Electrocrystallisation and Crystal Structure Determination of $Ph_4PC_{60}{\cdot}Ph_4PCl$

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$Ph_4PC_{60}{\cdot}Ph_4PCl$ is prepared by electrocrystallisation and its structure determined by single crystal structure analysis.

Since the discovery of the fullerenes[1] their chemical behaviour has been studied extensively.[2] Although investigations have shown the possibility of their chemical[3] and electrochemical reduction in solution[4] (*i.e.* C_{60} down to $C_{60}{}^{6-}$) only few reports on fullerides as crystalline solids have appeared. Wudl *et al.* describe the synthesis of $Ph_4PC_{60}{\cdot}(Ph_4PCl)_2$, the composition of which was reportedly determined only by elemental analyses.[5] A second paper also refers to the same compound.[6] Another solid containing $C_{60}{}^{-}$ obtained electrochemically is $[(Ph_3P)_2N]C_{60}$.[7] Here we report the novel fulleride $Ph_4PC_{60}{\cdot}Ph_4PCl$ and its single crystal structure determination.

Coarse crystalline samples were prepared by electrocrystallisation at ambient temperature. Direct current electrolysis was carried out on a solution of 1,2-dichlorobenzene containing 10^{-3} mol dm^{-3} C_{60} and 10^{-2} mol dm^{-3} Ph_4PCl, applying 2 V to platinum wires (10 mm^2 surface). After 24 h black, air-stable, tetragonal bipyramidal crystals of $[(C_6H_5)_4P]C_{60}{\cdot}[(C_6H_5)_4P]Cl$ formed. Magnetic measurements† showed the presence of unpaired spins.

Single crystal structure analysis‡ confirmed the analytically determined composition. Except for the fulleride anion all atoms (including hydrogen) are in fully occupied positions with thermal parameters as expected for an ordered molecular crystal structure. The packing of the complex cations provides sites which may be occupied by $C_{60}{}^{-}$ in two different orientations. These are, however, geometrically equivalent, and thus have the same potential energy and are occupied to the same extent. Attempts to refine the structure assuming twinning failed. The disorder must therefore be local, either static or dynamic, the latter being most probable. Refinement using a split atom model yielded low residual electron densities and reasonable temp. factors.

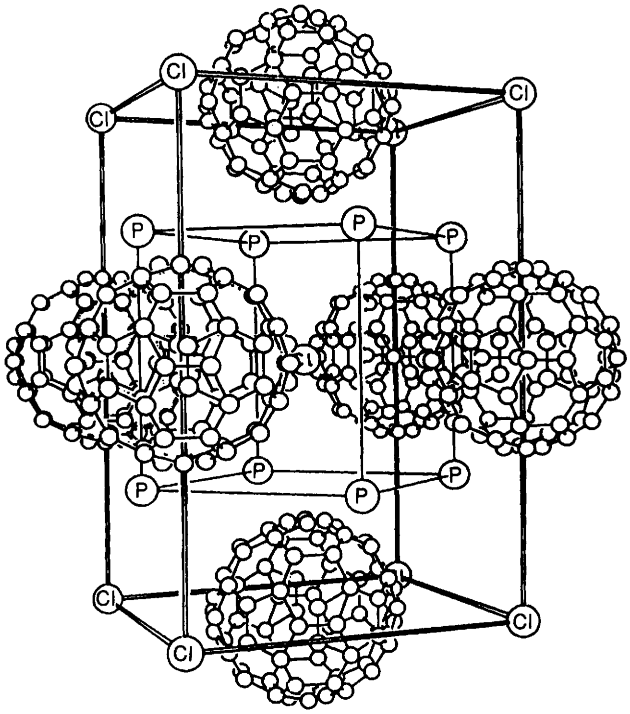

Fig. 1 Unit cell of $Ph_4PC_{60}{\cdot}Ph_4PCl$, showing the pseudo-cubic sublattice of the phosphorus atoms. For clarity the phenyl rings are omitted.

Fig. 1 provides a view at the unit cell of $Ph_4PC_{60}{\cdot}Ph_4PCl$. The barycentres of the constituents form a CsCl-like structure by substituting Cs^+ for $(Ph_4P)^+$ and Cl^- for $C_{60}{}^{-}$ or Cl^-. The approximately cubic primitive lattices of the cations and anions, respectively, have the dimensions 9 × 9 × 10 Å. Neighbouring P_8-cubes are occupied by $C_{60}{}^{-}$ and Cl^- in an alternating fashion.

The considerable difference in the size of the anions is compensated for by the orientation of the phenyl groups: they are directed towards the centres of the P_8-cubes occupied by chlorine (*cf.* Fig. 2), while the phenyl rings coordinating the fulleride anion lie outside the P_8-cube containing $C_{60}{}^{-}$. The shortest distances from fulleride to phenyl carbons are

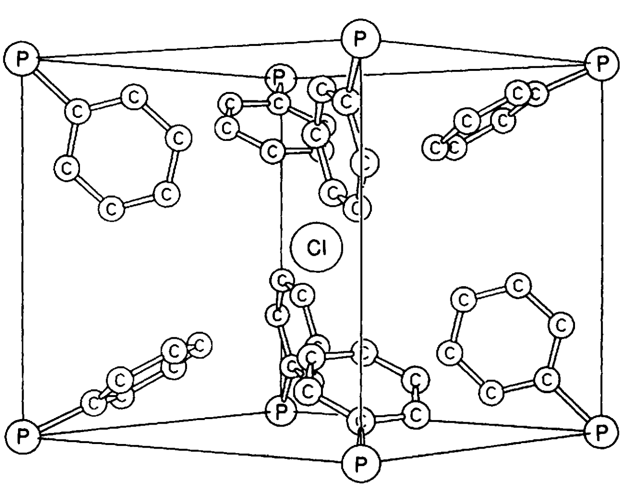

Fig. 2 A view upon the arrangement of phenyl groups around chlorine with the P-phenyl-bonds pointing towards the anion

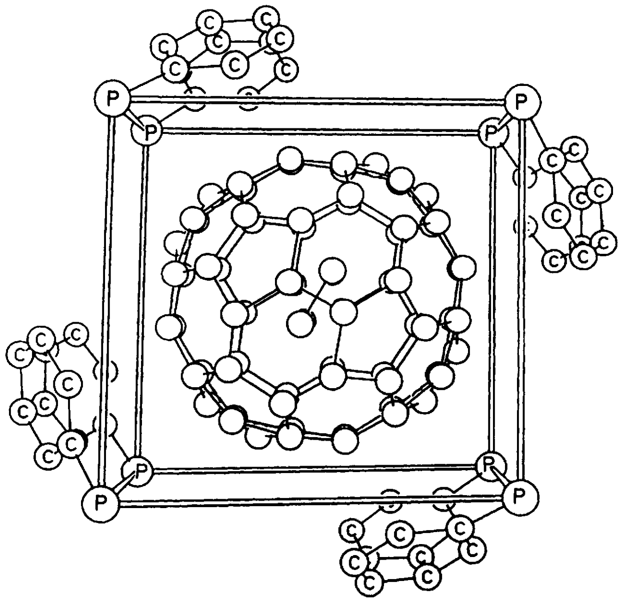

Fig. 3 The coordination of the fulleride anion by the phenyl groups is shown. The phenyl rings lie outside this P_8-cube and are oriented in a face to face manner with respect to the fulleride's hexagons.

3.83–4.06 Å, due to eight of the hexagons of the fulleride being oriented face to face with eight phenyl rings, as can be seen in Fig. 3 (dihedral angles being 4.8–6.0°). Although there are only two orientations for the fulleride, no reliable bond lengths for the fulleride anion can be obtained. This is a consequence of the interchange of the hexagons and pentagons upon switching between the two orientations.

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Footnotes

† Magnetic measurements were carried out between 2 and 300 K on a SQUID magnetometer MPMS 5, Quantum Design, and indicate two phase transitions at 120 and 240 K, respectively.

‡ *Crystal data* for $C_{108}H_{40}P_2Cl$; $M = 1434.79$, tetragonal, $I4/m$, $a = b = 12.5731$ (9), $c = 20.1415$ (25) Å; $T = 293$ K, $V = 3184.0$ Å^3, $Z = 2$, $F(000) = 1470$, Cu-Kα, $\mu = 1.49$ mm^{-1}; data were collected on an Enraf-Nonius CAD4 diffractometer, 14799 reflections measured, 1742 independent with $I \geq 2\sigma(I)$ used, 174 refined parameters; $R1 = 5.14$, $wR2 = 10.95$, final difference Fourier = 0.39 Å^3. Cell constants were determined from X-ray powder data using 35 indexed reflections; calculated and observed X-ray powder diffraction pattern are in accordance. Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Centre. See Information for Authors, Issue No. 1.

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