

A Very Large Metallocapsule with Cube-like 4^3 Topology Assembled from Twelve Cu(II) Centers and Eight Tri-Bidentate Tri-Anionic Ligands Derived from 2,4,6-Triphenylazo-1,3,5-trihydroxybenzene

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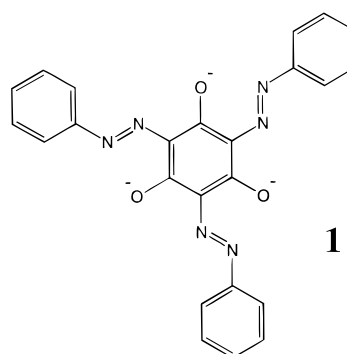
Numerous recent reports make it abundantly clear that coordination chemistry offers rich scope for the facile generation of self-organizing nanosystems of widely variable topology and architecture via spontaneous metal/ligand association. The types of self-assembling coordinative conglomerates that have been described include grids, helices, and a number of enclosure-like structures possessing some sort of cavity capable of accommodating guests.¹ Trail-blazing examples in the enclosure category, clearly indicating the general promise provided by coordination chemistry for the facile formation of such structures by self-assembly, were Fujita's M_4L_4 square corral, with metal centers, M , at the four corners and with 4,4'-bipyridine (bipy) ligands providing the four fence-like sides of the corral,² and Lehn's eleven-component "molecular cylinder" consisting of six metal centers, two 3-connecting ligands, and three ligands of a second type.³

A number of enclosure-like systems with the topology of the tetrahedron (3^3 or $\{3,3\}$) have been generated recently by metal/ligand self-assembly. M_4L_6 conglomerates in which the metal centers provide the four 3-connecting nodes characteristic of this topology, have been reported by Saalfrank⁴ and by Raymond.⁵ Compositionally and geometrically different but topologically identical M_6L_4 assemblies in which ligand molecules, rather than metal centers, provide the four 3-connecting nodes have been described by Fujita using tripyridyltriazine, tpt, as the 3-connecting ligand⁶ and by Steel using a tri-pyrazolyl 3-connecting ligand.⁷

The topological essence of the cube (4^3 or $\{4,3\}$) is eight 3-connecting nodes linked together by twelve node-to-node connections so as to generate six closed circuits each containing four nodes. Two M_8L_{12} examples of coordinative assemblies with this topology have been reported very recently. Thomas⁸ has presented NMR evidence for the generation of a cubelike arrangement with eight Ru corners and twelve bipy edges, a 3D extension of Fujita's $M_4(\text{bipy})_4$ corral, while Rauchfuss⁹ has confirmed by crystallography the assembly of a much smaller

cube with bridging cyano ligands along the twelve edges, a discrete molecular version of the cubelike $M_8(\text{CN})_{12}$ structural unit present in extended cyano networks of the Prussian Blue type. Similar parallels in which the same bridging ligand has been used by independent researchers to generate metallocapsules on one hand and coordination polymers on the other are evident in recent developments in these two areas, e.g., the $M_4(\text{bipy})_4$ corral and a Zn/bipy coordination polymer containing an infinite 2D collection of almost identical corrals¹⁰ were generated independently and essentially contemporaneously as were two related tpt derivatives, namely, the discrete $M_6(\text{tpt})_4$ cage with 3^3 topology mentioned earlier⁶ and a Cu(I)/tpt coordination polymer containing an infinite 3D collection of cages basically of the same type.¹¹

We report here a crystallographically characterized example of an $M_{12}L_8$ enclosure with cubelike 4^3 topology in which ligands rather than metals provide the eight 3-connecting nodes; the ligand is the trianion, **1** (tapp^{3-}), derived from 2,4,6-triazophenyl-1,3,5-



trihydroxybenzene (H_3tapp), which acts as a tri-bidentate chelator. Dark brown crystals of solvated $\text{Cu}_{12}(\text{tapp})_8$ suitable for study by single-crystal X-ray diffraction grew directly over a period of several days from a DMF solution containing H_3tapp , $\text{Cu}(\text{NO}_3)_2$, and tetramethylammonium hydroxide in 2:3:6 proportions.¹² As can be seen in Figures 1a and 2, every ligand is attached to three Cu(II) centers, in each case by a bidentate N,O chelating system, and each Cu is in turn chelated by two ligands acquiring a somewhat distorted trans N_2O_2 square-planar coordination environment. The centroids of the eight ligands are located very close to the corners of a cube (inscribed inside the cage in Figure 1a), each of whose solid diagonals are very close to perpendicular to the central C_6 rings of two of the ligands. Distances from the cavity center to the ligand centroids are in the range 6.3–6.5 Å. The twelve Cu's are located very close to the corners of a cuboctahedron, 6.9–7.1 Å from the cavity center. These twenty building blocks, disposed in 3D space approximately symmetrically around a central point, generate an approximately spherical shell and because the six cube faces are effectively blocked off by four phenyl groups from four separate ligands,

(1) The reader is directed to a number of up-to-date reviews of this vigorously expanding area. (a) Fujita, M. *Chem. Soc. Rev.* **1998**, 27, 417–425. (b) Jones, C. J. *Chem. Soc. Rev.* **1998**, 27, 289–299. (c) Stang, P. J. *Chem. Eur. J.* **1998**, 4, 19–27. (d) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1707–1728. (e) Albrecht, M. *Chem. Soc. Rev.* **1998**, 27, 281–287.

(2) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, 112, 5645–5647.

(3) Baxter, P.; Lehn, J.-M.; DeCian, A. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 69–72.

(4) (a) Saalfrank, R. W.; Stark, A.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 851–852. (b) Saalfrank, R. W.; Stark, A.; Bremer, M.; Hummel, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 311–314. (c) Saalfrank, R. W.; Horner, B.; Stalke, D.; Salbeck, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1179–1182.

(5) Beissel, T.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1084–1086.

(6) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, 378, 469–471.

(7) Hartshorn, C. M.; Steel, P. J. *Chem. Commun.* **1997**, 541–542.

(8) Roche, S.; Haslem, C.; Adams, H.; Heath, S. L.; Thomas, J. A. *Chem. Commun.* **1998**, 1681–1682.

(9) Klausmeyer, K. K.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 1694–1696.

(10) Gable, R. W.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1990**, 1677–1678.

(11) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1690–1692.

(12) To the ligand H_3tapp (20 mg) in DMF (10 mL) was added NMe_4OH (50 mg of a 25 wt % solution in methanol). This solution was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (17 mg) in DMF (10 mL) to give a dark brown solution. These concentrations, which directly provided dark brown crystals suitable for X-ray study over a period of several days, were arrived at by trial and error, more concentrated solutions giving unsuitable finer material more rapidly. Yield after drying in air, 22 mg, 64%. Anal. Calcd for $\text{C}_{264}\text{H}_{296}\text{O}_{52}\text{N}_{72}\text{Cu}_{12}$, i.e., $\text{Cu}_{12}(\text{tapp})_8 \cdot 24\text{DMF} \cdot 4\text{H}_2\text{O}$: C, 52.2; H, 4.9; N, 16.6; Cu, 12.6. Found: C, 52.6; H, 3.6; N, 16.2; Cu, 12.4. Crystallographic data: orthorhombic, *Pcca*, dark brown crystals with a metallic green iridescence, $a = 23.939(5)$ Å, $b = 31.949(2)$ Å, $c = 40.837(8)$ Å, $T = 130\text{K}$, $Z = 4$, $wR2 = 0.3666$, $R1 = 0.1170$, $\text{GOF} = 1.033$.

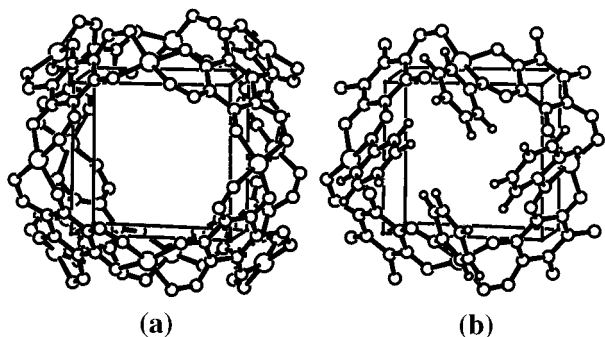


Figure 1. (a) A view of the $\text{Cu}_{12}(\text{tapp})_8$ cage, from which the 24 terminal C_6H_5 residues have been omitted for clarity, revealing the 4^3 cubelike topology. The cube inscribed here is defined by the centroid of a ligand at each corner. (b) A view, from the same angle as in part a, of the four ligands and four Cu's defining one of the six cube faces, showing how four ligand phenyl groups arranged edge-to-face block off the face of the cube.

which are arranged in close edge-to-face contact as shown in Figure 1b, the shell is essentially windowless and capsule-like. The volume of the void space inside the inner van der Waals surface of the capsule is estimated, using the PLATON program,¹³ to be ca. 816 \AA^3 , sufficient in principle to accommodate ca. 6 DMF molecules if they behaved like liquid DMF, which under ordinary conditions has a volume per molecule of 128 \AA^3 . The volume per formula unit of the void space outside the outer van der Waals surface of the capsules is likewise estimated to be ca. 3190 \AA^3 , a space technically capable of accommodating ca. 25 DMF molecules if they were liquidlike. Elemental analysis and analysis of the X-ray diffraction data are in agreement in indicating the order of 24 DMF molecules per cage (inside and outside). A large number of peaks of electron density are apparent inside the cage consistent with 5–6 DMF molecules, two of which are well-resolved. All five non-hydrogen atoms of several DMF molecules located between capsules are clearly resolved, but other molecules are very disordered even at 130 K. Some of the DMF molecules, both internal and external, appear to interact weakly via their oxygen atom with Cu centers ($\text{O}\cdots\text{Cu}$, 2.5–2.8 \AA). Individual cages are chiral, but the crystal as a whole is racemic.

(13) PLATON Program: Spek, A. L. *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

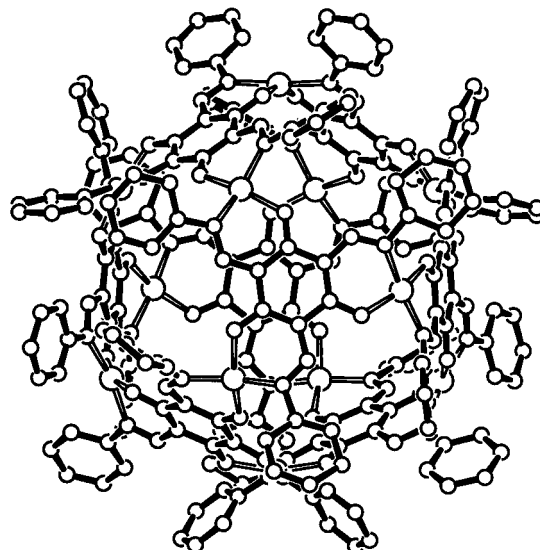


Figure 2. The complete $\text{Cu}_{12}(\text{tapp})_8$ cage.

This is the largest discrete coordinative capsule with an effectively windowless shell that we are aware of. The only example known to us of a larger coordinative cage providing complete encapsulation is that seen in another infinite 3D coordination polymer of the earlier mentioned tpt ligand of composition $\text{Zn}(\text{tpt})_{2/3}(\text{CN})(\text{NO}_3)$ in which the completely sealed off cavities were large enough to enclose approximately 18 CHCl_3 + 4 MeOH molecules in one case and 9 $\text{C}_2\text{H}_2\text{Cl}_4$ + 9 MeOH molecules in another case.¹⁴

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Supporting Information Available: Figure of the $\text{Cu}_{12}(\text{tapp})_8$ cage with anisotropic displacement ellipsoids along with crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1995**, *117*, 5385–5386.