Synthesis and Characterisation of the Inclusion Complex $\{(P_4)_2C_{60}\}$

Richard E. Douthwaite, Malcolm L. H. Green,* Stephen J. Heyes, Matthew J. Rosseinsky and John F. C. Turner

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

Incorporation of elemental phosphorus into hexagonal-packed C_{60} gives the new phase $\{(P_4)_2C_{60}\}$; characterisation by powder diffraction and multinuclear solid-state NMR studies show the P_4 tetrahedra occupy trigonal prismatic sites and confirm the retention of the molecular nature of the P_4 guest.

Inclusion and intercalation complexes of the fullerene C_{60} are well established and may occur without net electron transfer. Previously reported examples include $\{[Fe(\eta\text{-}C_5H_5)_2]_2C_{60}\}$,[1] $\{(I_2)_2C_{60}\}$[2] and the benzene solvate $[C_{60}.4C_6H_6]$.[3,4] Also, C_{60} can readily undergo reduction and the mono- to hexa-anions have been detected by low temperature cyclic voltammetry.[5] Intercalation of alkali metals by reduction of the fullerene host gives the fullerides $\{A_nC_{60}\}$ (for example, A = Li–Cs, n = 0.5–6).[6] Here we report the synthesis and characterisation of the phase $\{(P_4)_2C_{60}\}$. This is the first example of which we are aware of host–guest chemistry of molecular P_4.

Treatment of a toluene solution of C_{60} with an excess of purified white phosphorus in CS_2 results in the immediate precipitation of a black-blue solid with the composition $\{(P_4)_2C_{60}\}$ **1**.† The solid **1** shows solubility characteristics which are similar to both C_{60} and P_4, being soluble in dichloromethane and to a lesser extent in toluene. The phase was analytically pure.

X-ray powder diffraction¶ showed **1** to be highly crystalline. The data could be indexed on a hexagonal/trigonal cell ($a = b$ = 10.09, c = 10.11 Å), which suggested an AAA stacking of close packed C_{60} layers, as previously reported for $\{(I_2)_2C_{60}\}$.[2] A series of Rietveld analyses was performed to locate the phosphorus atoms within this array. Initial refinements showed a scattering density corresponding to four phosphorus atoms located in the trigonal prismatic sites, of which there are two per unit cell. Difference Fourier syntheses and Rietveld refinement (Fig. 1) lead to a structural model in which a P_4 tetrahedron occupies each trigonal prismatic site with one of its C_3 axes parallel to the [001] direction (Fig. 2), corresponding to the composition $\{(P_4)_2C_{60}\}$. Unconstrained refinement of the apical [2(d)] and basal [6(g)] atoms of the tetrahedron gives bond lengths of 2.12(4) Å (apex to basal plane) and 2.16(4) Å (within the triangular basal plane). The diffraction pattern of a sample exposed to the air for a week showed essentially no change, implying that the crystalline phase is quite stable to air and that any minor aerial oxidation generates a non-crystalline product.

Solid state ^{31}P MAS NMR spectroscopy§ reveals a single phosphorus resonance at −490 ppm ($\Delta\nu_{1/2}$ = 55 Hz). The band is slightly upfield from the shift of −462 ppm observed for crystalline white phosphorus.[7] This implies that no charge transfer has occurred in **1**. The difference in chemical shielding from crystalline white phosphorus is probably due to environment effects in the lattice, such as ring current shifts from the presence of neighbouring C_{60} molecules. At ambient temperature, the wideline ^{31}P spectrum shows a sharp singlet ($\Delta\nu_{1/2}$ = 814 Hz). Clearly the P_4 molecules are dynamic in such a way as to render all the phosphorus atoms equivalent on the NMR timescale and such that the chemical shift anisotropy (CSA) is removed by effectively isotropic reorientation. Wideline ^{31}P NMR studies at lower temperatures show line broadening effects indicating a slowing of the exchange process or processes but even at the lowest temperature available, 98 K, the spectrum was not fully in the slow exchange limit on the CSA timescale and is substantially narrower than that of crystalline white phosphorus at the same temperature.[8]

Similarly, the ^{13}C MAS NMR spectroscopy shows a single

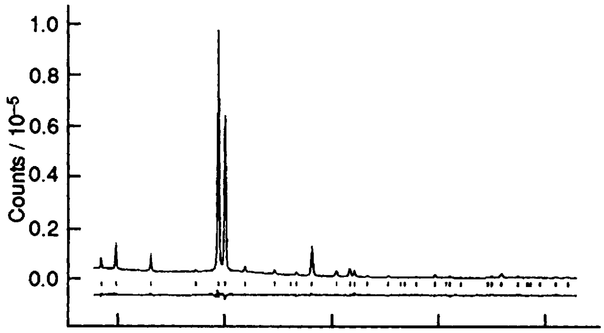

Fig. 1 Rietveld fit to diffraction data in space group *P6/mmm*, a = 10.0837(6), c = 10.1028(7) (R_w = 4.7%, χ^2 = 3.0)

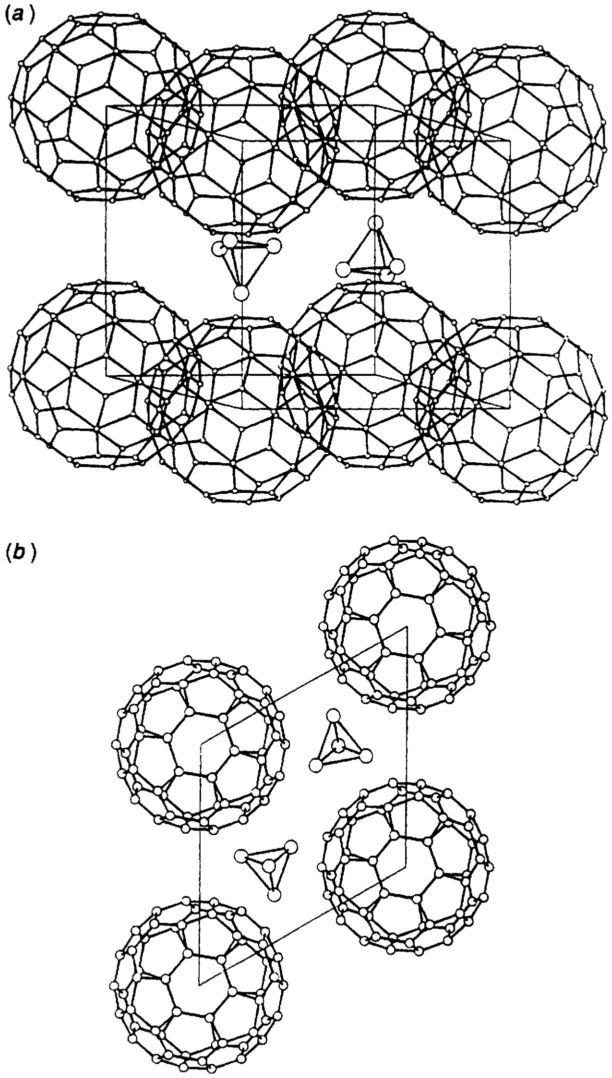

Fig. 2(*a*) Structure of $\{(P_4)_2C_{60}\}$. Only one orientation of the P_4 tetrahedron at each trigonal prismatic site is shown, corresponding to the space group $P\bar{3}$. (*b*) View of the cell along the c axis.

sharp peak at 146 ppm ($\Delta\nu_{1/2} = 15$ Hz) and even in the absence of MAS, $\Delta\nu_{1/2} = 235$ Hz, indicating rapid effectively isotropic averaging of the CSA by the motion of the C_{60} molecules. Lower temperature studies also show a slowing of the rapid room temperature exchange process and at 98 K, the slow exchange limit is not achieved.

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Footnotes

† All manipulations were performed under dry dinitrogen by Schlenk techniques or in a glove box. White phosphorus was distilled under dinitrogen before use. In a typical preparation, 205 mg C_{60} was dissolved in *ca.* 200 ml of dry degassed toluene and 12 equivalents of white phosphorus in CS_2 (0.137 mol dm^{-3} solution) were added rapidly *via* a cannula. The resulting fine precipitate was allowed to settle, filtered under N_2, and dried under a dynamic vacuum. Yield, 248 mg, 90% based on C_{60}.

¶ Powder X-ray diffraction data were collected on a sample sealed in a 0.5 mm capillary under dinitrogen, using a Siemens D5000 diffractometer equipped with a linear position sensitive detector and a primary Ge monochromator (Cu-Kα radiation). *R* values are calculated using only regions of the profile which have Bragg peak contributions. Data were analysed using GSAS software.

§ Solid state NMR spectra were measured on a Bruker MSL200 pulse spectrometer using an Oxford Instruments 4.7-T wide bore solenoid superconducting magnet. ^{13}C and ^{31}P spectra were recorded at 50.32 and 80.92 MHz respectively. The MAS samples were contained in a Kel-F insert inside a Kel-F capped zirconia rotor, the samples for wideline spectra in a 7 mm o.d. glass tube sealed under vacuum. Chemical shifts are relative to tetramethylsilane *via* a secondary adamantane reference for ^{13}C and to 85% H_3PO_4 for ^{31}P.

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