Closed-surface hexameric metal–organic nanocapsules derived from cavitand ligands†

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Assembly of cavitand ligands, $\mathbf{1}^{4-}$, and Zn^{2+} ions yields a one-dimensional polymer comprised of hexameric, closed-surface, metal–organic nanocapsules.

For over two decades now, spheroidal, container-like molecules[1] have captivated chemists across the disciplines, presenting both challenges and opportunities for synthetic chemists and serving as a playground for modern physical organic chemistry. Avenues of practical interest include their study as possible drug delivery agents,[2] reaction nanovessels and catalysts,[3] storage materials,[4] and as environments within which to protect and study reactive intermediates.[5] With respect to synthesis, there is a growing recognition that supramolecular approaches based upon dynamic chemistry—*e.g.* dynamic covalent chemistry,[6] hydrogen bonding[7] and, particularly, metal–ligand coordination[8,9]—are the most viable means of accessing nanometre-plus sized, many component containers. As the diameters of such species extend significantly into the nanometre regime their structures often more resemble cages than capsules, allowing ready exchange of small molecule guests. Much utility, though (*e.g.* storage, protection, *etc.*), remains rooted in the closed-surface nature of nanocontainers, providing kinetic barriers to the ingress/egress of guests. Moreover, chirality remains rare in these systems.[7a] We report herein the synthesis and X-ray single crystal structure of chiral, closed-surface, metal–organic hexameric nanocapsules derived from the assembly of Zn^{2+} ions and upper-rim carboxylate functionalized cavitand ligands, $\mathbf{1}^{4-}$. The nanocapsules are condensed into one-dimensional polymers in the solid-state.

Given the present current interest in metal–organic framework materials, and particularly in metal–carboxylates,[10] we have been exploring the synthesis of frameworks derived from cavitand and container-like carboxylate ligands.[4b] We reasoned that reaction of the C_{4v} symmetric tetra-carboxylic acid functionalized cavitand $H_4\mathbf{1}$[11] with transition metals would yield either polymeric frameworks or discrete metal–organic capsules, depending upon the choice of metal salt and reaction conditions (Fig. 1). Simple Zn^{II}–arylcarboxylates tend toward octahedral $[Zn_4(\mu_4\text{-}O)(ArCOO)_6]$ clusters, four-fold symmetric paddle-wheel type $[Zn_2(ArCOO)_4]$ clusters, or three-fold symmetric $[Zn_2(ArCOO)_3L_n]$ (L = OH^-, $ArCOO^-$, *etc.*; **A** in Fig. 1) clusters. Notably, simple molecular models exclude, on steric grounds, the possibility of Zn^{2+} complexes of $\mathbf{1}^{4-}$ forming the octahedral or four-fold symmetric clusters. Moreover, Yaghi and co-workers have established the tendancy for bulky 2,6-disubstituted aryl carboxylate ligands, such as $\mathbf{1}^{4-}$, to adopt the less crowded three-fold symmetric cluster.[12]

Reaction of $H_4\mathbf{1}$ with $Zn(NO_3)\cdot 6H_2O$ at room temperature in acetone led to the precipitation of colorless, phase pure, crystalline $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7\cdot$solvent in *ca.* 21% yield. X-Ray analysis of single crystals of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7\cdot$solvent‡[13] established the presence of hexameric nanocapsules based upon core $[Zn_{16}(\mathbf{1})_6]^{8+}$ assemblies consisting of sixteen Zn^{2+} ions and six $\mathbf{1}^{4-}$ ligands. The $[Zn_{16}(\mathbf{1})_6]^{8+}$ hexamers are sustained primarily by the formation of eight three-fold symmetric **A**-type $[Zn_2(ArCOO)_3]^+$

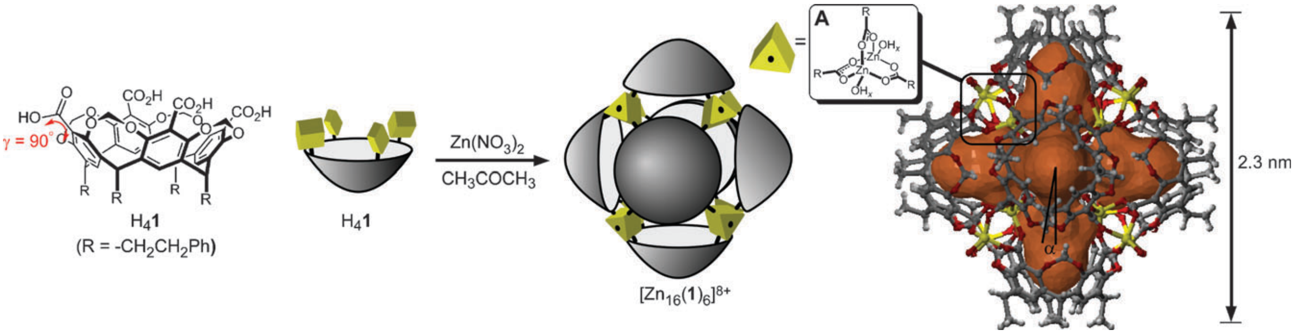

Fig. 1 (Left) Assembly of sixteen Zn^{2+} ions with six cavitand ligands, $\mathbf{1}^{4-}$, yields hexameric $[Zn_{16}(\mathbf{1})_6]^{8+}$ nanocapsules sustained by $[Zn_2(ArCOO)_3]^+$ coordination clusters. (Right) The capsular entity from the X-ray single crystal structure of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7\cdot$solvent. The solvent accessible internal cavity volume is depicted in orange. For clarity, the phenethyl substituents of **1** are depicted as methyl groups.

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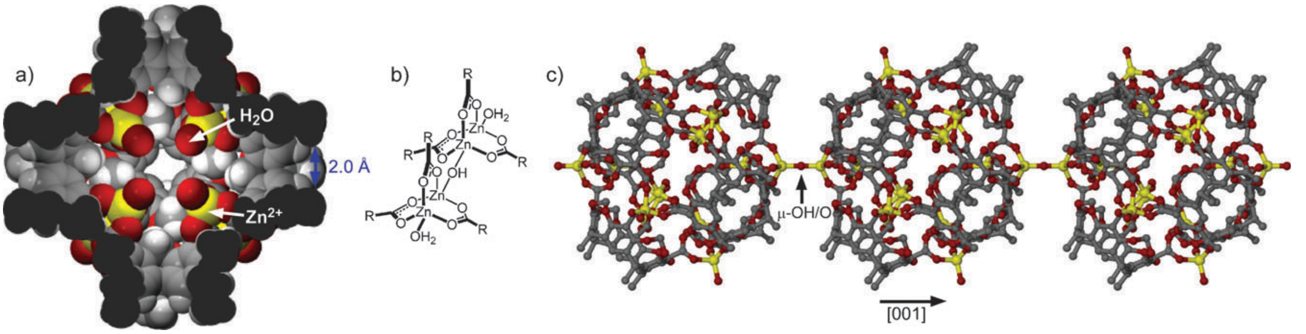

Fig. 2 (a) Cross sectional view of the nanocapsule (phenethyls omitted), (b) the μ-OH (or μ-O) linkage resulting in (c) 1D polymerization of the nanocapsules.

clusters (Fig. 1). Neglecting the ancillary ligands (*vide infra*), the capsules are in fact chiral (racemic), closely approximating 432 (*O*) point group symmetry. Indeed, the three-fold symmetric **A**-type clusters complement the four-fold symmetric cavitand ligands such that each $[Zn_{16}(\mathbf{1})_6]^{8+}$ capsule is most accurately described, according to the classification system of MacGillivray and Atwood,[1a] as an Archimedean snub cube—one of only two possible convex uniform polyhedra constructed from regular 3- and 4-gons (the other possibility being a rhombicuboctahedron). The feature differentiating a snub cube-like structure from a rhombicuboctahedron is an approximate 10° clockwise (or counterclockwise) rotation of the cavitand ligands about the four-fold symmetry axis (α, Fig. 1). Thus, the chirality does not arise from the individual constituents, but from their spatial arrangement. The cavitands are turned so as to alleviate steric interactions between the O–CH_2–O methylenic bridges that line the rim of the cavitands. The result, remarkably, is a closed-surface carcerand-like species, the largest portals being the 2.0 Å diameter windows at the base of the cavitand ligands themselves (Fig. 2).

Due to extensive crystallographic disorder, the interiors of the nanocapsules are somewhat poorly defined. Each of the eight $[Zn_2(ArCOO)_3L_n]^+$ clusters projects one of its apical water (or hydroxyl) ligands, L, toward the center of the internal cavity, thereby segregating the *ca.* 680 $Å^3$ cavity into seven nearly discrete compartments (Fig. 1, Fig. 2a). Six of the compartments are defined by the bowl-shaped cavitand ligands and are each occupied by either an acetone molecule or a nitrate anion, which are crystallographically indistinguishable, but the former is deemed more likely for electrostatic reasons. The central compartment is smaller, but appears to be of sufficient size to house an additional molecule of acetone.

Each of the eight $[Zn_2(ArCOO)_3L_n]^+$ clusters also projects an apical ligand away from the surface of the capsules. Six of these clusters are clearly terminated by water ligands whereas two serve to connect adjacent nanocapsules *via* linear μ-hydroxy (or μ-oxo) linkages (Fig. 2b,c). The nanocapsules are thus formally polymerized into 1D chains propagating along the [001] crystallographic axis. It is likely, in fact, that crystal growth is instigated by the polymerization process; the needle shaped crystals are longest along the [001] direction. It is therefore suspected that discrete $[Zn_{16}(\mathbf{1})_6(H_2O)_{16}{\subset}\text{guests}]^{n+}$ capsules are initially formed in solution and ultimately condense *via* slow deprotonation/dehydration under the acidic reaction conditions. Though preliminary experiments (^1H NMR, ESI-MS, MALDI) have offered no evidence for the existence of discrete $[Zn_{16}(\mathbf{1})_6(H_2O)_{16}{\subset}\text{guests}]^{n+}$ capsules, efforts to characterize and exploit the cavities of such species continue. Moreover, the polymeric material may itself have applications, among others, in the storage of gases and/or volatile organic compounds. The storage properties of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7{\cdot}$solvent and related materials derived from container molecules are currently being explored.

Notes and references

‡ Crystal data for $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7{\cdot}$solvent (solvent ≈ $12CH_3COCH_3$, $47H_2O$): M = 10034.98, colorless needle, 1.20 × 0.21 × 0.21 mm^3, trigonal, $R\bar{3}$ (No. 148), $a = b = 44.783(6)$, $c = 22.093(6)$ Å, $V = 38373(12)$ $Å^3$, $Z = 3$, $D_c = 1.3037$ g cm^{-3}, $F_{000} = 15684$, Siemens SMART 1 K CCD, MoKα, $\lambda = 0.71073$ Å, $T = 85(2)$ K, $2\theta_{max} = 42.0°$, 33517 reflections collected, 9145 unique ($R_{int} = 0.1169$). Final $GooF = 0.914$, $R1 = 0.0913$, $wR2 = 0.2431$, R indices based on 4599 reflections with $I > 2\sigma(I)$ (refinement on F^2), 424 parameters. Lp and absorption corrections applied, $\mu = 0.827$ mm^{-1}. CCDC 662426. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715273f
Anal. calc. (%) for $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7{\cdot}12CH_3COCH_3{\cdot}47H_2O$, $Zn_{16}C_{444}H_{507}O_{191}N_7$, C 53.09, H 5.09, N 0.98; obs. C 49.91, H 5.39, N 1.23, indicating the presence of some $Zn(NO_3)_2$ impurity.

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