Organic Alloys: Diamondoid Networks in Crystalline Complexes of 1,3,5,7-Tetrabromoadamantane, Hexamethylenetetramine and Carbon Tetrabromide

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1,3,5,7-Tetrabromoadamantane and hexamethylenetetramine (hmt) co-crystallise to form a diamondoid-type 1 : 2 molecular complex but one of the two hmt molecules is disordered and can be substitutionally replaced by CBr_4 to give the corresponding 1 : 1 : 1 complex.

The typical organic molecule adopts low-symmetry crystal systems[1,2] but molecules with S_4 or pseudo-S_4 symmetry and a tendency to form directional intermolecular interactions can be elaborated into highly symmetrical diamondoid networks.[3] Owing to the large hollows of the 'super-adamantoid' cages inherent in such a construction, these supramolecular networks are catenated in order that gross violations of the space-filling principle do not occur.[1] A continuing challenge in the engineering of diamondoid molecular solids is to design inclusion compounds such that the diamondoid network acts as a cage, more or less like an organic zeolite instead of being catenated by other identical networks. However, this challenge has been largely unfulfilled. In this communication we report on the diamondoid molecular complexes formed by 1,3,5,7-tetrabromoadamantane ($AdBr_4$), hexamethylenetetramine (hmt), and CBr_4 where clathration rather than catenation occurs.

This study followed from our earlier observations on the 1 : 1 complex hmt–CBr_4 in which two-non-connected N···Br mediated diamondoid networks are catenated.[4] To obviate the disorder caused by the similarity in molecular dimensions of hmt and CBr_4 in this structure, hmt (subl. 280 °C) and $AdBr_4$ (mp 260 °C)[5] were co-crystallised from $CHCl_3$ to obtain cubic crystals of the 1 : 2 complex **1** (mp 260 °C). X-Ray data were collected and the structure was solved and refined successfully.† Fig. 1 is a schematic view of the structure and Fig. 2 is a stereoview of the actual structure. The molecules are colour-coded. The structure is face-centred cubic with $AdBr_4$ molecules at the cell corners and hmt molecules tetrahedrally situated in the alternating octants (as in cubic ZnS). We will refer to these hmt molecules as hmt (1/4, 1/4, 1/4). Interestingly these molecules are held together by four sets each of three equivalent C–H···N hydrogen bonds (C···N 3.77 Å, θ 151°) rather than by N···Br interactions as in the hmt–CBr_4 complex. In these 12 identical C–H···N bonds, the H atoms are provided by $AdBr_4$ and the N atoms by hmt. These alternating $AdBr_4$ and hmt (1/4, 1/4, 1/4) molecules form a super-adamantoid cage shown in Fig. 1 and because of the relatively distant spacing of molecules in this cage, there is sufficient room within for a second type of hmt molecule at the cell-centre. This is referred to as hmt (1/2, 1/2, 1/2). Significantly, the hmt (1/2, 1/2, 1/2) molecules are disordered about a molecular inversion centre, the space group being non-centrosymmetric.

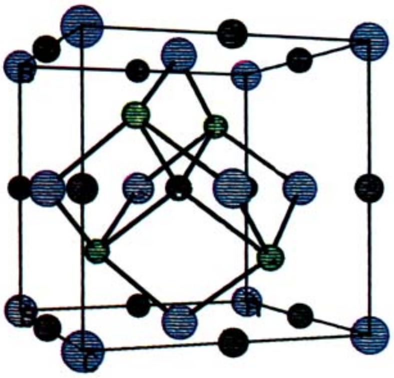

Fig. 1 Schematic representation of the crystal structure of complex **1**. Molecules are shown as circles: blue ($AdBr_4$); green (hmt 1/4, 1/4, 1/4); black (hmt 1/2, 1/2, 1/2). The super-adamantoid cage is marked as is the co-ordination between the two types of hmt molecule.

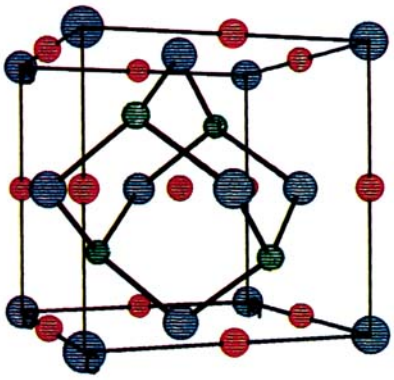

Fig. 3 Schematic representation of the crystal structure of complex **2**. Compare this with Fig. 1. CBr_4 molecules are shown as red circles.

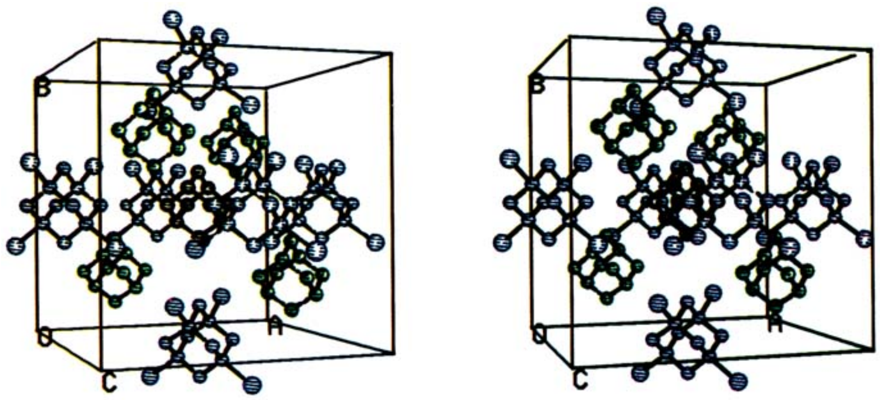

Fig. 2 Stereoview of the structure of complex **1** showing inclusion of the hmt (1/2, 1/2, 1/2) molecule in the super-adamantoid cage. The hmt (1/2, 1/2, 1/2) molecule is shown in one of its two possible orientations.

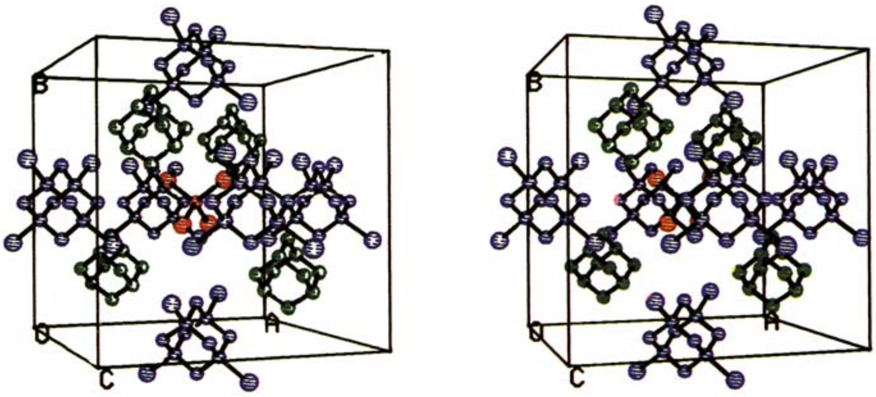

Fig. 4 Stereoview of the structure of complex **2** showing inclusion of the CBr_4 molecule. Notice that the CBr_4 molecule makes contacts with the bromine-clusters formed by the $AdBr_4$ molecules.

Two questions are of structural interest: (*i*) Why are only alternate octants occupied by hmt (1/4, 1/4, 1/4) molecules? (*ii*) Why are the hmt (1/2, 1/2, 1/2) molecules disordered? To answer the first question, it is relevant to note that four $AdBr_4$ molecules converge tetrahedrally to give six identical Br···Br contacts of 4.08 Å. This bromine-cluster occupies alternate octants leaving alternate octants for the hmt (1/4, 1/4, 1/4) molecules. Curiously, Br···Br interactions are of only minor importance in the plastic crystal structure of pure $AdBr_4$.[7] The disorder of the hmt (1/2, 1/2, 1/2) molecules is in turn rationalised because each hmt (1/2, 1/2, 1/2) molecule can have only 12 C–H···N contacts to the neighbouring hmt (1/4, 1/4, 1/4) molecules (C···N 3.74 Å, θ 148°), rather than the 24 such contacts possible for the hmt (1/4, 1/4, 1/4) molecules.‡ The enthalpic contribution from these interactions is probably insufficient to ensure ordering.

The disordered hmt (1/2, 1/2, 1/2) molecule is encapsulated within the super-adamantoid cages formed by $AdBr_4$ and hmt (1/4, 1/4, 1/4) but this clathrating behaviour is demonstrated more strikingly by substituting the hmt (1/2, 1/2, 1/2) by CBr_4 which is already known to be a good structural mimic for hmt.[4] As predicted, co-crystallisation of a equimolar mixture of $AdBr_4$, hmt and CBr_4 from $CHCl_3$ yielded exclusively crystals of the 1 : 1 : 1 complex **2** (mp 260 °C).

The crystal structure of complex **2**† is isostructural to that of complex **1** and is shown in Figs. 3 and 4. The CBr_4 molecule in complex **2** is, however, ordered unlike the hmt (1/2, 1/2, 1/2) molecule in complex **1**. The reason for this is that CBr_4 can form 12 Br···Br contacts of 3.90 Å with $AdBr_4$ molecules in only one orientation (which is found in here). Clearly, these 12 Br···Br interactions are of greater enthalpic significance than the 12 C–H···N interactions formed by hmt (1/2, 1/2, 1/2) in complex **1**.

The study reveals many significant topological similarities in the structural chemistry of organic and inorganic solids. Fig. 1 may be analysed in terms of a face-centred cubic array of spheres ($AdBr_4$) with a 50% occupancy of tetrahedral sites (hmt 1/4, 1/4, 1/4) and a 100% occupancy of octahedral sites (hmt 1/2, 1/2, 1/2 or CBr_4). An inorganic analogy is Cu_2Sb but here the octahedral and tetrahedral domains are layered.[8] An exact topological match is found in the LiAlSi group of solids which are able to adopt this structure type because of the mismatch of atomic sizes.[9] Continuing such analogies further, complex **1** contains hmt molecules in two crystallographic sites but only one is disordered. Such behaviour is reminiscent of sublattice disordering in intermetallic compounds.[10] The eventual goal in such crystal engineering studies would be to develop a family of materials where molecules may be removed or added at will to tailor properties such as clathration. Accordingly, we would like to designate such materials 'organic alloys'.

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Footnotes

† Complex **1**, $C_{10}H_{12}Br_4{\cdot}2(C_6H_{12}N_4)$, M = 732.2, cubic, $F\bar{4}3m$, a = 13.801(1) Å, V = 2628.3(3) Å^3, Z = 4, D_c = 1.85 g cm^{-3}, μ(MoKα) = 60.92 cm^{-1}, F(000) = 364.0, 135 observed non-zero reflections (3σ) out of 155 unique collected with 2 < 2θ < 50°, solution MULTAN, refinement RAELS89,[6] R = 0.032.

Complex **2**, $CBr_4{\cdot}C_{10}H_{12}Br_4{\cdot}C_6H_{12}N_4$, M = 923.6, cubic, $F\bar{4}3m$, a = 13.571(1) Å, V = 2499.1(1) Å^3, Z = 4, D_c = 2.45 g cm^{-3}, μ(MoKα) = 127.28 cm^{-1}, F(000) = 434.0, 135 observed unique reflections (3σ) out of 146 unique collected with 2 < 2θ < 50°, R = 0.028.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

‡ Each hmt (1/4, 1/4, 1/4) molecule forms 24 C–H···N hydrogen bonds. Of these, 12 are to $AdBr_4$ wherein hmt (1/4, 1/4, 1/4) acts as a hydrogen bond acceptor. The other 12 are to hmt (1/2, 1/2, 1/2) wherein hmt (1/4, 1/4, 1/4) acts as a hydrogen bond donor. All these latter 12 contacts are found in only one of the two disordered orientations of hmt (1/2, 1/2, 1/2).

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