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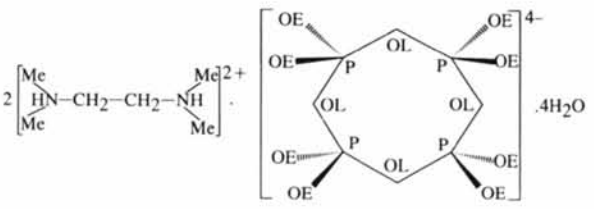

(I)

Acta Cryst. (1997). C**53**, 318–320

Bis(*N*,*N*,*N*′,*N*′-tetramethylethylenediammonium) Cyclotetraphosphate Tetrahydrate

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Abstract

The crystal structure of the title compound, $2C_6H_{18}N_2^{2+}.P_4O_{12}^{4-}.4H_2O$, can be described as typical $[(C_6H_{18}N_2)_2P_4O_{12}]_n$ layers at $y = \frac{1}{2}$ interconnected by water molecules *via* hydrogen bonding.

Comment

The crystal structure of the title compound, (I), has been determined as part of an investigation into the solid-state chemistry of organic phosphates. Among the saturated organic amines RNH_2, R_2NH and R_3N, which are similar in their donor properties, only RNH_2 has been intensively studied with counterions HPO_4^{2-} (Averbuch-Pouchot & Durif, 1987), $H_2PO_4^-$ (Kamoun, Jouini, Kamoun & Daoud, 1989), $P_2O_7^{4-}$ (Kamoun, Jouini & Daoud, 1992), $HP_2O_7^{3-}$ (Gharbi, Jouini, Averbuch-Pouchot & Durif, 1994), $H_2P_2O_7^{2-}$ (Averbuch-Pouchot & Durif, 1993), $P_3O_9^{3-}$ (Averbuch-Pouchot, Durif & Guitel, 1989), $P_4O_{12}^{4-}$ (Jouini, 1989) and $P_6O_{18}^{6-}$ (Durif & Averbuch-Pouchot, 1989). The alkylamine R_2NH has only been characterized three times, *i.e.* with monophosphate HPO_4^{2-} (Kamoun, Jouini & Daoud, 1990), cyclotetraphosphate $P_4O_{12}^{4-}$ (Bdiri & Jouini, 1989) and cyclohexaphosphate $P_6O_{18}^{6-}$ (Gharbi, Jouini & Durif, 1995). The first structure observed with alkylamine R_3N was *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium dihydrogendiphosphate dihydrate (Gharbi, Charfi & Jouini, 1996). The present work provides a second example of an R_3N compound comprising $C_6H_{18}N_2^{2+}$ cations and $P_4O_{12}^{4-}$ anions.

A projection of the atomic arrangement along the *b* axis is shown in Fig. 1. The two crystallographically independent organic $C_6H_{18}N_2$ entities and the P_4O_{12} groups are located around the inversion centres at $(0,\frac{1}{2},0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$, respectively. The $C_6H_{18}N_2^{2+}$ dication at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is linked to $P_4O_{12}^{4-}$ anions by hydrogen bonds, forming infinite anionic ribbons, $\{[(C_6H_{18}N_2)P_4O_{12}]_n\}^{2n-}$, along the **a** direction. The hydrogen bond involving the N2 atom of the remaining $C_6H_{18}N_2$ group at $(0,\frac{1}{2},0)$ acts as a link between ribbons forming a two-dimensional $[(C_6H_{18}N_2)_2P_4O_{12}]_n$ network parallel to the *ac* plane. The N—H···O hydrogen bonds of this structure are strong since the corresponding N···O distances [2.647 (3) and 2.700 (3) Å] are of the same order of magnitude as the O···O distances inside the PO_4 tetrahedra. In addition, the H···O acceptor distances [1.81 (4) and 1.85 (4) Å] are shortest

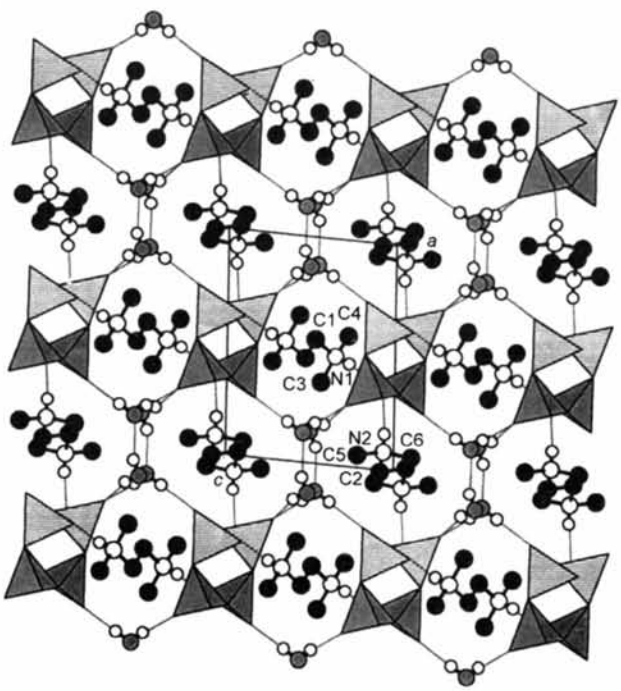

Fig. 1. Projection along the **b** direction of the structure of (I). P_4O_{12} groups are in polyhedral representation, with large white circles representing N atoms, small circles H atoms, grey circles O atoms and black circles C atoms. Hydrogen bonds are denoted by full and dotted lines.

in the present atomic arrangement. The hydrogen bonds involving the H atoms of the water molecules are responsible for the cohesion between the layers. One of them associates the two independent water molecules, as depicted in Fig. 2, and the remaining ones connect three P_4O_{12} groups. This second type of hydrogen bond is weaker than the first since the corresponding O···O distances range between 2.757 (3) and 2.921 (4) Å, whereas the H···O acceptor distances range between 1.93 (4) and 2.11 (5) Å.

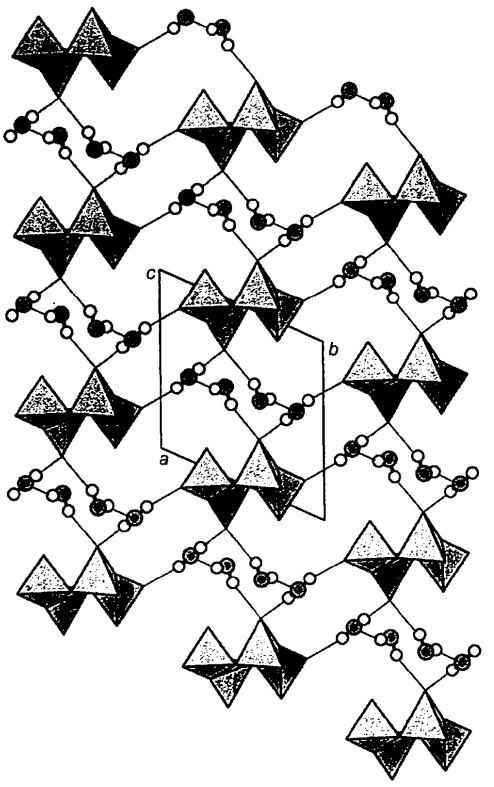

Fig. 2. Projection along the **c** direction of the P_4O_{12} groups located around the $(0,\frac{1}{2},\frac{1}{2})$ inversion centre, with the water molecules shown. Ring anions are in polyhedral representation, with grey circles representing O atoms and white circles H atoms. Hydrogen bonds are denoted by full and dotted lines.

Experimental

The title compound was prepared by neutralization of $H_4P_4O_{12}$ with *N,N,N′,N′*-tetramethylethylenediamine (Fluka Chemica, > 98%). A $H_4P_4O_{12}$ solution was synthesized using an aqueous solution of $Na_4P_4O_{12}$ and ion-exchange resins (Amberlite IR 120). Colourless single crystals appeared after evaporation of the solution at room temperature for a few days.

Crystal data

$2C_6H_{18}N_2^{2+}.P_4O_{12}^{4-}.4H_2O$
M_r = 624.39
Triclinic
$P\bar{1}$
a = 8.557 (4) Å
b = 9.064 (2) Å
c = 10.961 (3) Å
α = 66.830 (10)°
β = 75.36 (3)°
γ = 62.05 (2)°
V = 688.0 (4) Å^3
Z = 1
D_x = 1.507 Mg m^{-3}
D_m = 1.45 Mg m^{-3}
D_m measured by pycnometry (in toluene)
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 14–16°
μ = 0.349 mm^{-1}
T = 293 (2) K
Rectangular prism
0.35 × 0.30 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2726 measured reflections
2405 independent reflections
2139 reflections with $I > 2\sigma(I)$
R_{int} = 0.0266
θ_{max} = 25°
$h = -9 \rightarrow 10$
$k = -9 \rightarrow 10$
$l = 0 \rightarrow 12$
1 standard reflection
frequency: 120 min
intensity decay: 0.24%

Refinement

Refinement on F^2
$R(F)$ = 0.0413
$wR(F^2)$ = 0.1165
S = 1.189
2405 reflections
252 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.7404P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.619 e Å^{-3}
$\Delta\rho_{min}$ = −0.527 e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.042 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
P1	0.05954 (8)	0.26800 (7)	0.63805 (6)	0.0174 (2)
P2	0.13408 (8)	0.37012 (8)	0.34548 (6)	0.0199 (2)
OE11	−0.1114 (3)	0.2783 (3)	0.6224 (2)	0.0326 (5)
OE12	0.1763 (3)	0.1171 (2)	0.7384 (2)	0.0324 (5)
OL12	0.1796 (2)	0.2865 (2)	0.4977 (2)	0.0241 (4)
OL21	0.0311 (2)	0.4438 (2)	0.6619 (2)	0.0248 (4)
OE21	0.2907 (3)	0.3952 (3)	0.2638 (2)	0.0361 (5)
OE22	0.0658 (3)	0.2646 (2)	0.3170 (2)	0.0313 (5)
OW1	0.5036 (4)	0.3931 (4)	−0.1386 (3)	0.0566 (7)
OW2	0.5365 (3)	0.1700 (3)	0.1277 (2)	0.0375 (5)
N1	−0.3514 (3)	0.2584 (3)	0.5248 (2)	0.0273 (5)
N2	0.0577 (3)	0.2539 (3)	0.0761 (2)	0.0252 (5)
C1	−0.5300 (4)	0.5555 (4)	0.5447 (3)	0.0354 (7)
C2	0.0769 (4)	0.4193 (3)	−0.0138 (3)	0.0272 (6)
C3	−0.4349 (5)	0.1647 (5)	0.6437 (4)	0.0443 (8)
C4	−0.2735 (5)	0.1587 (5)	0.4274 (4)	0.0472 (8)
C5	0.2143 (5)	0.0977 (4)	0.0513 (4)	0.0422 (8)
C6	−0.1082 (5)	0.2479 (5)	0.0623 (4)	0.0403 (7)

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

P1—OE11	1.471 (2)	N1—C1^{ii}	1.493 (3)
P1—OE12	1.473 (2)	N1—C4	1.494 (4)
P1—OL21	1.612 (2)	N2—C5	1.488 (4)
P1—OL12	1.616 (2)	N2—C6	1.493 (4)

P2—*OE*21	1.473 (2)	N2—C2	1.494 (3)
P2—*OE*22	1.484 (2)	C1—C1^{ii}	1.508 (6)
P2—*OL*21^{i}	1.602 (2)	C2—C2^{iii}	1.519 (5)
P2—*OL*12	1.602 (2)	P1···P2	2.955 (1)
N1—C3	1.469 (4)	P1···P2^{i}	2.959 (1)
*OE*11—P1—*OE*12	120.90 (12)	P2—*OL*12—P1	133.37 (12)
*OE*11—P1—*OL*21	110.42 (11)	P2^{i}—*OL*21—P1	134.11 (12)
*OE*12—P1—*OL*21	106.81 (11)	P2—P1—P2^{i}	96.82 (3)
*OE*11—P1—*OL*12	110.62 (11)	P1—P2—P1^{i}	83.18 (3)
*OE*12—P1—*OL*12	106.54 (11)	C3—N1—C1^{ii}	115.3 (3)
*OL*21—P1—*OL*12	99.32 (10)	C3—N1—C4	110.2 (3)
*OE*21—P2—*OE*22	118.64 (12)	C1^{ii}—N1—C4	108.9 (2)
*OE*21—P2—*OL*21^{i}	110.82 (11)	C5—N2—C6	109.5 (3)
*OE*22—P2—*OL*21^{i}	105.71 (11)	C5—N2—C2	110.0 (2)
*OE*21—P2—*OL*12	106.89 (12)	C6—N2—C2	113.5 (2)
*OE*22—P2—*OL*12	109.73 (10)	N1^{ii}—C1—C1^{ii}	110.4 (3)
*OL*21^{i}—P2—*OL*12	104.14 (10)	N2—C2—C2^{iii}	111.1 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
*OW*1—H1*W*1···*OE*21^{i}	0.85 (5)	2.11 (5)	2.921 (4)	159 (4)
*OW*1—H2*W*1···*OW*2	0.77 (6)	2.09 (6)	2.816 (4)	158 (5)
*OW*2—H1*W*2···*OE*21	0.83 (4)	1.93 (4)	2.757 (3)	173 (4)
*OW*2—H2*W*2···*OE*12^{ii}	0.85 (5)	1.97 (5)	2.791 (3)	166 (4)
N1—HN1···*OE*11	0.85 (3)	1.81 (4)	2.647 (3)	173 (3)
N2—HN2···*OE*22	0.86 (4)	1.85 (4)	2.700 (3)	169 (4)
H1*W*1—*OW*1···H2*W*1	–	–	–	99 (5)
H1*W*2—*OW*2···H2*W*2	–	–	–	109 (4)

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

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). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Anilino-*N*-phenyl-1*H*-indole-2-carbothioamide

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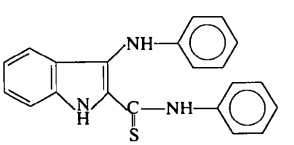
Abstract

The title compound, $C_{21}H_{17}N_3S$, prepared by the reaction of phenyl isothiocyanate with a low-valent titanium reagent, has an intramolecular N—H···N hydrogen bond between the two exocyclic NH groups and a C=S bond length of 1.660 (3) Å.

Comment

The reductive coupling of carbonyl compounds with low-valent titanium reagents is an attractive method for the formation of C—C bonds which has found considerable application in synthesis (Wei-Xing, 1993). Under the action of the low-valent titanium $TiCl_4$–Zn reagent, phenyl isothiocyanate was converted into the title compound, (I), *via* a trimolecular cyclodesulfuration reaction in *ca* 44% yield.



(I)