

Phase change in tetraphenylphosphonium perchlorate

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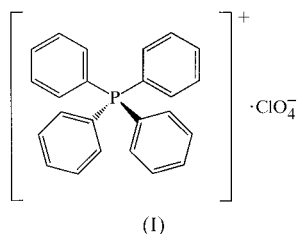
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The title compound, $C_{24}H_{20}P^+ \cdot ClO_4^-$, undergoes a sudden reversible phase change in the region of 173–180 K which involves ordering of three quarters of the perchlorate anions.

Comment

Simple ionic salts such as $Ph_4P^+ \cdot ClO_4^-$ are often produced as unwanted by-products of metal complexation reactions. The good crystal quality of many of these ionic salts means that they can often be inadvertently chosen from the reaction mixture for single-crystal X-ray diffraction analysis, particularly if the yield of usable crystals of the desired product for the reaction is low. Usually, however, the dimensions of the unit cell will be indicative of the by-product involved, and reference to published structures of these salts will prevent unnecessary collection of a full data set. However, with the advent of modern cryogenic techniques, the possibility of phase changes at low temperatures can result in a simple salt giving a unit cell with unrecognizable dimensions. We report such a case, with the observation of a reversible phase change at low temperature in $Ph_4P^+ \cdot ClO_4^-$, (I).



The structure of (I) has previously been reported at 293 K (RT phase) as tetragonal, $I\bar{4}$, $a = 12.383$ (3), $c = 7.188$ (2) Å, $V = 1102.2$ (5) Å³ and $Z = 2$ (Vittal & Dean, 1996). The data we collected at 123 K (LT phase) also gave a tetragonal cell, space group $I\bar{4}$, but with dimensions $a = 17.0481$ (4), $c = 13.7568$ Å, $V = 2998.2$ (2) Å³ and $Z = 8$. Further determinations of the unit cell at temperatures between 123 and 223 K indicated a reversible and sudden phase change between the two phases somewhere between 173 and 180 K.

The difference between the two phases involves ordering of the perchlorate anions. In the RT phase, there is only one crystallographically unique perchlorate anion, which is disor-

dered over three positions. Both the Cl and P atoms lie on crystallographic $\bar{4}$ axes. In the LT phase, there are four crystallographically unique perchlorate anions, but still only one crystallographically unique Ph_4P^+ cation (Fig. 1). All four Cl atoms still lie on crystallographic $\bar{4}$ axes, but the P atoms now lie on a general position. Also, now only one of the four perchlorates is disordered. It is centred on Cl4 and has been modelled as being disordered over two equal positions. Thus, the phase change is induced by ordering of three quarters of the perchlorate anions (Fig. 2). The cell dimensions of the LT (a, c, V) and HT (a', b', V') phases are related by $a = 2^{1/2}a'$, $b = 2b'$ and $V = 4V'$. Thus, accompanying the phase change is a contraction in cell dimensions of equivalent cells (*i.e.* the equivalent LT cell which has the same contents as the HT cell would have the dimensions $a = 12.055$, $b = 6.878$ Å and $V = 999.53$ Å³).

A number of other similar salts have been found at room temperature to have crystal structures isomorphous with the RT phase of (I) (Couldwell, 1979; Vittal & Dean, 1996, and references therein). It would be reasonable to expect a number of these to undergo similar phase changes at low temperatures.

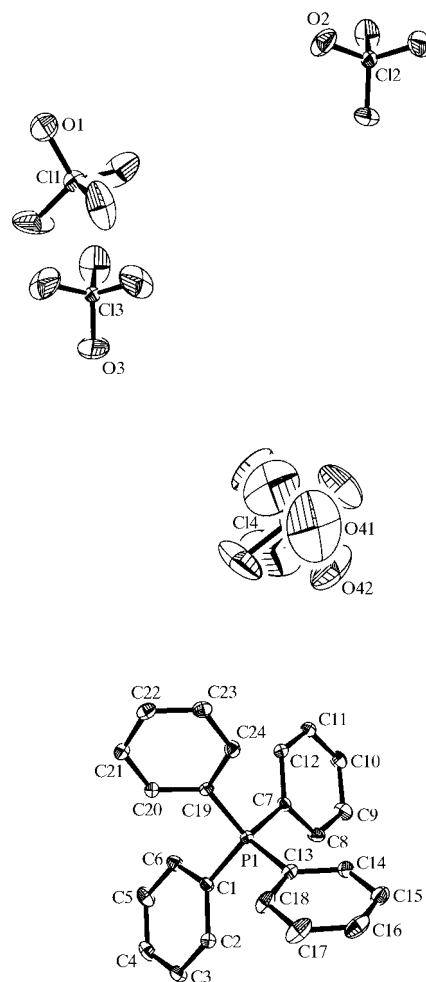


Figure 1

The atom-numbering scheme for the LT phase of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted. Unlabelled atoms are symmetry-related to those labelled.

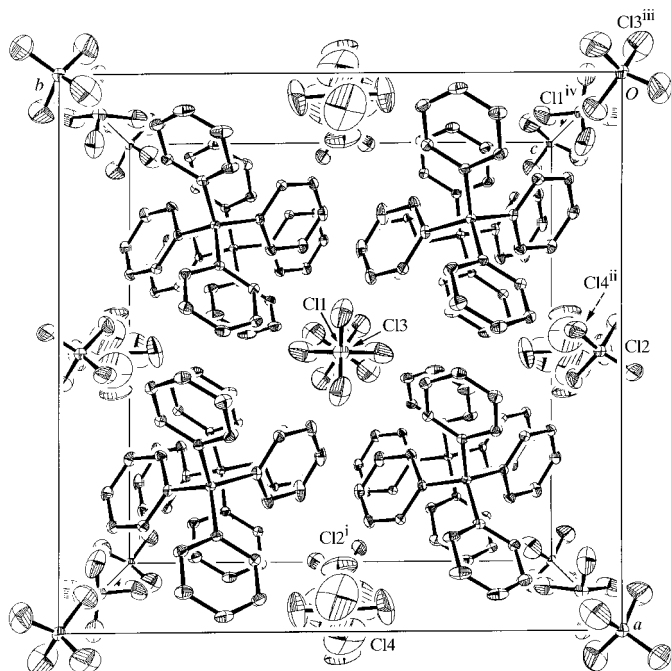


Figure 2
Packing diagram for the LT phase of (I). The Cl atoms of some of the perchlorate anions are labelled to indicate those related by symmetry; all Ph_4P^+ cations are crystallographically identical. Symmetry codes: (i) $1 + y, 1 - x, 1 - z$; (ii) $y, 1 - x, 1 - z$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$.

Experimental

The product was obtained as large colourless crystals from an acetonitrile solution containing $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $(\text{Ph}_4\text{P})[\text{N}(\text{CN})_2]$ and tetramethylpyrazine.

Crystal data

$\text{C}_{24}\text{H}_{20}\text{P}^+ \cdot \text{ClO}_4^-$	Mo $K\alpha$ radiation
$M_r = 438.82$	Cell parameters from 11973 reflections
Tetragonal, $I\bar{4}$	$\theta = 1.69\text{--}30.50^\circ$
$a = 17.0481(4) \text{ \AA}$	$\mu = 0.301 \text{ mm}^{-1}$
$c = 13.7568(3) \text{ \AA}$	$T = 123(2) \text{ K}$
$V = 3998.24(16) \text{ \AA}^3$	Block, colourless
$Z = 8$	$0.40 \times 0.28 \times 0.15 \text{ mm}$
$D_x = 1.458 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD diffractometer	5030 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.026$
Absorption correction: by integration (<i>XPREP</i> ; Siemens, 1994)	$\theta_{\text{max}} = 30.5^\circ$
$T_{\text{min}} = 0.913, T_{\text{max}} = 0.954$	$h = -24 \rightarrow 17$
11969 measured reflections	$k = -20 \rightarrow 24$
3177 independent reflections (plus 2804 Friedel-related reflections)	$l = -18 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 1.5872P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.052$	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
5981 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
279 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.03 (5)

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cl1—O1	1.4224 (15)	P1—C7	1.7940 (14)
Cl2—O2	1.4347 (14)	P1—C19	1.7940 (14)
Cl3—O3	1.4128 (17)	P1—C1	1.7952 (15)
Cl4—O41	1.303 (4)	P1—C13	1.7966 (15)
Cl4—O42	1.463 (4)		
C7—P1—C19	109.81 (6)	C7—P1—C13	110.36 (7)
C7—P1—C1	107.76 (7)	C19—P1—C13	107.63 (7)
C19—P1—C1	110.29 (6)	C1—P1—C13	111.00 (7)

The perchlorate anion centred on Cl4 was disordered and was modelled over two equal positions.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1294). Services for accessing these data are described at the back of the journal.

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