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Hexakis(3,4-dichlorobenzylammonium) cyclohexaphosphate hexahydrate

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Key indicators

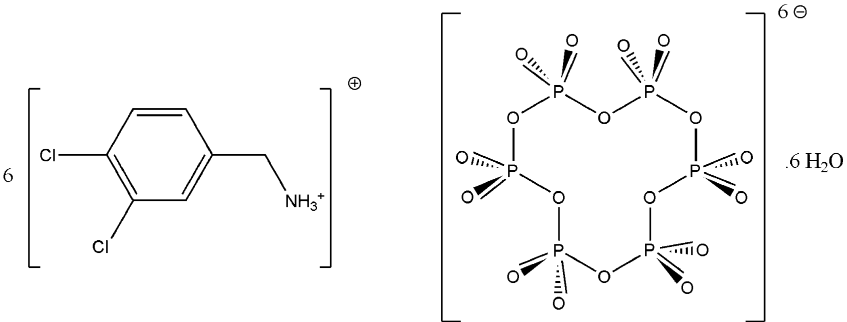
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.122
Data-to-parameter ratio = 18.6

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

Single crystals of the title new cyclohexaphosphate, $6C_7H_8Cl_2N^+\cdot P_6O_{18}{}^{6-}\cdot 6H_2O$, were synthesized and investigated by X-ray diffraction. The phosphate rings are centrosymmetric. The asymmetric unit consists of three cations, one half-anion and three water molecules. The three-dimensional network is built up from parallel layers of anionic P_6O_{18} rings and water molecules, between which the organic molecules are inserted. The 3,4-dichlorobenzylamine exercises an electrostatic interaction with the inorganic anions and establishes strong hydrogen bonds with the O atoms of the ring and the water molecules.

Comment

Hybrid materials with organic and inorganic components are of great interest in solid state chemistry due to their enormous variety of intriguing structural topologies and their fascinating properties, as well as their great potential applications in many fields, such as catalysis, medicine, sorption, electronic conductivity, magnetism and photochemistry (Xiao *et al.*, 2005).



(I)

The title compound, (I), was prepared as part of our ongoing structural studies of inorganic–organic cyclohexaphosphate systems. It consists of cyclic P_6O_{18} units, water molecules and 3,4-dichlorobenzylamine molecules (Fig. 1). The asymmetric unit consists of three cations, one half-anion and three water molecules.

The packing of (I) consists of layers perpendicular to the *a* axis built up from anionic P_6O_{18} rings connected *via* hydrogen bonds from interstitial water molecules. The protonated organic 3,4-dichlorobenzylammonium cations occupy the interlayer spaces (Fig. 2) and participate in the hydrogen-bonding scheme via the water molecules, with $N-H\cdots O$ and $O-H\cdots O$ interactions connecting the different entities of the structure, assuring the cohesion of the network (Fig. 3 and Table 2).

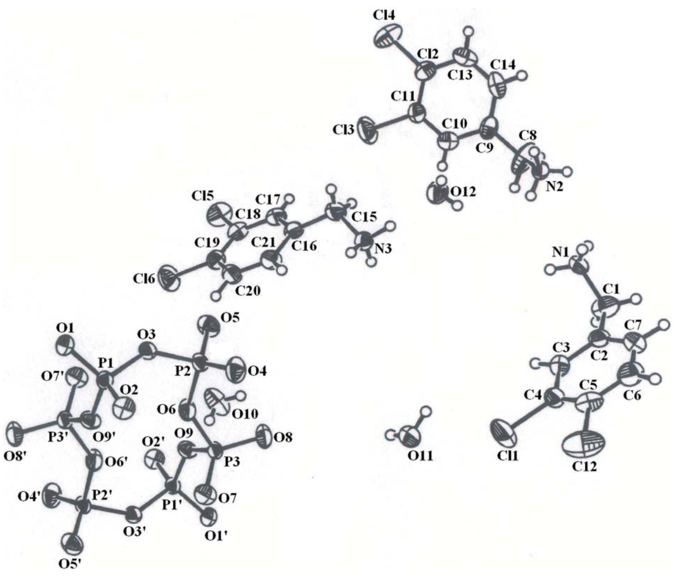


Figure 1
The asymmetric unit of (I), together with the other half of the anion, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. (Symmetry code for primed atoms: 1 − *x*, 1 − *y*, −*z*.)

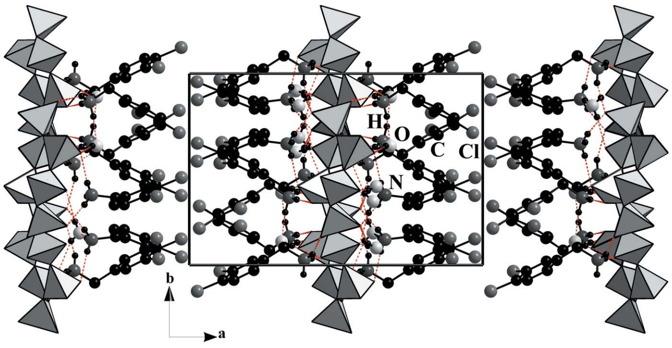


Figure 2
A projection of the structure of (I), along the *c* axis. The phosphate anions are shown in a tetrahedral representation. Hydrogen bonds are shown as dashed lines.

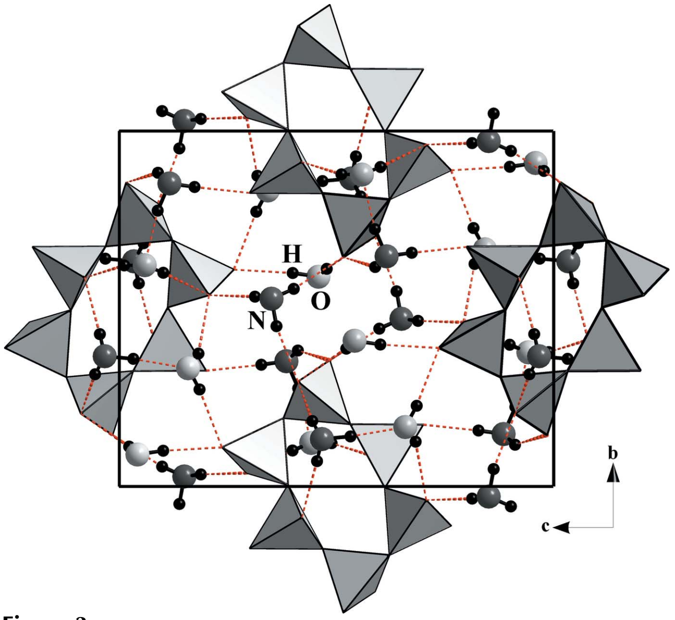


Figure 3
A projection, along the *a* axis, of the inorganic layer of (I). Organic cations have been omitted for clarity. Dashed lines represent hydrogen bonds.

Inside each such layer, the phosphate rings are located around inversion centres at ($\frac{1}{2}$, 0, 0) and are built up by six PO_4 tetrahedra. The P···P···P angles of 93.25 (1), 102.25 (1) and 131.87 (1)° show that the rings are significantly distorted from the ideal three-fold symmetry. It should be noted that these large deviations are commonly observed in cyclohexaphosphates with a ring of low local symmetry (*e.g.* only centrosymmetric) (Durif & Averbuch-Pouchot, 1990; Khedhiri *et al.*, 2003), as in the title compound. Nevertheless, this distortion is comparatively less important than that observed in $Cs_6P_6O_{18}\cdot6H_2O$, which shows the greatest distortion for the same angles, ranging between 93.2 and 145.5° (Averbuch-Pouchot & Durif, 1991). The great flexibility of the P_6O_{18} rings can probably explain the pronounced stability of cyclohexaphosphates compared with their smaller ring analogues. In spite of this distortion, examination of the main geometric features of the PO_4 tetrahedra (P—O distances and P—O—P or O—P—O angles, as well as P···P distances) shows that they are in accordance with values generally observed in condensed phosphate anions.

The 3,4-dichlorobenzylammonium cations involved in this structure with non-parallel orientations, as seen in Fig. 2, display no special features. They alternate with the inorganic anions to build, with the water molecules, a three-dimensional hydrogen-bonded network.

Experimental

The title compound was synthesized by neutralization of an acidic aqueous solution (10 ml) of $H_6P_6O_{18}$ (3.5 mmol) with an ethanolic solution (2.8 ml) of 3,4-dichlorobenzylamine (21 mmol, density 1.320 g ml^{-1}). The cyclohexaphosphoric acid used was produced from an $Li_6P_6O_{18}$ (Schulke & Kayser, 1985) solution using an ion-exchange resin (Amberlite IR 120). The resulting solution was allowed to evaporate slowly at room temperature for several days to give colourless single crystals of (I), which are stable under normal conditions of temperature and humidity.

Crystal data

$6C_7H_8Cl_2N^+\cdot O_{18}P_6^{6-}\cdot 6H_2O$
M_r = 1644.18
Monoclinic, $P2_1/c$
a = 19.384 (3) Å
b = 11.788 (5) Å
c = 15.447 (3) Å
β = 111.230 (18)°
V = 3290.1 (16) Å^3
Z = 2
Mo *Kα* radiation
μ = 0.73 mm^{-1}
T = 293 (2) K
0.7 × 0.4 × 0.2 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.774, T_{max} = 0.864
8608 measured reflections
7921 independent reflections
5615 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
2 standard reflections
frequency: 120 min
intensity decay: 4%

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Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.122$
$S = 1.02$
7921 reflections
427 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.4766 (19)	P2—O6	1.5937 (19)
P1—O2	1.4905 (19)	P2—O3	1.6095 (18)
P1—O3	1.5945 (17)	P3—O8	1.4743 (18)
P1—O9^{i}	1.5986 (18)	P3—O7	1.479 (2)
P2—O4	1.474 (2)	P3—O6	1.5943 (19)
P2—O5	1.483 (2)	P3—O9	1.6029 (18)
O1—P1—O2	118.86 (12)	O6—P2—O3	98.62 (10)
O1—P1—O3	105.79 (10)	O8—P3—O7	119.82 (12)
O2—P1—O3	110.69 (10)	O8—P3—O6	110.95 (11)
O1—P1—O9^{i}	111.72 (11)	O7—P3—O6	107.51 (12)
O2—P1—O9^{i}	104.44 (10)	O8—P3—O9	108.72 (11)
O3—P1—O9^{i}	104.53 (10)	O7—P3—O9	110.11 (10)
O4—P2—O5	119.62 (12)	O6—P3—O9	97.43 (11)
O4—P2—O6	111.24 (12)	P1—O3—P2	135.93 (11)
O5—P2—O6	109.24 (12)	P2—O6—P3	136.74 (12)
O4—P2—O3	111.00 (11)	P1^{i}—O9—P3	135.61 (12)
O5—P2—O3	104.90 (11)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*A*···O4^{ii}	0.833 (19)	2.04 (3)	2.815 (3)	154 (5)
O10—H10*B*···O2^{i}	0.821 (19)	2.21 (3)	2.919 (3)	145 (4)
O11—H11*A*···O7^{iii}	0.833 (18)	1.93 (2)	2.742 (3)	166 (4)
O11—H11*B*···O5^{ii}	0.827 (18)	2.100 (19)	2.924 (3)	175 (4)
O12—H12*A*···O5^{iii}	0.802 (19)	2.05 (3)	2.773 (3)	151 (4)
O12—H12*B*···O4^{iv}	0.825 (18)	2.07 (2)	2.886 (3)	172 (4)
N1—H1*A*···O8^{iii}	0.89	1.82	2.715 (3)	178
N1—H1*B*···O1^{iv}	0.89	2.23	3.001 (3)	144
N1—H1*C*···O11^{iii}	0.89	1.96	2.837 (4)	168
N2—H2*A*···O2^{iv}	0.89	2.08	2.888 (3)	151
N2—H2*B*···O1^{v}	0.89	1.91	2.749 (3)	156
N2—H2*C*···O5^{iii}	0.89	1.91	2.790 (3)	171
N3—H3*A*···O2^{ii}	0.89	1.96	2.842 (3)	169
N3—H3*B*···O12	0.89	1.93	2.810 (3)	172
N3—H3*C*···O7^{ii}	0.89	1.97	2.856 (3)	179

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

Water H atoms were located in difference Fourier maps and refined with an isotropic displacement parameter $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm O)$. O—H and H···H distances were restrained to 0.82 Å to ensure a reasonable geometry for the water molecules. All H atoms attached to C and N were treated as riding on their parent atoms, with C—H = 0.93 (CH) or 0.97 Å (CH_2) and N—H = 0.89 Å, and with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$ or $1.5U_{\rm eq}(\rm N)$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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