

Supramolecular Chemistry of $[M(\text{CO})_3(\mu_3\text{-OH})]_4$ ($M = \text{Mn, Re}$): Spontaneous Strict Self-assembly of Distorted Super-diamondoid Networks that are Capable of enclathrating Acetonitrile

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Cocrystallization of $[M(\text{CO})_3(\mu_3\text{-OH})]_4$ ($M = \text{Mn, Re}$) with the linear difunctional H-bond acceptor molecules 1,4-diaminobenzene and 4,4'-bipyridyl affords, respectively, twofold and fourfold tetragonally distorted super-diamondoid networks that contain microchannels which enclathrate acetonitrile.

Exploitation of network hydrogen bonding in order predictably to engineer ordered solids represents an area of considerable general and topical interest.¹ In this context, the ability of appropriately tetrafunctionalized organic molecules with approximate S_4 symmetry to form super-diamondoid networks has been a subject of recent interest.² These networks are structurally analogous to diamond but the linkages are self-assembled hydrogen bonds rather than C–C bonds. In order to fill available space in the crystal lattice the two prototypal organic diamondoid compounds, adamantane-1,3,5,7-tetracarboxylic acid^{2a} and 3,3-bis(carboxymethyl)glutaric acid ('methanetetraacetic acid'),^{2b} undergo self-inclusion to exist as three- and five-fold independent networks, respectively. The potential significance to inclusion chemistry was noted immediately^{2a} and has been realized by studies which demonstrate that such 'tectons'^{3d} can be modified to afford a lower level of interpenetration, thereby facilitating inclusion of guest molecules in the lattice.³ However, a considerable drawback concerns the very limited number of tetrafunctionalized molecules with the requisite symmetry and ability to self-assemble. We recently outlined⁴ an alternative approach that has the potential to be far more versatile and general than self-assembly: cocrystallization of a molecule which contains four hydrogen bond donor groups with two complementary difunctional hydrogen bond acceptor or 'spacer' molecules, *i.e.* strict self-assembly.⁵ The prototypal network, $[\text{Mn}(\text{CO})_3(\mu_3\text{-OH})]_4 \cdot 2\text{en}$ ($\text{en} = 1,2\text{-diaminoethane}$), $1 \cdot 2\text{en}$, is undistorted and consists of three interpenetrating networks in which $\text{OH} \cdots \text{en} \cdots \text{HO}$ hydrogen bonds serve the geometric function of C–C bonds. In this communication we demon-

strate that the strict self-assembly approach to construction of super-diamondoid networks is indeed quite general and versatile and can facilitate distortion of the diamondoid network, zeolite-like channels, and ready inclusion of solvent molecules.

Complex **1**,⁶ which may be prepared in 100% yield in one step from $\text{Mn}_2(\text{CO})_{10}$ ^{6b} and is a powerful and versatile hydrogen bond donor with T_d symmetry,⁷ cocrystallizes from hot acetonitrile with two equivalents of 4,4'-bipyridyl (bpy) to afford $1 \cdot 2\text{bpy} \cdot 2\text{MeCN}$ **2**.[†] The Re analogue **3**⁸ cocrystallizes with 1,4-diaminobenzene, diam, to afford $3 \cdot 2\text{diam} \cdot 4\text{MeCN}$ **4**.[†] The tertiary structure of **2** consists of four tetragonally

[†] *Crystal Data* for **2**: $M = 1018.4$, tetragonal, $P4_2/nnc$, $a = 13.984(4)$, $c = 23.416(9)$ Å, $U = 4579.1(22)$ Å³, $Z = 4$, $D_c = 1.48$ Mg m⁻³, $\mu = 11.0$ cm⁻¹, crystal dimensions $0.20 \times 0.20 \times 0.40$ mm. 665 reflections with $I > 3\sigma(I)$ converged at $R = 0.040$ and $R_w = 0.048$. There are four independent super-diamondoid networks which consist of molecules of **1** around 4 positions (15.22 Å apart) and molecules of bpy which lie around twofold axes.

Crystal Data for **4**: $M = 1529.5$, tetragonal, $P4_2/n$, $a = 15.1361(22)$, $c = 9.9037(21)$ Å, $U = 2269.0(6)$ Å³, $Z = 2$, $D_c = 2.24$ Mg m⁻³, $\mu = 108.4$ cm⁻¹, crystal dimensions $0.20 \times 0.40 \times 0.80$ mm. 1281 reflections with $I > 3\sigma(I)$ converged at $R = 0.051$ and $R_w = 0.059$. There are two independent super-diamondoid networks which consist of molecules of **3** around 4 positions (11.79 Å apart) and molecules of diam which lie around inversion centres.

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.

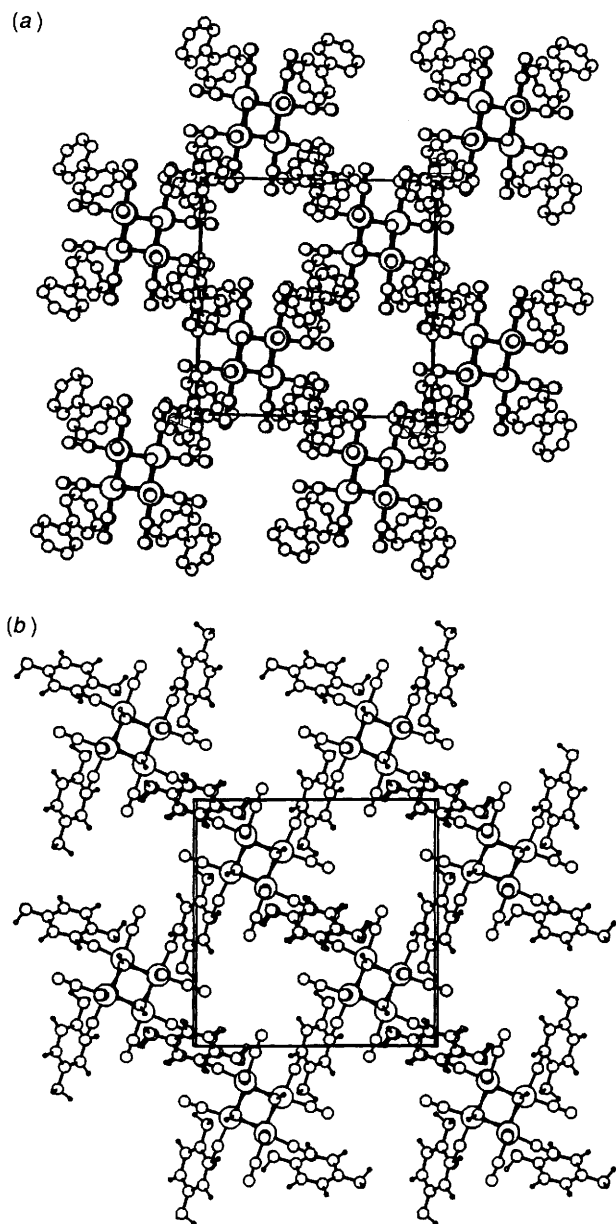


Fig. 1 Cross-section of the *ab* planes in (a) **2** and (b) **4**. The solvent molecules lie in the microchannels that exist because the interweaved diamondoid networks cannot occupy all the space in the crystal. O...N-H bond separations are 2.744(9) and 2.608(18) Å for **2** and **4**, respectively.

elongated super-diamondoid networks that are disposed around a fourfold crystallographic axis [Fig. 1(a)]. The fourfold axis, which is parallel to the *c* axis, therefore represents a microchannel that stretches through the crystal. This microchannel contains two sites which are occupied by acetonitrile molecules that appear to be dynamically disordered.‡ There are two acetonitrile molecules per molecule of **1**. Compound **4** crystallizes as a tetragonally contracted twofold diamondoid network, reflecting the different geometric characteristics of diam compared to bpy (smaller separation of cubes and different orientation of bridging lone pairs). Nevertheless, the structure is similar to that of **2** in that a

microchannel containing acetonitrile molecules passes through the crystal parallel to the *c* axis [Fig. 1(b)]. Compound **4** contains four molecules of acetonitrile per molecule of **3**.

In summary, the nature of super-diamondoid networks formed by strict self-assembly of **1** and **3** with difunctional hydrogen bond acceptor 'spacer' molecules is profoundly influenced by the 'spacer' molecule. We consider the salient feature of the results reported herein to be the observation that strict self-assembly works in a general sense and therefore, as it relies upon noncovalent bonding, supramolecular architectures can be modified without the need for covalent modification of the tecton. Furthermore, we have demonstrated that suitable 'spacer' molecules can facilitate 3-D super-diamondoid networks that have structural characteristics similar to zeolites⁹ even though their chemical nature is markedly different (in particular, the cavities formed are hydrophobic in nature). Generation of a wide range of super-diamondoid networks with low levels of interpenetration appears to be an attainable and desirable goal, especially one-fold networks that could in principle have up to 50% of their volume as space for enclathration of guest molecules. Finally, the results described herein also have relevance in the context of properties of solids, given that KH_2PO_4 , a well-known ferroelectric and nonlinear optic active material,¹⁰ is a polar twofold super-diamondoid network.

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References

- Recent representative reports: (a) C. V. Krishnamohan, K. Panneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 832; (b) F. Garcia-Tallado, S. J. Geib, S. Goswami and A. D. Hamilton, *J. Am. Chem. Soc.*, 1991, **113**, 9265; (c) S. J. Geib, S. C. Hirst, C. Vicent and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1991, 1283; (d) X. Zhao, Y.-L. Chang, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1990, **112**, 6627; (e) J.-M. Lehn, M. Mascal, M. A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 479; (f) M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; (g) C. B. Aakeroy, P. B. Hitchcock and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1992, 553; (h) G. R. Desiraju, in *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989; (i) J. A. Zerkowski, C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1992, **114**, 5473.
- (a) O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747; (b) O. Ermer and A. Eling, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 829.
- (a) O. Ermer and L. Lindenberg, *Helv. Chim. Acta*, 1988, **71**, 1084; (b) O. Ermer and L. Lindenberg, *Chem. Ber.*, 1990, **123**, 1111; (c) O. Ermer and L. Lindenberg, *Helv. Chim. Acta*, 1991, **74**, 825; (d) M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
- S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719.
- J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153.
- (a) M. Herberhold, F. Wehrmann, D. Neugebauer and G. Huttner, *J. Organomet. Chem.*, 1978, **152**, 329; (b) M. D. Clerk and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1991, 1607.
- M. D. Clerk, S. B. Copp, S. Subramanian and M. J. Zaworotko, *Supramolecular Chem.*, 1992, **1**, 7.
- M. Herberhold and G. Suss, *Angew. Chem., Int. Ed. Engl.*, 1975, **87**, 750.
- Microchannels and micropores are characteristic structural features of zeolites and zeolite-like solids: (a) R. M. Barrer, in *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, New York, 1978; (b) L. A. Mundi and R. C. Haushalter, *Chem. Mater.*, 1992, **4**, 31.
- (a) S. Endo, T. Chino, S. Tsuboi and K. Koto, *Nature*, 1989, **340**, 452, and references therein; (b) see discussion section of ref. 2(b).

‡ The ¹H NMR spectrum of a solid sample of **2** displays two singlets at δ 4.39 and 3.53, consistent with the two crystallographic environments observed for MeCN.