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(m-$CH_3C_6H_4NH_3)_6P_6O_{18}$

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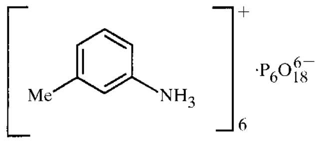
In hexakis(m-toluidinium) cyclohexaphosphate, $6C_7H_{10}N^+\cdot P_6O_{18}{}^{6-}$, the atomic arrangement is typical of a layer structure. Layers including the centrosymmetric P_6O_{18} ring anions develop around the (100) planes at $x = \frac{1}{2}$. The hydrogen-bond distribution is described.

Comment

The title compound, (I), has been isolated as part of an investigation into salts formed between toluidine and cyclohexaphosphoric acid. According to the relative position of the methyl group with respect to the amine function, we can separate three phases with different crystal structures. Two of these have already been studied: (o-$CH_3C_6H_4NH_3)_6$-$P_6O_{18}\cdot 2H_2O$ (Laarafa *et al.*, 1997) and (p-$CH_3C_6H_4NH_3)_6$-$P_6O_{18}\cdot 8H_2O$ (Ben Nasr & Rzaigui, 1999). We report in this contribution the crystal structure of m-toluidine and cyclohexaphosphoric acid salt.



(I)

The main geometrical features such as intramolecular bond distances and angles are reported in Table 1. A view of the asymmetric unit is shown in Fig. 1. The atomic arrangement is typical of a layer structure. Layers including the P_6O_{18} ring anions develop around the (100) planes at $x = \frac{1}{2}$. Between these layers, separated by a distance of 14.622 (3) Å, organic cations establish hydrogen bonds (Table 2) to interconnect the different P_6O_{18} anions (Fig. 2). The $N(1)H_3$ groups produce the internal P_6O_{18} ring cohesion through hydrogen bonds involving external O atoms of each PO_4 tetrahedron. The two other groups, $N(2)H_3$ and $N(3)H_3$, are linked to three different P_6O_{18} rings and so contribute to the intralayer cohesion of this compound. Inside such a layer, the phosphoric ring develops around the inversion centre located at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and thus presents a -1 internal symmetry. The main geometrical features of this ring are reported in Table 1. This atomic arrangement is the third type of structure obtained with toluidine and cyclohexaphosphoric acid in aqueous solution. It is worth noticing that according to the relative position of the methyl group on the phenyl ring, the toluidine cyclohexaphosphate crystallizes with different degrees of hydra-

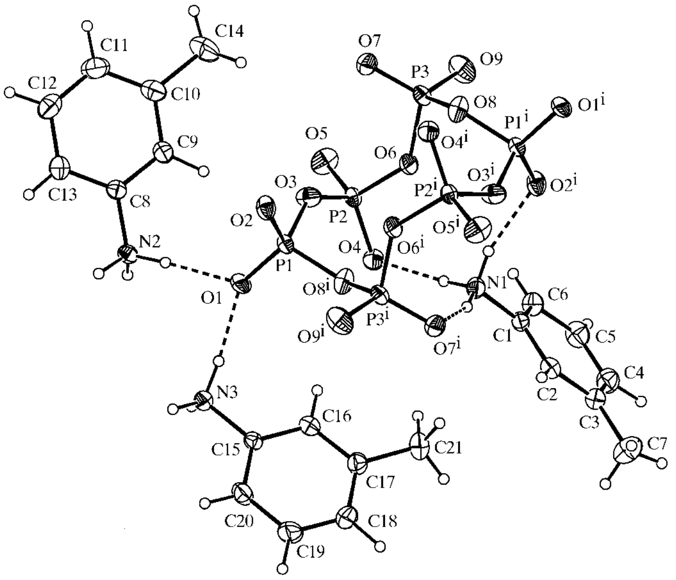


Figure 1
A view of the centrosymmetric $(P_6O_{18})^{6-}$ anion and the three m-toluidinium cations of the asymmetric unit. Displacement ellipsoids are plotted at the 30% probability level. The hydrogen bonds are shown as dashed lines.

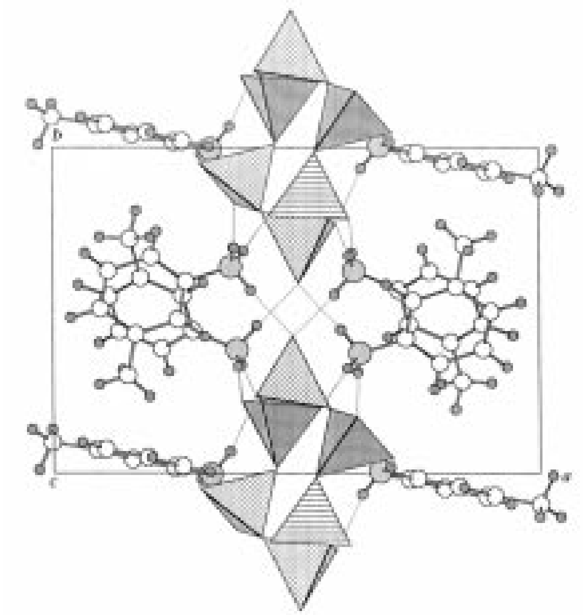


Figure 2
The atomic arrangement of (I) in projection along the c axis. The phosphoric anion is given in a tetrahedral representation. All constituents of the organic molecules are represented: the small empty circles are H atoms, the larger empty ones are C atoms and the hatched circles represent N atoms.

tion: the *meta* isomer gives an anhydrous compound, whereas the *ortho* and *para* isomers lead to di- and octahydrate salts respectively, giving additional hydrogen bonds inside the anionic layers.

Experimental

The title compound was prepared according to the following reaction: an aqueous solution of cyclohexaphosphoric acid was first obtained by passing a solution of $Li_6P_6O_{18}$ through an ion-exchange resin in its H-state (Amberlite IR 120). The lithium salt was prepared according to the process described by Schulke & Kayser (1985), using 'purum p.a. Fluka chemical reagents'. This solution was then added drop by drop to distilled *p*-toluidine (purum p.a. Fluka) under continuous stirring until the solution exhibited a light greenish aspect. The solution was slowly evaporated until large prismatic crystals of (m-$CH_3C_6H_4NH_3)_6P_6O_{18}$ formed.

Crystal data

$6C_7H_{10}N^+\cdot P_6O_{18}^{6-}$
$M_r = 1122.81$
Triclinic, $P\overline{1}$
$a = 14.622$ (3) Å
$b = 10.656$ (4) Å
$c = 9.216$ (4) Å
$\alpha = 112.72$ (3)°
$\beta = 91.29$ (3)°
$\gamma = 89.68$ (3)°
$V = 1324.2$ (8) Å^3
$Z = 1$
$D_x = 1.408$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–13.0°
$\mu = 0.278$ mm^{-1}
$T = 296.2$ K
Prism, colourless
0.40 × 0.29 × 0.16 mm

Data collection

CAD-4 diffractometer
ω–2θ scans
9286 measured reflections
4643 independent reflections
3185 reflections with $I > 3\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 24.97$°
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$
2 standard reflections every 400 reflections intensity decay: 4.17%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.050$
$S = 1.280$
3185 reflections
325 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00123|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

All H atoms were found by difference Fourier synthesis and fixed at their positions with common isotropic displacement parameters ($U_{iso} = 0.08$ Å^2). The range of C—H distances is 0.72 to 1.02 Å.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *TEXSAN* for *Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN* for *Windows*; molecular graphics: *MOLVIEW* (Cense, 1990); software used to prepare material for publication: *TEXSAN* for *Windows*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1058). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.469 (2)	C3—C4	1.377 (5)
P1—O2	1.477 (2)	C3—C7	1.489 (4)
P1—O3	1.578 (2)	C4—C5	1.375 (5)
P1—O8	1.577 (2)	C5—C6	1.383 (4)
P2—O3	1.589 (2)	C8—C9	1.373 (4)
P2—O4	1.483 (2)	C8—C13	1.371 (4)
P2—O5	1.458 (2)	C9—C10	1.380 (4)
P2—O6	1.576 (2)	C10—C11	1.390 (5)
P3—O6	1.604 (2)	C10—C14	1.504 (5)
P3—O7	1.467 (2)	C11—C12	1.371 (5)
P3—O8^{i}	1.609 (2)	C12—C13	1.384 (5)
P3—O9	1.451 (2)	C15—C16	1.370 (4)
N1—C1	1.454 (3)	C15—C20	1.375 (4)
N2—C8	1.461 (3)	C16—C17	1.372 (4)
N3—C15	1.455 (3)	C17—C18	1.383 (4)
C1—C2	1.371 (4)	C17—C21	1.505 (4)
C1—C6	1.372 (4)	C18—C19	1.376 (5)
C2—C3	1.400 (4)	C19—C20	1.375 (4)
O1—P1—O2	117.50 (12)	O5—P2—O6	111.40 (13)
O1—P1—O3	109.84 (13)	O6—P3—O7	110.61 (11)
O1—P1—O8^{i}	109.48 (11)	O6—P3—O8	98.70 (11)
O2—P1—O3	105.23 (11)	O6—P3—O9	107.92 (13)
O2—P1—O8^{i}	111.29 (10)	O7—P3—O8	105.95 (11)
O3—P1—O8^{i}	102.33 (11)	O7—P3—O9	121.22 (13)
O3—P2—O4	109.77 (11)	O8—P3—O9	110.11 (13)
O3—P2—O5	107.09 (12)	P1—O3—P2	137.20 (13)
O3—P2—O6	101.21 (12)	P2—O6—P3	134.46 (12)
O4—P2—O5	120.20 (11)	P1^{i}—O8—P3	133.27 (12)
O4—P2—O6	105.54 (10)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2^{i}	0.88	1.86	2.721 (3)	164
N1—H2$\cdots$O4	0.88	1.93	2.771 (3)	175
N1—H3$\cdots$O7^{i}	0.91	1.84	2.733 (3)	164
N2—H11$\cdots$O9^{ii}	0.94	1.74	2.664 (3)	168
N2—H12$\cdots$O1	0.93	1.88	2.807 (3)	177
N2—H13$\cdots$O4^{iii}	0.89	1.84	2.735 (3)	176
N3—H21$\cdots$O5^{iii}	0.85	1.81	2.657 (3)	176
N3—H22$\cdots$O1	0.95	1.80	2.748 (3)	174
N3—H23$\cdots$O2^{iv}	0.94	1.80	2.741 (3)	176

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

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