N,N,N',N'-Tetramethylethylenediammonium Dihydrogendiphosphate Dihydrate

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Abstract

The crystal structure of the title compound, $C_6H_{18}N_2^{2+}.H_2P_2O_7^{2-}.2H_2O$, can be described as a typical thick-layered organization of molecules built up from all the components of the structure and centered on the (101) planes. Strong hydrogen bonds connect molecules within the layers.

Comment

A large number of diphosphates with mineral cations are presently known and a systematic survey of their main crystallographic data has been reported recently (Durif, 1995). However, to date, a relatively small number of organic cation diphosphates has been characterized. Among the nine well known structural investigations, three were recently reported by this laboratory: $(C_2H_{10}N_2)_3(HP_2O_7)_2.2H_2O$ (Kamoun, Jouini & Dabbabi, 1990), $(C_2H_{10}N_2)_2P_2O_7$ (Kamoun, Jouini & Daoud, 1992) and $Cu_2(C_2H_{10}N_2)(HP_2O_7)_2(C_2H_8N_2)_2.$-$3H_2O$ (Gharbi, Jouini, Averbuch-Pouchot & Durif, 1994). Acidic diphosphate anions $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ are often observed in this type of compound. We have undertaken the study of organic diphosphates in order to investigate the atomic arrangements of infinite chains, ribbons or layers of $[H_2P_2O_7^{2-}]_n$, which are generally present in diphosphate chemistry. The crystal structure of the title compound provides a new and interesting example of infinite layers of $[H_2P_2O_7(H_2O_2)]^{2-}$ where the diphosphate groups are interconnected by strong hydrogen bonds (Blessing, 1986; Brown, 1976).
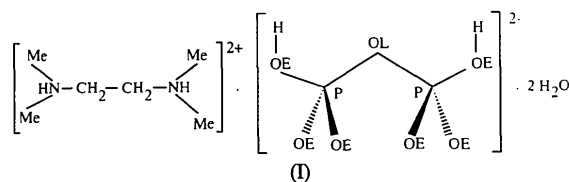
cations are connected to these planes by strong hydrogen bonds. Within a plane containing the acidic diphosphate anions, one can observe the formation, around the inversion center, of a cluster comprising two $H_2P_2O_7^{2-}$ anions. The two $H_2P_2O_7$ groups are linked by a strong acidic hydrogen bond, the O···O distance being of the same order of magnitude as the O···O distances in the PO_4 tetrahedra. In addition, the H···O distance observed in these clusters [1.80 (3) Å] is the shortest in the hydrogen-bond network. Each cluster is connected to six adjacent neighbours by hydrogen bonds from six pairs of water molecules, giving rise to infinite $[H_2P_2O_7(H_2O)_2]_n$ layers projected along the [101] direction, as depicted in Fig. 2. The organic groups are linked to these mineral planes by strong hydrogen bonds with N···O distances of 2.616 (2) and 2.681 (2) Å. The atomic arrangement can therefore be described as a stacking of thick layers perpendicular to the [101] direction and containing all the components of the cell. This structure has a strong tendency to assemble within an infinite network since the calculated compactness is 35%. The P—O distances within a PO_4 tetrahedron of $H_2P_2O_7$ are similar to those commonly observed in dihydrogen diphosphate anions. Three main types of P—O distances can be observed: the P—OL bonds (mean 1.59 Å) corresponding to the bridging O atoms are longer than the P—OH bonds (mean 1.56 Å) involving acidic H atoms which are themselves longer than the P—OE bonds (mean 1.48 Å) corresponding to the external O atoms. The N—C and C—C distances and C—N—C and C—C—N angles are
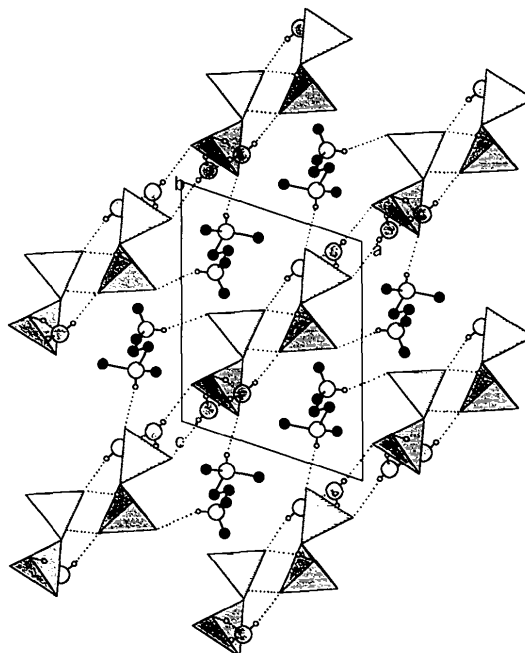

Fig. 1. Projection along the **b** direction of the thick layer profile of the title compound. $H_2P_2O_7^{2-}$ anions are represented by polyhedra. The large circles represent O and N atoms, and black ones C atoms. Hydrogen bonds are denoted by full and dotted lines.
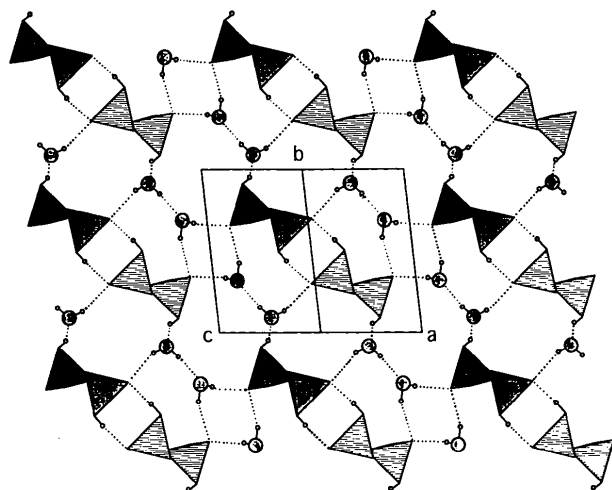
The atomic arrangement in $C_6N_2H_{18}.H_2P_2O_7.2H_2O$ is a typical layer organization. As can be seen from the projection along the *b* axis in Fig. 1, the (101) planes contain $H_2P_2O_7$ groups and water molecules. Organic

Fig. 2. Projection along the [101] direction of the $[H_2P_2O_7(H_2O)_2]_n$ layer, in polyhedral representation. The large circles represent O water molecules, the small ones H atoms. Hydrogen bonds in the layer are denoted by full and dotted lines.

similar and lie within the ranges 1.477 (3)–1.501 (3) Å and 109.8 (2)–113.3 (2)°, respectively. The title structure contains both short strong (N—H⋯O, O—H⋯O) and long weak [O(W)—H⋯O] hydrogen bonds. The range of N(O)⋯O distances is quite narrow, 2.562 (2)–2.681 (2) Å, whereas the O(W)⋯O distances range from 2.715 (2) to 2.968 (2) Å. There are therefore two types of N(O)—H donors, namely the weaker water molecules O(W)—H and the stronger N—H and O—H donors.

Experimental

The preparation of $(C_6H_{18}N_2)H_2P_2O_7.2H_2O$ involved the neutralization of $H_4P_2O_7$ with N,N,N',N'-tetramethylethylenediamine (Fluka Chemica, >97%) in a 1:1 molar ratio. The solution of $H_4P_2O_7$ was prepared using an aqueous solution of $Na_4P_2O_7$ and ion-exchange resins Amberlite IR 120. The resulting solution was then slowly evaporated at room temperature for several weeks. Crystals obtained in this way were stable in normal conditions of temperature and humidity.

Crystal data

$C_6H_{18}N_2^{2+}.H_2P_2O_7^{2-}.2H_2O$
$M_r = 330.21$
Triclinic
$P\bar{1}$
$a = 8.407 (2)$ Å
$b = 9.181 (2)$ Å
$c = 10.950 (3)$ Å
$\alpha = 69.03 (1)°$
$\beta = 68.57 (2)°$
$\gamma = 77.71 (1)°$
$V = 731.3 (3)$ Å³
$Z = 2$
$D_x = 1.500$ Mg m⁻³
$D_m = 1.42$ Mg m⁻³
D_m measured by picnometry

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.338$ mm⁻¹
$T = 293 (2)$ K
Transparent
$0.25 \times 0.20 \times 0.15$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2794 measured reflections
2600 independent reflections
2324 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0069$
$\theta_{max} = 25.23°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 13$
1 standard reflection
frequency: 120 min
intensity decay: 0.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0277$
$wR(F^2) = 0.0786$
$S = 1.051$
2600 reflections
269 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.3225P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.265$ e Å⁻³
$\Delta\rho_{min} = -0.255$ e Å⁻³
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0331 (30)
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(Å^2)$

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
P1	0.30039 (5)	0.67415 (5)	0.53991 (4)	0.02402 (15)
P2	0.21049 (5)	0.73348 (5)	0.79851 (4)	0.02454 (15)
OE22	0.3128 (2)	0.6742 (2)	0.89524 (12)	0.0347 (3)
OE23	0.1607 (2)	0.9133 (2)	0.7674 (2)	0.0447 (4)
OE11	0.1412 (2)	0.7634 (2)	0.51574 (13)	0.0387 (3)
OE12	0.4614 (2)	0.70118 (15)	0.42141 (12)	0.0326 (3)
OE21	0.0551 (2)	0.6572 (2)	0.83328 (13)	0.0369 (3)
OE13	0.2722 (2)	0.4968 (2)	0.6008 (2)	0.0441 (4)
OL12	0.3394 (2)	0.7146 (2)	0.65549 (13)	0.0377 (3)
N1	0.2491 (2)	0.6745 (2)	1.1475 (2)	0.0297 (3)
N2	-0.1914 (2)	0.7568 (2)	0.6677 (2)	0.0319 (4)
C4	0.2621 (2)	0.3869 (2)	1.2227 (2)	0.0314 (4)
C1	0.1797 (2)	0.5325 (2)	1.2620 (2)	0.0334 (4)
C5	-0.2382 (4)	0.7928 (4)	0.5410 (3)	0.0540 (6)
C2	0.4293 (3)	0.6863 (3)	1.1297 (2)	0.0446 (5)
C3	0.1382 (4)	0.8174 (3)	1.1694 (3)	0.0513 (6)
C6	-0.2461 (3)	0.8911 (3)	0.7226 (3)	0.0517 (6)
OW1	0.3383 (2)	1.0877 (2)	0.8034 (2)	0.0513 (4)
OW2	-0.1529 (2)	0.6857 (2)	1.0827 (2)	0.0590 (5)

Table 2. *Selected geometric parameters* $(Å, °)$

P1—OE11	1.4731 (13)	P1—P2	2.872 (1)
P1—OE12	1.4853 (13)	N1—C2	1.479 (3)
P1—OE13	1.5569 (15)	N1—C3	1.480 (3)
P1—OL12	1.5932 (13)	N1—C1	1.493 (2)
P2—OE21	1.4758 (13)	N2—C6	1.477 (3)
P2—OE22	1.4870 (13)	N2—C5	1.484 (3)
P2—OE23	1.5570 (15)	N2—C4'	1.487 (2)
P2—OL12	1.5908 (13)	C4—C1	1.501 (3)
OE11—P1—OE12	117.18 (8)	OE23—P2—OL12	104.25 (8)
OE11—P1—OE13	108.44 (9)	P2—OL12—P1	128.88 (8)
OE12—P1—OE13	110.61 (8)	C2—N1—C3	111.4 (2)
OE11—P1—OL12	110.76 (8)	C2—N1—C1	112.0 (2)
OE12—P1—OL12	103.99 (7)	C3—N1—C1	110.4 (2)
OE13—P1—OL12	105.17 (9)	C6—N2—C5	110.7 (2)

OE21—P2—OE22	118.33 (8)	C6—N2—C4ⁱ	109.8 (2)
OE21—P2—OE23	108.29 (9)	C5—N2—C4ⁱ	113.3 (2)
OE22—P2—OE23	111.39 (8)	N2ⁱ—C4—C1	111.99 (15)
OE21—P2—OL12	108.28 (7)	N1—C1—C4	110.44 (15)
OE22—P2—OL12	105.29 (7)		

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

Table 3. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O(W1)—H1W1···O(W2ⁱ)	0.82 (4)	1.90 (4)	2.715 (2)	172 (3)
O(W1)—H2W1···OE12ⁱⁱ	0.80 (3)	1.97 (3)	2.757 (2)	168 (3)
O(W2)—H1W2···OE21	0.79 (3)	1.94 (3)	2.722 (2)	179 (3)
O(W2)—H2W2···OE21ⁱⁱⁱ	0.74 (3)	2.29 (3)	2.968 (2)	152 (3)
N1—HN1···OE22	0.87 (2)	1.77 (2)	2.616 (2)	165 (2)
N2—HN2···OE11	0.79 (2)	1.93 (2)	2.681 (2)	159 (2)
OE13—HE13···OE12ⁱᵛ	0.77 (3)	1.80 (3)	2.562 (2)	170 (3)
OE23—HE23···OW1	0.84 (3)	1.80 (3)	2.617 (2)	161 (3)

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

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Tris(1,4-butanediyldiammonium) Bis(cyclotriphosphate) Tetrahydrate

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Abstract

The atomic arrangement in the title compound, $3C_4H_{14}N_2^{2+}.2P_3O_9^{3-}.4H_2O$, is described as a three-dimensional network of hydrogen bonds connecting all the components of the structure. Ring anions are linked by hydrogen-bonded water molecules to form infinite ribbons and hydrogen bonds from the organic groups establish the three-dimensional cohesion.

Comment

Fig. 1 is a projection of the $[(P_3O_9)_2(H_2O)_4]^{6-}$ anions of the title structure, (I), along the **a** direction. It illustrates the connection established by $H_2O(2)$ hydrogen bonds between adjacent P_3O_9 groups giving rise to infinite chains extending along the **b** direction. Hydrogen bonds from $H_2O(1)$ assemble these chains along the **c** axis, constructing very linear $[(P_3O_9)_2(H_2O)_4]^{6-}$ ribbons spreading along the **b** direction. The projection along the [010] direction, depicted in Fig. 2, clearly shows the hydrogen bonds from the organic groups interconnecting the ribbons into a three-dimensional network.

(I)
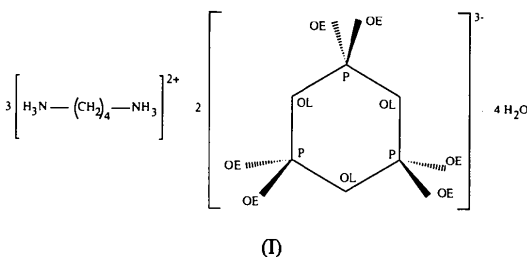
As is always the case in triclinic compounds, the triphosphoric ring anion has no internal symmetry. Three independent PO_4 tetrahedra, linked by three O atoms, form the P_3O_9 group. The main geometric features of this group are the P···P distances and the P···P···P and P—O—P angles. The P···P distances fall within the range 2.857 (1)–2.885 (1) Å, which is in good agreement with the corresponding values found in condensed phosphate chemistry. The overall average value for the P···P···P angles is 60.00°; P···P···P angles in the literature do not deviate significantly from