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Hydroxonium 1-ammonioethylidene-1,1-bisphosphonate

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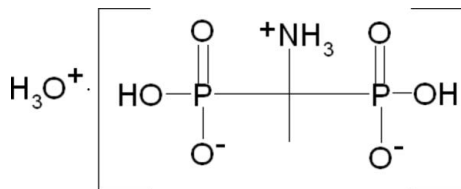
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 Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.095; data-to-parameter ratio = 17.2.

The title compound, $\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_8\text{NO}_6\text{P}_2^-$, contains a disordered H_3O^+ cation and an $\text{NH}_3\text{C}(\text{CH}_3)(\text{PO}_3\text{H})_2$ anion. The three H atoms of the H_3O^+ cation are statistically distributed over four positions with occupancies of 0.75, resulting in a pseudo tetrahedron. Multiple $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds generate an intricate three-dimensional network.

Related literature

For related literature, see: Bollinger & Roundhill (1993); Chai *et al.* (1980); Clearfield (2002); Fernández *et al.* (2003); Li *et al.* (2008); Finn *et al.* (2003); Yin *et al.* (2005).



Experimental

Crystal data

 $\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_8\text{NO}_6\text{P}_2^-$
 $M_r = 223.06$

 Triclinic, $P\bar{1}$
 $a = 5.6379$ (5) Å

 $b = 8.9712$ (8) Å

 $c = 9.2302$ (8) Å

 $\alpha = 102.111$ (1)°

 $\beta = 100.499$ (1)°

 $\gamma = 101.342$ (1)°

 $V = 435.22$ (7) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 0.50$ mm⁻¹
 $T = 293$ (2) K

 $0.36 \times 0.32 \times 0.27$ mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

 $T_{\min} = 0.839$, $T_{\max} = 0.876$

2811 measured reflections

1946 independent reflections

 1871 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.009$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.095$
 $S = 1.08$

1946 reflections

113 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.58$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O3}^{\text{ii}}$	0.89	2.02	2.798 (2)	145
$\text{N1}-\text{H1B}\cdots\text{O2}^{\text{ii}}$	0.89	2.00	2.766 (2)	144
$\text{N1}-\text{H1C}\cdots\text{O6}^{\text{i}}$	0.89	1.93	2.771 (2)	156
$\text{O1}-\text{H1}\cdots\text{O3}^{\text{iii}}$	0.82	1.69	2.501 (2)	168
$\text{O4}-\text{H4}\cdots\text{O2}^{\text{iv}}$	0.82	1.84	2.635 (2)	164
$\text{O1W}-\text{H9}\cdots\text{O1}^{\text{v}}$	0.89	2.06	2.923 (2)	164
$\text{O1W}-\text{H10}\cdots\text{O5}$	0.89	1.88	2.737 (2)	164
$\text{O1W}-\text{H11}\cdots\text{O6}^{\text{i}}$	0.88	1.94	2.781 (2)	159
$\text{O1W}-\text{H12}\cdots\text{O5}^{\text{vi}}$	0.89	2.01	2.901 (3)	180

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2098).

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supplementary materials

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Hydroxonium 1-ammonioethylidene-1,1-bisphosphonate

Y. Wu and D.-L. Yin

Comment

Phosphonic acids are interesting ligands. They can complex various metal ions and a series of organic-inorganic hybrid materials containing phosphonic acids have been prepared and characterized. Such materials have potential applications in catalysts, sensors, sorbents, magnetic and luminescent materials (Finn *et al.*, 2003). In addition, introduction of some functional groups to phosphonic acids, such as crown ether, $-\text{COOH}$, $-\text{OH}$, $-\text{NR}_2$ or mixed group will modify their complexing ability (Clearfield, 2002). 1-Aminoethylidene-1,1-diphosphonic acid (AEDPH₄) exists as a zwitterion and is inclined to transfer one proton to the amino group (Bollinger & Roundhill, 1993; Fernández *et al.*, 2003; Li *et al.*, 2008). Its deprotonation would result in predictable hydrogen aggregates from stronger $\text{P}-\text{O}-\text{H}\cdots\text{O}-\text{P}$ to weaker $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. However, its crystal structure is still unknown (Yin *et al.*, 2005). Herein, we report the structure of the title compound, (I).

The asymmetric unit of (I) is built up from one deprotonated AEDPH₄ anion and a disordered H_3O^+ cation which are linked through $\text{OW}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 1, Table 1). Two of the four protons of phosphonates are used in the protonation of one for the amino group, the other for H_3O^+ cation. The deprotonated AEDPH₃⁻ anions form two-dimensional (2D) H-bonded layer along the *bc*-plane. The strongest H-bond is $\text{O1}-\text{H1}\cdots\text{O3}^{\text{iii}}$ (with $\text{O1}\cdots\text{O3}$ distance 2.501 (2) Å), which links the AEDPH₃⁻ anions into dimers which form an infinite chain along the *b* axis by hydrogen bond $\text{O4}-\text{H4}\cdots\text{O2}^{\text{iv}}$ ($\text{O4}\cdots\text{O2}$ distance 2.635 (2) Å). Furthermore, three $\text{N}-\text{H}\cdots\text{O}$ H-bonds connect these chains to obtain a 2D layer. The H_3O^+ anions bond to the adjacent layers with five $\text{Ow}-\text{H}\cdots\text{O}$ bonds and stabilize the structure. The occurrence of different hydrogen bond interactions, $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$ and $\text{OW}-\text{H}\cdots\text{O}$ results in the formation of an intricate three dimensional network (Fig. 2, Table 1).

Experimental

The title compound was synthesized according to the US Patent 4239695 (Chai *et al.*, 1980). It was crystallized unexpectedly when 4,4-bipyridine was added into the AEDPH₄ H₂O solution to synthesize the complex. However, the 4,4-bipyridine was not present in the final product.

Refinement

All H atoms attached to C atoms, N atom and O(hydroxyl) atoms were fixed geometrically and treated as riding with $\text{C}-\text{H} = 0.96$ Å (C), $\text{N}-\text{H} = 0.86$ Å and $\text{O}-\text{H} = 0.82$ Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{N} \text{ or } \text{O})$. H atoms of the H_3O^+ cation were located in difference Fourier maps and included in the subsequent refinement using restraints ($\text{O}-\text{H} = 0.86$ (1) Å) with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$; in the final stages of refinement their coordinates were fixed. The three hydrogen atoms of the H_3O^+ cation are statistically distributed over four positions with occupation factor of 0.75, resulting in a pseudo tetrahedron.

Figures

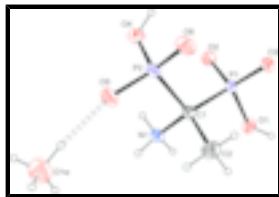


Fig. 1. The asymmetric unit of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bond is shown as dashed line.

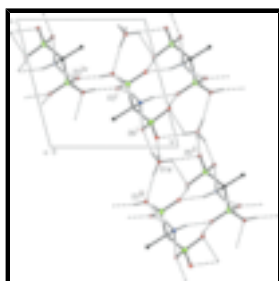
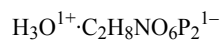


Fig. 2. Partial packing view of compound (I), showing the formation of the three dimensional network built from hydrogen bonds. For clarity, H atoms not involved in hydrogen bonding have been omitted. [symmetry codes: (i) 1+x, y, z; (ii) 2-x, 2-y, z; (iii) x, y, z-1; (iv) 1-x, 1-y, 1-z].

Hydroxonium 1-ammonioethylidene-1,1-bisphosphonate

Crystal data



$M_r = 223.06$

Triclinic, *PT*

Hall symbol: -P 1

$a = 5.6379$ (5) Å

$b = 8.9712$ (8) Å

$c = 9.2302$ (8) Å

$\alpha = 102.111$ (1)°

$\beta = 100.499$ (1)°

$\gamma = 101.342$ (1)°

$V = 435.22$ (7) Å³

$Z = 2$

$F_{000} = 232$

$D_x = 1.702$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2523 reflections

$\theta = 2.4$ – 29.6 °

$\mu = 0.50$ mm⁻¹

$T = 293$ (2) K

Plate, colorless

$0.36 \times 0.32 \times 0.27$ mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer

Monochromator: graphite

$T = 298$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.839$, $T_{\max} = 0.876$

2811 measured reflections

1946 independent reflections

1871 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 2.3$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 11$

$l = -11 \rightarrow 8$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.5124P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
1946 reflections	$(\Delta/\sigma)_{\max} < 0.001$
113 parameters	$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
P1	0.64618 (8)	0.73089 (5)	0.49332 (5)	0.01519 (14)	
P2	0.58222 (8)	0.83546 (6)	0.19085 (5)	0.01897 (14)	
C1	0.7352 (3)	0.7236 (2)	0.3101 (2)	0.0159 (3)	
C2	0.6859 (4)	0.5520 (2)	0.2183 (2)	0.0263 (4)	
H2A	0.7448	0.5493	0.1268	0.039*	
H2B	0.5106	0.5046	0.1924	0.039*	
H2C	0.7717	0.4950	0.2784	0.039*	
N1	1.0110 (3)	0.79403 (19)	0.34632 (18)	0.0177 (3)	
H1A	1.0884	0.7500	0.4126	0.027*	
H1B	1.0421	0.8971	0.3866	0.027*	
H1C	1.0657	0.7766	0.2612	0.027*	
O1	0.8136 (2)	0.63586 (16)	0.57120 (16)	0.0207 (3)	
H1	0.7371	0.5435	0.5513	0.031*	
O2	0.7185 (3)	0.89740 (16)	0.58704 (16)	0.0234 (3)	
O3	0.3743 (2)	0.64928 (16)	0.46080 (17)	0.0218 (3)	
O4	0.6364 (3)	1.00594 (17)	0.29828 (18)	0.0267 (3)	
H4	0.5123	1.0175	0.3295	0.040*	
O5	0.7259 (3)	0.8501 (2)	0.07158 (17)	0.0295 (3)	
O6	0.3106 (3)	0.75734 (19)	0.14090 (16)	0.0262 (3)	
O1W	1.0469 (3)	0.8192 (2)	-0.1160 (2)	0.0403 (4)	
H9	1.0002	0.7549	-0.2088	0.061*	0.75
H10	0.9220	0.8286	-0.0718	0.061*	0.75
H11	1.1434	0.7837	-0.0515	0.061*	0.75

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H12 1.1157 0.9206 -0.1025 0.061* 0.75

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0131 (2)	0.0149 (2)	0.0193 (2)	0.00319 (17)	0.00587 (17)	0.00642 (17)
P2	0.0151 (2)	0.0268 (3)	0.0203 (3)	0.00901 (19)	0.00713 (18)	0.01124 (19)
C1	0.0124 (7)	0.0172 (8)	0.0194 (8)	0.0038 (6)	0.0051 (6)	0.0057 (6)
C2	0.0297 (10)	0.0204 (9)	0.0257 (10)	0.0056 (8)	0.0055 (8)	0.0005 (7)
N1	0.0128 (7)	0.0209 (7)	0.0223 (8)	0.0054 (6)	0.0068 (6)	0.0083 (6)
O1	0.0173 (6)	0.0195 (6)	0.0253 (7)	0.0040 (5)	0.0017 (5)	0.0094 (5)
O2	0.0265 (7)	0.0170 (7)	0.0275 (7)	0.0043 (5)	0.0119 (6)	0.0033 (5)
O3	0.0132 (6)	0.0226 (7)	0.0334 (8)	0.0043 (5)	0.0073 (5)	0.0138 (6)
O4	0.0239 (7)	0.0241 (7)	0.0376 (8)	0.0104 (6)	0.0125 (6)	0.0106 (6)
O5	0.0297 (8)	0.0425 (9)	0.0283 (8)	0.0162 (7)	0.0175 (6)	0.0184 (7)
O6	0.0162 (7)	0.0401 (8)	0.0239 (7)	0.0087 (6)	0.0033 (5)	0.0112 (6)
O1W	0.0390 (9)	0.0496 (11)	0.0344 (9)	0.0119 (8)	0.0101 (7)	0.0127 (8)

Geometric parameters (\AA , $^\circ$)

P1—O2	1.4952 (14)	C2—H2B	0.9600
P1—O3	1.5081 (13)	C2—H2C	0.9600
P1—O1	1.5686 (14)	N1—H1A	0.8900
P1—C1	1.8417 (18)	N1—H1B	0.8900
P2—O5	1.4928 (14)	N1—H1C	0.8900
P2—O6	1.4947 (14)	O1—H1	0.8200
P2—O4	1.5765 (15)	O4—H4	0.8200
P2—C1	1.8497 (19)	O1W—H9	0.8869
C1—N1	1.505 (2)	O1W—H10	0.8852
C1—C2	1.537 (2)	O1W—H11	0.8841
C2—H2A	0.9600	O1W—H12	0.8888
O2—P1—O3	115.72 (8)	C1—C2—H2B	109.5
O2—P1—O1	108.61 (8)	H2A—C2—H2B	109.5
O3—P1—O1	111.06 (8)	C1—C2—H2C	109.5
O2—P1—C1	109.30 (8)	H2A—C2—H2C	109.5
O3—P1—C1	108.25 (8)	H2B—C2—H2C	109.5
O1—P1—C1	103.15 (8)	C1—N1—H1A	109.5
O5—P2—O6	118.42 (9)	C1—N1—H1B	109.5
O5—P2—O4	106.13 (9)	H1A—N1—H1B	109.5
O6—P2—O4	112.40 (8)	C1—N1—H1C	109.5
O5—P2—C1	105.96 (8)	H1A—N1—H1C	109.5
O6—P2—C1	108.21 (8)	H1B—N1—H1C	109.5
O4—P2—C1	104.72 (8)	P1—O1—H1	109.5
N1—C1—C2	107.76 (14)	P2—O4—H4	109.5
N1—C1—P1	106.97 (11)	H9—O1W—H10	113.6
C2—C1—P1	110.19 (13)	H9—O1W—H11	112.2
N1—C1—P2	107.45 (12)	H10—O1W—H11	102.3
C2—C1—P2	109.40 (13)	H9—O1W—H12	120.3

P1—C1—P2	114.79 (9)	H10—O1W—H12	98.6
C1—C2—H2A	109.5	H11—O1W—H12	107.6

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1A···O3 ⁱ	0.89	2.02	2.798 (2)	145
N1—H1B···O2 ⁱⁱ	0.89	2.00	2.766 (2)	144
N1—H1C···O6 ⁱ	0.89	1.93	2.771 (2)	156
O1—H1···O3 ⁱⁱⁱ	0.82	1.69	2.501 (2)	168
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Fig. 1

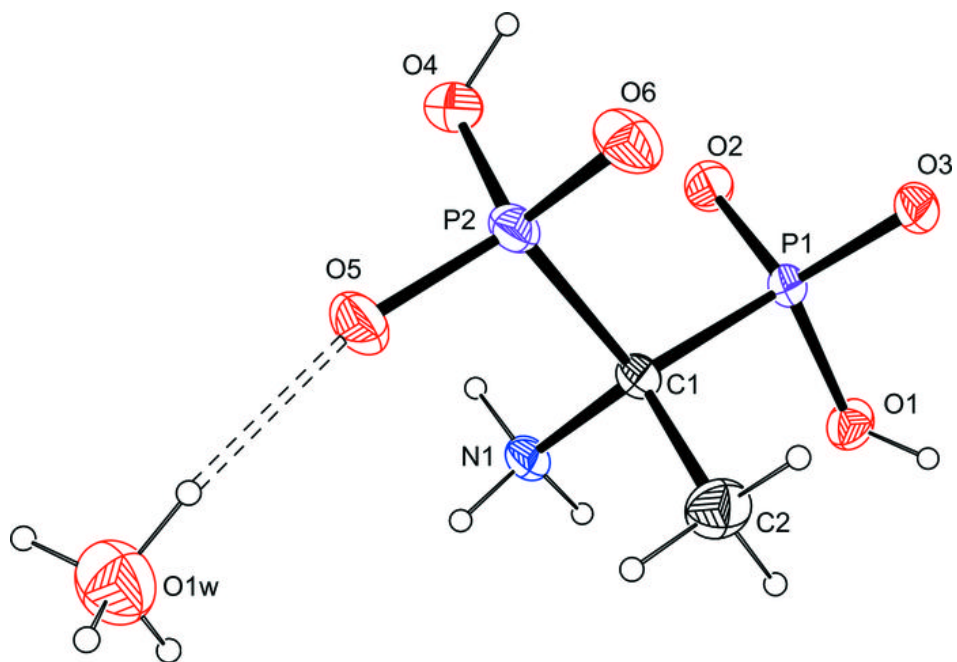


Fig. 2

