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A New Polymeric Framework Formed by the Self Assembly of 5,10,15,20-tetra(3-pyridyl)porphyrin, HgI_2 And C_{60}

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The X-ray structure of $H_2T(3\text{-}Py)P{\cdot}HgI_2{\cdot}C_{60}$, cocrystallized from a chlorobenzene/methanol solvent mixture containing 5,10,15,20- tetra(3-pyridyl)porphyrin, HgI_2 and C_{60}, has been determined. A new two dimensional arrangement of the tetra(3-pyridyl)porphyrin molecules joined by coordination to HgI_2 is formed. These assemblies are connected by close C_{60}-porphyrin $\pi-\pi$ interactions leading to the alignment of the porphyrins into linear alternating fullerene porphyrin columns. The structure is compact with no significant cavities.

Keywords: Mercury iodide; Pyridyl; Methanol; Porphyrins; Fullerenes

INTRODUCTION

Assemblies of porphyrins and fullerenes are readily formed through the attraction of the planar pi surface and the curved pi surface of the two photoactive molecules [1]. The nature of this attractive interaction is driven by dispersive forces associated with $\pi-\pi$ interactions augmented by weaker electrostatic interactions associated with the relative orientation of the two molecules. This new supramolecular recognition element is the basis of a rapidly growing class of fullerene–porphyrin cocrystallates which contain a variety of tape, sheet and 3D structural motifs [1–8]. Additional supramolecular forces often augment the fullerene–porphyrin interaction and can determine the particular motif that is observed. In nearly all structures determined so far, a fullerene is centered over a porphyrin (or metalloporphyrin) with unusually close atom-to-atom approaches and this is appears to be a major structure-determining element.

The construction of multiporphyrin arrays using the coordination of the 4-pyridyl functionalized porphyrins, $H_2T_{py}P$, to external Cd(II) and Cu(I) metal ions originated from the work of Robson [9,10]. There are now many examples of tapes, sheets and 3-D structures using metal ions with varying coordination geometries [11–17]. We have found that the fullerene–porphyrin interaction is sufficiently strong to act as a structure-defining element when combined with such sheets and tapes [4]. When fullerenes are intercalated between tapes and sheets of metal-linked tetra-*p*-pyridylporphyrins they act as pillars increasing the interlayer spacing. The 6:6 ring juncture bonds of C_{60} are centred over the porphyrins bringing the tapes and sheets into strict tetragonal register [4].

In this paper, we report the first coordination polymer of 5,10,15,20-tetra(3-pyridyl)porphyrin formed with mercury iodide cocrystallised with the fullerene C_{60}.

EXPERIMENTAL SECTION

$H_2T(3\text{-}Py)P{\cdot}HgI_2{\cdot}C_{60}$

Crystals of $H_2T(3\text{-}Py)P{\cdot}HgI_2{\cdot}C_{60}$ were grown by diffusion of a layered methanol solution of HgI_2 into a chlorobenzene solution of $H_2T(3\text{-}Py)P$ [18] and C_{60} followed by slow evaporation of the solvent mixture. A black fragment of a prism was used for the single crystal x-ray diffraction study. X-ray data were collected at 150 K on a Siemens SMART CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz

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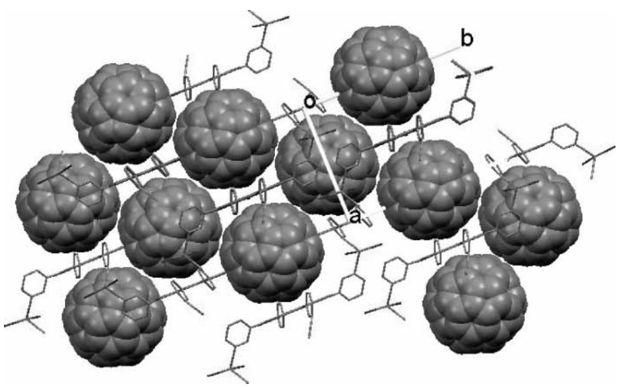

FIGURE 1 View of crystal packing along c axis of H_2T(3-Py)P·HgI_2·C_{60} showing the C_{60} molecules interleaved between porphyrin sheets.

and polarisation effects and absorption corrections were applied to the raw intensity data using the SADABS program [21]. The structure was solved by direct methods using WINGX [20] with SHELXS-97 [21].

Empirical formula, $C_{50}H_{13}HgI_2N_4$, fw; 1124.03, monoclinic, $P2_1/n$, $a = 12.26190(10)Å$, $b = 16.7845(2)Å$, $c = 16.7916(2)Å$, $\alpha = 90°$, $\beta = 90.1010(10)°$, $\gamma = 90°$, $V = 3455.87(6)Å^3$, $Z = 4$, $D_c = 2.160\,g/cm^3$, $\mu = 6.287\,mm^{-1}$, $F(000) = 2108$; crystal 0.26 × 0.24 × 0.22 mm^3, $\Theta_{max} = 25.18°$, ranges $14 \leq = h \leq = 14$, $-20 \leq = k \leq = 20$, $-19 \leq = l \leq = 19$; reflections collected = 30307, independent reflections = 6367 (R(int) = 0.0522), data / restraints / parameters 6367 / 611 / 572. All non-hydrogen atoms were identified after isotropic refinement of the initial solution. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. Full matrix least-squares refinement on F^2 was carried out to give R indices $[I > 2\sigma(I)]$, $R_1 = 0.0424$, $wR_2 = 0.1036$ and $GOF = 1.036$. Although the diffraction data showed pronounced Laue tetragonal $4/mmm$ Laue symmetry, no solutions could be found; nor any in orthorhombic space groups, consistent with absences $h00$ $h = 2n + 1$, $0k0$ $k = 2n + 1$, $00l$ $l = 2n + 1$ (n an integer). Data were reprocessed in the monoclinic crystal system and twinning was considered. Structure solution and initial refinements were conducted in space group $P2_1$, and then in $P2_1/n$. The twin law $[-1\,0\,0/\,0\,0\,1/\,0\,-1\,0]$ leads to overlapping of reflections h0l, obscuring the underlying n-glide plane. The four twin components had fractional volumes of 0.2356(17), 0.2041(17) 0.2393(18) and 0.3210. The HgI_2 moiety and a 3-pyridyl group were disordered; the C_{60} is ordered and its geometry was restrained to two distinct C–C separations (final values 1.353(8) and 1.467(5)Å). The stereochemistry of the porphyrin moiety was also restrained, with each chemically distinct C–C and C–N bond assigned a refinable constrained value by means of free variables, and pyrrole and phenyl rings were tightly restrained to planarity. Because of disorder, twinning, which created high correlations among parameters, and the domination of structure factors by the HgI_2 moiety, ISOR, SIMU and DELU restraints were applied to atomic displacement parameters of light atoms. Refinements then proceeded smoothly to convergence to values for R_1 that were commensurate with the quality of the diffraction data. Figs. were created using The Cambridge Crystallographic Database Mercury visualization software [22]. In each Fig. the major ordered component of the HgI_2 moiety(67.9%) and 3-pyridyl fragment(67.9%) are shown.

A completed CIF file has been deposited with the Cambridge Crystallographic Data centre (deposition number 281034).

RESULTS AND DISCUSSION

When a chlorobenzene solution of $H_2T_{3\text{-}Py}$ P and C_{60} is layered with a methanol solution of HgI_2 crystals of $H_2T_{3\text{-}Py}$ P·HgI_2·C_{60} are formed. The solution of the x-ray crystal structure involved problems in both pseudo-merohedral twinning and disorder.

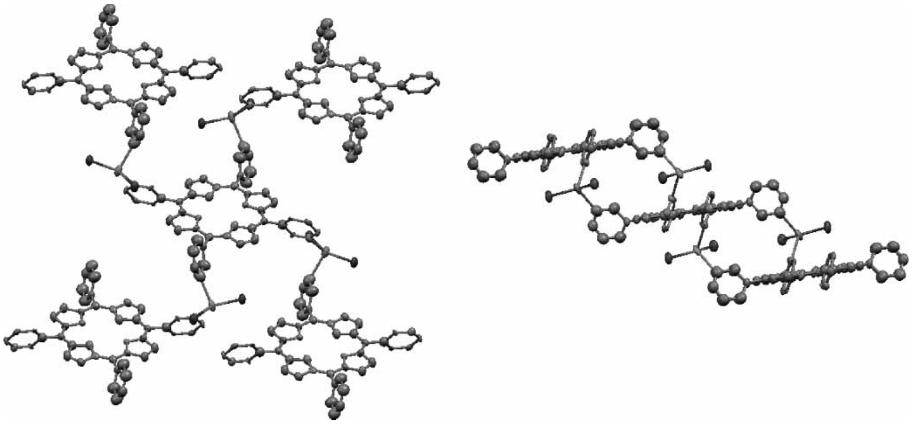

FIGURE 2 Ball and stick views of the two dimensional HgI_2 linked porphyrin assemblies.

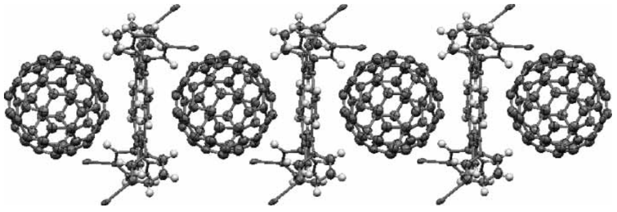

FIGURE 3 Linear alternating columnar array of porphyrins and fullerenes viewed perpendicular to a axis (thermal ellipsoids probability level 50%).

The structure is formed from a combination of a two-dimensional assembly of 3-pyridyl porphyrins, connected by coordination of each pyridine nitrogen to a separate mercury(II) iodide molecule, and C_{60} molecules interleaved between each layer, Fig. 1. Unlike one dimensional porphyrin tapes and two dimensional sheets formed from the corresponding 4-pyridyl porphyrins [4], the layers are distinctly non planar. The angle formed between the porphyrin planes and the plane formed from the centroids of the porphyrin molecules in each sheet is 37.8°. Each porphyrin is coordinated to four mercury iodide molecules. The fourfold coordination geometry about the mercury atom is completed by coordination of a further pyridine from another porphyrin. This gives connection of each porphyrin to four others with two lying above and two below the porphyrin plane in an α, α, β, β arrangement, Fig. 2. Bond lengths and angles about the four-coordinate mercury atom (Hg–I, 2.635(3)Å, 2.661(3)Å; Hg–N, 2.455(14)Å, 2.516(15)Å; I–Hg–I, 151.0(2)°; N–Hg–N, 100.3(3)°) are similar to those observed in other bis-pyridine HgI_2 complexes (Average values: Hg–I, 2.647 Å,; Hg–N, 2.451 Å; I–Hg–I, 147.9°; N–Hg–N, 90.1°) [4,23–28].

The C_{60} molecules are sandwiched between the porphyrin layers. The porphyrin–porphyrin separation, 12.26 Å, is in keeping with the van der Waals diameter of C_{60}.The porphyrins encapsulating a C_{60} molecule are observed to be parallel and in alignment with each other. The tetragonal register of these porphyrins leads to alternating linear columns with C_{60}, Fig. 3, as is found in other supramolecular fullerene porphyrin frameworks. A fullerene 6:6 ring juncture "double" bond closely approaches the porphyrin with closest carbon atoms to mean 24-atom plane distances of 2.60 and 2.72 Å, Fig. 4. The fullerene is centered over the porphyrin. There are several short fullerene carbon to porphyrin distances (2.92–3.40 Å) at or less than the van der Waals contact distance. The C_{60} encapsulation is completed by four 3-pyridyl groups surrounding the equatorial region of the column, two from each of the neighbouring two dimensional porphyrin assemblies, Fig. 5.

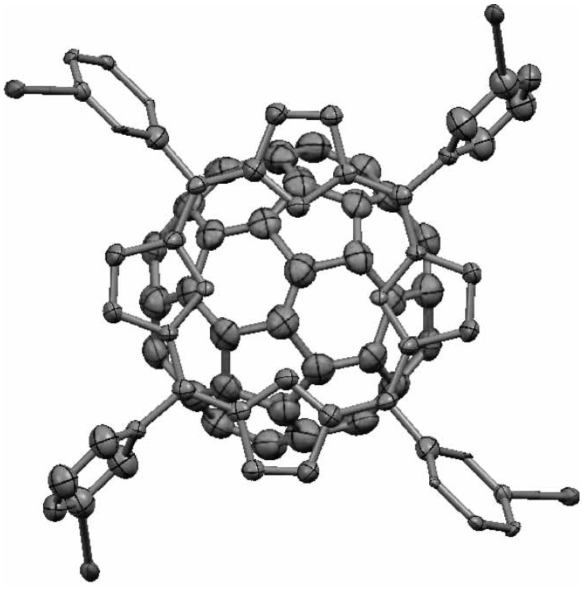

FIGURE 4 Close approach and orientation of C_{60} over the tetra(3-pyridyl)porphyrin (thermal ellipsoids probability level 50%).

CONCLUSION

The attraction of C_{60} to a porphyrin provides an extra supramolecular recognition element for use in the modification of metal organic frameworks. In the example reported here the crystal structure is compact with no voids available for solvent occupation. This is unlike other coordinatively linked fullerene–porphyrin framework structures which generally contain channels and cavities with solvents of crystallization [4].

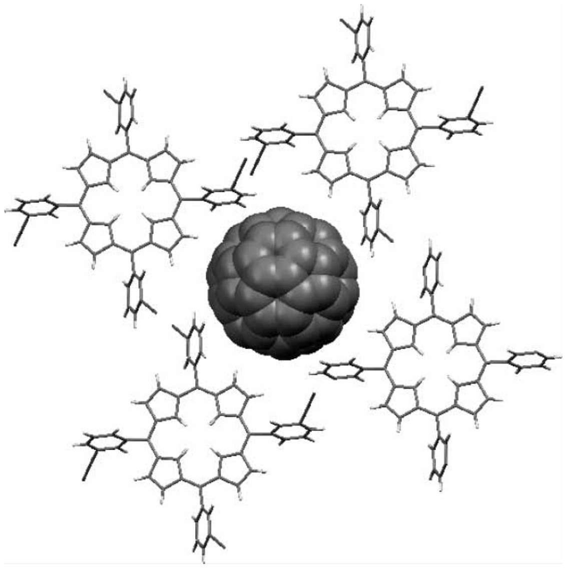

FIGURE 5 Arrangement of 3-pyridyl groups around the equator of the linear fullerene porphyrin columns viewed along a axis. Iodine atoms omitted for clarity.

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