way by a twofold rotation axis form a cyclic hydrogen-bonded head-to-tail $R_2^2(14)$ dimer, where carboxyl O1 at (x, y, z) acts as a hydrogen-bond donor to phosphonate O5 at $(-x, -y, z)$ (Table 2; Fig. 5). These dimer units form (001) sheets in combination with the cations, but, as with the anions, only certain combinations of cation sites can be occupied. Thus if the cation site at (x, y, z) is occupied, that at $(1 - x, y, z)$, which is related to the first by the mirror plane at $x = \frac{1}{2}$, cannot be occupied, since atom C14 lies on this plane. Similarly, if the cation site at (x, y, z) is occupied, that at $(\frac{1}{2} - x, \frac{1}{2} - y, z)$,

which is related to the first by the twofold rotation axis along $(\frac{1}{4}, \frac{1}{4}, z)$, cannot be occupied, as once again impossibly short contacts and atom overlaps would occur. Subject to these constraints, each cation is linked by N—H...O hydrogen bonds to two anion dimers, while each anion dimer is linked to four cations. Thus N1 in the cation at (x, y, z) acts as a hydrogen-bond donor to phosphonate O4 in the anion at (x, y, z) , which is part of the dimer across $(0, 0, z)$, and N12 in the same cation acts as a donor to carboxyl O2 in the anion at $(\frac{1}{2}, -x, \frac{1}{2} - y, z)$, which is part of the anion dimer across $(\frac{1}{2}, \frac{1}{2}, z)$. Propagation of these three hydrogen bonds, one O—H...O and two N—H...O, thus generates a (001) sheet built from $R_2^2(14)$ and $R_{10}^{10}(46)$ rings, which alternate in checkerboard fashion (Fig. 5). Note that the arrangement of occupied sites depicted in Fig. 5 is just one of two possible arrangements: the alternative arrangement, which occurs with equal probability within each crystal, is the mirror image of that depicted, as reflected in either the

(100) or, equivalently, the (010) plane.

While there is complete correlation of the occupied sites within a given (001) sheet, this is not the case for the sites in different sheets. The sheets are linked by O—H...O hydrogen bonds that involve the water molecule, but there are two

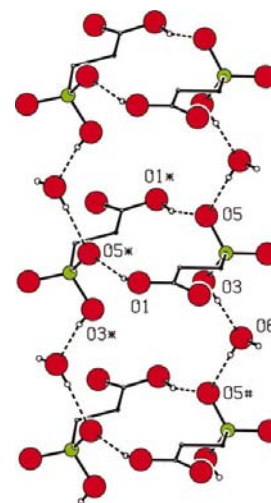


Figure 6

Part of the crystal structure of (2) showing the formation of a [001] stack of anion dimers and water molecules. For the sake of clarity, H atoms bonded to C, and the unit-cell box, are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, -y, z)$ and $(x, y, -1 + z)$, respectively.

possible arrangements of these hydrogen bonds, which permit alternative mutual orientations of adjacent (001) sheets. Phosphonate O3 in the anion at (x, y, z) acts as a hydrogen-bond donor to water O6 at two alternative sites, (x, y, z) and $(x, -y, z)$. We consider first the water at (x, y, z) , which involves the shorter of the two O3—H3···O6 hydrogen bonds (Table 2). Water O6 at (x, y, z) acts as a hydrogen-bond donor, *via* H61, to phosphonate O5 at $(x, y, -1 + z)$, so generating by translation a $C_2^2(6)$ chain that runs parallel to the [001] direction. These two hydrogen bonds would therefore generate a stack of anion dimers that are in register along the line $(0, 0, z)$ (Fig. 6) and hence would force successive (001) sheets of cation and anions (Fig. 5) also to be in register. Water O6 at (x, y, z) also acts as a hydrogen-bond donor, this time *via* H62, to phosphonate O4 at $(\frac{1}{2} - x, -y, -\frac{1}{2} + z)$, which lies in

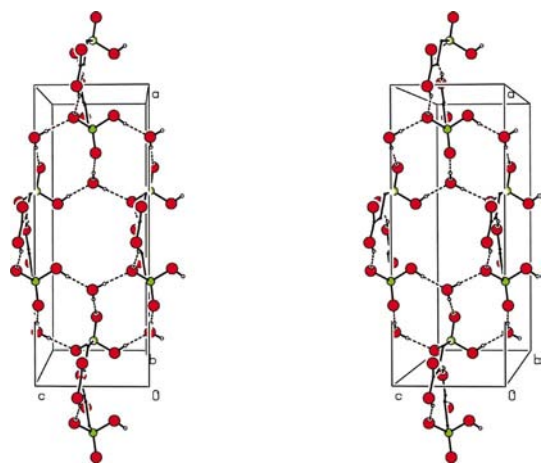


Figure 7
Stereoview of part of the crystal structure of (2) showing the formation of a (010) sheet formed by anions and water molecules. For the sake of clarity, H atoms bonded to C are omitted.

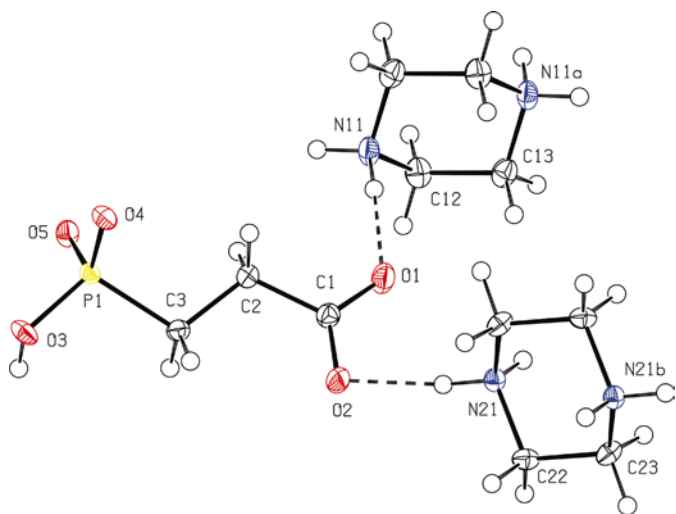


Figure 8
The molecular components of (3) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' and 'b' are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(1 - x, 1 - y, -z)$, respectively.

the anion/water stack along $(\frac{1}{2}, 0, z)$, and in this manner the [001] stacks are linked into a (010) sheet (Fig. 7).

If, however, the phosphonic O3 acts instead as a hydrogen-bond donor to water O6 at the alternative site $(x, -y, z)$, then this in turn will act as a hydrogen-bond donor to phosphonate O5, which is also at $(x, -y, z)$. In these circumstances the two successive anion dimers will not be in register and related simply by translation, but will be out of register as if reflected across (100) or (010) before translation along [001]. Consequently, the two adjacent (001) sheets of cations and anions (Fig. 5) will be out of register, with opposite orientations.

It is reasonable to suppose that the relative abundance of the two alternative O3—H3···O6 hydrogen bonds is at least roughly proportional to their relative strengths, as judged by the H···O and O···O distances. If this assumption is true then successive occurrences of the stronger of these two interactions would generate a series of cation/anion layers that are all in register, while each occurrence of the weaker interaction would switch the sequence to a block of layers that have the alternative orientation. Provided only that the manifestation of the weaker hydrogen bond occurred at random, regardless of its frequency, then there would be no predictable correlation of the layer orientations over medium to long distances. This lack of ordered correlation between layers is required by the space group $Fmm2$. The orthorhombic F lattice is not compatible with a fully ordered sequence of (001) layers. Note that, of the symmetry elements present in $Fmm2$, the twofold axes along $(0, 0, z)$ and $(\frac{1}{2}, \frac{1}{2}, z)$ are manifest in a single (001) sheet, but those at $(\frac{1}{4}, \frac{1}{4}, z)$ *etc.* are not. Similarly, the single

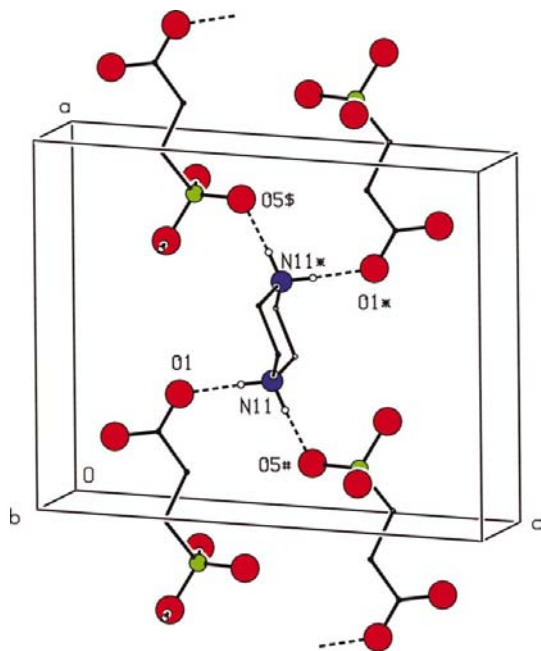


Figure 9
Part of the crystal structure of (3) showing the linking of the [010] anion chains by the type 1 cations. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-x, 1 - y, 1 - z)$ and $(1 + x, y, z)$, respectively.

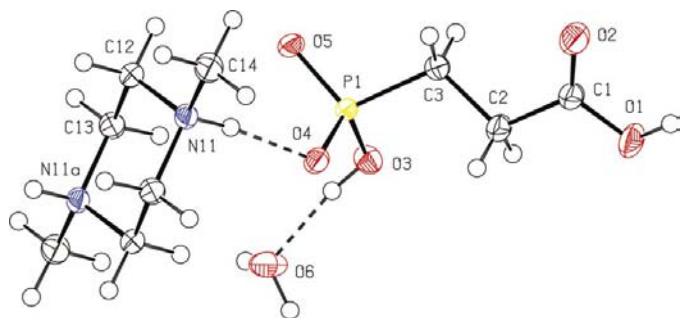


Figure 10
The molecular components of (4) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atom marked with 'a' is at the symmetry position $(1-x, 1-y, 1-z)$.

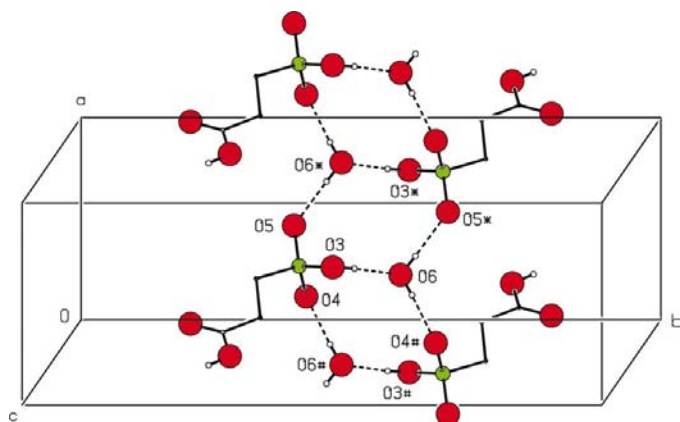


Figure 11
Part of the crystal structure of (4) showing the formation of a molecular ladder along [100]. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1-x, 1-y, -z)$ and $(-x, 1-y, -z)$, respectively.

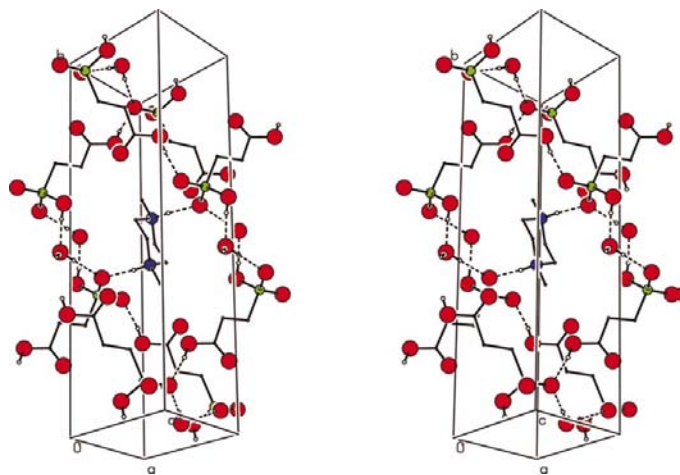


Figure 12
Stereoview of part of the crystal structure of (4) showing the cation lying in a void within the anion-water framework. For the sake of clarity, H atoms bonded to C are omitted.

sheet exhibits two sets of glide planes, at $x = \frac{1}{4}$ and $\frac{3}{4}$ and at $y = \frac{1}{4}$ and $\frac{3}{4}$, but no mirror planes.

3.3.2. The anions form simple chains. The chains are linked into a three-dimensional framework by the cations. The anion substructure in (3) (Fig. 8) still involves only the phosphonate groups, and it is generated by the action of a screw axis. Phosphonate O3 in the anion at (x, y, z) acts as a hydrogen-bond donor to O4 at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so producing a $C(4)$ spiral chain around the 2_1 screw axis along $(-\frac{1}{4}, y, \frac{1}{4})$ (Fig. S1). Two such chains, which are related to one another by the inversion centres and hence have opposite senses, run through each unit cell. The two independent centrosymmetric cations link these chains into a single three-dimensional framework by means of four $N-H \cdots O$ hydrogen bonds (Table 2).

In the type 1 cation (which contains N11) centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ N11 at (x, y, z) acts as a hydrogen-bond donor, via H11A and H11B, respectively, to O1 in the anion at (x, y, z) and to O5 in the anion at $(-x, 1-y, 1-z)$. These anions lie in the chains along $(-\frac{1}{4}, y, \frac{1}{4})$ and $(\frac{1}{4}, -y, \frac{3}{4})$, respectively. The symmetry-related N11 in the same cation is at $(1-x, 1-y, 1-z)$, and it similarly acts as a donor to O1 in the anion at $(1-x, 1-y, 1-z)$ and to O5 in the anion at $(1+x, y, z)$. These two anions, respectively, form part of the chains along $(\frac{3}{4}, -y, \frac{3}{4})$ and $(\frac{3}{4}, y, \frac{1}{4})$ (Fig. 9). Similarly, the type 2 cation (which contains N21) centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ forms $N-H \cdots O$ hydrogen bonds to anions lying in the four chains along $(-\frac{1}{4}, y, \frac{1}{4})$, $(\frac{3}{4}, y, \frac{1}{4})$, $(\frac{3}{4}, -y, -\frac{1}{4})$ and $(\frac{1}{4}, -y, -\frac{1}{4})$ (Fig. S2). In this manner, each cation is directly linked to four different [010] chains, and each anion is directly linked to four different cations; propagation by the space group of the $N-H \cdots O$ hydrogen bonds links all of the [010] chains into a continuous framework.

A cation-templated framework built from anions and water molecules only. Compound (4) is a hydrated salt $[(\text{MeNC}_4\text{H}_8\text{NMe})\text{H}_2]^{2+} \cdot [(\text{C}_3\text{H}_6\text{O}_5\text{P})^-]_2 \cdot (\text{H}_2\text{O})_2$ (Fig. 10). The cation lies across a centre of inversion, which is selected for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the anion and the water molecule both lie in general positions. The anions alone form a simple head-to-tail chain, and the anions and water molecules together generate a continuous three-dimensional framework that encapsulates large voids within which the cations lie. The cations are linked to the anion-water framework by $N-H \cdots O$ hydrogen bonds.

Carboxyl O1 in the anion at (x, y, z) acts as a hydrogen-bond donor to phosphonate O5 in the anion at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, and propagation of this hydrogen bond produces a $C(7)$ chain that runs parallel to the [201] direction. This chain is generated by the glide plane at $y = \frac{1}{4}$ and lies in the domain $0.04 < y < 0.46$ (Fig. S3). A similar but antiparallel chain lying in the domain $0.54 < y < 0.96$ is generated by the glide plane at $y = \frac{3}{4}$. The behaviour of the anion and water molecules together is most simply analysed in terms of a second one-dimensional substructure and thence of the interaction of this with the [201] anion chains.

Within the asymmetric unit, phosphonic O3 acts as a hydrogen-bond donor to water O6 (Fig. 10). O6 in turn acts as a donor, via H61, to phosphonate O4 at $(-x, 1-y, -z)$, so producing an $R_2^2(12)$ ring centred at $(0, \frac{1}{2}, 0)$, and via H62 to

phosphonate O5 at $(1 - x, 1 - y, -z)$, so producing a second $R_2^2(12)$ ring, this time centred at $(\frac{1}{2}, \frac{1}{2}, 0)$. Propagation by inversion of these hydrogen bonds generates a chain of edge-fused rings, or a molecular ladder, that runs along the line $(x, \frac{1}{2}, 0)$ (Fig. 11). Within this reference ladder carboxyl O1 atoms at (x, y, z) and $(-x, 1 - y, -z)$ act as hydrogen-bond donors within [201] chains to atoms O5 in the anions at $(-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively, and these anions lie in the [100] molecular ladders along $(x, 0, -\frac{1}{2})$ and $(x, 1, \frac{1}{2})$, respectively. The action of the translation operators generates further such connections between the $(x, \frac{1}{2}, 0)$ ladder and the

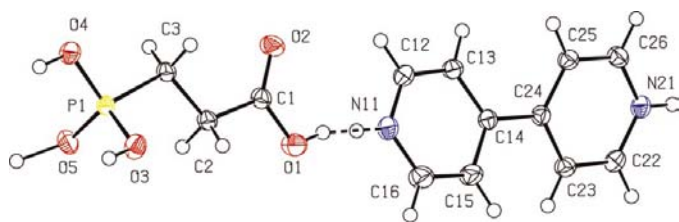


Figure 13

The molecular components of (5) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The H-atom sites adjacent to O3, O4, O5 and N21 all have 0.5 occupancy: the H-atom sites adjacent to O1 and N11 (atoms H1 and H11) have occupancies 0.78 (4) and 0.22 (4), respectively.

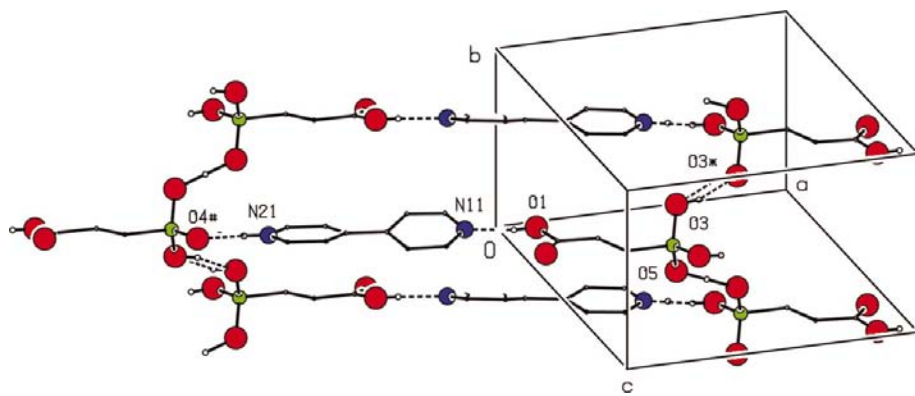


Figure 14

Part of the crystal structure of (5) showing the formation of a $(10\bar{3})$ sheet. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(-\frac{3}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

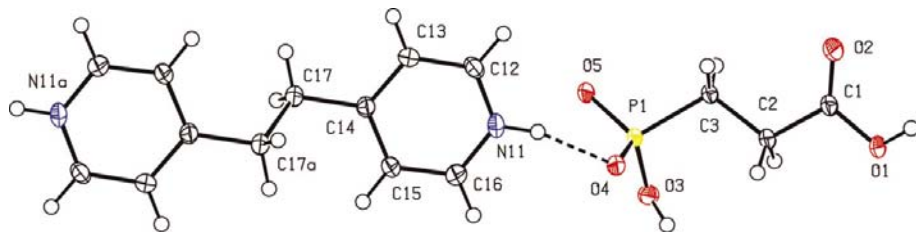


Figure 15

The molecular components of (6) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(1 - x, 1 - y, 2 - z)$.

ladders along $(x, 0, \frac{1}{2})$ and $(x, 1, -\frac{1}{2})$, so linking all of the [100] ladders into a continuous three-dimensional framework. This framework, which is built from anions and water molecules only, occupies only *ca.* 65.1% of the unit-cell volume, which leaves two large voids per cell to contain the cations. Each cation is linked to the anion–water framework by two symmetry-related $N-H \cdots O$ hydrogen bonds (Fig. 12).

3.3.3. The anions form a simple chain containing pseudo-rings. Although the H atoms associated with N and O atoms in (5) (Fig. 13) exhibit considerable disorder (see §3.1), the one-dimensional anion structure is nonetheless relatively straightforward. Atom H5 lies at the centre of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$, mid-way between phosphonate O5 atoms of the anions at (x, y, z) and $(1 - x, -y, 1 - z)$. By contrast, phosphonate O3 atoms in the anions at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are linked by a conventional $O-H \cdots O$ hydrogen bond but with the H disordered over two centrosymmetrically related sites. Propagation of these two hydrogen bonds generates, *via* the successive centres of inversion, a $C_2^2(8)$ chain that runs parallel to [010] (Fig. S4). For any pair of adjacent O3 sites, only one of the associated H sites can be occupied, but the average structure deduced from the diffraction data (where the occupancy averaging is certainly spacial and possibly temporal) displays apparent, but not real, four-membered rings. Two $C_2^2(8)$ chains run through each unit cell, along $(\frac{1}{2}, y, \frac{1}{2})$ and $(0, y, 0)$, and these [010] chains are linked into sheets by $N-H \cdots O/O-H \cdots N$ hydrogen bonds that involve disordered H-atom sites.

Within the asymmetric unit, atoms O1 and N1 are linked by an $N-H \cdots O/O-H \cdots N$ hydrogen bond (Table 2). Another such bond links N21 in the cation at (x, y, z) and O4 in the anion at $(-\frac{3}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z)$, which is a part of the anion chain along $(-1, \frac{1}{2}, 0)$. Propagation of these $N-H \cdots O/O-H \cdots N$ hydrogen bonds thus generates a $C_2^2(16)$ chain parallel to the [301] direction, and the combination of the [010] and [301] chains generates a $(10\bar{3})$ sheet built from $R_6^2(40)$ rings (Fig. 14). Three such sheets are required in order to define the structure fully, and adjacent sheets are linked by two $C-H \cdots O$ hydrogen bonds. Atom C26 in the cation at (x, y, z) acts as a hydrogen-bond donor to carboxyl O1 in the anion at $(-1 + x, y, z)$, so linking adjacent sheets, by translation, in a $C_2^2(10)$ chain (Fig. S5). In addition, atom C23 in the cation at (x, y, z) , which lies in the sheet passing through $(\frac{1}{2}, y, \frac{1}{2})$, acts as a hydrogen-bond donor to carboxyl O2 in the anion at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$,

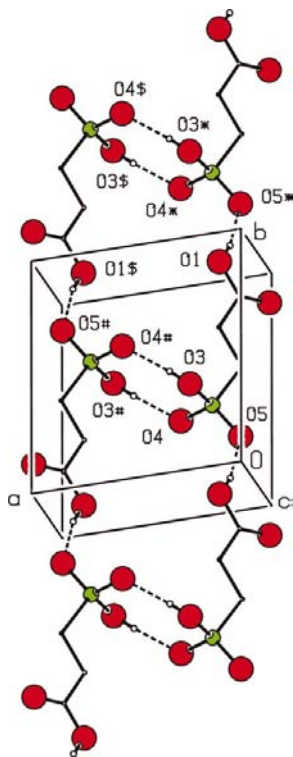


Figure 16

Part of the crystal structure of (6) showing the formation of a chain of anions along [010]. This chain contains fused $R_2^2(8)$ and $R_4^4(22)$ rings. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, 1 + y, z)$, $(1 - x, 1 - y, 1 - z)$ and $(1 - x, 2 - y, 1 - z)$, respectively.

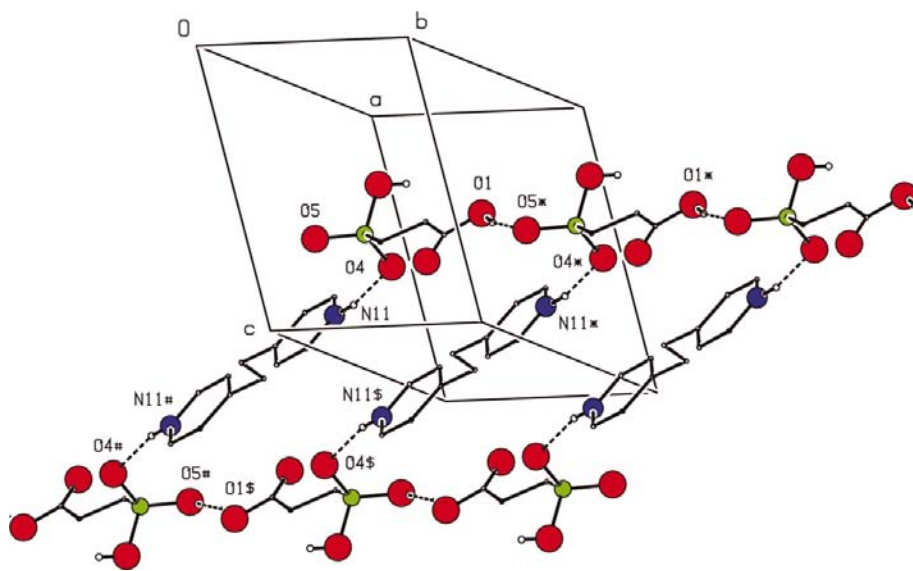


Figure 17

Part of the crystal structure of (6) showing the linking of the [010] anion chains by the cations to form a (100) sheet. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, 1 + y, z)$, $(1 - x, -1 - y, 2 - z)$ and $(1 - x, -y, 2 - z)$, respectively.

which lies in the sheet passing through $(\frac{3}{2}, y, \frac{1}{2})$ (Fig. S5). Hence each sheet is linked to the two adjacent sheets so that a continuous three-dimensional framework is formed.

3.3.4. The anions form chains of edge-fused rings (molecular ladders). In (6) (Fig. 15) the anions alone form a chain of fused rings, the cations link the anion chains into sheets by means of $N-H \cdots O$ hydrogen bonds, and these sheets are then linked to form three-dimensional structures by $C-H \cdots O$ hydrogen bonds. Both the carboxyl group and the phosphonate group are involved in the chain formation in (6). Phosphonic O3 in the anion at (x, y, z) acts as a hydrogen-bond donor to phosphonate O4 in the anion at $(1 - x, 1 - y, 1 - z)$, so forming an $R_2^2(8)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. At the same time, carboxyl O1 at (x, y, z) acts as a donor to phosphonate O5 at $(x, 1 + y, z)$, so producing by translation a $C(4)$ chain that runs parallel to the [010] direction. The combination of these two hydrogen bonds generates a chain of edge-fused rings along [010] that contains alternating $R_2^2(8)$ rings centred at $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_4^4(22)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 16).

In the linking of these chains to form a (100) sheet, pyridinium N11 at (x, y, z) acts as a hydrogen-bond donor to phosphonate O4 within the asymmetric unit (Fig. 15). With the reference anion chain running along $(\frac{1}{2}, y, \frac{1}{2})$, the cation is then centred at $(\frac{1}{2}, -\frac{1}{2}, 1)$. The symmetry-related N11 in the same cation lies at $(1 - x, -1 - y, 2 - z)$, and this N11 acts as a donor to O4 in the anion at $(1 - x, -1 - y, 2 - z)$, which lies in the anion chain along $(\frac{1}{2}, y, \frac{3}{2})$. Propagation of this $N-H \cdots O$ hydrogen bond by inversion and translation thus generates a (100) sheet, within which adjacent pairs of cations enclose centrosymmetric $R_6^6(44)$ rings (Fig. 17).

Two significant $C-H \cdots O$ hydrogen bonds link the (100) sheets into a three-dimensional framework. Atoms C12 and C13 at (x, y, z) are components of the (100) sheet centred at $x = \frac{1}{2}$. These atoms act as hydrogen-bond donors, respectively, to carboxyl O2 in the anion at $(-x, 1 - y, 2 - z)$ and phosphonate O5 in the anion at $(-x, -y, 2 - z)$. Both of these atoms lie in the sheet centred at $x = -\frac{1}{2}$ (Fig. S6). The symmetry-related C12 and C13 atoms, which lie in the same cation centred at $(\frac{1}{2}, -\frac{1}{2}, 1)$, are at $(1 - x, -1 - y, 2 - z)$. These atoms act, respectively, as donors to O2 at $(1 + x, -2 + y, z)$ and to O5 at $(1 + x, -1 + y, z)$, both of which lie in the sheet centred at $x = \frac{3}{2}$. Hence these $C-H \cdots O$ hydrogen bonds link each (100) sheet to the two neighbouring sheets.

3.3.5. The anion substructure is two-dimensional. *Compound (7): a structural hierarchy.* In (7) (Fig. 18) all

of the components lie in general positions. Each of the anions (type 1 contains P1 and type 2 contains P2) individually forms a one-dimensional substructure; the two anions together form a two-dimensional substructure; and the cation and anions together form a three-dimensional framework. There is thus a hierarchy of N -component N -dimensional structures for $N = 1$ –3; this type of structure has previously been noted in the hydrated adducts of 4,4'-bipyridyl and ethane-1,2-diphosphonic acid (Glidewell *et al.*, 2000) and of N,N' -dimethylpiperazine and tartaric acid (Zakaria *et al.*, 2002).

The one-dimensional substructures are simple chains that are generated by translation. Carboxyl O11 in the type 1 anion

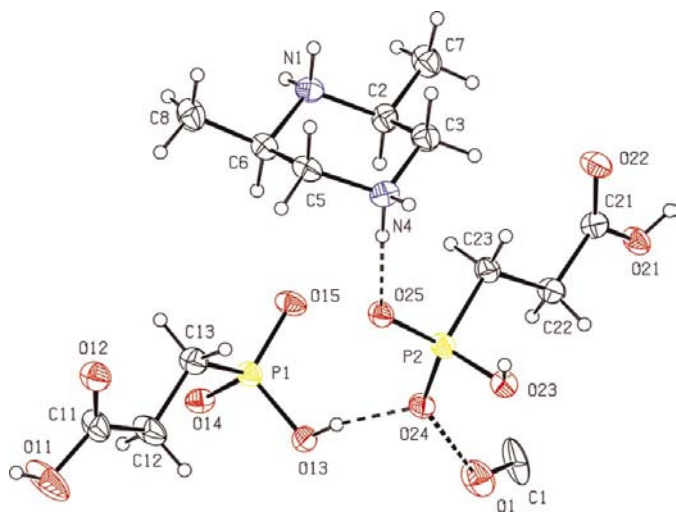


Figure 18

The molecular components of (7) and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The methanol component (atoms C1 and O1) has occupancy 0.337 (13).

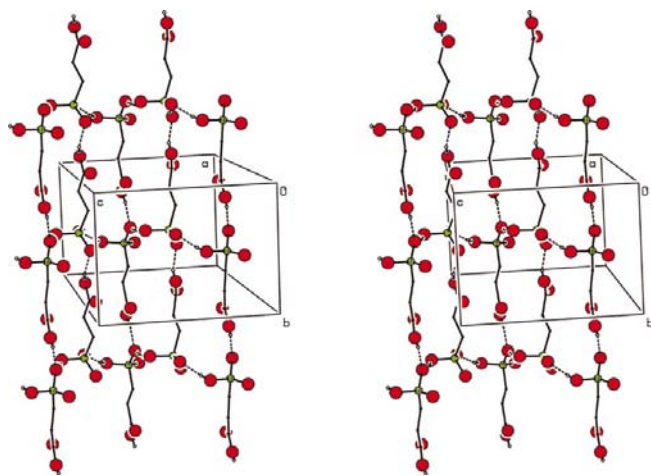


Figure 19

Stereoview of part of the crystal structure of (7) showing the formation of a (100) sheet of anions built from $R_4^3(20)$ and $R_4^4(22)$ rings. For the sake of clarity, H atoms bonded to C are omitted.

at (x, y, z) acts as a hydrogen-bond donor to phosphonate O15 in the corresponding anion at $(x, 1 + y, z)$, while carboxyl O21 in the type 2 anion at (x, y, z) likewise acts as a donor to phosphonate O25 in the type 2 anion at $(x, -1 + y, z)$, so producing in each case a $C(7)$ chain that runs parallel to the [010] direction (Fig. 19). Two further short O—H...O hydrogen bonds link the two types of chain into a sheet. Phosphonic O13 acts as a hydrogen-bond donor to phosphonate O24 within the asymmetric unit, while phosphonic O23 in the type 2 anion at (x, y, z) acts as a donor to phosphonate O15 in the type 1 anion at $(\frac{1}{2} - x, y, \frac{1}{2} + z)$. The combination of these two hydrogen bonds produces a $C_2^2(8)$ chain that runs parallel to the [001] direction and is generated by the c -glide plane at $x = \frac{1}{4}$ (Fig. 19).

The combination of the [010] and [001] chains generates a (100) sheet that is built from alternating columns of $R_4^3(20)$ and $R_4^4(22)$ rings (Fig. 19). This rather puckered sheet lies in the domain $0.04 < x < 0.46$, and a second such sheet lies in the domain $0.54 < x < 0.96$. Successive sheets are linked into a continuous framework by the cations, all four of whose N—H bonds are engaged in the formation of N—H...O hydrogen bonds. In the cation at (x, y, z) N4 acts as a hydrogen-bond donor, *via* H4A and H4B, respectively, to O25 in the type 2 anion, which is also at (x, y, z) , and to O14 in the type 1 anion at $(\frac{1}{2} - x, y, \frac{1}{2} + z)$. Both of these anions lie in the $0.04 < x < 0.46$ sheet. In the same cation N1 acts as a donor in a nearly planar three-centre N—H...O₂ system, *via* H1A, to both O23 and O24 in the type 2 anion at $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$, which also lies in the $0.04 < x < 0.46$ sheet. N1 also acts as a hydrogen-bond donor, *via* H1B, to O14 in the type 1 anion at $(\frac{1}{2} + x, 1 - y, z)$, which lies in the $0.54 < x < 0.96$ sheet. Similarly, the cation at $(-\frac{1}{2} + x, 1 - y, z)$ acts as a hydrogen-bond donor, *via* H1B and H4B, respectively, to O14 in the type 1 anion at (x, y, z) and to O25 in the type 2 anion at $(-\frac{1}{2} + x, 1 - y, z)$; these anions lie, respectively, in the $0.04 < x < 0.46$ and $-0.46 < x < -0.04$ sheets. Hence propagation by the space group of the N—H...O hydrogen bonds links all of the (100) sheets into a single framework (Fig. 20). The linking of the sheets, *via* the N1 atom in the cation, can alternatively be envisaged in terms of a $C_3^3(8)$ chain that runs parallel to the [100] direction.

Although the hard hydrogen bonds, of O—H...O and N—H...O types, suffice to generate the framework structure, there are two reasonably strong C—H...O hydrogen bonds (Table 2) that reinforce the [100] and [010] chains.

The H atoms of the partial-occupancy methanol could not be located, despite extensive searches of difference maps. However, the O1...O24 distance within the asymmetric unit, 2.957 (12) Å, may be indicative of a weak O—H...O hydrogen bond with O1 acting as the donor. There are no other potential hydrogen-bond-donor sites within bonding distance of O1, so the methanol molecules are simply pendent from the framework rather than integrated within it. Possibly the methanol is simply occupying an otherwise vacant space.

3.3.6. General comments on the substructures. Three motifs dominate the anion substructures in (1)–(7). The first is the head-to-head chain motif, which involves only the phos-

phonate units of $C(4)$ type in (3) and of $C_2^2(8)$ type in (5) and (7). The $C(4)$ motif is a characteristic feature of both simple phosphonic acids (Weakley, 1976; Lis, 1997) and simple aliphatic carboxylic acids (Jones & Templeton, 1958; Nahrungbauer, 1970; Jönsson, 1971). The second motif is a $C(7)$ head-to-tail chain, which is present in (4), (6) and (7). Finally there are cyclic dimer motifs, with head-to-head phosphonate dimers of $R_2^2(8)$ type, in (1) and (6): this motif is also present in phenylphosphonic acid (Weakley, 1976). The head-to-tail $R_2^2(12)$ dimer that involves both phosphonate and carboxyl groups, which is present also in phosphonoacetic acid (Lis, 1997), occurs in (2). Note that the $R_2^2(8)$ carboxyl motif that is characteristic of many carboxylic acids is absent throughout. Hence the variations of the hydrogen-bonding patterns in the acid substructures within this series pose a real challenge to methods aimed at the computation from first principles of the crystal structures of molecular systems.

3.3.7. Comparison of phosphonopropionate salts with phosphonoacetate analogues. The adducts formed by phosphonoacetic acid, $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{COOH}$, with four of the amines employed in the present study, namely N,N' -dimethylpiperazine, 4,4'-bipyridyl, 1,2-bis(4-pyridyl)ethane and 2,2'-dipyridylamine, have recently been structurally characterized (Farrell *et al.*, 2001; Bowes *et al.*, 2003), and it is of interest to compare the structural variation within each of these three pairs of compounds.

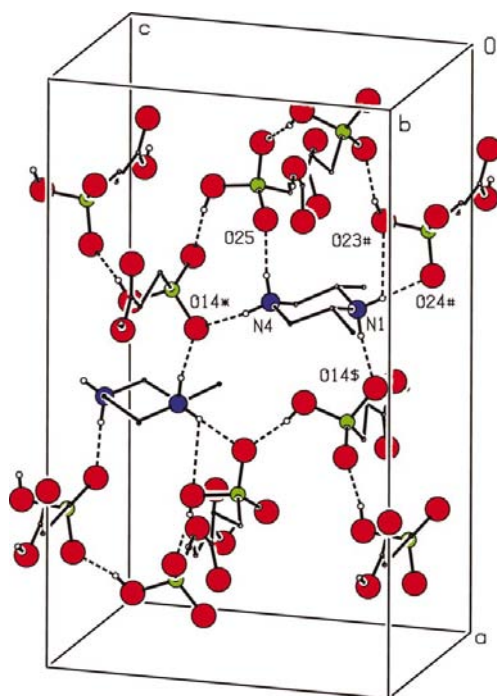


Figure 20
Part of the crystal structure of (7) showing the linking of the (100) sheets by the cations. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(\frac{1}{2} - x, y, \frac{1}{2} + z)$, $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$ and $(\frac{1}{2} + x, 1 - y, z)$, respectively.

In contrast to the extensive H-atom disorder observed here in the 4,4'-bipyridyl compound (5), the phosphonoacetate analogue is a simple salt that shows no disorder at all, thus $[\{(\text{C}_{10}\text{H}_8\text{N}_2)\text{H}\}^+][(\text{C}_2\text{H}_4\text{O}_5\text{P})^-]$. Despite this lack of disorder, and despite the very different unit-cell dimensions, there are some clear similarities between the overall supramolecular structures of the two salts. In each, the anion substructure is a chain; in each, the cations link the anion chains into sheets built from a single type of ring [$R_6^6(38)$ in the phosphonoacetate and $R_6^6(40)$ in the phosphonopropionate, where the difference in ring size arises solely from the additional C atom in the backbone of the latter acid]; and in each, the sheets are linked into a continuous framework by means of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

The two 1:2 salts derived from 1,2-bis(4'-pyridyl)ethane both contain centrosymmetric $[\{(\text{C}_{12}\text{H}_{12}\text{N}_2)\text{H}_2\}^{2+}]$ cations, but the phosphonoacetate crystallizes in space group $P2_1/c$, as opposed to $P\bar{1}$ for (6), and the $[(\text{C}_2\text{H}_4\text{O}_5\text{P})^-]$ anions in the phosphonoacetate form sheets of alternating $R_2^2(12)$ and $R_2^2(12)$ rings, as opposed to the molecular ladders formed by the anions in (6). Neither of these salts has a supramolecular structure that in any way resembles that of (1), which is formed by the analogous 1,2-bis(4'-pyridyl)ethene and in which even the stoichiometry and the molecular constitution are different.

With phosphonoacetic acid, N,N' -dimethylpiperazine forms a solvent-free salt in which the anions form sheets built from $R_6^6(28)$ rings. These are effectively templated by the cations, which lie at the ring centres. In the hydrated analogue (4) described here, the structure can similarly be interpreted in terms of a templated three-dimensional framework built of anions and water molecules with, again, centrosymmetric cations generating, and occupying, the spaces within the anion substructure.

Possibly the biggest contrast between these corresponding phosphonoacetate and phosphonopropionate derivatives is found in the salts formed with 2,2'-dipyridylamine. The phosphonoacetate is a solvent-free salt that crystallizes in space group $P\bar{1}$, where the anion substructure takes the form of a molecular ladder, and the ladders are linked by the cations to form sheets. This structure contrasts strongly with the orthorhombic monohydrate (2), where the anion substructure is a finite dimer. While in each structure the cations and anions together generate sheets, these sheets are linked to form a continuous framework by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds in the phosphonoacetate but by water molecules in (2).

4. Concluding comments

The results reported here, for a series of adducts formed by a single acid with a range of rather simple and closely related amines, encompass a wide variety of molecular constitutions and supramolecular arrangements. The nature of the acid components present, whether monoanions or dianions, is not readily predictable: nor is the nature of the diamine, where both monocations, as in (2) and (5), and mixtures of cations

and neutral diamines, as in (1), can occur in addition to the dications found in (3), (4), (6) and (7). There are also unexpected solvent molecules in (2), (4) and (7); in (2) and (4) the solvent molecules are stoichiometric and integral components of the framework structure, while in (7) the solvent sites are only partially occupied and these molecules are merely pendent from the cation–anion framework. Similarly, the acid substructures exhibit wide variation, and there are, in addition, significant structural differences between analogous phosphonoacetate and phosphonopropionate salts. Taken together, all these findings mean that no one supramolecular structure could readily have been predicted, even with detailed foreknowledge of all the others in this series. This fact in turn may mean that attempts to apply simple principles of crystal engineering to the design and construction of specific supramolecular structures in systems such as those described here will require predictive models that are considerably more sophisticated than those currently available.

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