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Bis(1,6-hexanediaminium) cyclotetraphosphate dihydrate

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The title compound, $2C_6H_{18}N_2^{2+}\cdot P_4O_{12}^{4-}\cdot 2H_2O$, has been synthesized at room temperature and studied by single-crystal X-ray diffraction. The asymmetric unit consists of two hexanediaminium cations, four PO_4 tetrahedra and two water molecules. The organic cations are linked to the cyclic $P_4O_{12}^{4-}$ anions *via* N—H···O hydrogen bonds to form two-dimensional layers, and are further linked by water molecules to form a three-dimensional network.

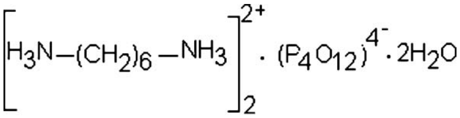
Key indicators

Single-crystal X-ray study
T = 546 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.102
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Phosphate salts of organic cations have been intensively studied due to their uses in various fields, such as catalysis, fuel cells, nonlinear optics and protonic conductors (Kita *et al.*, 1995; Casciola *et al.*, 1986). These structures assemble largely by way of hydrogen bonding between the phosphate anions and the organic cations, which contain donor centres. Water molecules often also play an important role in the cohesion and stability of such structures. Here, we report a structural investigation of the title salt, (I) (Fig. 1), formed from the diprotonated aliphatic diamine, $H_3N(CH_2)_6NH_3^{2+}$, with two donor centres, and cyclotetraphosphate.



$$\left[H_3N-(CH_2)_6-NH_3\right]_2^{2+}\cdot(P_4O_{12})^{4-}\cdot 2H_2O$$

(I)

From a general point of view, the structure of this phosphate could be described as a succession of two types of layers (Fig. 2) parallel to the $(\overline{1}01)$ plane. The first layer, located at $z = 0$, is formed from the $P_4O_{12}^{4-}$ anions and the first organic cation, with atoms N1 and N2. The second (at $z = \frac{1}{2}$), is formed from the water molecules and the second organic cation, with atoms N3 and N4.

In this structure, the cyclic $P_4O_{12}^{4-}$ anion is built up from four crystallographically independent PO_4 tetrahedra. Within each PO_4 tetrahedron, two types of P—O distances are observed. The P—O*L* bonds that link the P atoms to form the P_4O_4 ring are substantially longer than the P—O bonds on the periphery. The P atoms of the $P_4O_{12}^{4-}$ anion form an approximately ideal square [P—P—P angles vary from 88.80 (3) to 90.54 (2)°]. The O—P—O angles average 109.30° around P1, 109.17° around P2, 109.19° around P3 and 109.23° around P4. All these distances and angles are similar to those commonly observed for other anions in condensed phosphate chemistry (Durif, 1995; Soumhi & Jouini, 1995*a*,*b*, 1996*a*,*b*,*c*; Soumhi *et al.*, 1999*a*,*b*, 2001).

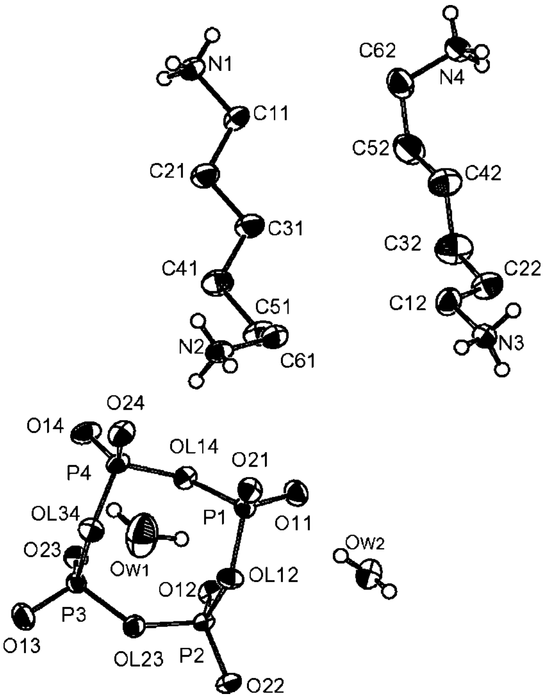


Figure 1

The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. C-bound H atoms have been omitted.

The atomic arrangement of $C_{12}H_{36}N_4P_4O_{12}\cdot 2H_2O$ contains two independent $(C_6H_{18}N_2)^{2+}$ cations. The N—C and C—C distances and N—C—C and C—C—C angles also correspond to values generally observed in this family of materials (Soumhi *et al.*, 1998).

The structure of (I) contains 16 hydrogen bonds. Cation 1 establishes five hydrogen bonds with the $P_4O_{12}^{4-}$ anion in the same layer through atoms N1 and N2, and one hydrogen bond with a water molecule (N1—H2N1···O*W*2). This extends the layer containing the $P_4O_{12}^{4-}$ anions and N1/N2 cations into two dimensions. The N3/N4 cation establishes five hydrogen bonds with $P_4O_{12}^{4-}$ anions in one layer and one hydrogen bond (N3—HN3···O12) with a $P_4O_{12}^{4-}$ anion in an adjacent layer. The four remaining hydrogen bonds involve water molecules and are also responsible for the cohesion between the first type of layers by means of O*W*—H···O—P bonds. While it is clear that these hydrogen bonds contribute significantly to stabilizing the structure of this salt, it should nevertheless be noted that, according to accepted criteria (Blessing, 1986; Brown, 1976), all 16 of these hydrogen bonds are weak.

Experimental

The title compound, (I), was prepared by neutralizing $H_4P_4O_{12}$ with 1,6-hexanediamine in a 2:1 molar ratio. The $H_4P_4O_{12}$ solution was prepared using an aqueous solution of $Na_4P_4O_{12}\cdot 4H_2O$ and an ion-exchange resin (Amberlite IR-120). Colourless single crystals of (I) appeared after evaporation of the solution at room temperature for a few days.

Crystal data

$2C_6H_{18}N_2^{2+}\cdot O_{12}P_4^{4-}\cdot 2H_2O$
$M_r = 588.36$
Monoclinic, $P2_1/n$
$a = 9.676$ (3) Å
$b = 19.118$ (6) Å
$c = 13.882$ (3) Å
$\beta = 95.90$ (2)°
$V = 2554.2$ (13) Å^3
$Z = 4$

$D_x = 1.530$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.37$ mm^{-1}
$T = 546$ (2) K
Plate, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5890 measured reflections
5566 independent reflections
4554 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 27.0°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 24$
$l = -17 \rightarrow 17$
2 standard reflections frequency: 60 min intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.05$
5566 reflections
457 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 2.0372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.59$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

P1—O11	1.482 (2)	P4—O*L*14	1.620 (2)
P1—O21	1.491 (2)	N1—C11	1.487 (3)
P1—O*L*12	1.609 (2)	N2—C61	1.499 (3)
P1—O*L*14	1.613 (2)	N3—C12	1.491 (3)
P2—O22	1.485 (2)	N4—C62	1.491 (3)
P2—O12	1.487 (2)	C11—C21	1.501 (3)
P2—O*L*23	1.603 (2)	C21—C31	1.532 (3)
P2—O*L*12	1.617 (2)	C31—C41	1.520 (4)
P3—O13	1.474 (2)	C41—C51	1.524 (4)
P3—O23	1.490 (2)	C51—C61	1.514 (4)
P3—O*L*23	1.612 (2)	C12—C22	1.514 (4)
P3—O*L*34	1.629 (2)	C22—C32	1.521 (4)
P4—O24	1.487 (2)	C32—C42	1.540 (4)
P4—O14	1.486 (2)	C42—C52	1.511 (4)
P4—O*L*34	1.610 (2)	C52—C62	1.491 (4)
O11—P1—O21	118.48 (9)	O24—P4—O14	119.9 (1)
O11—P1—O*L*12	110.42 (9)	O24—P4—O*L*34	107.53 (9)
O21—P1—O*L*12	107.00 (8)	O14—P4—O*L*34	110.11 (9)
O11—P1—O*L*14	106.75 (9)	O24—P4—O*L*14	110.32 (9)
O21—P1—O*L*14	110.11 (8)	O14—P4—O*L*14	105.69 (9)
O*L*12—P1—O*L*14	103.02 (8)	O*L*34—P4—O*L*14	101.90 (8)
O22—P2—O12	119.84 (9)	N1—C11—C21	111.0 (2)
O22—P2—O*L*23	105.12 (8)	C11—C21—C31	112.4 (2)
O12—P2—O*L*23	111.81 (8)	C41—C31—C21	112.0 (2)
O22—P2—O*L*12	107.42 (9)	C31—C41—C51	113.6 (2)
O12—P2—O*L*12	110.03 (9)	C61—C51—C41	115.4 (2)
O*L*23—P2—O*L*12	100.84 (8)	N2—C61—C51	111.6 (2)
O13—P3—O23	120.27 (9)	N3—C12—C22	110.2 (2)
O13—P3—O*L*23	107.08 (9)	C12—C22—C32	113.5 (3)
O23—P3—O*L*23	109.28 (8)	C22—C32—C42	113.8 (3)
O13—P3—O*L*34	107.65 (9)	C52—C42—C32	111.5 (3)
O23—P3—O*L*34	109.67 (8)	C62—C52—C42	115.1 (3)
O*L*23—P3—O*L*34	101.20 (8)	C52—C62—N4	111.4 (2)

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···O11^{i}	0.95	1.89	2.826 (3)	167 (1)
O*W*1—H2*W*1···O14^{ii}	0.99	2.27	3.252 (4)	172 (1)
O*W*2—H1*W*2···O11	0.90 (4)	1.90 (4)	2.760 (3)	160 (4)
O*W*2—H2*W*2···O13^{iii}	0.81 (4)	2.09 (4)	2.875 (3)	163 (4)
N1—H1N1···O21^{iv}	0.89 (3)	1.95 (3)	2.827 (3)	171 (3)
N1—H2N1···O*W*2^{v}	0.89 (4)	2.00 (4)	2.888 (3)	173 (3)
N1—H3N1···O14^{vi}	0.89 (3)	2.03 (3)	2.926 (3)	178 (3)
N2—H1N2···O23^{ii}	0.84 (4)	1.93 (4)	2.761 (3)	170 (3)
N2—H2N2···O22^{iv}	0.86 (3)	2.01 (4)	2.869 (3)	175 (3)
N2—H3N2···O24	0.92 (4)	2.13 (4)	3.022 (3)	163 (3)
N3—H1N3···O12^{ii}	0.87 (4)	1.95 (4)	2.810 (3)	168 (3)
N3—H2N3···O24^{iii}	0.91 (3)	2.10 (4)	2.997 (3)	168 (3)
N3—H3N3···O22^{vii}	0.94 (4)	1.94 (4)	2.828 (3)	157 (3)
N4—H1N4···O21^{vii}	0.88 (4)	2.03 (4)	2.871 (3)	160 (3)
N4—H2N4···O14^{v}	0.97 (4)	2.22 (4)	3.189 (4)	179 (3)
N4—H3N4···O12^{v}	0.84 (4)	2.05 (4)	2.836 (3)	155 (4)

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

All H atoms, except for those on atoms O*W*1 and C52, were refined without constraints. The atomic coordinates of atoms H1*W*1 and H2*W*2 were fixed, as were their displacement parameters. For atoms H152 and H252, the C—H distances were restrained> to 0.92 (1) Å and their displacement parameters fixed at 0.050 Å^2.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1995) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

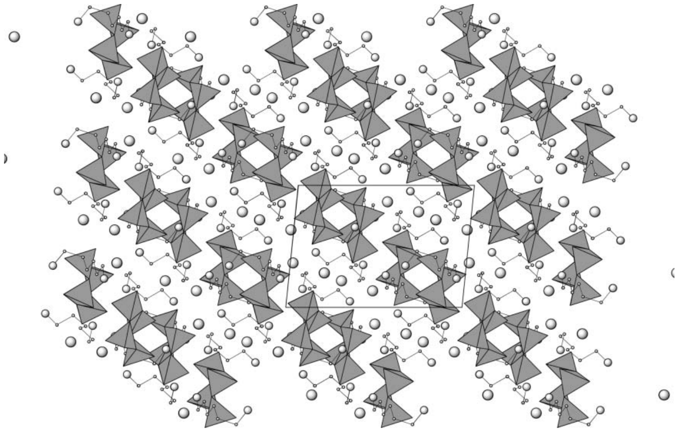

Figure 2
A projection along the *b* axis of the structure of (I). In order of decreasing size, the circles represent water molecules, N and C atoms, respectively. H atoms have been omitted for clarity.

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