

Ethene-*trans*-1,2-bis(4-pyridinium) Dihydrogenphosphite and Dihydrogenphosphate Compounds Exhibiting Cooperative and Directed Hydrogen Bonds between Cations and Anions: $\text{H}_2\text{bpe}(\text{H}_2\text{PO}_3)_2$ and $\text{H}_2\text{bpe}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

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$\text{H}_2\text{bpe}(\text{H}_2\text{PO}_3)_2$ (**1**) and $\text{H}_2\text{bpe}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (**2**) (H_2bpe = ethene-*trans*-1,2-bis(4-pyridinium), H_2PO_3^- = dihydrogenphosphite, and H_2PO_4^- = dihydrogenphosphate) have been prepared and structurally characterized. In compound **1**, the dihydrogenphosphite anions form dimers, with a P...P distance of 4.2073(7) Å, by two O–H...H hydrogen bonds, and the dimeric dihydrogenphosphite units interact with the H_2bpe cations by way of N–H...O and O–H...O hydrogen bonds, resulting in a one-dimensional chain. The chains are held together by C–H...O interactions. In compound **2**, the phosphate ions are connected by O–H...O hydrogen bonds into an unusual 2D square grid-type framework with P...P separations ranging from 4.7533(7) to 4.9506(8) Å. The H_2bpe cations crosslink the dihydrogen phosphate layers by N–H...O hydrogen bonds, forming a three-dimensional supramolecular network with channels. The water molecules in compound **2** occupy these channels and make O–H...O bonds to adjacent phosphate O atoms and also O–H...O bonds to the next water O atom in the channel.

Key words: Dihydrogenphosphites, Dihydrogenphosphates, Ethene-*trans*-1,2-bis(4-pyridinium) Cations, Hydrogen Bonds, Crystal Structure

Introduction

In the formation of organic-templated phosphates, protonated organic amines play an important role. For example, they act as structure-directing agents, usually occupying the available voids or channels, and stabilize the structure *via* hydrogen bonding and other intermolecular interactions [1–4]. Furthermore, the organic amine acts as a ligand to metal ions and it has been shown that the number of amino groups has significant effects on these materials and the use of diamines, triamines or tetramines seems to be more effective than that of monoamines [5–8]. Sometimes, organic ammonium phosphates are formed as intermediates or by-products in the synthesis of organic-templated metal phosphates [9–11]. They exhibit interesting crystal packing motifs strongly influenced by N–H...O and O–H...O hydrogen bonds [12–16]. In some cases, hydrogen bonding results in a three-dimensional supramolecular array of phosphate ions

and the organic ammonium cations are encapsulated in the channels of the framework [17, 18].

As a part of our work on the preparation and structural characterization of organic ammonium phosphates, in this paper, we report the characterization and structures of two ionic compounds of the ethene-*trans*-1,2-bis(4-pyridinium) dication (H_2bpe) with dihydrogenphosphite and dihydrogenphosphate anions, namely $\text{H}_2\text{bpe}(\text{H}_2\text{PO}_3)_2$ (**1**) and $\text{H}_2\text{bpe}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (**2**).

Results and Discussion

Description of the crystal structures

The structure of **1** is built up from $[\text{H}_2\text{PO}_3]^-$ dihydrogenphosphite anions and ethene-*trans*-1,2-bis(4-pyridinium) cations. The latter species is generated from the asymmetric unit by inversion symmetry (Fig. 1). Selected geometrical data are presented in Table 1. The $[\text{H}_2\text{PO}_3]^-$ moiety adopts its usual pseudo-

Table 1. Selected bond lengths and angles, and hydrogen bonding geometry of **1**^a.

<i>Bond lengths (Å) and angles (°)</i>				
P1–O1	1.4976 (13)	O1–P1–O2	116.45 (8)	
P1–O2	1.5026 (13)	O1–P1–O3	111.14 (7)	
P1–O3	1.5725 (14)	O2–P1–O3	108.10 (7)	
P1–H1	1.3200			
<i>Hydrogen bonds</i>				
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O3–H2...O1 ⁱ	0.83 (2)	1.71 (2)	2.5361 (19)	177 (2)
N1–H3...O2 ⁱⁱ	0.92 (2)	1.66 (2)	2.5703 (18)	175 (19)
C4–H4...O1 ⁱⁱⁱ	0.95	2.28	3.227 (2)	177
C5–H5...O3 ^{iv}	0.95	2.42	3.319 (2)	158
C6–H6...O1 ^v	0.95	2.35	3.296 (2)	177

^a Symmetry operations: ⁱ $1-x, 1-y, -z$; ⁱⁱ $x-1, y, z$; ⁱⁱⁱ $x, 1/2-y, 1/2+z$; ^{iv} $-x, y-1/2, 1/2-z$; ^v $1-x, 1/2+y, 1/2-z$.

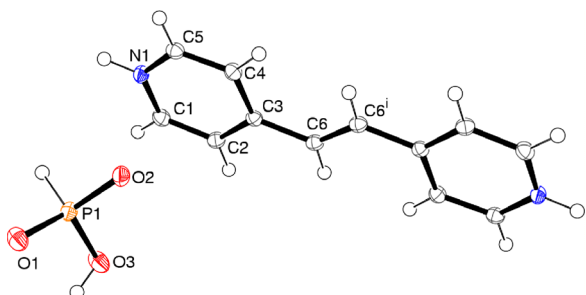


Fig. 1. A view of the asymmetric unit of **1** in the crystal, showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Symmetry code: $1-x, 1-y, 1-z$.

pyramidal geometry, and the P–O bond lengths and angles are normal [mean P–O = 1.524(2) Å]. As expected, the protonated P1–O3 link is significantly longer than the unprotonated bonds.

As well as by electrostatic and van der Waals forces, the components in **1** interact by way of N–H...O and O–H...O hydrogen bonds to result in a crystal structure with strong one-dimensional character. The anions are self assembled into dimers [P1...P1ⁱ = 4.2073(7) Å], linked by two O3–H2...O1ⁱ (see Table 1 for symmetry codes) hydrogen bonds (Fig. 2). Then, the cations form N–H...O bonds to result in a chain of alternating ([H₂PO₃][−])₂ dimers and [C₁₂H₁₄N₂]²⁺ cations that propagates in [201]. The unit-cell packing diagram in Fig. 2 shows that the chain orientations alternate between [201] and [20 $\bar{1}$] with respect to the *b* direction resulting in a pseudo layered structure. Along with the conventional hydrogen bonds, there are also some very short, nearly linear C–H...O interactions (Table 1), which may provide some additional crosslinking in [010] between the pseudo-layers. Any π ... π stacking interactions in **1** must be

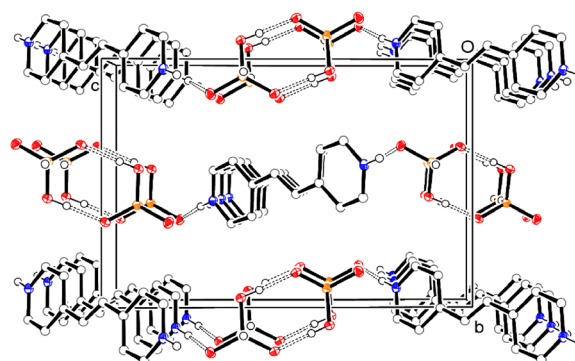
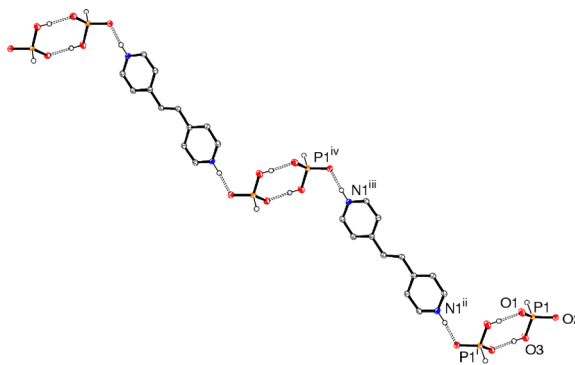


Fig. 2. Top: Interaction of the cations and anions via N–H...O and O–H...O hydrogen bonds, generating a one-dimensional chain of **1**. Symmetry codes (i) = $1-x, 1-y, -z$, (ii) = $-x, 1-y, -z$, (iii) = $x-1, y, z-1$ and (iv) = $x-2, y, z-1$. Bottom: Packing diagram of **1** viewed along the *a* axis. All C–H hydrogen atoms have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

very weak, with a minimum ring-centroid separation of 4.67 Å.

The structure of **2** contains hydrogenphosphate anions, ethene-*trans*-1,2-bis(4-pyridinium) cations and water molecules. As with **1**, the complete dication is generated by inversion symmetry (Fig. 3). Table 2 gives selected geometrical data. The [H₂PO₄][−] group is normal, with the two P–OH vertices showing the expected lengthening relative to the P–O bonds which have formal partial double bond character [mean P–O = 1.538(2) Å].

Again, hydrogen bonds appear to play a key role in establishing the crystal packing in **2**. Both P–OH vertices participate in H bonds to nearby anions to result (Fig. 4) in an unprecedented square network of phosphate ions. The graph theory notation [19] for this configuration is an $R^4_4(16)$ loop, and the nodal P atom

Table 2. Selected bond lengths and angles, and hydrogen bonding geometry of **2**^a.

<i>Bond lengths (Å) and angles (°)</i>				
P1–O1	1.4963 (14)	O1–P1–O2	116.64 (8)	
P1–O2	1.5168 (14)	O1–P1–O3	112.10 (9)	
P1–O3	1.5660 (15)	O2–P1–O3	105.25 (8)	
P1–O4	1.5707 (16)	O1–P1–O4	106.02 (8)	
		O2–P1–O4	109.76 (8)	
		O3–P1–O4	106.71 (9)	
<i>Hydrogen bonds</i>				
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O5–H4...O1	0.94	1.98	2.894 (2)	164
O3–H1...O2 ⁱ	0.82 (3)	1.76 (3)	2.576 (2)	176 (3)
O4–H2...O1 ⁱⁱ	0.86 (3)	1.75 (3)	2.586 (2)	164 (3)
O5–H5...O5 ⁱⁱⁱ	0.97	1.89	2.862 (4)	173
O5–H6...O5 ^{iv}	1.06	1.71	2.774 (3)	175
N1–H3...O2 ^v	0.93 (2)	1.72 (3)	2.639 (2)	173 (2)
C1–H1a...O4	0.95	2.48	3.273 (2)	141
C5–H5a...O1 ^{vi}	0.95	2.38	3.254 (2)	152

^a Symmetry operations: ⁱ $1/2 - x, 1/2 + y, 3/2 - z$; ⁱⁱ $x, -y, 1/2 + z$; ⁱⁱⁱ $-x, y, 2 - z$; ^{iv} $-x, -y, 1 - z$; ^v $1/2 - x, 1/2 - y, 2 - z$; ^{vi} $x, 1 - y, 1/2 + z$.

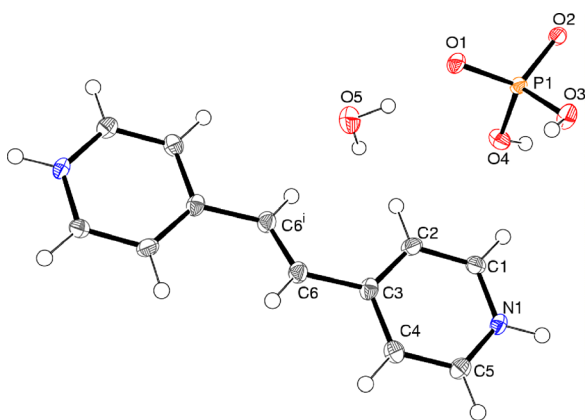


Fig. 3. A view of the asymmetric unit of **2** in the crystal with 50% displacement ellipsoids (arbitrary spheres for the H atoms). Symmetry codes (i) = $x, 1 - y, -z$.

separations are $P1 \cdots P1^i = 4.7533(7)$ and $P1 \cdots P1^{ii} = 4.9506(8)$ Å ($i = x, -y, 1/2 - z$, $ii = 1/2 - x, y - 1/2, 3/2 - z$). The organic dication forms an N–H...O hydrogen bond from each of its N atoms to crosslink the (100) dihydrogenphosphate sheets in the *a* direction (Fig. 4). This connectivity of the $[H_2PO_4]^-$ and $[C_{12}H_{14}N_2]^{2+}$ moieties results in a three-dimensional supramolecular scaffold that encloses channels propagating in [001]. These channels are occupied by the water molecules, which make O–H...O bonds (*via* H4) to adjacent phosphate O atoms and also O–H...O bonds (*via* the disordered H5 and H6) to the next water O atom in the channel. Locally each [001] column of water molecules has ordered H bonds as

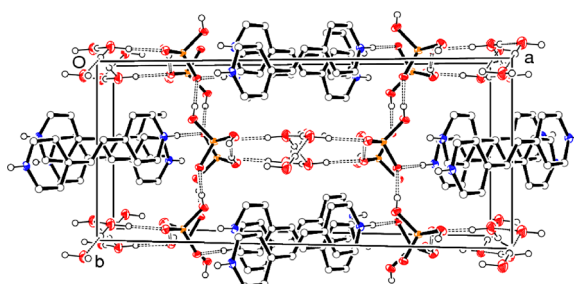
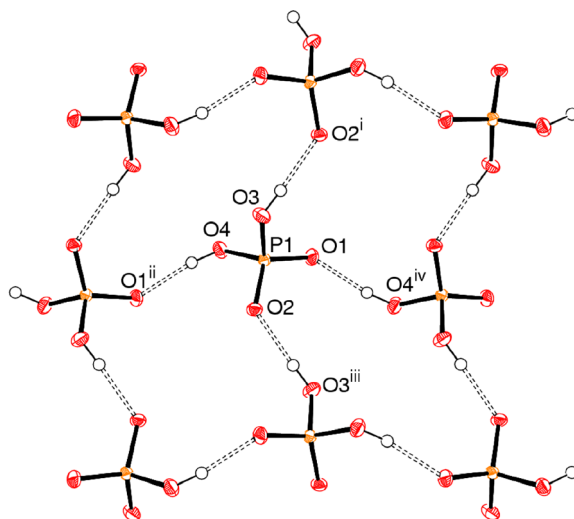


Fig. 4. Top: The two-dimensional phosphate framework of **2** formed by O–H...O hydrogen bonds. Symmetry codes (i) = $1/2 - x, 1/2 + y, 3/2 - z$, (ii) = $x, -y, z + 1/2$, (iii) = $1/2 - x, y - 1/2, 3/2 - z$ and (iv) = $x, -y, z - 1/2$. Bottom: Packing diagram of **2**, showing hydrogen bonds. All C–H hydrogen atoms have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

either $\cdots O5-H5 \cdots O5-H6 \cdots O5-H5 \cdots$ or $\cdots H5-O5 \cdots H6-O5 \cdots H5-O5 \cdots$, but, as modelled here, there is no coherence between channels. Attempts to refine an ordered distribution of H bonds in lower symmetries were not successful. As in **1**, some short C–H...O contacts are present in **2** (Table 2), although their role, perhaps helping to anchor the dications to the (100) phosphate sheets, is not so clear-cut as in **1**.

IR spectra

The IR spectra of compounds **1** and **2** are almost identical. The $\nu(O-H)$ and $\nu(N-H)$ vibrations are expected to appear above 3000 cm^{-1} , but they are observed as a strong single band centered at 3055 cm^{-1} for **1** and at 3030 cm^{-1} for **2**, due to overlapping. The

	1	2
Empirical formula	C ₁₂ H ₁₆ N ₂ O ₆ P ₂	C ₁₂ H ₂₀ N ₂ O ₁₀ P ₂
<i>M</i> _r	346.20	414.24
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	4.655 (1)	20.640 (1)
<i>b</i> [Å]	10.331 (1)	9.033 (1)
<i>c</i> [Å]	15.435 (1)	9.320 (1)
β [°]	91.393 (3)	102.269 (3)
<i>V</i> [Å ³]	741.98 (4)	1698.00 (14)
<i>Z</i>	2	4
<i>D</i> _c [g/cm ³]	1.550	1.620
μ [mm ^{−1}]	0.324	0.314
<i>F</i> (000)	360	861
Crystal size [mm ³]	0.34 × 0.07 × 0.05	0.40 × 0.12 × 0.02
θ Range [°]	3.94–27.54	3.19–27.53
Index range (<i>h, k, l</i>)	−6/5, −13/13, −19/20	−26/24, −11/11, −12/11
Reflections collected	9203	10244
Independent reflections (<i>R</i> _{int})	1691 (0.0416)	1952 (0.0453)
Absorption correction	multi-scan	multi-scan
Min. and max. transmission	0.898 and 0.984	0.885 and 0.995
Data / parameters	1691 / 107	1952 / 128
Goodness-of-fit on <i>F</i> ²	1.094	1.098
<i>R</i> Indices [<i>I</i> > 2σ(<i>I</i>)]	0.0349	0.0404
<i>wR</i> 2 (all data)	0.0809	0.0998
Largest diff. peak and hole [e.Å ^{−3}]	0.32 and −0.41	0.33 and −0.49

Table 3. Crystallographic data for **1** and **2**.

sharp and strong band at 2336 cm^{−1} is assigned to the P–H stretching vibration of the phosphite group of **1**, and the medium bands at 1651 and 1523 cm^{−1} are attributed to the ring stretching vibrations of the H₂bpe dication in both **1** and **2**. Three distinct and strong bands at 1191, 1089 and 911 cm^{−1} correspond to the P–O stretching vibrations of the phosphite anions of **1**, whereas the strong bands at 1217, 1089 and 962 cm^{−1} characterize the P–O stretching vibrations of the phosphate anions of **2**.

Experimental Section

Materials and measurements

All reagents were commercially available and used without further purification. Elemental analyses (C, H, and N) were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{−1} by using a JASCO FT/IR-430 spectrophotometer.

Synthesis of H₂bpe(H₂PO₃)₂ (**1**)

5 ml of an aqueous solution of H₃PO₃ (0.16 g, 2 mmol) was added dropwise to an aqueous mixture (10 ml) of 1,2-di(4-pyridyl)ethene (0.182 g, 1 mmol) and stirred for 20 min at 50 °C. The resulting solution was then left to crystallize at r.t. Colorless crystals of **1** were collected, washed

with a small amount of water, and dried in air. Yield 50%. C₁₂H₁₆N₂O₆P₂ (346.20): calcd. C 41.63, H 4.66, N 8.09; found C 41.79, H 4.76, N 7.87.

Synthesis of H₂bpe(H₂PO₄)₂ · H₂O (**2**)

The preparation method for **2** was the same as described for **1** with H₃PO₄ replacing H₃PO₃. Yield 58%. C₁₂H₂₀N₂O₁₀P₂ (414.24): calcd. C 34.79, H 4.87, N 6.76; found C 34.92, H 4.68, N 6.90.

X-ray crystallography

The data collections were performed at 120 K for both compounds on a Nonius Kappa-CCD diffractometer with graphite monochromated Mo-*K*_α radiation (λ = 0.71073 Å). The structures were solved by Direct Methods using SHELXS-97 [20] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [20]. All non-hydrogen atoms were easily found on the difference Fourier map and refined anisotropically. For both compounds, the P–OH and N–H hydrogen atoms were located in difference maps and their positions were freely refined. The C–H = 0.95 Å and refined as riding atoms. The water H atoms for **2** were located in difference maps and refined as riding in their as-found relative positions. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) was applied in all cases. The details of data collection, refinement and crystallographic data are summarized in Table 3.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-299941 (**1**) and CCDC-299942 (**2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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