

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Hydroxonium 1-ammonioethane-1,1-diylidiphosphonate

Ming Li,* Wen Wen, Wuzu Ha and Liang Chang

 Department of Chemical Engineering, Wuhan University of Science and Engineering, Wuhan 430073, People's Republic of China
 Correspondence e-mail: lim@wuse.edu.cn

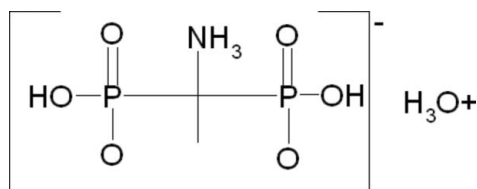
Received 9 October 2008; accepted 10 March 2009

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.097; data-to-parameter ratio = 14.5.

The title complex, $\text{H}_3\text{O}^+\cdot\text{NH}_3\text{C}(\text{CH}_3)(\text{PO}_3\text{H})_2^-$, contains a hydroxonium ion and an $\text{NH}_3\text{C}(\text{CH}_3)(\text{PO}_3\text{H})_2^-$ anion. The three H atoms of H_3O^+ form a pseudo-tetrahedron by being distributed over four positions with occupation factors of 0.75. Multiple $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in the crystal structure form an intricate three-dimensional supra-molecular network.

Related literature

For the structures of organophosphonates, see: Clearfield (2002); Finn *et al.* (2003). For similar bisphosphonates, see: Fernández *et al.* (2003); For complexes with 1-aminoethylidene-1,1-diphosphonic acid, see: Yin *et al.* (2005); Ding *et al.* (2006); Li *et al.* (2008). For the synthesis, see: Chai *et al.* (1980).



Experimental

Crystal data

 $\text{H}_3\text{O}^+\cdot\text{C}_2\text{H}_8\text{N}_2\text{O}_6\text{P}_2^-$
 $M_r = 223.06$
 Monoclinic, $P2_1/c$
 $a = 7.3372$ (6) Å
 $b = 10.6553$ (8) Å
 $c = 10.6128$ (8) Å
 $\beta = 97.705$ (1)°

 $V = 822.22$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.53$ mm⁻¹
 $T = 293$ K
 $0.36 \times 0.27 \times 0.18$ mm

Data collection

 Bruker SMART 4K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)
 $T_{\min} = 0.831$, $T_{\max} = 0.910$
 5340 measured reflections
 1972 independent reflections
 1837 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.097$
 $S = 1.10$
 1972 reflections
 136 parameters
 4 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.61$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1C}\cdots\text{O2}^{\text{I}}$	0.89	1.98	2.809 (2)	155
$\text{N1}-\text{H1A}\cdots\text{O5}^{\text{I}}$	0.89	1.90	2.713 (2)	151
$\text{N1}-\text{H1B}\cdots\text{O3}^{\text{II}}$	0.89	2.01	2.824 (2)	152
$\text{O4}-\text{H3}\cdots\text{O3}^{\text{II}}$	0.73 (4)	1.86 (4)	2.591 (2)	176 (4)
$\text{O1}-\text{H4}\cdots\text{O6}^{\text{III}}$	0.71 (3)	1.84 (3)	2.550 (2)	172 (4)
$\text{O1W}-\text{H5}\cdots\text{O5}^{\text{IV}}$	0.893 (10)	1.954 (15)	2.804 (2)	159 (3)
$\text{O1W}-\text{H8}\cdots\text{O1}^{\text{V}}$	0.888 (10)	2.64 (4)	3.061 (2)	110 (3)
$\text{O1W}-\text{H8}\cdots\text{O3}^{\text{VI}}$	0.888 (10)	2.27 (2)	3.041 (2)	145 (3)
$\text{O1W}-\text{H6}\cdots\text{O2}^{\text{VII}}$	0.896 (10)	1.935 (11)	2.828 (2)	175 (3)
$\text{O1W}-\text{H7}\cdots\text{O6}^{\text{III}}$	0.900 (10)	1.920 (11)	2.815 (2)	173 (3)

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008b); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

This work was supported financially by the Foundation of Education Department of Hubei Province (No. Q20081705).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2053).

References

- Bruker (2001). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chai, B. J., Covina, W. & Muggee, F. D. (1980). US Patent No. 4 239 695.
- Clearfield, A. (2002). *Recent Opin. Solid Mater. Sci.* **6**, 495–506.
- Ding, D., Yin, M., Lu, H., Fan, Y., Hou, H. & Wang, Y. (2006). *J. Solid State Chem.* **179**, 747–752.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fernández, D., Vega, D. & Ellena, J. A. (2003). *Acta Cryst.* **C59**, o289–o292.
- Finn, R. C., Zubieta, J. & Haushalter, R. C. (2003). *Prog. Inorg. Chem.* **51**, 421–601.
- Li, M., Xiang, J. F., Chen, S. P., Wu, S. M., Yuan, L. J., Li, H., He, H. J. & Sun, J. T. (2008). *J. Coord. Chem.* **61**(3), 372–383.
- Sheldrick, G. M. (2008a). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008b). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Yin, P., Wang, X. C., Gao, S. & Zheng, L. M. (2005). *J. Solid State Chem.* **178**, 1049–1053.

supplementary materials

Acta Cryst. (2009). E65, o787 [doi:10.1107/S1600536809008770]

Hydroxonium 1-ammonioethane-1,1-diylidiphosphonate

M. Li, W. Wen, W. Ha and L. Chang

Comment

Organophosphonic acids and their compounds have attracted tremendous interest. A series of phosphonate hybrid materials have been prepared and show potential applications in catalysts, sensors, sorbents, magnetic and luminescent materials. Such materials also illustrate a variety of structures from one-dimensional chains, two-dimensional layers to three-dimensional porous frameworks. (Finn *et al.*, 2003). Introduction of some functional groups to phosphonic acids, such as crown ether, $-\text{COOH}$, $-\text{OH}$, $-\text{NR}_2$ or mixed groups will modify their complexing ability and construct a great number of novel phosphonates (Clearfield, 2002). Compared with other phosphonic acids, 1-aminoethylidene-1,1-diphosphonic acid (AEDPH₄) is easier to synthesize. However, little attention has been paid to the structural study of metal-AEDP compounds (Yin *et al.*, 2005; Ding *et al.*, 2006). In our recent paper, it is found that AEDPH₄ is inclined to transfer one proton to the amino group, which is in agreement with Fernández's results on similar bisphosphonates. (Li *et al.*, 2008; Fernández *et al.*, 2003). Deprotonation of it will 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. Herein, we report its structure, (I).

The asymmetric unit of (I) is built up from one deprotonated AEDPH₃ anion and a disordered H_3O^+ cation, which are linked through four types of $\text{Ow}-\text{H}\cdots\text{O}$ hydrogen bonds (Fig. 1, Table 1). Two of the four protons of phosphonates are used in protonation, one for the amino group, the other for the H_3O^+ cation. The combination of different hydrogen bond interactions, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ results in the formation of an intricate three dimensional supramolecular network (Fig.2, Table 1).

Experimental

The AEDPH₄ was synthesized according to the US Patent 4239695 (Chai *et al.*, 1980). It was crystallized directly from the AEDPH₄ aqueous solution. When the mixture was heated for 24h, colorless crystals were obtained.

Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding with $\text{C}-\text{H} = 0.96 \text{ \AA}$ (C), $\text{N}-\text{H} = 0.89 \text{ \AA}$ with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C},\text{N})$. The H atoms of hydroxyl were located in difference Fourier maps and included in the subsequent refinement.

The three hydrogen atoms of the H_3O^+ cation are statistically distributed over four positions with occupation factor of 0.75, building a pseudo tetrahedron.

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.8715P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
1972 reflections	$(\Delta/\sigma)_{\max} = 0.001$
136 parameters	$\Delta\rho_{\max} = 0.40 \text{ e } \text{Å}^{-3}$
4 restraints	$\Delta\rho_{\min} = -0.61 \text{ e } \text{Å}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.023 (2)

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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.9948 (2)	0.56114 (16)	0.24265 (16)	0.0131 (3)	
C2	0.9672 (3)	0.62357 (19)	0.36861 (18)	0.0209 (4)	
H2A	1.0741	0.6722	0.3993	0.031*	
H2B	0.9488	0.5602	0.4299	0.031*	
H2C	0.8615	0.6774	0.3556	0.031*	
N1	1.0165 (2)	0.66564 (14)	0.14939 (14)	0.0152 (3)	
H1A	0.9151	0.7124	0.1391	0.023*	
H1B	1.0347	0.6329	0.0750	0.023*	
H1C	1.1124	0.7131	0.1792	0.023*	
O1W	0.4462 (2)	0.70203 (18)	0.52441 (17)	0.0363 (4)	
O1	0.63612 (19)	0.57626 (13)	0.17124 (14)	0.0209 (3)	
O2	0.75556 (18)	0.37252 (13)	0.27913 (13)	0.0208 (3)	
O3	0.80235 (18)	0.42568 (13)	0.05066 (12)	0.0208 (3)	
O4	1.23166 (19)	0.41015 (14)	0.13108 (14)	0.0209 (3)	
O5	1.20389 (18)	0.37077 (13)	0.35944 (13)	0.0204 (3)	
O6	1.36080 (17)	0.56986 (13)	0.29441 (13)	0.0199 (3)	
P1	0.78594 (6)	0.47061 (4)	0.18354 (4)	0.01339 (15)	
P2	1.21301 (6)	0.47175 (4)	0.26319 (4)	0.01358 (15)	
H3	1.227 (5)	0.456 (3)	0.079 (3)	0.051 (10)*	
H4	0.562 (5)	0.568 (3)	0.208 (3)	0.049 (10)*	
H5	0.5658 (17)	0.698 (3)	0.554 (3)	0.018 (7)*	0.75
H6	0.386 (4)	0.673 (3)	0.587 (2)	0.018 (7)*	0.75
H7	0.426 (4)	0.663 (2)	0.4485 (15)	0.013 (7)*	0.75
H8	0.422 (5)	0.7827 (13)	0.509 (4)	0.038 (10)*	0.75

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0145 (7)	0.0114 (7)	0.0138 (7)	-0.0006 (6)	0.0032 (6)	0.0007 (6)
C2	0.0254 (9)	0.0214 (9)	0.0164 (8)	0.0030 (7)	0.0042 (7)	-0.0040 (7)
N1	0.0165 (7)	0.0123 (7)	0.0173 (7)	-0.0002 (5)	0.0040 (5)	0.0017 (5)
O1W	0.0356 (9)	0.0393 (10)	0.0331 (9)	0.0008 (8)	0.0010 (7)	-0.0001 (7)
O1	0.0155 (6)	0.0200 (7)	0.0283 (7)	0.0043 (5)	0.0073 (5)	0.0065 (5)
O2	0.0210 (6)	0.0164 (6)	0.0261 (7)	0.0001 (5)	0.0068 (5)	0.0073 (5)
O3	0.0217 (6)	0.0236 (7)	0.0169 (6)	-0.0005 (5)	0.0022 (5)	-0.0037 (5)
O4	0.0248 (7)	0.0184 (7)	0.0201 (7)	0.0019 (5)	0.0051 (5)	-0.0036 (5)
O5	0.0191 (6)	0.0189 (6)	0.0227 (7)	0.0010 (5)	0.0005 (5)	0.0066 (5)
O6	0.0148 (6)	0.0193 (6)	0.0259 (7)	-0.0038 (5)	0.0037 (5)	-0.0049 (5)
P1	0.0127 (2)	0.0124 (2)	0.0152 (2)	-0.00029 (15)	0.00251 (16)	0.00126 (15)
P2	0.0123 (2)	0.0125 (2)	0.0158 (2)	0.00017 (15)	0.00167 (16)	0.00006 (15)

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

C1—N1	1.512 (2)	O1W—H6	0.896 (10)
C1—C2	1.531 (2)	O1W—H7	0.900 (10)
C1—P1	1.8479 (17)	O1W—H8	0.888 (10)
C1—P2	1.8505 (17)	O1—P1	1.5666 (14)
C2—H2A	0.9600	O1—H4	0.71 (3)
C2—H2B	0.9600	O2—P1	1.4940 (13)
C2—H2C	0.9600	O3—P1	1.5093 (13)
N1—H1A	0.8900	O4—P2	1.5706 (14)
N1—H1B	0.8900	O4—H3	0.73 (4)
N1—H1C	0.8900	O5—P2	1.4914 (13)
O1W—H5	0.893 (10)	O6—P2	1.5106 (13)
N1—C1—C2	106.82 (14)	H5—O1W—H7	109 (3)
N1—C1—P1	108.51 (11)	H6—O1W—H7	118 (3)
C2—C1—P1	108.82 (12)	H5—O1W—H8	106 (3)
N1—C1—P2	106.91 (11)	H6—O1W—H8	111 (3)
C2—C1—P2	109.54 (12)	H7—O1W—H8	106 (3)
P1—C1—P2	115.87 (9)	P1—O1—H4	116 (3)
C1—C2—H2A	109.5	P2—O4—H3	113 (3)
C1—C2—H2B	109.5	O2—P1—O3	116.77 (8)
H2A—C2—H2B	109.5	O2—P1—O1	113.10 (8)
C1—C2—H2C	109.5	O3—P1—O1	107.04 (8)
H2A—C2—H2C	109.5	O2—P1—C1	109.10 (8)
H2B—C2—H2C	109.5	O3—P1—C1	108.44 (8)
C1—N1—H1A	109.5	O1—P1—C1	101.18 (8)
C1—N1—H1B	109.5	O5—P2—O6	116.47 (8)
H1A—N1—H1B	109.5	O5—P2—O4	109.10 (8)
C1—N1—H1C	109.5	O6—P2—O4	109.82 (8)
H1A—N1—H1C	109.5	O5—P2—C1	109.54 (8)
H1B—N1—H1C	109.5	O6—P2—C1	104.71 (8)

H5—O1W—H6	107 (3)	O4—P2—C1	106.71 (8)
N1—C1—P1—O2	-176.13 (11)	N1—C1—P2—O5	177.18 (11)
C2—C1—P1—O2	-60.25 (14)	C2—C1—P2—O5	61.79 (14)
P2—C1—P1—O2	63.66 (11)	P1—C1—P2—O5	-61.75 (11)
N1—C1—P1—O3	55.70 (13)	N1—C1—P2—O6	51.57 (12)
C2—C1—P1—O3	171.58 (12)	C2—C1—P2—O6	-63.82 (13)
P2—C1—P1—O3	-64.51 (11)	P1—C1—P2—O6	172.64 (9)
N1—C1—P1—O1	-56.68 (12)	N1—C1—P2—O4	-64.85 (12)
C2—C1—P1—O1	59.20 (13)	C2—C1—P2—O4	179.76 (12)
P2—C1—P1—O1	-176.89 (9)	P1—C1—P2—O4	56.22 (11)

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—H1C···O2 ⁱ	0.89	1.98	2.809 (2)	155
N1—H1A···O5 ⁱ	0.89	1.90	2.713 (2)	151
N1—H1B···O3 ⁱⁱ	0.89	2.01	2.824 (2)	152
O4—H3···O3 ⁱⁱ	0.73 (4)	1.86 (4)	2.591 (2)	176 (4)
O1—H4···O6 ⁱⁱⁱ	0.71 (3)	1.84 (3)	2.550 (2)	172 (4)
O1W—H5···O5 ^{iv}	0.893 (10)	1.954 (15)	2.804 (2)	159 (3)
O1W—H8···O1 ^v	0.888 (10)	2.64 (4)	3.061 (2)	110 (3)
O1W—H8···O3 ^{vi}	0.888 (10)	2.27 (2)	3.041 (2)	145 (3)
O1W—H6···O2 ^{vii}	0.896 (10)	1.935 (11)	2.828 (2)	175 (3)
O1W—H7···O6 ⁱⁱⁱ	0.900 (10)	1.920 (11)	2.815 (2)	173 (3)

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

Fig. 1

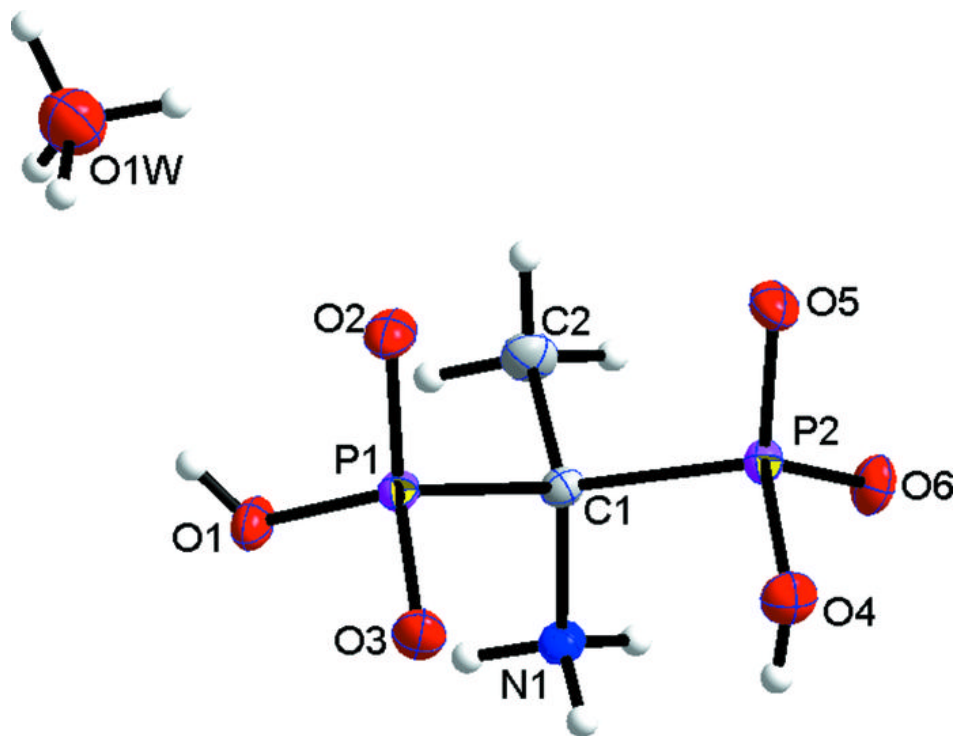


Fig. 2

