O*E*21—P2—O*E*22	118.33 (8)	C6—N2—C4^{i}	109.8 (2)
O*E*21—P2—O*E*23	108.29 (9)	C5—N2—C4^{i}	113.3 (2)
O*E*22—P2—O*E*23	111.39 (8)	N2^{i}—C4—C1	111.99 (15)
O*E*21—P2—O*L*12	108.28 (7)	N1—C1—C4	110.44 (15)
O*E*22—P2—O*L*12	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(W2^{i})	0.82 (4)	1.90 (4)	2.715 (2)	172 (3)
O(W1)—H2W1···O*E*12^{ii}	0.80 (3)	1.97 (3)	2.757 (2)	168 (3)
O(W2)—H1W2···O*E*21	0.79 (3)	1.94 (3)	2.722 (2)	179 (3)
O(W2)—H2W2···O*E*21^{iii}	0.74 (3)	2.29 (3)	2.968 (2)	152 (3)
N1—HN1···O*E*22	0.87 (2)	1.77 (2)	2.616 (2)	165 (2)
N2—HN2···O*E*11	0.79 (2)	1.93 (2)	2.681 (2)	159 (2)
O*E*13—HE13···O*E*12^{iv}	0.77 (3)	1.80 (3)	2.562 (2)	170 (3)
O*E*23—HE23···O*W*1	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: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The authors would like to express their gratitude to Dr T. Jouini, Département de Chimie, Faculté des Sciences, Tunisia, for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blessing, R. H. (1986). *Acta Cryst.* B**42**, 613–621.
Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.
Durif, A. (1995). In *Crystal Chemistry of Condensed Phosphates*. New York: Plenum.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Gharbi, A., Jouini, A., Averbuch-Pouchot, M. T. & Durif, A. (1994). *J. Solid State Chem.* **111**, 330–337.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kamoun, S., Jouini, A. & Dabbabi, A. (1990). *Acta Cryst.* C**46**, 420–422.
Kamoun, S., Jouini, A. & Daoud, A. (1992). *J. Solid State Chem.* **99**, 18–28.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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

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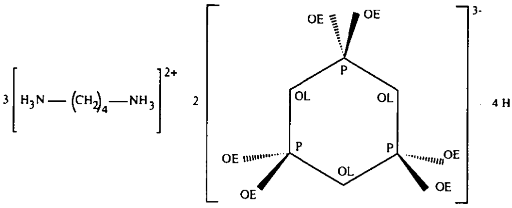
Abstract

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

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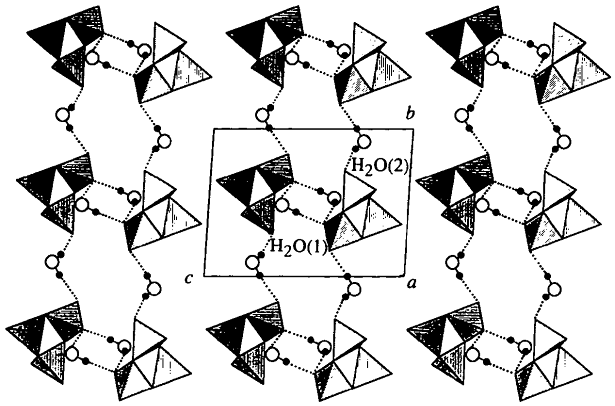

Fig. 1. Projection along the **a** direction, of the $[(P_3O_9)_2(H_2O)_4]^{6-}$ ribbon anions. P_3O_9 groups are represented by polyhedrons. Large white circles represent water O atoms and small black ones water H atoms. Hydrogen bonds are denoted by full and dotted lines.

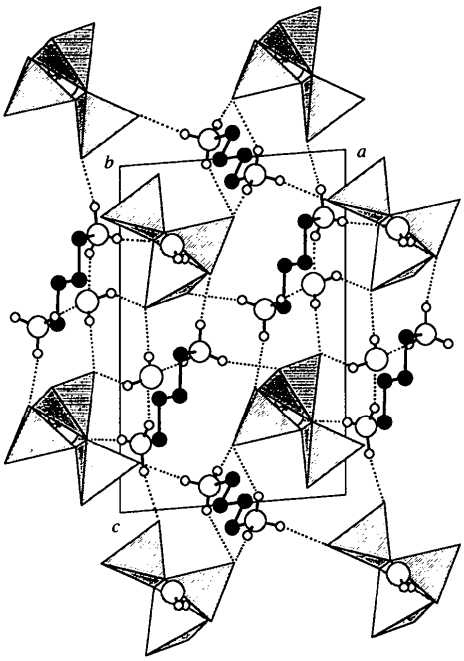

Fig. 2. Projection along the **b** direction of atomic arrangement. Cyclotriphosphate groups are represented as polyhedrons. Large empty circles represent water O atoms, grey circles N atoms, black ones C atoms and small white circles H atoms. Hydrogen bonds are denoted by full and dotted lines.

this value. For the P—O—P angles, the average value is 126.59 (8)°. Thus, for this small ring, there are no large deviations from the average values observed in larger rings, mainly P_6O_{18} (Gharbi, Jouini & Durif, 1995) since geometrical strain decreases with ring size. Distances (C—C, N—C) and angles (N—C—C, C—C—C) relating to the conformation of the organic dication are reported in Table 2. They are similar to the main geometric features of this organic group observed in other phosphoric anions [HPO_4^{2-} (Kamoun & Jouini, 1990), $H_2P_2O_7^{2-}$ (Bartoszak & Jaskolski, 1990), $P_4O_{12}^{4-}$ (Thabet, Bdiri, Jouini & Durif, 1995)] in that they lie within the ranges 1.481 (2)–1.520 (4) Å and 110.5 (2)–112.4 (2)°, respectively. The title structure contains long weak N(O)—O···O hydrogen bonds; the N(O)—O distances are in the range 2.710 (2)–2.982 (3) Å.

Experimental

$(C_4H_{14}N_2)_3(P_3O_9)_2.4H_2O$ was prepared by neutralization of $H_3P_3O_9$ with 1,4-diaminobutane (Fluka chemicals, >97%) in 3:2 molar ratio. $H_3P_3O_9$ solution was synthesized using an aqueous solution of $Na_3P_3O_9$ and ion-exchange resin Amberlite IR 120. This solution was then slowly evaporated at room temperature for one month. The crystals obtained in this way were stable in normal conditions of temperature and humidity.

Crystal data

$3C_4H_{14}N_2^{2+}.2P_3O_9^{3-}.4H_2O$
$M_r = 816.40$
Triclinic
$P\overline{1}$
$a = 8.243\,(2)$ Å
$b = 9.0790\,(10)$ Å
$c = 12.0390\,(10)$ Å
$\alpha = 92.930\,(10)°$
$\beta = 93.310\,(10)°$
$\gamma = 104.466\,(8)°$
$V = 869.0\,(2)$ Å^3
$Z = 1$
$D_x = 1.560$ Mg m^{-3}
$D_m = 1.52$ Mg m^{-3}
D_m measured by pycnometry (toluene as pycnometric liquid)

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 0.398$ mm^{-1}
$T = 293\,(2)$ K
Truncated prism
0.25 × 0.20 × 0.18 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3230 measured reflections
3072 independent reflections
2808 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0126$
$\theta_{\rm max} = 25.08°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 14$
1 standard reflection frequency: 120 min intensity decay: 0.89%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0263$
$wR(F^2) = 0.0766$
$S = 1.076$
3072 reflections
309 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.4746P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.283$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.280$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0435 (25)
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 (Å²)*

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

	x	*y*	*z*	U_{eq}
P1	0.38412 (5)	0.57986 (5)	0.25518 (4)	0.02344 (14)
P2	0.22845 (5)	0.29839 (5)	0.34538 (4)	0.02411 (14)
P3	0.09604 (6)	0.37352 (5)	0.13570 (4)	0.02651 (14)
O*E*11	0.4015 (2)	0.71604 (15)	0.33127 (11)	0.0356 (3)
O*E*12	0.5045 (2)	0.58629 (15)	0.16791 (11)	0.0333 (3)
O*L*12	0.3877 (2)	0.43657 (14)	0.32636 (11)	0.0339 (3)
O*L*13	0.19577 (15)	0.53501 (13)	0.19889 (10)	0.0276 (3)
O*E*21	0.2976 (2)	0.17137 (15)	0.37985 (11)	0.0368 (3)
O*E*22	0.1117 (2)	0.3539 (2)	0.41437 (12)	0.0432 (4)
O*L*23	0.1481 (2)	0.25726 (14)	0.22033 (10)	0.0320 (3)
O*E*31	−0.0831 (2)	0.3637 (2)	0.14078 (14)	0.0486 (4)
O*E*32	0.1714 (2)	0.3528 (2)	0.03005 (11)	0.0425 (4)
O*W*1	0.1433 (2)	0.4755 (2)	0.62967 (15)	0.0477 (4)
O*W*2	0.2338 (2)	0.9106 (2)	0.24067 (15)	0.0502 (4)
N1	−0.3981 (2)	0.3511 (2)	0.05530 (14)	0.0285 (3)
N2	0.6437 (2)	0.2481 (2)	0.44668 (15)	0.0332 (4)
N3	0.0938 (2)	0.2556 (2)	−0.19197 (15)	0.0352 (4)
C1	0.5011 (2)	0.8048 (2)	−0.0692 (2)	0.0300 (4)
C2	−0.4445 (2)	0.0801 (2)	−0.0031 (2)	0.0327 (4)
C3	−0.2707 (3)	0.1220 (2)	0.4425 (2)	0.0322 (4)
C4	−0.2664 (3)	0.0595 (2)	0.3246 (2)	0.0312 (4)
C5	0.8238 (3)	0.9326 (2)	0.3199 (2)	0.0325 (4)
C6	0.8248 (3)	0.8724 (2)	0.2006 (2)	0.0338 (4)

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

P1—O*E*11	1.4727 (13)	P2—P3	2.874 (1)
P1—O*E*12	1.4796 (13)	O*W*1—H1*W*1	0.88 (3)
P1—O*L*12	1.5993 (13)	O*W*1—H2*W*1	0.75 (4)
P1—O*L*13	1.6031 (13)	O*W*2—H1*W*2	0.88 (3)
P2—O*E*22	1.4700 (14)	O*W*2—H2*W*2	0.86 (4)
P2—O*E*21	1.4755 (13)	N1—C1^{i}	1.481 (2)
P2—O*L*23	1.5964 (13)	N2—C3^{ii}	1.487 (2)
P2—O*L*12	1.6098 (13)	N3—C6^{iii}	1.482 (3)
P3—O*E*31	1.462 (2)	C1—C2^{i}	1.506 (3)
P3—O*E*32	1.4712 (14)	C2—C2^{iv}	1.520 (4)
P3—O*L*13	1.6174 (13)	C3—C4	1.508 (3)
P3—O*L*23	1.6193 (13)	C4—C5^{v}	1.519 (3)
P1—P2	2.857 (1)	C5—C6	1.512 (3)
P1—P3	2.885 (1)		
O*E*11—P1—O*E*12	118.42 (8)	O*E*32—P3—O*L*23	107.35 (8)
O*E*11—P1—O*L*12	109.44 (8)	O*L*13—P3—O*L*23	100.17 (6)
O*E*12—P1—O*L*12	108.34 (8)	P1—O*L*12—P2	125.82 (8)
O*E*11—P1—O*L*13	107.31 (7)	P1—O*L*13—P3	127.26 (8)
O*E*12—P1—O*L*13	109.81 (7)	P2—O*L*23—P3	126.68 (8)
O*L*12—P1—O*L*13	102.34 (7)	P1—P2—P3	60.46 (2)
O*E*22—P2—O*E*21	120.48 (9)	P1—P3—P2	59.46 (2)
O*E*22—P2—O*L*23	110.06 (8)	P2—P1—P3	60.06 (2)
O*E*21—P2—O*L*23	107.92 (8)	H1*W*1—O*W*1—H2*W*1	103 (4)
O*E*22—P2—O*L*12	109.95 (9)	H1*W*2—O*W*2—H2*W*2	100 (3)
O*E*21—P2—O*L*12	106.08 (8)	N1^{i}—C1—C2^{i}	110.5 (2)
O*L*23—P2—O*L*12	100.44 (7)	C1^{i}—C2—C2^{iv}	111.8 (2)
O*E*31—P3—O*E*32	122.31 (9)	N2^{vi}—C3—C4	111.7 (2)
O*E*31—P3—O*L*13	106.68 (8)	C3—C4—C5^{v}	111.8 (2)
O*E*32—P3—O*L*13	109.29 (8)	C6—C5—C4^{vii}	110.3 (2)
O*E*31—P3—O*L*23	108.81 (8)	N3^{iii}—C6—C5	112.4 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H1*W*1···O*E*22	0.88 (3)	1.87 (4)	2.737 (2)	171 (3)
O*W*1—H2*W*1···O*E*22^{i}	0.75 (4)	2.24 (4)	2.946 (2)	158 (4)
O*W*2—H1*W*2···O*E*21^{ii}	0.88 (3)	1.87 (3)	2.750 (2)	178 (2)
O*W*2—H2*W*2···O*E*11	0.86 (4)	1.88 (4)	2.732 (2)	169 (3)
N1—H1N1···O*E*12^{iii}	0.88 (2)	1.91 (3)	2.780 (2)	170 (2)
N1—H2N1···O*E*12^{iv}	0.88 (3)	2.05 (3)	2.906 (2)	163 (2)
N1—H3N1···O*E*31	0.90 (2)	1.82 (3)	2.710 (2)	168 (2)
N2—H1N2···O*E*11^{v}	0.93 (3)	1.82 (3)	2.734 (2)	166 (2)
N2—H2N2···O*W*1^{v}	0.89 (3)	2.02 (3)	2.907 (3)	172 (2)
N2—H3N2···O*E*21	0.88 (3)	1.97 (3)	2.820 (2)	165 (2)
N3—H1N3···O*W*1^{vi}	0.94 (3)	2.09 (3)	2.982 (3)	159 (2)
N3—H2N3···O*E*32	0.93 (3)	1.84 (3)	2.759 (2)	169 (2)
N3—H3N3···O*W*2^{iv}	0.89 (3)	1.89 (3)	2.757 (2)	163 (2)

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

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*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

The authors wish to express their most grateful thanks to Dr T. Jouini, Département de chimie, Faculté des Sciences, Tunisia, for the X-ray data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bartoszak, E. & Jaskolski, M. (1990). *Acta Cryst.* C**46**, 2158–2160.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Gharbi, A., Jouini, A. & Durif, A. (1995). *J. Solid State Chem.* **114**, 42–51.

Kamoun, S. & Jouini, A. (1990). *J. Solid State Chem.* **89**, 67–74.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Thabet, H., Bdiri, M., Jouini, A. & Durif, A. (1995). *J. Soc. Chim. Tunis.* **III**, 693–708..

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1,6-Hexanediammonium *cyclo*-Hexaphosphate Hexahydrate

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Abstract

The atomic arrangement of the title compound, $3C_6H_{18}N_2^{2+}.P_6O_{18}^{6-}.6H_2O$, is described as a stacking of P_6O_{18} groups and organic entities. The stability of such an arrangement results from a network of weak hydro-