

# A structural hierarchy in the hydrogen-bonded adduct ethane-1,2-diphosphonic acid–4,4'-bipyridyl–water (1/1/2): an *N*-component *N*-dimensional structure (*N* = 3) with substructures having *N* = 1 and 2

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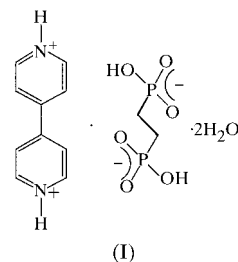
The title compound, 4,4'-bipyridinium ethane-1,2-diyl-1,2-diphosphonate dihydrate, is a hydrated salt,  $C_{10}H_{10}N_2^{2+} \cdot C_2H_6O_6P_2^{2-} \cdot 2H_2O$ , in which the components are linked by extensive hydrogen bonding. The cations and anions lie on inversion centres and with the water molecules each form separate one-component one-dimensional chains along [100]: the anions and the water molecules form a two-component two-dimensional substructure, (001) sheets, while the cations and anions form a second two-component two-dimensional substructure, (011) sheets. All three components combine to form a three-dimensional framework.

## Comment

Phenylphosphonic acid,  $PhPO(OH)_2$ , 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, so forming the anion  $[PhPO_2(OH)]^-$ : 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 investigated the bisphosphonic acid ethane-1,2-diphosphonic acid,  $(HO)_2P(O)CH_2CH_2P(O)(OH)_2$ , and we report here the structure of the hydrated 1:1 adduct formed with 4,4'-bipyridyl, (I). The structure of (I) consists of a three-dimensional hydrogen-bonded framework, which can be most conveniently described by means of the substructure approach (Gregson *et al.*, 2000).

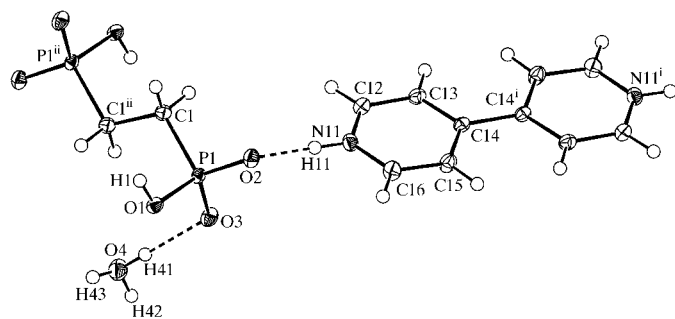
It is possible to identify in the three-dimensional structure of (I) three distinct one-component one-dimensional substructures and two distinct two-component two-dimensional substructures.



The constitution of the adduct (I) is that of a salt  $HNC_5H_4C_5H_4NH_2^{2+} \cdot (HO)PO_2CH_2CH_2PO_2(OH)^{2-} \cdot 2H_2O$ : the cation and anion both lie across centres of inversion, so that the asymmetric unit consists of one half of each ion, together with one water molecule. In the water molecule, one of the H atoms is disordered over two sites having equal occupancy, but all the other H atoms in (I) are fully ordered (Fig. 1). Each of the individual molecular components forms chains running parallel to the [100] direction. The anions form molecular ladders in which *C*(4) hydrogen-bonded chains form the uprights and the *P*–*C*–*C*–*P* backbones of the anions form the treads: O1 at (*x*, *y*, *z*) acts as hydrogen-bond donor to O3 at (*1* + *x*, *y*, *z*), while the symmetry-related O1 in the same anion, which is at (*2* – *x*, –*y*, *1* – *z*) acts as donor to O3 at (*1* – *x*, –*y*, *1* – *z*). In this manner, a ladder is formed in which the anions centred at (*n*, 0,  $\frac{1}{2}$ ) (*n* = zero or integer) enclose  $R_2^2(14)$  rings centred at (*n* +  $\frac{1}{2}$ , 0,  $\frac{1}{2}$ ) (*n* = zero or integer) (Fig. 2).

A second [100] chain is formed by the water molecules (Fig. 2): the half-occupancy H atoms H42 and H43 at (*x*, *y*, *z*) form hydrogen bonds with the water O4 atoms at (*1* – *x*, –*1* – *y*, *1* – *z*) and (*2* – *x*, –*1* – *y*, *1* – *z*), respectively, so forming a series of  $R_2^2(4)$  rings centred at (*n* +  $\frac{1}{2}$ , – $\frac{1}{2}$ ,  $\frac{1}{2}$ ) and (*n*, – $\frac{1}{2}$ ,  $\frac{1}{2}$ ), respectively (*n* = zero or integer). Similar continuous chains of partially disordered water molecules have been observed also in *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–terephthalic acid–water (1/1/4) (Lough *et al.*, 2000).

It may be assumed that at the local level only, one of the H sites between each pair of O atoms is occupied at any instant:



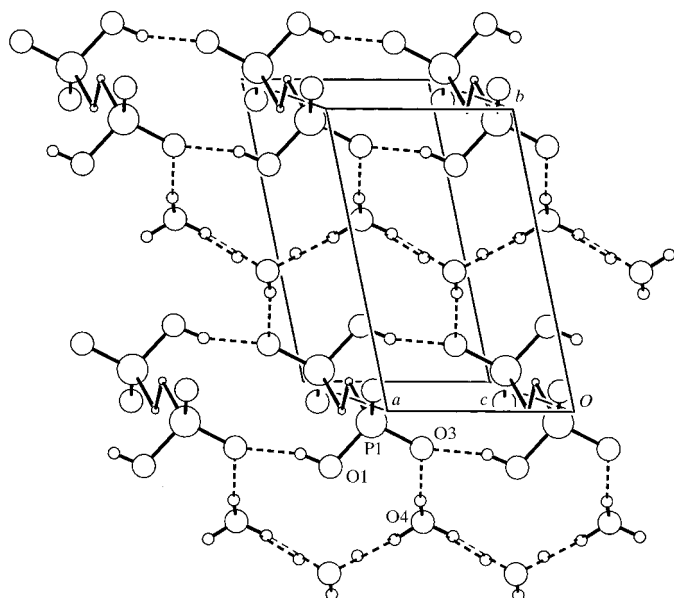
**Figure 1**

The molecular components of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms H42 and H43 each have a site-occupation factor of 0.5. Symmetry codes are the same as those given in Table 1.

simultaneous occupation of both would not only disrupt the hydrogen bonding, but would require the two H atoms concerned to be within covalent bonding distance of one another. Instantaneous occupation of either H-atom site between a given pair of O atoms thus precludes occupation of the other. If it is further assumed that the O atom in each water molecule forms, at any time, two and only two covalent bonds, then occupation of any one of the disordered sites within a particular chain necessarily defines the occupancy (unity or zero) of all other such sites within that chain. Hence, on this basis, the 0.5 occupancy modelled from the X-ray diffraction data can be regarded as resulting from spacial averaging of the H-atom site occupancy. It is also possible that there is temporal averaging: if the potential energy function describing the motion of a single H atom along the line between a pair of water O atoms exhibits two well defined equivalent minima, separated by a barrier insufficiently high to prevent tunnelling, then temporal averaging of the H-atom sites will again reproduce the observed 0.5 occupancy. Both spacial and temporal averaging mechanisms may be operating concurrently: in any event, at the local level, the centres of inversion embedded within these chains must be a reflection of the overall averaging process.

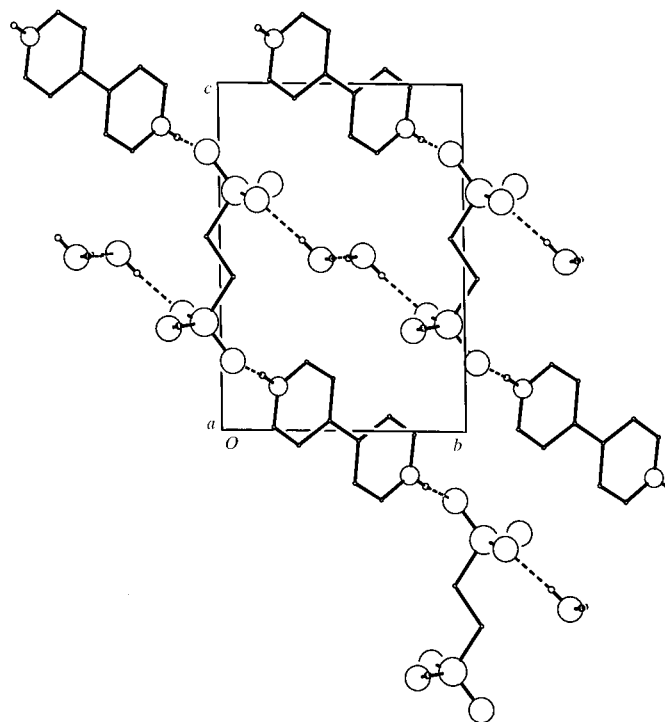
These two components, the anions and the water molecules, thus independently generate strings parallel to the [100] direction and alternating along the [010] direction: the anion ladders run along the lines  $(x, n, \frac{1}{2})$  ( $n = \text{zero or integer}$ ) while the water chains run along  $(x, n + \frac{1}{2}, \frac{1}{2})$ .

The third one-dimensional substructure is formed by the cations: aromatic  $\pi \cdots \pi$  stacking interactions between adjacent cations generate a third type of [100] chain. The pyridine ring at  $(x, y, z)$ , part of the cation centred at  $(0, \frac{1}{2}, 0)$ , interacts with that at  $(1 - x, 1 - y, -z)$  which is part of the cation centred at  $(1, \frac{1}{2}, 0)$ : the perpendicular spacing between



**Figure 2**

Part of the crystal structure of (I) showing the cation-free (001) net built from anion ladders and water chains.



**Figure 3**

Part of the crystal structure of (I) in projection along the  $a$  direction showing the formation of the three-dimensional framework from the two-component (001) and (011) sheets.

neighbouring rings is  $3.467(4) \text{ \AA}$  and the centroid offset is  $1.055(4) \text{ \AA}$ . Propagation of these interactions by the action of the inversion centres means that each cation forms  $\pi \cdots \pi$  stacking interactions with its two neighbours along [100].

Two distinct two-component, two-dimensional substructures can be identified, resulting from two distinct pairwise combinations of the one-dimensional chains. The anion chains, uniquely, are directly linked to both of the other types of chain. The chains built from anions and from water molecules are linked by further  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds to form cation-free sheets parallel to (001) built from  $R_5^4(12)$  and  $R_2^2(14)$  rings (Fig. 2). Atom O4 at  $(x, y, z)$  acts as hydrogen-bond donor, *via* the fully ordered H41 to O3 also at  $(x, y, z)$ , and propagation of this interaction by means of the centres of inversion links together the water and anion chains into a cation-free two-dimensional substructure. This sheet lies in the domain  $0.20 < z < 0.80$ , while the cation stacks lie in the domain  $-0.28 < z < 0.28$  when H atoms are included, or  $-0.20 < z < 0.20$  when H atoms are excluded. A second two-component sheet is built from the cations and anions: the cation centred at  $(0, \frac{1}{2}, 0)$  is directly linked to the two anions centred at  $(1, 0, \frac{1}{2})$  and  $(-1, 1, -\frac{1}{2})$ , which form parts of two distinct anion ladders. In this manner, purely ionic sheets are formed parallel to (011) (Fig. 3).

The formation of the single three-dimensional framework can be regarded either as the linking of the cation-free (001) sheets by the cations, or as the linking of the purely ionic (011) sheets by the water molecules (Fig. 3). Thus N11 at  $(x, y, z)$  is donor to O2 also at  $(x, y, z)$ , a component of the sheet centred

at  $z = \frac{1}{2}$ : the symmetry-related N11 in the same cation, which is centred at  $(0, \frac{1}{2}, 0)$ , acts as donor to O2 at  $(-x, 1 - y, -z)$ , a component of the sheet centred at  $z = -\frac{1}{2}$ . Again propagation of this interaction by the centres of inversion links each (001) sheet to its two immediate neighbours, thus generating a single three-dimensional framework. The connections between neighbouring (001) sheets are further reinforced by C—H $\cdots$ O hydrogen bonds in which the donors are C12 and C16, the two C atoms adjacent to the protonated N: C12—H12 and C16—H16 are thus expected to be the most acidic C—H bonds in the structure. C12 at  $(x, y, z)$  is donor to O4 at  $(1 - x, -y, 1 - z)$ , a component of the  $z = \frac{1}{2}$  sheet, while C16 at  $(x, y, z)$  is donor to O2 at  $(2 - x, -y, -z)$ , a component of the  $z = -\frac{1}{2}$  sheet.

The N—H $\cdots$ O hydrogen bond involving cationic N and anionic O is particularly short for its type: of the O—H $\cdots$ O hydrogen bonds, the shortest by far is that between anions. These two hydrogen bonds are thus expected to be particularly strong, although none of the hydrogen bonds in this structure can be classified as weak. Not only are the  $D\cdots A$  distances all short or very short for their types, but the  $D—H\cdots A$  angles all exceed  $160^\circ$  (Table 2).

There are no examples of the  $[(\text{HO})\text{PO}_2\text{CH}_2\text{CH}_2\text{PO}_2(\text{OH})]^{2-}$  anion recorded in the Cambridge Structural Database (Allen & Kennard, 1993): however, the structure of the parent acid  $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$  has been reported (Peterson *et al.*, 1977). The presence of the centre of inversion in the anion means that the P—C—C—P backbone necessarily has a *trans* planar conformation, but there are no symmetry constraints on the orientation of the  $\text{PO}_2(\text{OH})$  fragment. This group in fact exhibits a slight rotation from perfect staggering with the adjacent  $\text{CH}_2$  group, with one of the anionic O atoms antiperiplanar to the C—C bond (Table 1). In the parent acid, also centrosymmetric, one of the hydroxyl groups is antiperiplanar to C—C. The P—O bond lengths in the anion show a clear distinction between the P—O(H) bond and those in the  $\text{PO}_2^-$  group (Table 1). Within the  $\text{PO}_2^-$  fragment, the O—P—O angle is significantly larger than tetrahedral: this may be compared with similar wide angles in the O—S—O unit in sulfones and in the  $\text{CO}_2^-$  unit in carboxylate anions. In all these systems, there is a significant net negative charge on the paired O atoms. The other bond lengths and angles within the anion have values similar to those in the neutral parent acid (Peterson *et al.*, 1977). In the cation, the C—N—C angle is greater than  $120^\circ$ , as typically found in protonated pyridines, whereas in unprotonated pyridines, this angle is generally significantly less than  $120^\circ$ : the other internal dimensions of the cation are unexceptional.

## Experimental

Equimolar quantities of ethane-1,2-diphosphonic acid and of 4,4'-bipyridyl were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, exposed to air, producing analytically pure crystals of the adduct (I). Analysis: found C 37.8, H 5.6, N 7.1%;  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_8\text{P}_2$  requires C 37.7, H 5.5, N 7.3%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

## Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_2^{2+}\cdot\text{C}_2\text{H}_6\text{O}_6\text{P}_2^{2-}\cdot 2\text{H}_2\text{O}$   
 $M_r = 382.24$   
 Triclinic,  $P\bar{1}$   
 $a = 4.8297$  (2) Å  
 $b = 7.9967$  (5) Å  
 $c = 11.0644$  (6) Å  
 $\alpha = 89.022$  (3) $^\circ$   
 $\beta = 80.294$  (3) $^\circ$   
 $\gamma = 78.500$  (3) $^\circ$   
 $V = 412.69$  (4) Å $^3$

$Z = 1$   
 $D_x = 1.538$  Mg m $^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 7018 reflections  
 $\theta = 3.2\text{--}30.0^\circ$   
 $\mu = 0.308$  mm $^{-1}$   
 $T = 100$  (1) K  
 Needle, pale yellow  
 $0.28 \times 0.12 \times 0.08$  mm

## Data collection

KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan  
 (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.919$ ,  $T_{\text{max}} = 0.976$   
 7018 measured reflections  
 2364 independent reflections

1893 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 30^\circ$   
 $h = 0 \rightarrow 6$   
 $k = -10 \rightarrow 11$   
 $l = -15 \rightarrow 15$   
 Intensity decay: negligible

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.125$   
 $S = 1.100$   
 2364 reflections  
 121 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.3686P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.36$  e Å $^{-3}$   
 $\Delta\rho_{\text{min}} = -0.56$  e Å $^{-3}$

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

N11—C12	1.334 (3)	C14—C14 <sup>i</sup>	1.494 (4)
C12—C13	1.383 (3)	P1—O1	1.573 (2)
C13—C14	1.395 (3)	P1—O2	1.522 (2)
C14—C15	1.397 (3)	P1—O3	1.509 (2)
C15—C16	1.381 (3)	P1—C1	1.798 (2)
C16—N11	1.335 (3)	C1—C1 <sup>ii</sup>	1.537 (4)
C12—N11—C16	120.8 (2)	C1 <sup>ii</sup> —C1—P1	113.2 (2)
O1—P1—O2	109.46 (8)	O1—P1—C1	105.83 (9)
O2—P1—O3	114.98 (9)	O2—P1—C1	108.97 (9)
O3—P1—O1	106.53 (8)	O3—P1—C1	110.65 (9)
O1—P1—C1—C1 <sup>ii</sup>	−57.8 (2)	O3—P1—C1—C1 <sup>ii</sup>	57.2 (2)
O2—P1—C1—C1 <sup>ii</sup>	−175.5 (2)		

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

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N11—H11 $\cdots$ O2	0.88	1.65	2.528 (2)	173
O1—H1 $\cdots$ O3 <sup>i</sup>	0.84	1.73	2.536 (2)	160
O4—H41 $\cdots$ O3	0.86	1.92	2.783 (2)	173
O4—H42 $\cdots$ O4 <sup>ii</sup>	0.86	1.89	2.749 (3)	174
O4—H43 $\cdots$ O4 <sup>iii</sup>	0.86	1.92	2.778 (3)	174
C12—H12 $\cdots$ O4 <sup>iv</sup>	0.95	2.34	3.273 (3)	166
C16—H16 $\cdots$ O2 <sup>v</sup>	0.95	2.50	3.440 (3)	168

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

Compound (I) crystallized in the triclinic system; space group  $P\bar{1}$  was assumed and confirmed by the analysis. H atoms were treated as riding atoms with C—H 0.95 and 0.99, N—H 0.88 and hydroxy

O—H 0.82 Å. It was apparent from difference maps that one of the water H atoms was disordered over two sites with equal occupancy and the three water H atoms (H41, H42, H43) were included in the refinement with a *DFIX* free-variable restraint [which refined to 0.86 (2) Å] for the three O—H distances. Examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1999); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1384). Services for accessing these data are described at the back of the journal.

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