New Non-molecular Poly-adamantanoid Crystal Structures of $Cd(SAr)_2$. Zeolitic $Cd_4(SC_6H_4Me\text{-}4)_8$, and Solvated $Cd_8(SC_6H_4Br\text{-}4)_{16}(DMF)_3$ (DMF = dimethylformamide), in Relation to the Molecular Structures of Aggregates in Solution

Ian G. Dance,* Robert G. Garbutt, Don C. Craig, Marcia L. Scudder, and Trevor D. Bailey

School of Chemistry, The University of New South Wales, PO Box 1, Kensington, NSW 2033, Australia

Crystalline $Cd_4(SC_6H_4Me\text{-}4)_8$ contains a three-dimensionally non-molecular zeolitic lattice of vertex-linked adamantanoid cages, while crystalline $Cd_8(SC_6H_4Br\text{-}4)_{16}(DMF)_3$ (DMF = dimethylformamide) contains a derived two-dimensionally non-molecular lattice with linkages interrupted by CdSAr and $Cd(DMF)_3$ terminal co-ordination: Cd n.m.r. spectra of $Cd(SC_6H_4X\text{-}4)_2$ (X = H, F, Cl, Br, Me) in DMF solution indicate the existence of temperature-dependent equilibria between large and small molecular aggregates.

We recently reported[1] that $Cd(SPh)_2$ (**1**) crystallises from dimethylformamide (DMF) in the three-dimensionally non-molecular structure $^3_\infty\{(\mu\text{-}SPh)_6Cd_4(\mu\text{-}SPh)_{4/2}\}$, in which large tetrahedral adamantanoid cages are vertex-linked in the same helical conformation as the SiO_4 tetrahedra in cristobalite. We now report investigation of four derivatives, $Cd(SC_6H_4X\text{-}4)_2$, X = F (**2**), Cl (**3**), Br (**4**), and Me (**5**). The fluoro derivative (**2**) adopts the structure of (**1**), although with higher crystallographic symmetry,† but the other three compounds have distinctly different properties.

With X = Me, (**5**) also crystallises† with the ubiquitous adamantanoid cages $\{(\mu\text{-}SAr)_6Cd_4(\mu\text{-}SAr)_{4/2}\}$ vertex-linked to four others through doubly-bridging thiolate ligands, but in a quite different three-dimensionally non-molecular structure. The cage linkages occur in closed cycles, namely 4-rings, 6-rings, and 8-rings, instead of the helices of (**1**) and (**2**), and the lattice contains large polyhedral cavities such that the complete Cd–S network resembles a three-dimensional zeolite structure. Figure 1 shows one such cavity. The twelve adamantanoid tetrahedra are connected in two 4-rings (centrosymmetric) and four 6-rings around the centrosymmetric cavities (see Figure 1). Figure 2 presents the complete lattice as connected centroids of adamantanoid cages, and shows that the decahedral cavities are stacked along the *b* axis, sharing 4-rings. A consequence of the edge sharing of the cavities is that they are not close-packed, but enclose channels (see Figure 2) parallel to *b*. The walls of the channels are the 6-ring access ports to the cavities, while the shortest connections around the channels are puckered centrosymmetric 8-rings.

The internal surface of the cavity is composed of four triangular faces of adamantanoid tetrahedra at each of the upper and lower 4-rings, and by four edges of adamantanoid tetrahedra in the equatorial belt. In terms of the individual CdS_4 co-ordination tetrahedra, the internal surface of the cavity is lined by 44 sulphur atoms, connected by 32 cadmium atoms. S–S diagonals through the inversion centre of the cavity range from 16.6 to 19.1 Å. The cavity is populated by ten aryl substituents. We have calculated that in this lattice only 10% of the crystal volume is occupied by Cd and S atoms, and that the remaining 90% is substantially more than the volume of the substituents.‡§ Therefore the analogy between (**5**) and the microporous aluminosilicate networks is sustained by both the three-dimensional structural framework and its partial emptiness.

The ^{113}Cd n.m.r. spectra of (**1**)—(**5**) in DMF solution are very similar to each other. At low temperatures (*ca.* 220 K) one line predominates, at 593 ± 3 p.p.m. [reference $Cd(NO_3)_2(aq)$], diagnostic of $\{Cd(SAr)_4\}$ co-ordination. As temperature increases there is line broadening, followed by re-sharpening at the highest temperatures of measurement (*ca.* 340 K) to a line at 450 ± 10 p.p.m. attributed to $\{Cd(SAr)_3(DMF)_n\}$ co-ordination.¶ Therefore it appears that

† *Crystal data:* (**2**) $Cd_4(SC_6H_4F)_8$, tetragonal, space-group $P4_1$, a = 15.793(2), c = 21.121(5) Å, Z = 16, 3816 data, Mo-K_α, R = 0.035; (**5**) $Cd_4(SC_6H_4Me)_8$, monoclinic, space group $P2_1/c$, a = 27.196(9), b = 15.722(5), c = 37.046(13) Å, β = 132.03(3), Z = 8, 12003 data, Mo-K_α, R = 0.065; (**4**) $Cd_8(SC_6H_4Br)_{16}(DMF)_3$, monoclinic, space group $P2_1/c$, a = 27.331(13), b = 15.303(4), c = 39.110(20) Å, β = 126.43(2), Z = 8, 4873 data, Mo-K_α, R = 0.053. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ In comparison, total volumes excluded by the TO_4 (T = Si, Al) tetrahedra of typical zeolites range from 20 to 50%.

§ Similarly, in (**1**), the Cd and S atoms exclude 12% of the crystal volume, leaving 139 Å^3 per C_6H_5 substituent compared with 127 Å^3 per molecule in crystalline benzene.

¶ Estimated by interpolation between −35 p.p.m. for $[Cd(DMF)_n]^{2+}$ $[Cd(BF_4)_2$ in DMF] and 593 p.p.m. for $\{Cd(SAr)_4\}$ sites in various compounds.

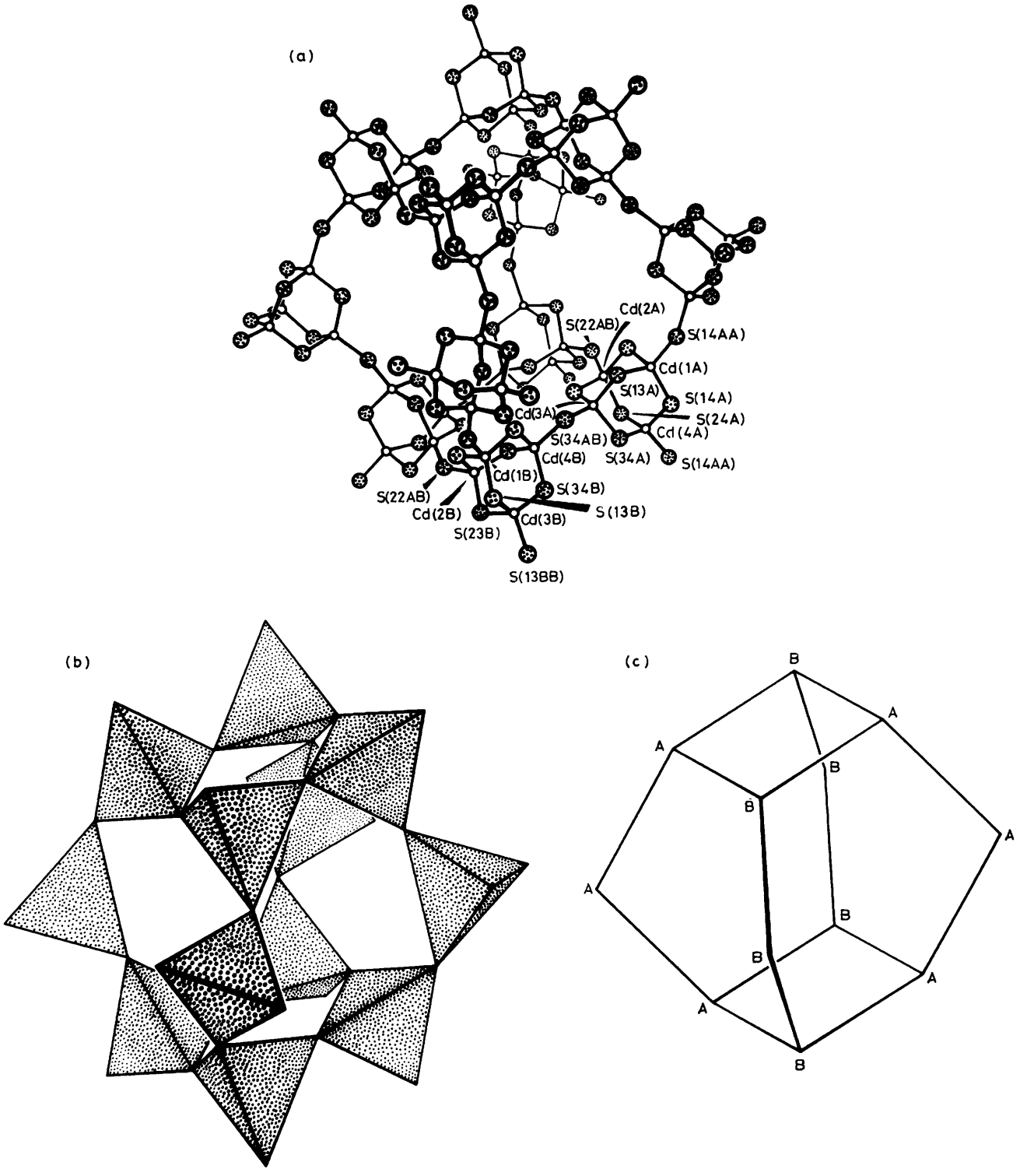

Figure 1. One polyhedral cavity composed of twelve adamantanoid cages in (**5**), showing (a) the Cd and S atoms, (b) the vertex-linked adamantanoid tetrahedra, and (c) the bi-truncated octahedron created by the centroids of the adamantanoid tetrahedra, and composed of 4- and 6-rings. The three diagrams have the same orientation, and the letters A,B refer to the crystallographically independent cages.

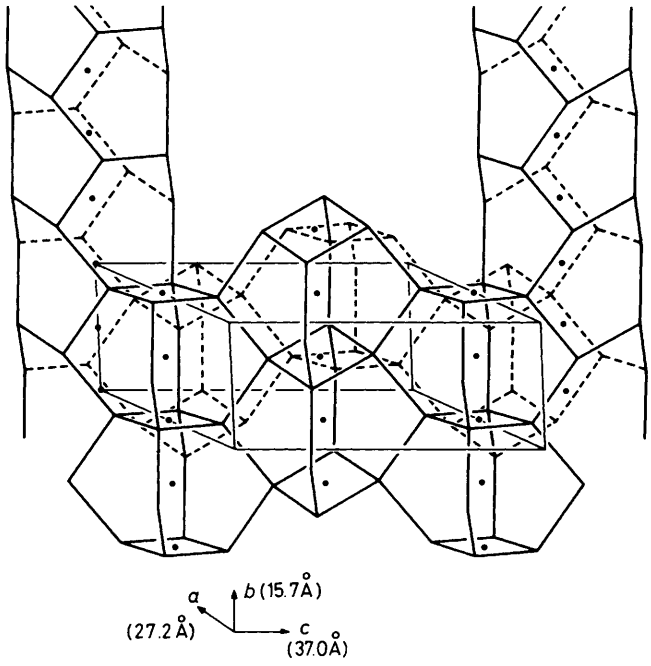

Figure 2. The crystal lattice of (**5**), drawn as the lines connecting the centroids of the adamantanoid cages which share vertices. Broken lines represent rear connections, dots are centres of symmetry. The 12-vertex decahedral cavities which are stacked along *b* are emphasised in the central part of the Figure, and the channels (encycled by 8-rings) between them are outlined on the sides.

these solutions contain various aggregated species in equilibria of the type in equation (1). At the lowest temperatures, the

$$\begin{matrix}\text{larger aggregates,}\\ \text{extensive SR}\\ \text{bridges}\end{matrix} + \text{DMF} \underset{k_{agg}}{\overset{k_{deagg}}{\rightleftharpoons}} \begin{matrix}\text{smaller aggregates,}\\ \text{with less bridging and}\\ \text{DMF co-ordination}\end{matrix} \quad (1)$$

equilibria are to the left ($k_{agg} \gg k_{deagg}$) and in n.m.r.-slow exchange. However at the upper temperatures, there are higher proportions of deaggregated species ($k_{deagg} > k_{agg}$) in n.m.r.-fast exchange. ^{13}C N.m.r. data on the distribution of bridging and terminal SAr ligands in these solutions are not entirely consistent with postulated structures for aggregates in solution, and the n.m.r. investigations are continuing.

The unexpected modification of the crystal structure due to the 4-methyl substituent in (**5**) was investigated further in crystals of (**3**) and (**4**) from DMF solution. Crystalline (**3**) is unique, decomposing rapidly in *X*-rays, but (**4**) is stable. The lattice of (**4**)† is a two-dimensionally non-molecular modification of that of (**5**), involving the incorporation of some DMF co-ordination according to the composition $\{(\mu\text{-SAr})_{15}Cd_6\}\{CdSAr\}\{Cd(DMF)_3\}$. In the crystal structure, shown schematically in Figure 3, there are two different types of adamantanoid cages, one (A) linked to three neighbours by doubly-bridging thiolate and with terminal thiolate at the fourth Cd atom, and the other (B) linked by three doubly-bridging thiolates and terminated by three DMF ligands at the fourth Cd atom which has unusual pseudo-octahedral stereochemistry. The significance of the structure of (**4**) is that it reveals the type of DMF co-ordination resulting in deaggregation that is likely to occur in the solutions of $Cd(SAr)_2$ in DMF at higher temperatures.

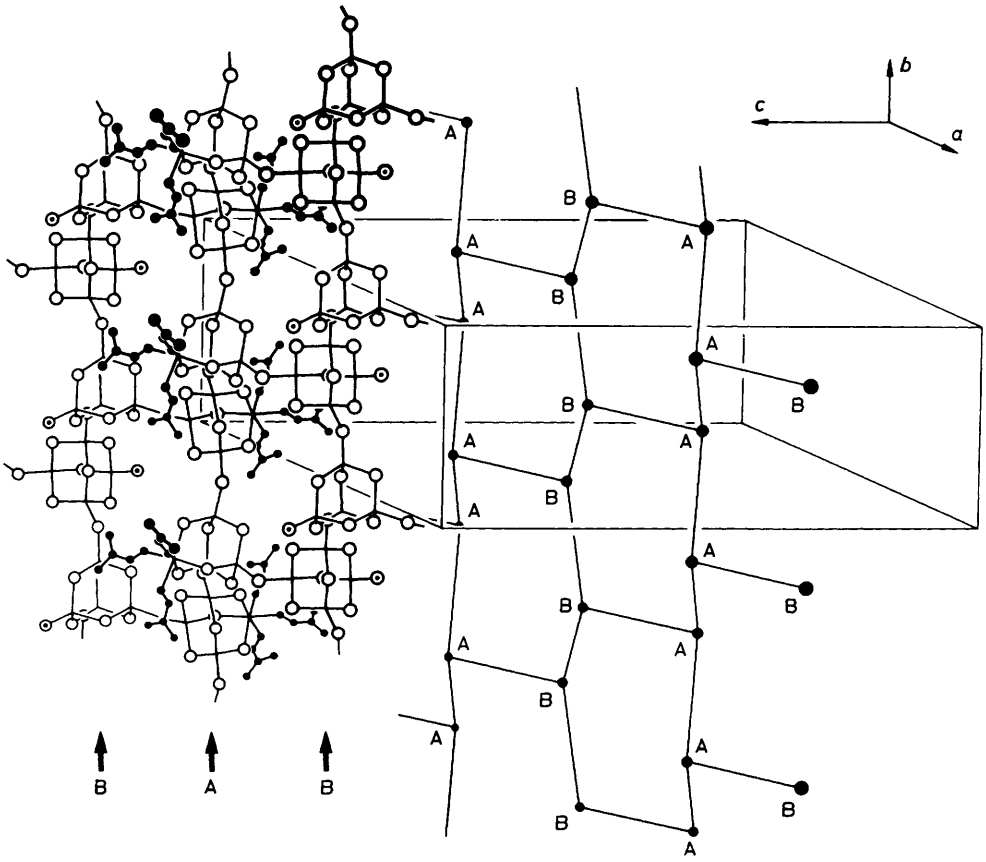

Figure 3. Representation of the crystal structure of (**4**), $\{(\mu\text{-SAr})_{15}Cd_6\}\{CdSAr\}\{Cd(DMF)_3\}$. Linked adamantanoid cages are shown on the left, with DMF atoms (on cages A) as filled circles and terminal S atoms (on cages B) as dotted circles. The connections of the centroids of the adamantanoid cages are shown on the right.

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Reference

1 D. Craig, I. G. Dance, and R. Garbutt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 165.