Tetrakis(chloromethyl)phosphonium chloride monohydrate

Ralf Weisbarth[a] and Martin Jansen[b]*

[a]Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany, and [b]Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Correspondence e-mail: m.jansen@fkf.mpg.de

Tetrakis(chloromethyl)phosphonium chloride monohydrate, $C_4H_8Cl_4P^+\cdot Cl^-\cdot H_2O$ or $P(CH_2Cl)_4^+\cdot Cl^-\cdot H_2O$, is the first crystal structure determination of a tetrakis(halogenomethyl)-phosphonium compound to date. The only comparable structures known so far are of phosphonium ions containing just one halogenomethyl group. The solvent water molecule interacts with the Cl^- anion *via* hydrogen bonds, with $O\cdots Cl$ distances of 3.230 (2) and 3.309 (2) Å. The structure also contains several $C-H\cdots Cl^-$ and $C-H\cdots O$ contacts, though with longer $D\cdots A$ distances [$D\cdots A$ 3.286 (3)–3.662 (2) Å] or bent $D-H\cdots A$ angles. For these reasons, the $C-H\cdots Cl^-$ and $C-H\cdots O$ interactions should not be considered as strong hydrogen bonds.

Comment

Hoffman (1921, 1930) reported on the formation of tetrakis(chloromethyl)phosphonium chloride as water-free needle-shaped crystals which melt at 466 K. We have now discovered that tetrakis(chloromethyl)phosphonium chloride also forms the title monohydrate, (I). Compound (I) can be obtained by dissolving tetrakis(chloromethyl)phosphonium chloride in organic solvents and then slowly removing the solvent in air. Monohydrate (I) can be distinguished from the anhydrous compound by its crystal habit and melting point. By recrystallization of (I) from methanol/ethyl acetate (3:16), needle-shaped crystals of the anhydrous material can be recovered.
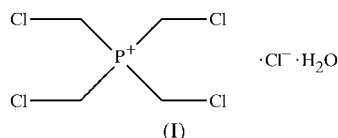
The present crystal structure determination of (I) is the first such structure reported to date, and the only comparable structures known so far are of phosphonium ions containing just one halogenomethyl group (Cambridge Structural Database, Version 5.22 of October 2001; Allen & Kennard, 1993).

In the cation of (I), P is coordinated tetrahedrally by C atoms (Fig. 1). The $Cl-C-PR_2-R$ conformations are all staggered, with torsion angles ranging from 161.8 (1) to 179.6 (1)°. The coordination of the Cl^- anions by water molecules presents an interesting feature, which is shown in Fig. 2. The $O-H\cdots Cl^-$ hydrogen bonds establish an approximately planar eight-membered ring, with a maximum deviation of 0.04 (2) Å from the best plane for atom H2. The $O-H\cdots Cl^-$ hydrogen bonds are nearly linear.
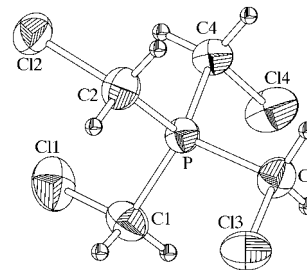

Figure 1
A view of the cation of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Additional coordination of Cl^- ions *via* $C-H\cdots Cl^-$ interactions should be weaker than the $O-H\cdots Cl^-$ bonds for polarization reasons. This is confirmed by the longer $H\cdots Cl^-$ distances and the bent $C-H\cdots Cl$ angle, compared with the geometry of the $O-H\cdots Cl^-$ contacts (Table 2).
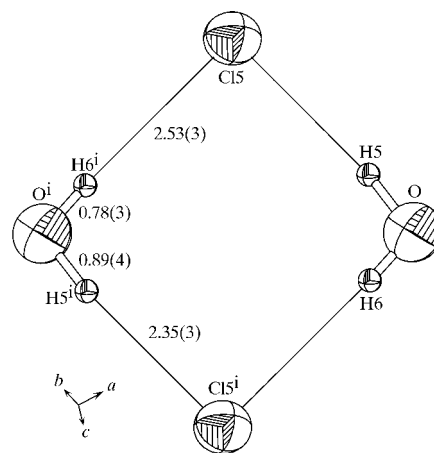

Figure 2
The coordination of the Cl^- anions in (I) by water molecules. Displacement ellipsoids are drawn at the 50% probability level and bond lengths are given in Å. [Symmetry code: $1 - x$, $1 - y$, $1 - z$.]

Experimental

Tetrakis(chloromethyl)phosphonium chloride (100 mg) was prepared according to the method of Hoffman (1921, 1930) and Reeves *et al.* (1955), and dissolved in a mixture of methanol and ethyl acetate (3:16, 50 ml). The solvent was removed slowly at room temperature in an open vessel. After 5 d, colourless prism-shaped crystals of (I) formed (m.p. 401 K).

organic compounds

$C_4H_8Cl_4P^+ \cdot Cl^- \cdot H_2O$
$M_r = 282.34$
Orthorhombic, $Pbca$
$a = 13.0928\,(2)$ Å
$b = 12.6946\,(2)$ Å
$c = 13.2335\,(2)$ Å
$V = 2199.51\,(6)$ Å^3
$Z = 8$
$D_x = 1.705$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 36 817
  reflections
$\theta = 1.0–26.0°$
$\mu = 1.41$ mm^{-1}
$T = 293\,(2)$ K
Prismatic block, colourless
$0.12 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector
  diffractometer
φ and ω scans
50 779 measured reflections
2171 independent reflections
1929 reflections with $I > 2\sigma(I)$

$R_{int} = 0.058$
$\theta_{max} = 26°$
$h = -16 \rightarrow 16$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.08$
2171 reflections
140 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2$
  $+ 1.3871P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

All H-atom positions were found on the difference Fourier map and refined independently [C—H range 0.89 (3)–1.00 (2) Å] with isotropic displacement parameters.

Table 1
Selected geometric parameters (Å, °).

P—C1	1.804 (2)	C1—Cl1	1.774 (2)
P—C2	1.802 (2)	C2—Cl2	1.775 (2)
P—C3	1.802 (2)	C3—Cl3	1.773 (2)
P—C4	1.803 (2)	C4—Cl4	1.7726 (19)
C1—P—C2	112.20 (11)	C3—P—C4	109.04 (10)
C1—P—C3	107.88 (11)	P—C1—Cl1	111.64 (12)
C1—P—C4	110.19 (10)	P—C2—Cl2	110.30 (11)
C2—P—C3	106.55 (10)	P—C3—Cl3	108.66 (11)
C2—P—C4	110.83 (10)	P—C4—Cl4	107.02 (10)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O—H5$\cdots$Cl5	0.88 (3)	2.35 (3)	3.230 (2)	173 (3)
O—H6$\cdots$Cl5^i	0.78 (3)	2.53 (3)	3.309 (2)	175 (3)
C1—H1$B\cdots$Cl5^{ii}	0.89 (3)	2.65 (3)	3.512 (2)	165 (2)
C2—H2$B\cdots$Cl5^{iii}	0.96 (2)	2.76 (2)	3.598 (2)	146.6 (19)
C3—H3$B\cdots$Cl5^{iv}	0.89 (3)	2.79 (3)	3.662 (2)	166 (2)
C4—H4$B\cdots$Cl5^{iii}	0.95 (2)	2.69 (2)	3.493 (2)	142.9 (18)
C1—H1$A\cdots$O^v	0.95 (2)	2.40 (2)	3.286 (2)	154.5 (19)
C4—H4$A\cdots$O^i	0.99 (2)	2.50 (2)	3.486 (3)	169.9 (18)

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1998).

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