N···Br Mediated Diamondoid Network in the Crystalline Complex Carbon Tetrabromide: Hexamethylenetetramine

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CBr_4 and hexamethylenetetramine cocrystallise to form a 1 : 1 molecular complex in which the component molecules are linked with N···Br interactions of 2.61(6) Å to form two non-connected but catenated diamondoid networks.

Supramolecular architecture of diamondoid networks has been an area of interest ever since Ermer's seminal study of crystalline adamantane-1,3,5,7-tetracarboxylic acid.[1] Such networks are well known in purely inorganic systems[2] and have since been engineered in coordination[3] and organometallic compounds.[4] These fascinating solids have not only a purely topological appeal but also potential for a number of applications in materials chemistry.

Diamondoid solids have, hitherto, been assembled with very strong metal–ligand bonds[3] or in the case of organic linkages, with strong O–H···O[1] and O–H···N[4b] hydrogen bonds. A continuing challenge in current crystal engineering and molecular recognition strategies has been to extend the scope of such chemistry to weaker intermolecular forces.[5] Can regular networks be built with supramolecular glue which is not so 'sticky'? Previous experience with C–H···O,[6] C–H···N[7] and C≡N···Cl[8] interactions indicated that this indeed might be the case. Diamondoid networks are necessarily built with molecules with S_4 (or pseudo-S_4) symmetry or tetrahedral bonding. Our search for new diamondoid networks concentrated therefore on molecules with S_4 symmetry and a propensity to form weak yet directional interactions. Short N···Br interactions have been described by Hassel in the structure of $CHBr_3$–hexamethylenetetramine (HMT).[9] More recently, Kochi has studied these interactions in the structures of the DABCO (1,4-diazabicyclo[2.2.2]octane) and quinuclidine complexes of CBr_4.[10] Despite the presence of short N···Br contacts, none of these structures has diamondoid networks because one of the two components in the mixed crystal falls short of S_4 symmetry and in this sense acts as a 'network stopper' in the solid. Building on this earlier work, we cocrystallised an equimolar mixture of the two S_4-symmetry molecules, CBr_4 (m.p. 90 °C) and HMT (subl. 280 °C) from $CHCl_3$ to obtain complex **1**.

Complex **1** (m.p. 235 °C) was obtained in two morphologies, tetrahedral wedges and rhombic dodecahedra. The two have identical m.p.s and examination of both types of crystal on a diffractometer showed that they have the same crystal structure. Thus, the morphologies are simply different types of the same crystalline material. X-Ray data were collected on a crystal exhibiting the rhombic dodecahedral morphology and the structure was solved and refined successfully.[†]

[†] *Crystal data* for: complex **1**, $CBr_4 : C_6H_{12}N_4$, $M = 471.8$, cubic, $I\bar{4}3m$, $a = 6.9558(7)$ Å, $V = 336.54(4)$ Å^3, $Z = 1$, $D_c = 2.33$ g cm^{-3}, μ(Mo-Kα) = 118.2 cm^{-1}, $F(000) = 222.0$ $T = 293$ K, 63 observed unique reflections (3σ) out of 72 unique collected with $2 < 2\theta < 50$ °, solution MULTAN, refinement BLOCKLS, $R = 0.034$, $R_w = 0.034$ C, N, Br anisotropic, H isotropic.

Structure determination: Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized molybdenum radiation (λ 0.7107 Å). Data were corrected for absorption using Gaussian integration on a 12 × 12 × 12 grid. Reflections with $I > 3\sigma(I)$ were considered observed. The presence of only one molecule in an I-centred cell suggests the structure is disordered with the CBr_4 and the tetramine effectively translationally disordered over the $\bar{4}3m$ sites at 0,0,0 and 1/2,1/2,1/2. The space group for the corresponding ordered structure would then be $P\bar{4}3m$. The disorder causes data with $h + k + l = 2n + 1$ to be scaled by a factor $(1 - 2a)$ where a is the fraction of the structure with the alternative origin. A 1 : 1 disorder causes $1–2a$ to be 0. The structure was solved from a Fourier based on a structure factor calculation with a carbon atom at 0,0,0 and a bromine at x,x,x with $x = 0.16$, corresponding to a C–Br distance of *ca.* 1.93 Å. The hydrogen atom was included in a calculated position. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least-squares analysis. Reflection weights used were $1/\sigma^2(F_0)$, with $\sigma(F_0)$ being derived from $\sigma(I_0) = [\sigma^2(I_0) + (0.04I_0)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_0{}^2)^{1/2}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

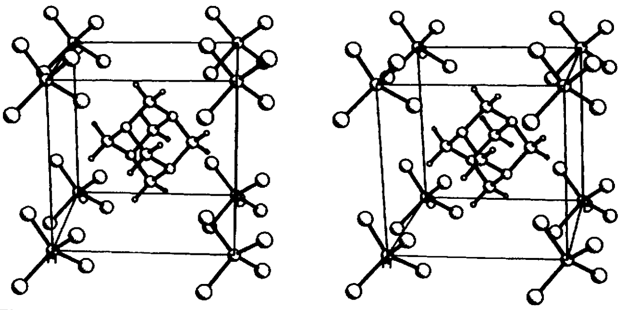

Fig. 1 Stereoview of the crystal structure of complex **1** (CBr_4 : HMT). The CBr_4 molecules have been placed at the cell corners and the HMT molecules at the cell centre to show the N···Br interactions. This is an idealised view of the structure, which in reality adopts a disordered body centred cubic packing.

Notably, the body-centred cubic structure contains CBr_4 and HMT molecules disordered at each of the lattice positions. The crystallographic evidence for the body-centred cell was unequivocal and a detailed search for larger unit cells (of possibly lower symmetry) yielded no alternative possibility. We are therefore confident about the existence of body centring and with it, the disorder of CBr_4 and HMT species. Fig. 1 is obtained by placing the CBr_4 molecules at the unit cell corners and the HMT molecule at the cell centre. This creates two non-connected but catenated diamondoid (actually sphalerite) networks as shown in Fig. 2. It is important to note that each sphere in Fig. 2 (shaded or unshaded) represents a complete molecule of CBr_4 or HMT and that the shaded and unshaded lines represent the N···Br interactions. The catenation is therefore completely supramolecular and each network is formed with N···Br interactions of 2.61(6) Å. These interactions are tetrahedrally disposed about the CBr_4 and HMT molecules and are constrained by crystallographic symmetry to lie exactly on the body diagonal of the unit cell.

A random positioning of CBr_4 and HMT molecules at all the lattice sites in other words, a solid solution structure for complex **1** would yield the observed body centring. However, there is good evidence that the networks are largely ordered as shown in Figs. 1, 2. First, there is a precedent for N···Br interactions of length similar to that observed here in CBr_4–DABCO (2.88, 2.76 Å),[10a] CBr_4–quinuclidine (2.53 Å),[10a] CBr_4–2,3-diazabicyclo[2.2.2]octene (2.91 Å)[10b] $CHBr_3$–HMT (3.00 Å)[9] and others. Secondly, the mixed crystals obtained from 3 : 1, 1 : 1 and 1 : 3 mixtures of CBr_4 and HMT in solution have identical melting points and IR spectra and were found (by elemental analysis) to have CBr_4 : HMT ratios of 1 : 0.99, 1 : 1.06 and 1 : 1.23‡ showing the absence of solid solution behaviour.

Significantly, crystals of the complex obtained from solutions rich in HMT were found to contain a slight excess of HMT in the crystal but when the mother liquor was rich in CBr_4, this component was not correspondingly incorporated into the mixed crystal in excess. This observation, coupled with the fact that pure HMT crystallises in a unit cell of nearly the same dimensions as complex **1** and with the same space group $I\bar{4}3m$ (pure HMT is cubic, a = 7.02 Å),[11] provides a mechanism for the observed body centring in **1** while retaining a largely ordered network, which is chemically more reasonable than the solid solution model. In the crystal of pure HMT, molecules translated along the vector [1/2 1/2 1/2] are linked with sets of three identical C–H···N bonds (C···N 3.88 Å). We propose that the CBr_4–HMT networks in **1** are nearly ordered but that occasionally there is a misregistry of molecules, with two HMT molecules next to each other (as in the pure HMT crystal).§ This necessitates a switch of molecules within the network, which when averaged over the entire crystal produces the body-centring.

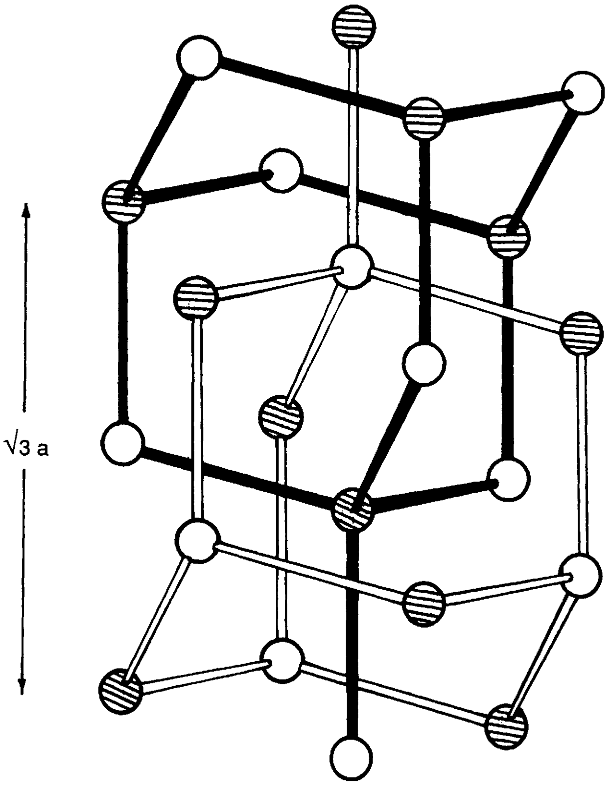

Fig. 2 Idealised ordered structure of complex **1** to show the two identical supramolecularly catenated diamondoid networks. Shaded and unshaded circles represent complete CBr_4 and HMT molecules while shaded and unshaded lines represent identical N···Br interactions. These are shaded and unshaded only to distinguish the two networks. The unit cell edge is 'a' and the body diagonal is shown.

This switching could be due to the coincidental equality of molecular sizes of CBr_4 and HMT and also because all the intermolecular interactions are very weak. The fact that little of the excess HMT can be incorporated in the crystal seems to suggest that the C–H···N interactions in an HMT···HMT linkage do not compete favourably with the (more electrostatic?) N···Br interaction in an HMT···CBr_4 linkage. Additionally, the fact that an excess of CBr_4 is not incorporated in these crystals shows that both N···Br and C–H···N interactions are perhaps stronger than Br···Br interactions. In decreasing order of 'stickiness' these interactions could be therefore N···Br > C–H···N > Br···Br. In effect, the N···Br interactions are sufficiently specific to create a largely ordered network but not so strong as to result in a fully ordered structure. Complex **1** is therefore an illustrative example of a supramolecular structure delicately poised between complete order and complete disorder.

The N···Br contact in complex **1** is of a very unusual length (2.61 Å) being short for an intermolecular interaction (3.2–3.4 Å)[13] and long for a covalent bond (1.9–2.3 Å)[14] and suggests extensive atomic polarisation or charge transfer. These N···Br interactions are in general the shortest to be found among the several CBr_4 complexes already reported. Further theoretical work on these interactions is desirable. Despite their undoubted significance in crystal structures, our results on complex **1**

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‡ A slight inequality of the CBr_4 and HMT content in the crystal is not necessarily incompatible with a body-centred structure.

§ The possibility of molecular misregistry occurring *via* two CBr_4 molecules situated next to each other is not so likely because of the failure of an excess of CBr_4 incorporation from 3 : 1 mixed solutions. Further, CBr_4 crystallises in two forms but neither is a mimic for structure **1** as is the crystal structure of HMT.[12]

indicate, however, that the strengths of these interactions N···Br and/or their directional properties are at the limit for achieving systematic supramolecular construction. Further studies are in progress on the crystals obtained from the 3 : 1 and 1 : 3 solutions, the frequency of molecular switching in all these solids and also on complexes obtained from other purely organic moieties with S_4 symmetry.

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