Monoclinic
$P2_1/n$
$a = 12.269\,(2)$ Å
$b = 6.081\,(1)$ Å
$c = 20.176\,(2)$ Å
$\beta = 102.629\,(9)^\circ$
$V = 1468.9\,(4)$ Å^3
$Z = 4$
$D_x = 1.841$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 9.56$–18.12°
$\mu = 2.552$ mm^{-1}
$T = 293\,(2)$ K
Irregular
$0.35 \times 0.20 \times 0.20$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.469$, $T_{\max} = 0.629$
2807 measured reflections
2726 independent reflections

2387 reflections with $F^2 > 2\sigma F^2$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25.46^\circ$
$h = -14 \rightarrow 14$
$k = -7 \rightarrow 0$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 30 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.086$
$S = 1.047$
2726 reflections
156 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 2.6277P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.797$ e Å^{-3}
$\Delta\rho_{\min} = -0.844$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Te—C1	2.119 (4)	Te—Cl2	2.4870 (13)
Te—C10	2.122 (4)	Te—Cl1	2.5096 (12)
C1—Te—C10	97.59 (17)	C1—Te—Cl1	86.28 (11)
C1—Te—Cl2	88.07 (11)	C10—Te—Cl1	87.17 (15)
C10—Te—Cl2	87.68 (15)	Cl2—Te—Cl1	171.78 (5)

H atoms were placed in calculated positions with fixed C—H distances (0.93 Å for Csp^2 and 0.96 Å for Csp^3), each riding on their carrier atoms with an isotropic displacement parameter of 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the equivalent isotropic displacement parameter of the attached atom. The highest peak and the deepest hole in the final difference Fourier map are 0.90 and 0.88 Å, respectively, from the Te atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1570). Services for accessing these data are described at the back of the journal.

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Tetrakis(cyclopropylammonium) cyclotetraphosphate tetrahydrate

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Abstract

In the structure of the title phosphate, $4C_3H_8N^+\cdot P_4O_{12}^{4-}\cdot 4H_2O$, the $(P_4O_{12})^{4-}$ cyclic anions are linked through OH$\cdots$O—P hydrogen bonds to build layers parallel to the *ab* plane. These layers are themselves interconnected by means of N—H$\cdots$O hydrogen bonds originating from the $(C_3H_5NH_3)^+$ cations.

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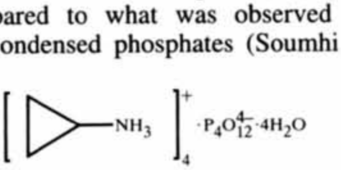
Comment

The structure of the title compound, (I) (Fig. 1), is unusual compared to what was observed in earlier homologous condensed phosphates (Soumhi & Jouini, 1996; Soumhi *et al.*, 1999). It can be described as a succession of two types of layers parallel to the *ab* plane. The first layer is formed solely by the organic cation containing N1. The second layer is composed of $(P_4O_{12})^{4-}$ cyclic anions, water molecules and the second independent organic cation containing N2. This type of structural sequence has been seen already in the diphosphate $(C_3H_5NH_3)_2H_2P_2O_7{\cdot}H_2O$, using the same organic cation (Soumhi *et al.*, 1998).



(I)

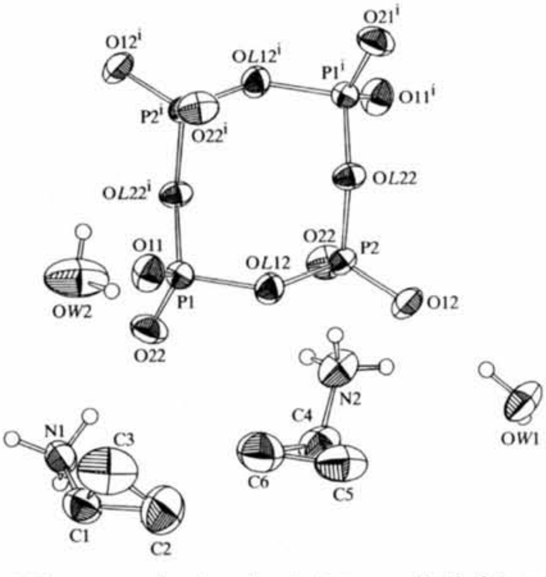


Fig. 1. The asymmetric unit and equivalent second half of the anion, with 50% probability ellipsoids.

Within the mixed layer, each P_4O_{12} ring is surrounded by four organic cations. The $(P_4O_{12})^{4-}$ anions lie on inversion centres located at $(\frac{1}{2},0,0)$ and $(0,\frac{1}{2},0)$. They contain two independent PO_4 tetrahedra. As is commonly observed in condensed cyclotetraphosphates associated with organic molecules in which the P_4O_{12} rings are centrosymmetric, the ring is significantly distorted (Durif, 1995). This type of internal symmetry generally leads to a large deviation of the P···P···P angles from the ideal value (90°). Indeed, the P···P···P angle in this case is 96.17 (2)°. An even larger value (98.89°) was observed in $[NH_3(CH_2)_3NH_3]_2P_4O_{12}{\cdot}2H_2O$ (Bdiri & Jouini, 1990). The values for the title compound are close to those observed in $(C_6H_{18}N_2)_2P_4O_{12}{\cdot}4H_2O$ (Thabet *et al.*, 1997). Furthermore, the P—O distances within the P_4O_{12} ring vary from 1.478 to 1.609 Å, while the P—O—P angle values are 132.93 (8) and 134.16 (7)°. Such values agree with those reported previously for other phosphates (Bdiri & Jouini, 1989).

Two crystallographically independent cyclopropylammonium groups are present in this structure, with different orientations (C—N bond directions). For one of them, containing N1, this bond is almost parallel to the [100] direction and located approximately at $z = \frac{1}{2}$, while the second is located approximately at $z = 0$ and oriented to the [001] direction (Fig. 2). The water molecules are interconnected as pairs. Each pair is linked by hydrogen bonds to two different phosphate groups to build layers parallel to the *ab* plane. The hydrogen bonds involving the H atoms of the $N1H_3$ group of the cyclopropylammonium cation are responsible for the cohesion between the layers, leading to a three-dimensional network. With the exception of two of

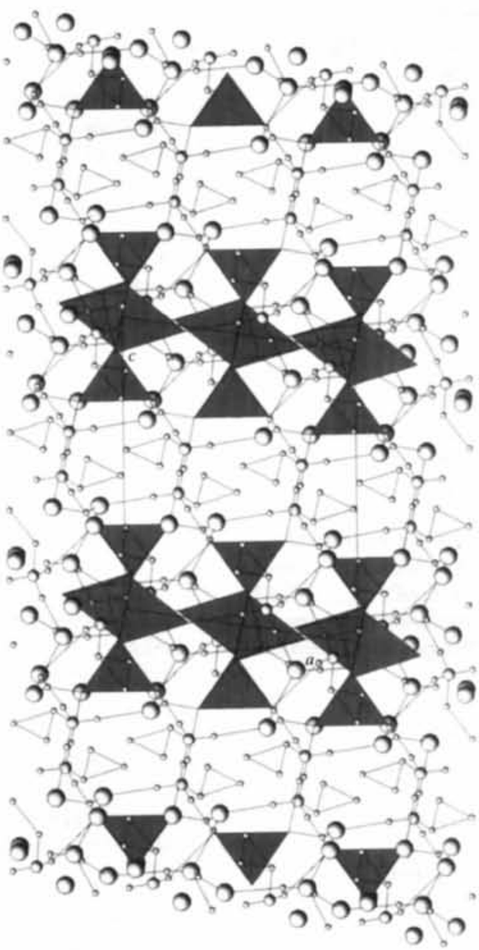


Fig. 2. Projection along the *b* axis. By order of decreasing size, the circles represent water molecules, N, C and H atoms. Hydrogen bonds are shown.

them, involving interactions between the organic cations and water molecules, all the hydrogen bonds involve terminal O atoms of the $(P_4O_{12})^{4-}$ anions. The hydrogen bond connecting the N2 cation to the phosphate group is bifurcated (Averbuch-Pouchot *et al.*, 1989). In the structure, only one hydrogen bond is considered as relatively strong, with O···O = 2.722 (2) Å; the others are weaker, with N···O and O···O distances ranging from 2.734 (2) to 3.069 (3) Å (Blessing, 1986; Brown, 1976).

Experimental

The title compound was prepared by neutralization of $H_4P_4O_{12}$ with cyclopropylamine (Fluka Chemicals, >97%) in a 4:1 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 IR120). Colourless single crystals appeared after evaporation of the solution at room temperature for a few days.

Crystal data

$4C_3H_8N^+ \cdot P_4O_{12}^{4-} \cdot 4H_2O$
$M_r = 620.36$
Monoclinic
$P2_1/a$
$a = 8.045 (2)$ Å
$b = 18.037 (2)$ Å
$c = 10.056 (1)$ Å
$\beta = 99.27 (1)^\circ$
$V = 1440.1 (4)$ Å^3
$Z = 2$
$D_x = 1.431$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.5–14.0^\circ$
$\mu = 0.333$ mm^{-1}
$T = 293 (2)$ K
Plate
$0.7 \times 0.6 \times 0.3$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical correction by ψ scans (North *et al.*, 1968)
$T_{min} = 0.882$, $T_{max} = 0.905$
3356 measured reflections
3132 independent reflections

2729 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 26.97^\circ$
$h = 0 \rightarrow 10$
$k = -23 \rightarrow 0$
$l = -12 \rightarrow 12$
2 standard reflections frequency: 120 min intensity decay: 5.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.091$
$S = 1.058$
3132 reflections
244 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.7448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.629$ e Å^{-3}
$\Delta\rho_{min} = -0.405$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.030 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P1—O11	1.479 (2)	P2—O12	1.478 (2)
P1—O21	1.481 (2)	P2—O22	1.480 (2)
P1—O*L*21	1.599 (2)	P2—O*L*12	1.604 (2)
P1—O*L*12	1.604 (2)	P2—O*L*21^{i}	1.609 (2)
O11—P1—O21	119.42 (8)	O12—P2—O*L*12	105.83 (7)
O11—P1—O*L*21	111.52 (7)	O22—P2—O*L*12	110.97 (7)
O21—P1—O*L*21	106.07 (7)	O12—P2—O*L*21^{i}	106.66 (7)
O11—P1—O*L*12	105.75 (7)	O22—P2—O*L*21^{i}	110.52 (7)
O21—P1—O*L*12	109.64 (8)	O*L*12—P2—O*L*21^{i}	99.64 (7)
O*L*21—P1—O*L*12	103.31 (6)	P2—O*L*12—P1	132.93 (8)
O12—P2—O22	121.00 (8)	P1—O*L*21—P2^{i}	134.16 (7)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···O12	0.86 (3)	1.88 (3)	2.722 (2)	168 (3)
O*W*1—H2*W*1···O12^{i}	0.83 (4)	2.06 (4)	2.855 (2)	160 (4)
O*W*2—H1*W*2···O21	0.92 (5)	1.88 (5)	2.758 (3)	158 (5)
O*W*2—H2*W*2···O*W*1^{ii}	0.85 (4)	1.97 (4)	2.811 (3)	172 (4)
N1—H1N1···O21	0.90 (2)	1.89 (3)	2.790 (2)	178 (3)
N1—H2N1···O11^{iii}	0.94 (3)	1.81 (3)	2.734 (2)	171 (3)
N1—H3N1···O*W*2^{iv}	0.86 (3)	1.91 (3)	2.759 (3)	170 (3)
N2—H1N2···O*W*1^{i}	0.90 (3)	2.05 (3)	2.914 (3)	162 (3)
N2—H2N2···O11^{v}	0.89 (3)	2.27 (3)	2.969 (2)	135 (3)
N2—H2N2···O22^{vi}	0.89 (3)	2.32 (3)	3.069 (2)	141 (3)
N2—H3N2···O22	0.86 (3)	1.93 (3)	2.787 (2)	178 (3)

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

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: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1294). Services for accessing these data are described at the back of the journal.

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