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Heptametallic Bowl-Shaped Complexes Derived from Conjugated Schiff-Base Macrocycles: Synthesis, Characterization, and X-ray Crystal Structures

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The reaction of chelating conjugated macrocycles **1a**–**c** with Zn(OAc)$_2$ gives bowl-shaped heptanuclear Zn complexes featuring Zn in tetrahedral, octahedral, and square-pyramidal geometries. Crystallographic and NMR results indicate that vacant Zn coordination sites within the bowl may be accessed, suggesting that these coordination complexes may be used as mimics for Zn fingers and carbonic anhydrase.

Supramolecular coordination chemistry is a gateway to new materials such as chemical sensors, molecular devices, and porous substances.[1−4] Grids and frameworks represent beautiful examples of harnessing coordination chemistry to direct self-assembly.[5,6] Organic macrocycles (e.g., crown ethers) and molecules with bowl, cone, or barrel structures (e.g., carceplexes, calixarenes, and cucurbiturils) have a rich history of host−guest chemistry.[7−9] Inorganic analogues that may be self-assembled using coordination chemistry promise to marry the selectivity and recognition of organic supramolecular chemistry with the useful catalytic, magnetic, and optical properties of the metal centers, producing functional materials.[10−12] An outstanding challenge in this field is to develop self-assembled capsules with accessible metal coordination sites to function as nanoreactors.[13]

Work on organic shape-persistent macrocycles has led to new substances capable of aggregating, forming liquid-crystalline phases, and yielding porous 3-D networks.[14] Although metal coordination to ligands inside and outside of macrocycles has been demonstrated,[15] the use of shape-persistent macrocycles as a template for assembling molecular clusters has received very little attention.

Here we report the first studies of the metalation of shape-persistent macrocycles **1a**−**c**, including the surprising discovery and crystallographic characterization of a hepta-

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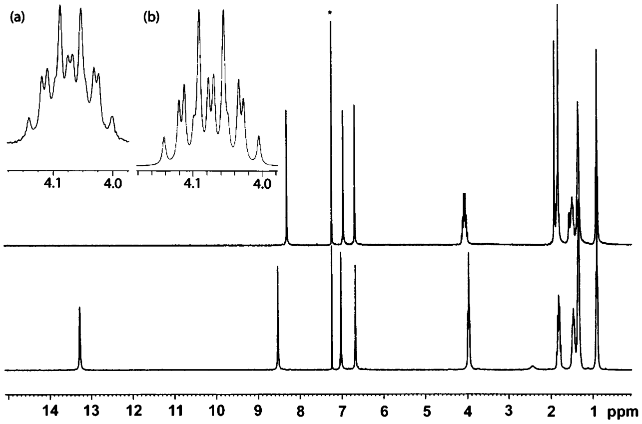
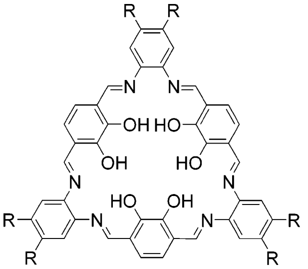


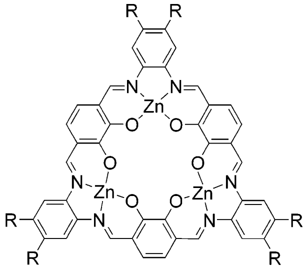
Figure 1. ^1H NMR spectra ($CDCl_3$, 300 MHz) of macrocycle **1c** (bottom) and compound **3c** (top). Inset: (a) experimental data and (b) simulation of the OCH_2 resonance for compound **3c** (* = $CHCl_3$).

metallic cluster complex. Preliminary evidence suggests that these new bowl-shaped complexes may be useful precursors for the self-assembly of metal-containing capsules and aggregates.

Macrocycles **1** are prepared by the [3 + 3] Schiff-base condensation of diformyldihydroxybenzene with substituted phenylenediamines.[16,17] Upon complexation to alkali-metal and ammonium ions, these macrocycles form supramolecular assemblies, with the cations complexed to the central hydroxyl groups.[16] We identified **1a**−**c** as potential precursors to flat, disc-shaped metallomacrocycles if transition metals are coordinated within their tetradentate N_2O_2 salen-type pockets. Reaction of **1c** with 3 equiv of $Zn(OAc)_2$ produced a product with a very broad ^1H NMR spectrum. Electrospray ionization mass spectrometry (ESI-MS) of the product indicated that compound **2c** formed but also showed many species that correspond to aggregates. These results suggested that the trimetalated macrocycle could be prepared but aggregates strongly in solution.



1a (R = OC_2H_5)
1b (R = $O^nC_5H_{11}$)
1c (R = $O^nC_6H_{13}$)



2a (R = OC_2H_5)
2b (R = $O^nC_5H_{11}$)
2c (R = $O^nC_6H_{13}$)

When shape-persistent macrocycle **1c** was reacted with an excess of $Zn(OAc)_2$, a single orange microcrystalline product **3c** precipitated from solution. The ^1H NMR spectrum of **3c** (Figure 1) indicates that the macrocyclic ligand retains its C_3 axis because the number of aromatic and imine CH resonances is unchanged from that for **1c**. Notably, the phenolic proton resonance of **1c** (δ 13.2) is absent in the spectrum for **3c**, as is expected if the ligand is bound to three metals. Two new peaks at δ 1.93 and 1.84, characteristic of acetate groups, are present in the spectrum of **3c** and integrate to six acetates per macrocycle (3:3 ratio).

Further examination of the ^1H NMR spectrum of **3c** revealed that the resonance assigned to OCH_2 (triplet in **1c**) of the peripheral alkoxy groups shows a complex coupling pattern (Figure 1, inset). The experimental data can be simulated as an ABX_2 spin system. In particular, the protons on the OCH_2 for **3c** are inequivalent and display both geminal and vicinal coupling.[18] Because the macrocycle in **3c** clearly exhibits C_3 rotational symmetry and there is only a single OCH_2 carbon environment (^{13}C NMR) in the molecule, the plane of symmetry perpendicular to the C_3 axis in the molecule must be absent, leading to diastereotopic H atoms in the OCH_2 group. This was our first indication that the metalated macrocycle is not flat.

ESI-MS of **3c** showed a single ion corresponding to $[\mathbf{2c}]Zn_2(OAc)_4Na^+$ (m/z = 1894), a species with five Zn^{2+} ions, but elemental analysis indicated clearly that compound **3c** contains seven Zn atoms per macrocycle. Unable to obtain crystals of **3c** that would diffract X-rays, we prepared analogous Zn complexes **3a** and **3b** from macrocycles **1a** and **1b**, respectively. Crystals of **3a** were obtained from dimethyl sulfoxide (DMSO)/ether, and a single-crystal X-ray diffraction (SCXRD) experiment was undertaken.[19] Figure 2 shows the solid-state structure of complex **3a**. The molecule has a bowl shape with nearly C_{3v} symmetry. The side of the bowl is formed by a trimetalated macrocycle with three Zn^{2+} ions in square-pyramidal geometry.[20,21] The metallomacrocycle adopts a cone shape as a result of the constrained geometry inside the macrocycle upon coordination to Zn^{2+} ions. O atoms in the interior of the shape-persistent macrocycle are further coordinated to a near-tetrahedral $[Zn_4O]^{6+}$ cluster (Figure 2c, red) that closes the bowl. The basic zinc acetate cluster is bridged by three μ-1,2 bidentate acetate ligands (Figure 2c, green). Three tridentate acetate ligands (Figure 2c, blue) bridge the Zn atoms in the macrocyclic N_2O_2 pockets with those at the base of the $[Zn_4O]^{6+}$ cluster.[22] These ligands bridge in the very rare μ-1,1,2 fashion with

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(19) Crystallographic data for **3a**·DMSO: red prism (0.50 × 0.30 × 0.20 mm), triclinic, space group $P1$, a = 12.0360(11) Å, b = 26.181(3) Å, c = 26.547(3) Å, α = 118.824(3)°, β = 93.440(3)°, γ = 90.154(3)°, V = 7310.9(14) Å^3, Z = 2, M_w = 2239.87, T = −100.0(1) °C, μ(Mo Kα) = 12.67 cm^{-1}, 60 844 observed (27 033 unique) reflections, 1202 variables, R1 = 0.1035, wR2 = 0.2056, GOF = 0.962. Crystallographic data for **3b**: red needle (0.30 × 0.10 × 0.05 mm), monoclinic, space group $C2/c$, a = 27.342(5) Å, b = 38.204(5) Å, c = 20.526(5), β = 113.343(5)°, V = 19686(7) Å^3, Z = 4, M_w = 2053.46, T = −100.0(1) °C, μ(Mo Kα) = 17.46 cm^{-1}, 90 372 observed (15 013 unique) reflections, 1031 variables, R1 = 0.1013, wR2 = 0.1489, GOF = 1.015. Full details are given in the Supporting Information.

(20) These molecules might be termed “nanobowls”. See ref 12a.

(21) In the structure, two Zn^{2+} ions in the macrocycle are square-pyramidal and the third is coordinated to DMSO (solvent), giving it an octahedral geometry in the solid state.

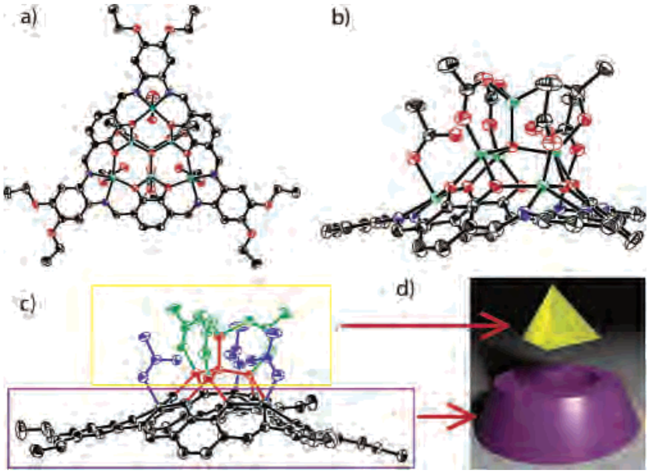

Figure 2. Depiction of the solid-state structure of complex **3a** (H atoms omitted) as obtained by SCXRD. (a) View of **3a** looking into the bowl (Zn, green; O, red; N, blue; C, black). (b) Side view of **3a** with ethoxy groups removed (colors as in part a). (c) Side view of **3a** showing the macrocycle (black), the $[Zn_4O]^{6+}$ tetrahedron (red), μ-1,1,2 acetates (blue), and μ-1,2 acetates (green). (d) Cartoon representation of the cluster-capped truncated-cone-shaped metallomacrocycle in **3a**. Thermal ellipsoids are all shown at 50% probability.

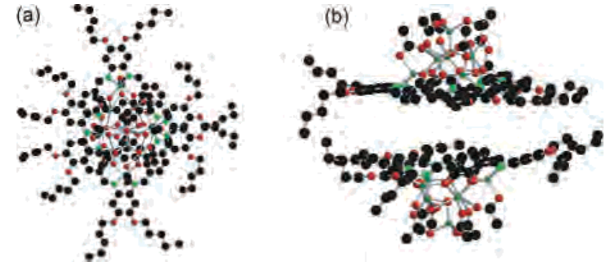

Figure 3. SCXRD structure of **3b** reveals face-to-face organization in the solid-state with a large cavity between the two adjacent molecules (black, C; red, O; bright green, N; dark green, Zn): (a) viewed from the top; (b) viewed from the side. H atoms have been removed for clarity.

monodentate and syn−anti bidentate bridges.[23] The structure may be viewed as a cluster-capped trimetalated truncated-cone-shaped macrocycle (Figure 2d). Overall, the molecule contains Zn^{2+} ions in tetrahedral, square-pyramidal, and octahedral coordination geometries.[24]

The solid-state structure of **3a** is consistent with the solution data (^{1}H and ^{13}C NMR) for complexes **3a**−**c**. Although ESI-MS of **3c** shows only $[\mathbf{2c}]Zn_2(OAc)_4Na^+$ $(=[\mathbf{3c}-Zn_2O(OAc)_2 + Na]^+)$ as the largest ion, we have observed $[\mathbf{3a}-OAc]^+$ and $[\mathbf{3b}-OAc]^+$ by ESI-MS or matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS. Other sensible fragments of the Zn_7 complexes are also observed.

The complexes are stable for several months in solution. Also, a high-temperature ^{1}H NMR experiment of **3c** in $(CDCl_2)_2$ showed no decomposition or dynamic motion in the complex at temperatures up to ca. 120 °C. Moreover, these molecules are insensitive to small quantities of water.

These multimetallic cluster complexes possess a concave surface of aromatic rings, creating a large void space. Interestingly, there is a DMSO molecule coordinated (via O) to one of the Zn^{2+} ions inside the bowl in the single-crystal structure of complex **3a**, but it is rapidly exchanging in solution because the ^{1}H NMR spectrum of **3a** in DMSO shows C_{3v} symmetry. A crystal structure of complex **3b** obtained from benzene shows the same overall structure as **3a**, but there is no solvent coordinated inside the bowl. In the solid state, **3b** is organized into pairs (Figure 3), with the molecules arranged such that they nearly form a capsule in the solid state, where two of the molecules are oriented face-to-face, with ca. 60° rotation. The molecules are not interlocked but are separated by 6−7 Å with disordered solvent in the space between them.

Preliminary NMR studies of the Zn_7 complexes indicate that they aggregate in solution. Whereas the ^{1}H NMR spectra of **3a**−**c** in $CDCl_3$, C_6D_6, and DMSO-d_6 are sharp, the spectra of these complexes in toluene-d_8 and xylenes-d_{10} are very broad, indicating short T_2 relaxation times that are characteristic of aggregates. Upon the addition of small (∼1%, v/v) quantities of coordinating solvents, the peaks in the ^{1}H NMR spectrum become sharp, as is expected for monomeric complexes. This suggests the possibility that the bowl-shaped compounds are assembling into dimers or larger aggregates in toluene and xylenes and that the aggregation is disrupted upon the addition of a solvent that can coordinate to the Zn^{II} centers.

In summary, metalation of shape-persistent Schiff-base macrocycles **1a**−**c** leads to the surprising formation of novel heptanuclear Zn cluster complexes. These molecules possess a bowl-shaped interior that contains Zn ions with accessible coordination sites inside the bowl, as indicated by SCXRD structures of the complexes with and without DMSO coordinated. The presence of vacant coordination sites within the bowl makes these attractive as site-constrained catalysts and as mimics of Zn-containing enzymes, such as carbonic anhydrase.[25] Studies are underway to explore the aggregation of complexes **3** in solution and to expand the coordination chemistry of the macrocycles to other transition metals.

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Supporting Information Available: Complete experimental details and spectra for compounds **3a**−**c**, and crystallographic data (CIF) for compounds **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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