

Ethane-1,2-diphosphonic acid as a building block in
supramolecular chemistry; a pillared-layer frame-
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The 1:1 adduct of piperazine and ethane-1,2-diphosphonic acid is a salt $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+} \cdot [\text{C}_2\text{H}_6\text{O}_6\text{P}_2]^{2-}$, in which both ions lie across centres of inversion in space group $P2_1/c$. The anions are linked by a single type of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond [$\text{O}\cdots\text{O}$, 2.562 (3) Å; $\text{H}\cdots\text{O}$, 1.73 Å, $\text{O}-\text{H}\cdots\text{O}$, 169°] into (6, 3) nets built from a single type of $R_4^4(22)$ ring. The cations lie between these nets, linked to them by two types of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond [$\text{N}\cdots\text{O}$, 2.635 (3) and 2.735 (3) Å; $\text{H}\cdots\text{O}$ 1.72 and 1.82 Å, $\text{N}-\text{H}\cdots\text{O}$, 175 and 177°] such that the cations link adjacent sheets, thus forming a pillared-layer framework. The aquated adduct formed between trimethylenedipiperidine and ethane-1,2-diphosphonic acid is also a salt $[\text{C}_{13}\text{H}_{28}\text{N}_2]^{2+} \cdot [\text{C}_2\text{H}_6\text{O}_6\text{P}_2]^{2-} \cdot 2.8[\text{H}_2\text{O}]$, in which there are 12 different types of hydrogen bond, eight $\text{O}-\text{H}\cdots\text{O}$ and four $\text{N}-\text{H}\cdots\text{O}$. The anions are linked into chains by pairs of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and these chains are linked by the water molecules into a continuous three-dimensional framework. Within the anion/water framework are large voids which contain pairs of cations, linked to the framework by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

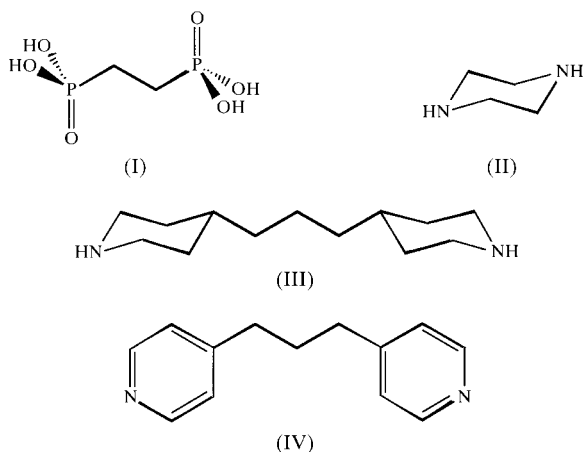
1. Introduction

The crystal structure of phenylphosphonic acid, $\text{PhP}(\text{O})(\text{OH})_2$, is built from continuous hydrogen-bonded sheets in which it is possible to identify both centrosymmetric $R[-\text{PO}(\text{OH})_2]_2$ dimer motifs and continuous $C(4)[\cdots\text{O}=\text{P}-\text{O}-\text{H}\cdots]_n$ motifs (Weakley, 1976). In both methylenediphosphonic acid $\text{CH}_2[\text{P}(\text{O})(\text{OH})_2]_2$ and ethane-1,2-diphosphonic acid $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ (Peterson *et al.*, 1977) the molecules are linked by hydrogen bonds into three-dimensional frameworks in which $C(4)$ chains are again a dominant motif.

Phenylphosphonic acid forms hydrogen-bonded adducts with a range of diamines, in which the supramolecular architecture can be one-, two- or three-dimensional (Ferguson *et al.*, 1998). A common feature of these adducts is the transfer of protons from the acid to the amine, thus forming the anion $[\text{PhP}(\text{O})_2(\text{OH})]^-$: the combination of ion formation, on the one hand, and on the other the ability of this anion to act as both hydrogen-bond donor and hydrogen-bond acceptor, leads to the formation of a rich diversity of strong, ionic hydrogen bonds.

Developing this theme we have now embarked on a study of ethane-1,2-diphosphonic acid (I), see scheme below, where at least as rich a structural variety may be expected as that previously observed in the adducts formed by phenyl phosphonic acid. We have already reported the structure of the hydrated 1:1 adduct formed by ethane-1,2-diphosphonic acid

with 4,4'-bipyridyl (Glidewell *et al.*, 2000). In this paper we report the synthesis of adducts with three further diamines: a non-solvated 1:1 adduct with piperazine (II) $[C_4H_{10}N_2] \cdot [(HO)_2P(O)CH_2CH_2P(O)(OH)_2]$ (1), and solvated adducts formed with two chain-extended diamines; $[C_{13}H_{26}N_2] \cdot [(HO)_2P(O)CH_2CH_2P(O)(OH)_2] \cdot 2.8H_2O$ (2) formed with the extended piperazine analogue 4,4-trimethylenedipiperidine (III) and $[C_{13}H_{14}N_2] \cdot [(HO)_2P(O)CH_2CH_2P(O)(OH)_2] \cdot [CH_4O] \cdot H_2O$ (3) formed with the corresponding extended 4,4-bipyridyl analogue 4,4-trimethylenedipyridine (IV). We report here the structures of (1) and (2), which prove to be the salts $[C_4H_{12}N_2]^{2+} \cdot [C_2H_6O_6P_2]^{2-}$ and $[C_{13}H_{28}N_2]^{2+} \cdot [C_2H_6O_6P_2]^{2-} \cdot 2.8H_2O$, respectively.



2. Experimental

2.1. Synthesis

2.1.1. Ethane-1,2-diphosphonic acid. Triisopropyl phosphite (83.3 g, 0.40 mol) was added dropwise, over a period of 45 min, to 1,2-dibromoethane (18.8 g, 0.10 mol) heated to 423 K: the mixture was held at this temperature until evolution of 2-bromopropane ceased. Tetraisopropyl ethane-1,2-diphosphonate was isolated by fractional distillation. NMR ($CDCl_3$): $\delta(H)$ 1.33 (24H, d, $J = 6.6$ Hz, $8 \times CH_3$), 1.92 (4H, m, $2 \times CH_2$), 4.70 (4H, m, $4 \times CH$); $\delta(C)$ 21.0 ($J_{PC} = 130$ Hz, CH_2), 24.6 (CH_3), 712.0 (CH); $\delta(P)$ 28.2. This ester was then refluxed for 4 h with an excess of concentrated aqueous hydrochloric acid: the mixture was then cooled and evaporated to dryness. The solid residue was recrystallized from water to give ethane-1,2-diphosphonic acid (I) in almost quantitative yield. Analysis: found C 12.8, H 4.1%; $C_2H_8O_6P_2$ requires C 12.6, H 4.2%. NMR ($CDCl_3$): $\delta(H)$ 1.93 (4H, m, $2 \times CH_2$), 3.30 (4H, br, $4 \times OH$); $\delta(C)$ 22.0 ($J_{PC} = 125$ Hz, CH_2); $\delta(P)$ 28.0.

2.1.2. Compounds (1)–(3). For each adduct, equimolar quantities of the acid (I) and the appropriate diamine, (II)–(IV), were separately dissolved in methanol: the solutions were mixed and set aside to crystallize, exposed to the laboratory atmosphere, producing (1)–(3), respectively. Analyses: (1) found C 26.0, H 6.6, N 9.9%; $C_6H_{18}N_2O_6P_2$ requires C 26.1, H 6.6, N 10.2%; (2) found C 40.3, H 9.3, N

6.1%; $C_{15}H_{34}N_2O_6P_2 \cdot 2.8H_2O$ requires C 40.0, H 8.9, N 6.2%; (3) found C 33.3, H 5.9, N 4.4%; $C_{17}H_{30}N_2O_{12}P_4 \cdot MeOH \cdot 2H_2O$ requires C 33.4, H 5.9, N 4.3%. Crystals of (1) and (2) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples: no suitable crystals of (3) have yet been obtained.

2.2. Data collection, structure solution and refinement

Diffraction data for (1) and (2) were collected at 100 (2) K using a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed (Ferguson, 1999; Gabe *et al.*, 1989; Johnson, 1976; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a,b*; Spek, 2000). For both compounds the space group $P2_1/c$ was uniquely determined from the systematic absences. The structures were solved by direct methods and refined with all data on F^2 . A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms in the organic components were located from difference maps and all were included in the refinements as riding atoms with O–H 0.84, N–H 0.92, C–H 0.99 (CH_2) and 1.00 Å (CH). It was apparent at an early stage in the refinements that two H atoms had been transferred from the acid units to the diamine units. In (2) three sites were located for O atoms of water molecules: of these, one, O3, is both fully occupied and fully ordered and the associated H atoms were located without difficulty. The O atom of a second water molecule was split over two closely adjacent sites and independent refinement of the two site-occupation factors led to values of 0.866 (11) and 0.134 (11), respectively, indicating that this pair of sites, taken together, accommodates a complete water molecule: the H atoms associated with the major site, designated O4, were located but those associated with the minor site, designated O41, could not be found. The O atom of the third water molecule was also found to be split over two closely adjacent sites for which the site occupation factors refined to 0.584 (10) and 0.209 (10): hence, this pair of sites accommodates significantly less than one complete water molecule. The H atoms associated with the major site O5 were located, but not those associated with the minor site, O51. All H atoms, including those on O3, O4 and O5 were fully ordered. The O–H distances were initially refined, to 0.85 Å, using a common free variable: in the final refinement cycles these distances were set to 0.85 (3) Å by use of a *DFIX* command.

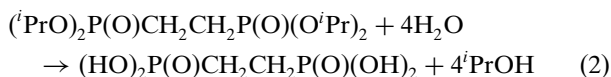
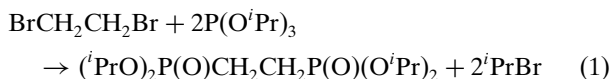
The diagrams were prepared with the aid of *PLATON* (Spek, 2000). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.¹ Figs. 1 and 2 show the molecular components, with the atom-labelling schemes. Figs. 3–7 illustrate aspects of the supramolecular structures.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0111). Services for accessing these data are described at the back of the journal.

3. Results and discussion

3.1. Syntheses and molecular constitutions

Ethane-1,2-diphosphonic acid (I) was prepared by hydrolysis of the corresponding isopropyl ester, which itself had been prepared by reaction of 1,2-dibromoethane with triisopropyl phosphite.



It was found necessary to use triisopropyl phosphite rather than the simpler and more obvious trimethyl phosphite. When $\text{P}(\text{OMe})_3$ was employed in the first step, the sole product isolated was the rearrangement product $\text{MeP}(\text{O})(\text{OMe})_2$, formed by the very rapid reaction of the ester with the initial by-product MeBr . Since secondary bromoalkanes react with $\text{P}(\text{OR})_3$ much more slowly than primary bromoalkanes, the use of the isopropyl ester effectively prevents this side reaction. Consistent with these observations, it has previously been reported (Moedritzer & Irani, 1961) that using the primary alkyl ester $\text{P}(\text{OEt})_3$ in reactions analogous to equation (1) gave only poor yields of $(\text{EtO})_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2$ when $n = 1$ or 2.

The acid (I) was identified by microanalysis and by NMR spectroscopy. The ^1H resonance of the $\text{PCH}_2\text{CH}_2\text{P}$ unit,

measured at 300 MHz, can be analysed as a second-order spectrum of the type $[\text{AX}_2]_2$ (Harris, 1964), in which $|^2J_{\text{HP}} + ^3J_{\text{HP}}|$ is 9.2 Hz. This spectrum is consistent with an antiperiplanar, effectively centrosymmetric conformation in solution, exhibiting no free rotation about the central C—C bond. It is interesting to note that in the solid state the molecules of this acid lie across centres of inversion (Peterson *et al.*, 1977), while molecular modelling of isolated molecules using the *HyperChem* package (Hypercube Inc., 1999) also led to the centrosymmetric form as the most stable conformer. A precisely similar pattern occurs in the ^1H spectrum of the isopropyl ester intermediate, where $|^2J_{\text{HP}} + ^3J_{\text{HP}}|$ is 9.3 Hz, again indicating a rigid and effectively centrosymmetric conformation.

Compounds (1) and (2), produced by co-crystallization of the acid (I) with the aliphatic diamines (II) and (III), respectively, are both 1:1 salts. However, while (1), $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}[\text{C}_2\text{H}_6\text{O}_6\text{P}_2]^{2-}$, contains no solvent molecules, (2) on the other hand crystallizes as an aquated salt, $[\text{C}_{13}\text{H}_{28}\text{N}_2]^{2+}[\text{C}_2\text{H}_6\text{O}_6\text{P}_2]^{2-} \cdot 2.8\text{H}_2\text{O}$. Microanalysis was unable to distinguish between 2.5 and 3.0 molecules of water per ion pair, but the structure analysis (see §3.2.2) showed that there were *ca.* 2.8 molecules of water per ion pair (see also §2.2), all of which are intimately bound into the supramolecular structure. In (3) the ratio of acid-to-diamine is 2:1 and the additional crystals contain one molecule of methanol and two of water per diamine: if the diamine is doubly protonated and the methanol and water molecules are unprotonated, then each acid has transferred only one proton rather than the two

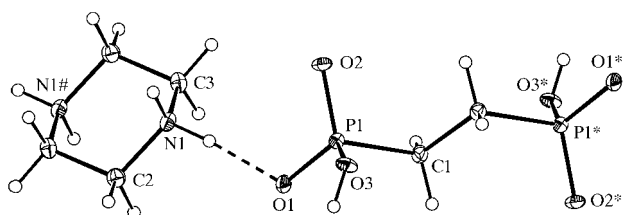


Figure 1
The molecular components of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms marked with a star (*) or hash (#) are at the symmetry positions $(2-x, 1-y, -z)$ and $(1-x, 1-y, 1-z)$, respectively.

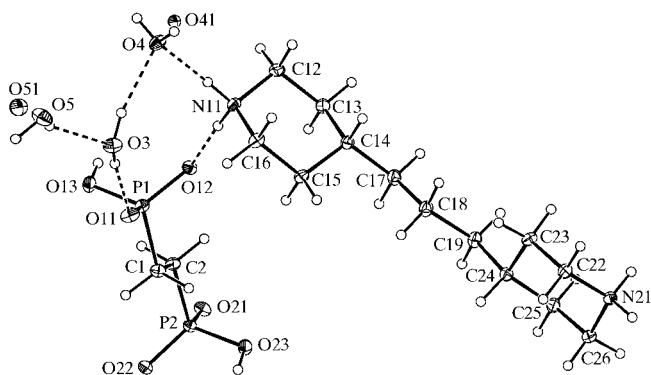


Figure 2
The asymmetric unit of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms associated with the minor occupancy sites O41 and O51 could not be located (see text).

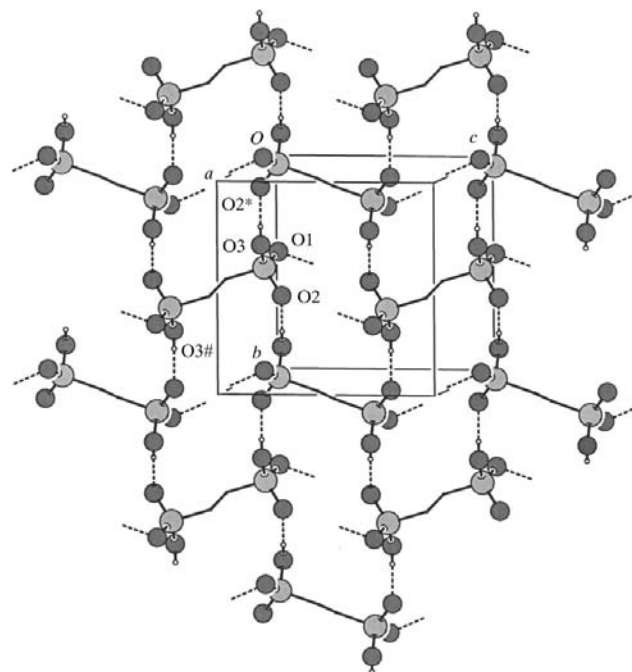


Figure 3
Part of the crystal structure of (1) showing formation of a (6, 3) net of anions, lying parallel to (100) and built from $R_4^2(22)$ rings. For the sake of clarity H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$ and $2-x, 1-y, -z$, respectively.

Table 1
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	C ₄ H ₁₂ N ₂ ·C ₂ H ₆ O ₆ P ₂	C ₁₃ H ₂₈ N ₂ ·C ₂ H ₆ O ₆ P ₂ ·2.8H ₂ O
Chemical formula weight	276.16	450.01
Cell setting, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3914 (6), 9.3343 (7), 9.3590 (6)	6.1218 (2), 20.6215 (7), 18.1831 (7)
α , β , γ (°)	90, 107.291 (4), 90	90, 99.942 (2), 90
<i>V</i> (Å ³)	616.53 (8)	2260.98 (14)
<i>Z</i>	2	4
<i>D</i> _x (Mg m ⁻³)	1.488	1.332
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	3237	13 672
θ range (°)	2.89–27.40	3.01–30.05
μ (mm ⁻¹)	0.368	0.237
Temperature (K)	150 (1)	120 (1)
Crystal form, colour	Needle, colourless	Block, colourless
Crystal size (mm)	0.20 × 0.06 × 0.02	0.30 × 0.12 × 0.12
Data collection		
Diffractometer	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan (Otwinowski & Minor, 1997)	Multi-scan (Otwinowski & Minor, 1997)
<i>T</i> _{min}	0.9300	0.9318
<i>T</i> _{max}	0.9927	0.9719
No. of measured, independent and observed parameters	3237, 1401, 947	13 672, 6599, 4617
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.057	0.033
θ _{max} (°)	27.40	30.05
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 9 0 → <i>k</i> → 12 -12 → <i>l</i> → 11	0 → <i>h</i> → 8 -29 → <i>k</i> → 0 -25 → <i>l</i> → 24
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0591, 0.1231, 1.038	0.0506, 0.1139, 1.022
No. of reflections and parameters used in refinement	1401, 74	6599, 284
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.6688P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 1.1810P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.000	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.372, -0.429	0.399, -0.388

transferred in (1) and (2). In the absence of structural data, further speculation on the constitution of this material is unlikely to be fruitful.

3.2. Supramolecular structures

3.2.1. Compound (1). In (1) the component ions [H₂N(CH₂CH₂)₂NH₂]²⁺ and [(HO)(O)₂PCH₂CH₂P(O)₂(OH)]²⁻ both lie across centres of inversion and, for the sake of convenience, the reference cation was centred at (½, ½, ½). In the asymmetric unit selected (Fig. 1) the reference anion is thus centred at (1, ½, 0). There are only three types of hydrogen bond in the structure, but each cation acts as a fourfold donor in N—H···O hydrogen bonds (Table 2) and each anion acts as

a double donor in O—H···O hydrogen bonds and hence acts as a sixfold acceptor of hydrogen bonds. Each cation is linked to four different anions: each anion is linked to four cations and four other anions.

The overall structure of (1) is most simply described in terms of the substructure formed by the anions alone, two-dimensional nets and then in terms of the linking of these nets by the cations to form a three-dimensional framework. The anions are linked by O—H···O hydrogen bonds into sheets lying parallel to (100). Atom O3 at (*x*, *y*, *z*), which is a component of the anion centred at (1, ½, 0), acts as a hydrogen-bond donor to O2 at (2 - *x*, -½ + *y*, ½ - *z*), a component of the anion centred at (1, 0, ½). O3 at (2 - *x*, -½ + *y*, ½ - *z*) in this same anion in turn acts as a donor to O2 at (*x*, -1 + *y*, *z*), thus producing a C(4) chain parallel to [010]. Each anion is, however, centrosymmetric and the propagation of the C(4) motif by the successive centres of inversion leads to the formation of a (6, 3) net (Batten & Robson, 1998) built from a single type of R₄^d(22) ring (Fig. 3). Within this net, the rings are centrosymmetric and the ring centres generate an A-face centring pattern. One net passes through each unit cell and the perpendicular distance between adjacent nets, *asin* β, is *ca* 7 Å.

The space between the van der Waals surfaces of adjacent nets is occupied by the cations, so that the overall supramolecular architecture is that of a pillared-layer structure (Fig. 4). The reference cation centred at (½, ½, ½) forms N—H···O hydrogen bonds (Table 2) to the anions centred at (1, ½, 0), (1, ½, 1), (0, ½, 1) and (0, ½, 0): of these anions, the first two are components of one layer, at *x* = 1, and the latter two are components of the adjacent layer, at *x* = 0. In this manner, all of the stacked layers are linked into a continuous framework, but there are no residual solvent-accessible voids in the structure. There are in addition two C—H···O hydrogen bonds involving one of the CH₂ groups adjacent to the charged N in the cation (Table 2). Of these, the C2—H2B···O3^{iv} [(iv) = -1 + *x*, *y*, *z*] interaction serves to reinforce the linking of the (100) sheets.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i>	H	<i>A</i>	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
(1)					
O3	H3	O2 ⁱ	1.73	2.562 (3)	169
N1	H1C	O2 ⁱⁱ	1.82	2.735 (3)	177
N1	H1D	O1	1.72	2.635 (3)	175
C2	H2A	O1 ⁱⁱⁱ	2.37	3.166 (4)	136
C2	H2B	O3 ^{iv}	2.36	3.285 (5)	155
(2)					
O13	H13	O22 ^{iv}	1.74	2.568 (2)	170
O23	H23	O12 ^v	1.76	2.598 (2)	173
O3	H31	O4	1.98 (2)	2.816 (3)	168 (2)
O3		O41		3.50 (2)	
O3	H32	O11	1.91 (2)	2.740 (2)	167 (2)
O4	H41	O11 ^{iv}	1.91 (2)	2.756 (3)	174 (2)
O41		O11 ^{iv}		2.65 (2)	
O4	H42	O21 ^{vi}	1.82 (2)	2.665 (2)	172 (3)
O41		O21 ^{vi}		2.61 (2)	
O5	H51	O3	2.09 (4)	2.813 (4)	143 (3)
O51		O3		2.956 (9)	
O5	H52	O11 ^{vii}	1.97 (3)	2.802 (4)	168 (3)
O51		O11 ^{vii}		2.86 (2)	
N11	H11A	O12	1.77	2.691 (2)	177
N11	H11B	O4	1.83	2.740 (3)	172
N11		O41		2.73 (2)	
N21	H21A	O21 ⁱⁱ	1.82	2.732 (2)	172
N21	H21B	O3 ^{viii}	1.89	2.800 (2)	169

Symmetry codes: (i) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, 1-y, 1-z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-1+x, y, z$; (v) $1+x, y, z$; (vi) $-1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $1-x, -y, 1-z$; (viii) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$.

3.2.2. Compound (2). In (2) all the components, both the ions $[\text{H}_2\text{NC}_5\text{H}_9(\text{CH}_2)_3\text{C}_5\text{H}_9\text{NH}_2]^{2+}$ and $[(\text{HO})(\text{O})_2\text{PCH}_2\text{-CH}_2\text{P}(\text{O})_2(\text{OH})]^{2-}$, as well as the neutral water molecules (Fig. 2) lie in general positions. The supramolecular structure analysis and description is complicated somewhat by the disorder and partial occupancy of some of the water sites (see §2.2). For the sake of simplicity, the structural description will consider only those water molecules containing O3, O4 and O5: the low occupancy O41 and O51 (adjacent to O4 and O5, respectively) will be ignored. Two reasons may be adduced in

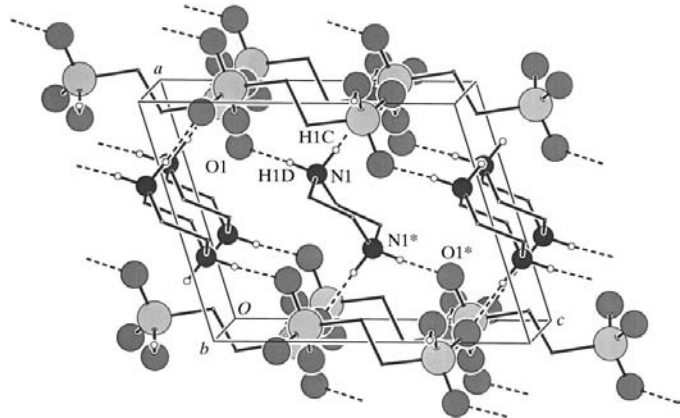


Figure 4
Part of the crystal structure of (1), showing the cation pillars connecting adjacent anionic layers. For the sake of clarity H atoms bonded to C are omitted. Atoms marked with a star (*) are at the symmetry position $1-x, 1-y, 1-z$.

support of this: first, the H atoms associated with the low occupancy O41 and O51 sites could not be located, secondly, the *D*...*A* distances involving O41 and O51 are, in general, very similar to the corresponding distances involving O4 and O5, respectively (Table 2). The sole significant difference arises in the O3...O4 and O3...O41 distances: these three sites are almost co-linear with O41 on the side of O4 remote from O3. Overall, the hydrogen-bonding behaviour of the low-occupancy water molecules can be expected with reasonable confidence to mimic that of the major components.

Subject to this constraint there are 12 distinct hydrogen bonds within the structure of either O—H...O or N—H...O types. Each cation acts as a fourfold donor in N—H...O hydrogen bonds; each anion acts as a twofold donor in O—H...O hydrogen bonds, as a twofold acceptor in N—H...O hydrogen bonds and as a sixfold acceptor in O—H...O hydrogen bonds. The water molecules containing O3 and O4 are both double donors and double acceptors of hydrogen bonds: that containing O5 is a double donor, but it is not an acceptor of significant hydrogen-bonding interactions.

As with (1), the substructure approach (Gregson *et al.*, 2000) provides the most straightforward route to an understanding of the structure. The anions are linked by paired O—H...O hydrogen bonds into a single-component chain; these chains are linked by the water molecules into a continuous three-dimensional two-component framework, which contains large voids, and these voids contain pairs of cations which themselves are linked to the water/anion framework by means of N—H...O hydrogen bonds. Each of these structural features will be described in turn.

In the formation of the anion chains O13 at (x, y, z) acts as a donor to O22 at $(-1+x, y, z)$ and O23 at $(-1+x, y, z)$ acts

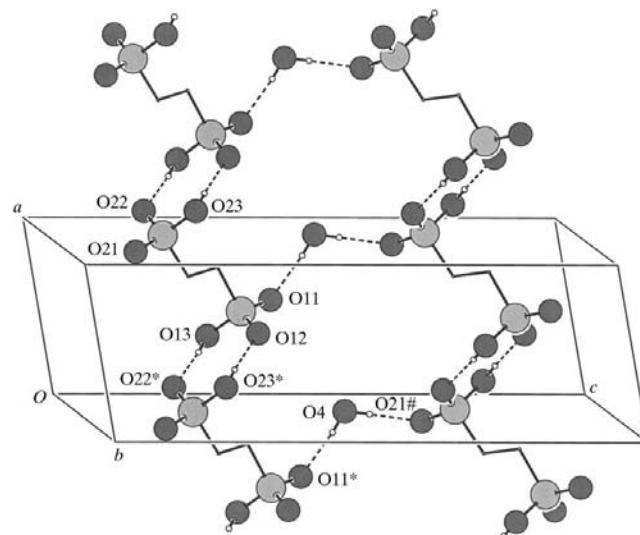


Figure 5
Part of the crystal structure of (2), showing the combination of $C(7)[R_2^2(8)]$ anion chains parallel to $[100]$ and $C_2^2(9)$ anion/water chains parallel to $[001]$ forming a (010) sheet built from $R_6^6(26)$ rings. For the sake of clarity H atoms bonded to C are omitted. Atoms marked with a star (*) or hash (#) are at the symmetry positions $-1+x, y, z$ and $-1+x, \frac{1}{2}-y, \frac{1}{2}+z$, respectively.

Table 3
Selected geometric parameters (Å, °).

(a) Cation geometries					
(1)					
N1—C2	1.487 (4)	N1—C3	1.482 (4)		
C2—C3 ⁱ	1.510 (5)				
(2)					
N11—C12	1.491 (2)	N21—C22	1.495 (2)		
N11—C16	1.494 (2)	N21—C26	1.486 (2)		
C12—C13—C14—C17	−178.9 (2)	C17—C18—C19—C24	−177.0 (2)		
C13—C14—C17—C18	171.7 (2)	C18—C19—C24—C25	177.8 (2)		
C14—C17—C18—C19	−175.6 (2)	C19—C24—C25—C26	174.6 (2)		
C15—C14—C17—C18	−66.4 (2)	C18—C19—C24—C23	−60.2 (2)		
(b) Anion geometries					
(1)					
P1—O1	1.504 (2)	P1—O11	1.508 (2)	P2—O21	1.511 (2)
P1—O2	1.514 (2)	P1—O12	1.519 (2)	P2—O22	1.507 (2)
P1—O3	1.575 (2)	P1—O13	1.571 (2)	P2—O23	1.586 (2)
P1—C1	1.802 (3)	P1—C1	1.809 (2)	P2—C2	1.806 (2)
C1—C1 ⁱⁱ	1.531 (6)	C1—C2	1.529 (3)		
(2)					
C1—P1—O1	109.0 (2)	C1—P1—O11	108.62 (8)	C2—P2—O21	106.51 (8)
C1—P1—O2	108.3 (2)	C1—P1—O12	107.92 (8)	C2—P2—O22	110.12 (8)
C1—P1—O3	105.4 (2)	C1—P1—O13	105.87 (8)	C2—P2—O23	105.50 (8)
O1—P1—O2	115.8 (2)	O11—P1—O12	114.59 (8)	O21—P2—O22	116.20 (8)
O2—P1—O3	106.4 (2)	O12—P1—O13	110.17 (7)	O22—P2—O23	110.58 (7)
O3—P1—O1	111.4 (2)	O13—P1—O11	109.30 (8)	O23—P2—O21	107.33 (8)
C1 ⁱⁱⁱ —C1—P1	113.7 (3)	C2—C1—P1	111.4 (2)	C1—C2—P2	116.2 (2)
C1 ⁱⁱⁱ —C1—P1—O1	178.9 (3)	C2—C1—P1—O11	−177.7 (8)	C1—C2—P2—O21	179.6 (2)
C1 ⁱⁱⁱ —C1—P1—O2	52.1 (4)	C2—C1—P1—O12	−52.9 (2)	C1—C2—P2—O22	52.8 (2)
C1 ⁱⁱⁱ —C1—P1—O3	−61.4 (4)	C2—C1—P1—O13	65.0 (2)	C1—C2—P2—O23	−66.5 (2)
		P1—C1—C2—P2	179.5 (2)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, -z$.

as a donor to O12 at (x, y, z) (Table 2). In this manner a $C(7)[R_2^2(8)]$ chain of rings running parallel to $[100]$ is generated by translation (Fig. 5). The conformation of the anion (Table 3, Fig. 2) is almost centrosymmetric, with the reference anion centred at approximately $(0.75, 0.25, 0.30)$, and the $R_2^2(8)$ rings are similarly almost centrosymmetric about $(n + 0.25, 0.25, 0.30)$ ($n = \text{zero or an integer}$). However, a search for possible additional symmetry showed that none was present and, indeed, the disposition of the water molecules alongside the anion chains effectively precludes this (Fig. 5). Four such chains run through each unit cell along the approximate lines $(x, 0.25, 0.30)$, $(x, 0.25, 0.80)$, $(x, 0.75, 0.20)$ and $(x, 0.75, 0.70)$, and the chains are linked into a single continuum by means of the water molecules. In total, six different O—H...O hydrogen bonds are involved in these links, utilizing all the donor capacity of the three independent water molecules.

The linking of the chains can itself be considered in two steps: the water molecules containing O4 link the $[100]$ chains into (010) sheets, and the water molecules containing O3 and O5 then together link the sheets into a three-dimensional framework. Atom O11 in the anion at (x, y, z) is an acceptor of an O—H...O hydrogen bond, *via* H41, from O4 at $(1+x, y, z)$: at the same time, O21 in the anion at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ accepts a hydrogen bond from the same water molecule, *via* H42. O11 in the anion at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ accepts

a hydrogen bond from O4 at $(1-x, \frac{1}{2}-y, \frac{1}{2}+z)$, as does O21 in the anion at $(x, y, 1+z)$. These hydrogen bonds give rise to a $C_2^2(9)$ chain, generated by the action of the glide plane and running parallel to the $[001]$ direction (Fig. 5). The combination of the $[100]$ anion chains and the anion/water chains along $[001]$ produces sheets parallel to (010) built from a single type of $R_6^6(12)$ ring (Fig. 5): two of these sheets pass through each unit cell, one in the domain $0 < y < \frac{1}{2}$ and the other in the domain $\frac{1}{2} < y < 1.0$.

Neighbouring sheets are linked by a very simple cyclic motif involving the O3 and O5 water molecules. Within the asymmetric unit (Fig. 2) O5 is a hydrogen-bond donor, *via* H51, to O3, which is itself a donor, *via* H32 to O11: O5 at (x, y, z) is also a donor, *via* H52, to O11 at $(1-x, -y, 1-z)$, thus producing an $R_6^6(12)$ ring (Fig. 6) which is centrosymmetric and almost planar. The anion at (x, y, z) is a component of the sheet in the domain $0 < y < \frac{1}{2}$ and the anion at $(1-x, -y, 1-z)$ is a component of the sheet in the domain $-\frac{1}{2} < y < 0$. Hence, these $R_6^6(12)$ rings link adjacent sheets, thus producing a continuous three-dimensional framework. An alternative view of the frame-

work is in terms of centrosymmetric $R_{14}^{12}(48)$ rings (Fig. 7) linked by $R_6^6(12)$ rings into (100) sheets and by $[100]$ chains.

The anion/water framework encapsulates large cavities, centred at the origin and at the A-face centres, which together represent *ca* 58% of the unit-cell volume: for comparison, the framework contains only half of the non-H atoms in the cell and less than 40% of all the atoms. These cavities are occupied by pairs of cations, each linked to the framework by four N—H...O hydrogen bonds and related to one another by centres of inversion: these cations thus serve to cross-brace the anion/water framework. Overall the structure contains no additional solvent-accessible void space.

3.2.3. General comments on the supramolecular structures. The substructure approach which has proven so fruitful in the descriptive analysis of other multicomponent structures (Gregson *et al.*, 2000; Glidewell *et al.*, 2000) has demonstrated the occurrence of a pillared-layer framework in (1). While this architecture is reasonably familiar in inorganic systems such as synthetic aluminosilicates, it is less common in organic materials. Nonetheless, several examples have recently been reported: for example, in piperazine–squaric acid–water (1/1/2), the squarate anions $[C_4O_4]^{2-}$ and the water molecules form hydrogen-bonded sheets built from $R_8^6(24)$ rings, and these sheets are linked by $[H_2N(CH_2CH_2)_2NH_2]^{2+}$ cations (MacLean *et al.*, 1999). Similarly in *meso*-5,5,7,12,12,14-

hexamethyl-1,4,8,11-tetraazacyclotetradecane-3,5-dihydroxybenzoic acid (1/2) the dihydroxybenzoate anions $[(\text{HO})_2\text{C}_6\text{H}_3\text{COO}]^-$ are linked into sheets containing alternating $R_2^2(14)$ and $R_6^4(30)$ rings, which are then linked by $[\text{C}_{16}\text{H}_{38}\text{N}_4]^{2+}$ cations, while in *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,4'-biphenol (1/3), neutral and anionic biphenol units form sheets, this time built from $R_8^6(70)$ rings, again linked by $[\text{C}_{16}\text{H}_{38}\text{N}_4]^{2+}$ cations (Gregson *et al.*, 2000).

In (2) the apparent complexity of the three-dimensional hydrogen bonding, involving no fewer than 12 distinct interactions (Table 2), can again be rather easily resolved using the substructure approach with the initial identification of a one-dimensional motif comprising a single molecular component, and building from this in steps towards the overall architecture. Some particularly elegant inorganic examples of the use of such an approach have recently been reported (Haile & Wuensch, 2000*a,b*). The two framework structures observed for (1) and (2) are radically different, not only from one another, but also from the framework structure found in the related adduct ethane-1,2-diphosphonic acid-4,4'-bipyridyl-water (1/1/2). In this compound each of the individual components forms a one-component, one-dimensional substructure and there are also two distinct two-component, two-dimensional substructures, which together all build the overall three-component, three-dimensional structure (Glidewell *et al.*, 2000).

3.3. Hydrogen-bond dimensions

In all of the hydrogen bonds (Table 2), the acceptor is O: all have $D\cdots A$ distances which are short for their types: in addition, with the sole exception of the O5—H51 \cdots O3 hydrogen bond in (2), all of the $D\cdots H\cdots A$ angles are greater than 165° .

The O—H \cdots O hydrogen bonds can be divided into three distinct categories. The anion \cdots anion hydrogen bonds have O \cdots O distances in the range 2.562 (3) Å in (1) to 2.598 (2) Å in (2), with a mean value of 2.576 Å; in the water \cdots anion hydrogen bonds in (2), the O \cdots O distances range from 2.665 (2) to 2.802 (4) Å with mean value 2.741 Å; the two water \cdots water hydrogen bonds in (2) have O \cdots O distances

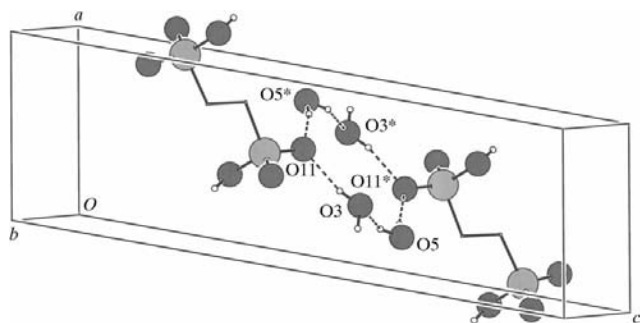


Figure 6
Part of the crystal structure of (2), showing one of the $R_6^4(12)$ rings linking adjacent (010) sheets. For the sake of clarity H atoms bonded to C are omitted. Atoms marked with a star (*) are at the symmetry position $1 - x, -y, 1 - z$.

2.813 (4) and 2.816 (3) Å. It is noteworthy that the ranges of these three types do not overlap. The N—H \cdots O hydrogen bonds, likewise, can be divided into two categories. The cation \cdots anion interactions where both components are charged all have very short N \cdots O distances, 2.635 (3)–2.735 (3) Å with mean 2.698 Å, while the cation \cdots water hydrogen bonds have N \cdots O distances 2.740 (3) and 2.800 (2) Å; again these types are separable in terms of their N \cdots O ranges. The pattern of the $D\cdots A$ distances in both the O—H \cdots O and the N—H \cdots O hydrogen bonds nicely conforms to the expectation (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994) that charged components will give short strong hydrogen bonds. With the exception of the outlier O5—H51 \cdots O3 interaction in (2), the pattern of the $D\cdots A$ distances closely follows that of the H $\cdots A$ distances, reflecting the near-linearity of the hydrogen bonds.

3.4. Molecular conformations and dimensions

The cations in (1) are centrosymmetric and thus are constrained to adopt the chair conformation (Fig. 1). The rings in the cation of (2) also adopt chair conformations with the $-(\text{CH}_2)_3-$ spacer unit occupying an equatorial site in each ring: this spacer unit has the usual extended-chain conformation. Indeed, there is a long sequence of C—C—C—C torsional angles of *ca* 180° defining a chain-extended sequence from C12 to C26 (Fig. 2; Table 3). The torsional angles C15—C14—C17—C18 and C18—C19—C24—C23, which define the location of the rings relative to this extended chain, have similar magnitudes and the same sign, so that the cation has approximately C_2 symmetry.

The anions in (1) are also centrosymmetric with the P—O(H) bond synclinal to C—C: precisely the same centro-

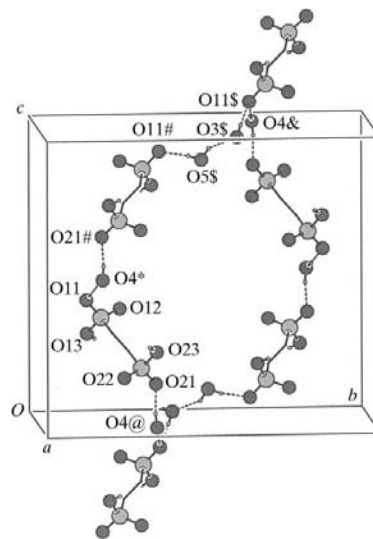


Figure 7
Part of the crystal structure of (2), showing one of the $R_{14}^{12}(48)$ rings bounding the cavities in the anion/water framework. For the sake of clarity H atoms bonded to C are omitted. Atoms marked with a star (*), hash (#), dollar (\$), at (@) or ampersand (&) signs are at the symmetry positions $1 + x, y, z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$; $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; $1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; $-x, \frac{1}{2} + y, \frac{3}{2} - z$, respectively.

symmetric conformation was observed in the salt formed with 4,4'-bipyridyl (Glidewell *et al.*, 2000). Although the anions in (2) lie in general positions, their conformation is close to centrosymmetric (Table 3). In particular, the P—C—C—P torsional angle is close to 180°, and the two independent P—O(H) bonds are synclinal to C—C and *trans* to one another: the corresponding C—C—P—O torsional angles for the two phosphonate groups have similar magnitudes, but opposite signs.

The P—O distances fall into two groups according to if the O does or does not carry a proton: the values observed here (Table 1) are comparable with those found in the salt formed with 4,4'-bipyridyl, P—O(H), 1.573 (2) Å and PO₂⁻, 1.509 (2) and 1.522 (2) Å. In the neutral acid (Peterson *et al.*, 1977) the P—O(H) distances are 1.543 (2) and 1.533 (2) Å, and the P=O distance is 1.501 (2) Å. Very similar values are found both in methylenediphosphonic acid (Peterson *et al.*, 1977) and in propane-1,3-diphosphonic acid (Gebert *et al.*, 1977). All of the P—O bonds in the ethane-1,2-diphosphonate anion are thus longer than the corresponding bonds in ethane-1,2-diphosphonic acid.

4. Concluding comments

The three framework structures formed by ethane-1,2-diphosphonic acid with the two bis-secondary amines reported here, and with 4,4'-bipyridyl, reported earlier, are all dominated by the hydrogen-bonding properties of the anion [(HO)P(O)₂CH₂CH₂P(O)₂(OH)]²⁻, which is either strictly or approximately centrosymmetric in all these compounds. This suggests that rather different supramolecular architectures must be expected in the corresponding adducts formed by these amines with either methanediphosphonic acid or propane-1,3-diphosphonic acid, since on both acids the tetrahedral geometry at the central C atom necessarily imposes a different molecular shape. Moreover, the structural versatility of the diphosphonate anion manifested in the present series of compounds indicates that further novel structure types are to be expected in organic salts formed from tri- and tetraphosphonic acids.

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