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Characterisation of a new 1:1 $(C_{60})(CHBr_3)$ intercalation complex

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The 1:1 crystalline intercalation complex $(C_{60})(CHBr_3)$ is an entirely new type of fullerene–haloform complex with an irregular structure comprised of C_{60} molecules interspersed with zigzag chains of disordered bromoform molecules.

Interest in simple solvates of C_{60} and other fullerenes has risen dramatically with reports of high temperature superconducting properties of fullerene–haloform crystalline materials.[1] The veracity of such studies is currently controversial,[2] and accordingly continued study of such systems is important. The structural chemistry of C_{60} intercalation complexes is rich, with materials containing small molecules such as haloforms,[3,4] through to larger molecules like ferrocene,[5] and curved or bowl shaped receptor molecules including many derivatised calixarenes,[6] cyclotriveratrylene,[7] and metal macrocycles.[8] The interplay of fullerenes at the van der Waals limit in these structures is complex and there have been recent advances in controlling how the arrays are built up.[9]

A number of fullerene-halogenated solvent complexes have been reported,[3,4,10] and in further understanding the interplay of fullerenes in such complexes we have reinvestigated fullerene–haloform complexes using a different synthetic approach, and show that a new solid state bromoform complex is readily accessible. It is a 1:1 complex, $(C_{60})(CHBr_3)$, which is particular noteworthy in that haloform complexes of the fullerene normally crystallise as 1:2 complexes, $(C_{60})(CHX_3)_2$, X = Cl, Br.

Dark red crystals of $(C_{60})(CHBr_3)$ were grown by slow diffusion of $CHBr_3$ into a toluene solution of C_{60}, the experimental set up involving a closed container with the haloform in an open vial standing in a toluene solution of C_{60}. The 1:2 complexes are prepared by evaporation of haloform solutions of the fullerene.[1,4] This has limitation because of the low solubility of the fullerene in such solvents. Moreover, the finding that the presence of another component, toluene, can result in a new type of fullerene complex, yet is not part of the resulting structure, further highlights the subtleties in crystallising complexes of C_{60}.[9]

Inter-grown needles of $(C_{60})(CHBr_3)$, up to 1 cm in length, were obtained using this approach. Interestingly, there was no evidence for formation of any of the previously reported 1:2 complex $(C_{60})(CHBr_3)_2$,[3,4] although adopting the same approach using chloroform in place of bromoform, resulted in formation of the previously reported 1:2 complex $(C_{60})(CHCl_3)_2$, as the exclusive product.

A single crystal X-ray structure of $(C_{60})(CHBr_3)$ was determined at low temperature. There was no indication of a phase change which is in contrast to the structure of $(C_{60})(CHX_3)_2$, X = Cl, Br which undergo a phase change from hexagonal to triclinic at ~ 150 K, with the low temperature form recently characterised using powder XRD methods.[4]

Structure solution of $(C_{60})(CHBr_3)$ gave a 1:1 stoichiometry which was confirmed by flotation density measurements, where $\rho_{calc} = 2.04$ and $\rho_{exp} = 1.99(2)$ g cm^{-3}. The crystals are stable at ambient temperature with respect to loss of haloform. The complex crystallises in an orthorhombic cell and the structure solved in the chiral space group $P2_12_12_1$.† The crystals were of extremely poor crystallographic quality, showing a very high mosaic spread with a final refined mosaicity of 1.606(3)°, and both molecular components of the structure are severely disordered. Nevertheless positioning of the molecular components was established unequivocally.

The asymmetric unit comprises one molecule of C_{60} and one of $CHBr_3$. The extended structure is shown in Fig. 1. The disordered $CHBr_3$ molecules (see below) run in zigzag chains along the *c* direction, and separate irregular layers of C_{60} molecules. Molecules of fullerene-C_{60} stack in columns in the *c* direction as would be anticipated from the *c* unit cell dimension of 10.0603(5) Å, a distance close to the van der Waals radii of C_{60}.[11] Each zigzag chain of $CHBr_3$ is contained within a channel of rectangular cross-section bordered by C_{60} molecules. The largest separation of C_{60} molecules from each other occurs

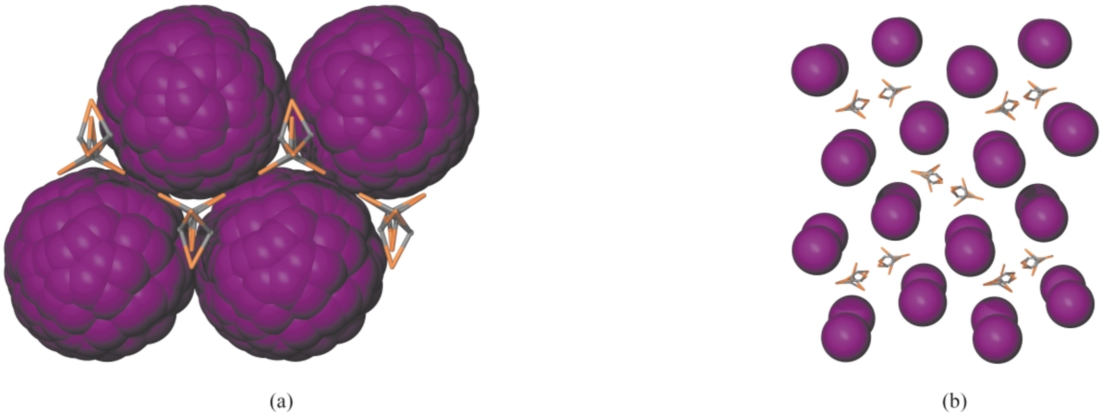
(a)
(b)

Fig. 1 Crystal packing in $(C_{60})(CHBr_3)$: (a) view slightly offset from *b* axis showing close contacts between C_{60} molecules and zigzag motif of disordered $CHBr_3$ molecules; (b) view down the *c* axis with C_{60} molecules shown as non-space filling spheres.

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here with centroid–centroid separations across the channel at 14.006 and 14.505 Å. The further separation is slightly higher than the increase in lattice spacing seen in $C_{60}(CHBr_3)_2$.

Packing of the C_{60} molecules within the lattice is somewhat irregular compared with the crystal packing of pristine C_{60} itself or $C_{60}(CHX_3)_2$. Unsolvated crystalline fullerene-C_{60} is polymorphic with the structure obtained largely dependent on crystallisation procedure and/or solvent. Numerous structural studies have shown hexagonal and face centred cubic structures,[12] and HRTEM has shown the co-existence of defect-free *fcc* and *hcp* phases within sublimed C_{60}.[13] Complex $C_{60}(CHX_3)_2$ has an hexagonal structure at room temperature, and undergoes a phase change to triclinic at low temperature, however the triclinic phases is closely related to the room temperature structure.[4] In $(C_{60})(CHBr_3)$ there are 10 close contacts between fullerene-C_{60} molecules at centroid separations ranging from 9.718 to 10.243 Å. The lower range are very short distances having previously been observed in a C_{60}-calix[4]arene complex, ascribed to dipole induction in a polar space group.[11] In this context we note that the present structure also crystallises in a polar space group, but the severe disorder limits analysis of the packing of the fullerenes with respect to the direction of the included molecule.

The structure may be considered to be a disruption of a close packed structure. Close packed and near close packed structures have each fullerene-C_{60} with van der Waals contacts to 12 nearest neighbour C_{60} molecules (6 in-plane, 3 above, 3 below). In $(C_{60})(CHBr_3)$ each fullerene has contacts with 4 in-plane fullerenes and 3 above and 3 below, however the above and below triads form an angle of 146° at the central fullerene, rather than 180° as would be expected for a true close packed array.

The C_{60} molecule is completely disordered and behaves as a shell of electron density and individual carbon positions could not be ascertained with any certainty. Such disordering of fullerenes is by no means unusual.[3,4,12] Disorder is also prevalent for the $CHBr_3$ molecules, being disordered over four sites, Fig. 2. Each of the six bromine positions is at 50% occupancy and is shared between two disordered carbon sites. The carbon atom is disordered over four positions with occupancies 0.3, 0,2, 0.35 and 0.15.

Incorporation of a small molecule into the C_{60} lattice leads to a disrupted packing motif. Such an effect has been claimed to influence electronic properties of similar materials, notably the 1:2 complex.[1] While the physical and electronic properties of $(C_{60})(CHBr_3)$ have yet to be established, the availability of a new class of fullerene–haloform complex has been established, and the synthetic approach may have ramifications for the synthesis of fullerene small molecule complexes in general.

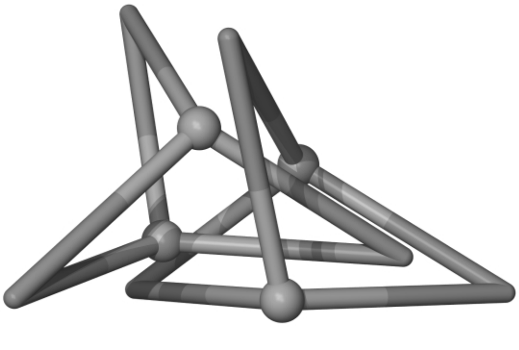

Fig. 2 Disordering of $CHBr_3$ molecules in $(C_{60})(CHBr_3)$ across four positions; carbon positions are shown as spheres and hydrogen atoms have been excluded for clarity.

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Notes and references

† Crystal Data for $(C_{60})(CHBr_3)$. Data were collected on a dark red needle of dimensions 0.53 × 0.30 × 0.26 mm at 150(1) K on a Nonius KappaCCD diffractometer with Mo-K_α radiation. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares on F^2 (SHELXL-97). Only the Br positions were refined anisotropically and hydrogen positions were included with a riding refinement. The disordered C_{60} molecule acts as a sphere of electron density and was refined over 120 positions each at 0.5 occupancy, this approach has also been used for other recently reported disordered fullerenes.[14] The disordered $CHBr_3$ was refined over 4 positions as described in the text. Refinement of a Flack parameter indicated that the crystal was an inversion twin. $C_{61}H_1Br_3$: Mr = 973.35, orthorhombic, $P2_12_12_1$, a = 16.3823(7), b = 19.1959(10), c = 10.0603(5) Å, U = 3163.7(3) Å^3, Z = 4, ρ_{calc} = 2.04 g mol^{-1}, ρ_{exp} = 1.99 g mol^{-1}, μ = 3.882 mm^{-1} (no correction), $F(000)$ = 1888, $\theta_{\max}$ = 26.39°, 20093 data collected, 6076 unique (R_{int} = 0.065), 552 parameters, R_1 = 0.1370 (4211 data $I > 2\sigma(I)$), wR_2 = 0.3795 (all data), GooF = 1.050, Flack parameter = 0.53(4). CCDC 207875. See http://www.rsc.org/suppdata/cc/b3/b303478j/ for crystallographic data in .cif or other electronic format.

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