Inorganic Chemistry
Editorial
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Editorial for the Virtual Issue on Inorganic Cages and Containers

A ship in a bottle rests on a mantelpiece, an object of beauty and mystery. How was such an intricate vessel with the complicated rigging of its sails placed inside a glass through such a tiny orifice? Molecular container compounds are molecules of mystery and beauty. How can a molecule be constructed that can completely encapsulate another molecule? What can be trapped inside? How long will it stay there? These are issues the molecular architect must address but on a much smaller scale than the craftsman who manages to slip that tiny ship into a bottle.

This virtual issue highlights very recent work on cage and container molecules that have an inorganic component. It follows three other *Inorganic Chemistry* virtual issues: Synthetic Inorganic Chemistry (http://pubs.acs.org/page/vi/2013/synthetic_inorganic.html) featuring the work of 17 young investigators, Models of Metalloenzymes (http://pubs.acs.org/page/vi/2013/models-of-metalloenzymes.html), and Quantum Molecular Magnets (http://pubs.acs.org/page/vi/2012/quantum-molecular-magnets.html).

In this virtual issue, our interest concerns not only how molecules might be placed in cages but also how those cages can be constructed and their shapes. Additionally, we want to know what they encapsulate, how selectively they bind particular molecules, and how binding alters the chemical and physical properties of the species trapped within. The dawn of the current work on container molecules can be traced back to the work of D. J. Cram, who began the construction of organic containers with curved interior surfaces.[1] Also, significant in the early stages of development were the design of cyclic polyethers that could surround and bind simple alkali and alkaline-earth ions by C. J. Pederson.[2] And before that, chelating ligands had been developed that surrounded metal ions in minicages. However, the work of Cram on various molecular capsules set a standard for the field. The demonstration that a cage molecule could be developed that could trap the elusive and reactive cyclobutadiene provided evidence that profound advances could be achieved using cage molecules.[3]

Four of the articles in our collection make use of a popular tetrahedral host with four metal centers at the vertices and either six bridging ligands along the edges of the tetrahedron to form M_4L_6 receptors or four bridging ligands that lie over the faces of the tetrahedron to produce M_4L_4 receptors. The design strategy for the construction of these hollow receptors was nicely delineated earlier in a review by Caulder and Raymond.[4]

Nitschke and co-workers prepared face-capped $\{Fe_4L_4\}^{8+}$ capsules using C_3-symmetric triamines combined with 2-formylpyridine and iron(II) to produce cages of different sizes.[5] Although four cages with void volumes of 31, 45, 229, and 823 Å^3 were obtained, only the intermediately sized cage with a volume of 229 Å^3 was found to encapsulate guests effectively. Those guests involved a range of compact, neutral molecules with molecular volumes in the 88−112 Å^3 range. The larger cage was not able to trap guests, and the authors suggested that the larger pore size that accompanied the large cage size was responsible for allowing molecules to pass through the cavity without entrapment. In contrast, the two smaller capsules simply lacked sufficient void volume to trap other molecules.

In a recent development, Bergman, Raymond, Toste, and their co-workers utilized a tetrahedral Ga_4L_6 assembly to trap the catalytically active $(Me_3PAu)^+$ ion.[6] Binding of this cation to the tetrahedral assembly was detected by ^1H NMR studies, which showed that identical spectra were obtained regardless of whether the gold complex was introduced as Me_3PAuCl, Me_3PAuBr, or $Me_3PAuNTf_2$. Thus, the anion dissociated, and the gold cation entered the cage. Furthermore, they demonstrate that the $(Me_3PAu)^+$ ion trapped in the cage shows catalytic activity for the hydroalkoxylation of allenes. Moreover, the encapsulated cation exhibited enhanced catalytic reactivity and longer lifetimes inside the cage.

In addition to the M_4L_6 and M_4L_4 receptors, Lustby and co-workers have designed an Ir_6L_4 cage with six $[Ir^{III}(2\text{-phenylatopyridine})_2]^+$ units at the corners of an octahedron and 1,3,5-tricyanobenzene bridging ligands positioned over four of the triangular faces of that octahedron.[7] The cluster that results has been crystallographically characterized and can accommodate four of the six counterions within the cavity of the ensemble. Homochiral capsules were obtained after the starting *rac*-$\{Ir^{III}(2\text{-phenylatopyridine})Cl\}_2$ was resolved into enantiopure samples. A comparison of the Ir_6L_4 cage with the mononuclear counterpart, $[Ir^{III}(2\text{-phenylatopyridine})_2(\text{benzonitrile})_2]^+$, reveals that the octahedral capsule is highly luminescent, whereas the mononuclear component shows a much more feeble emission. Thus, the cage structure plays a significant role in facilitating the emission processes.

A related $[Pd_6L_4]^{12+}$ cage with T_d symmetry has been assembled by Fujita and co-workers using 2,4,6-tri(4-pyridyl)-1,3,5-triazine and $Pd(\text{diamine})(NO_3)_2$.[8] The symmetry of its internal cavity allows this cage to be used to trap the twisted, purple-colored conformer of an overcrowded alkene.[9] The process begins with the yellow, antifolded conformer, which was suspended in an aqueous solution of the $[Pd_6L_4]^{12+}$ cage. Upon microwave heating, the solid, antifolded conformer dissolved and the solution became purple as the twisted conformer was trapped in the cage. Trapping could be confirmed by NMR and UV/vis spectroscopy. Remarkably, displacement of the guest by 1-adamantanol resulted in the precipitation of a purple solid containing the twisted conformer of the overcrowded alkene. However, heating this solid resulted in its reversion to the yellow, antifolded conformer. The twisted conformer could be permanently captured by bromination of the aromatic substituent on the overcrowded alkene within the cavity of the $[Pd_6L_4]^{12+}$ cage.

A paramagnetic cubic cluster with the composition $[Co^{II}_8L_{12}]^{16+}$ has been assembled by Hunter, Ward, and co-workers using a bis-bidentate bis(pyrazolylpyridine) as a bridge along each cube edge.[10,11] This $[Co^{II}_8L_{12}]^{16+}$ cage acts as a selective host for small organic molecules including coumarin and other bicyclic molecules with similar sizes. The para-

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magnetism of the cobalt ions results in a dispersal of the ^{1}H NMR spectrum, which facilitates studies of the strength of guest binding and the factors that promote the encapsulation of guests inside the capsule. Additional NMR studies have observed the separate processes of guest movement in and out of the cage and of guest movement within the cage.

Cui and co-workers have assembled a cage containing eight zinc ions using a chiral salan Schiff base ligand (L-salan) that forms a ZnN_2O_2 chelate with dangling arms that coordinate to two other zinc ions through pyridyl groups.[12] The entire Zn_8(L-salan)$_4Cl_8$ assembly shows a 10-fold enhancement in its ligand-based optical rotation. Additionally, this homochiral helicate cage displays enantioselective luminescence enhancement by amino acids in solution. The cage possesses a porous structure that allows the separation of small racemic molecules.

Continuing on in the development of cages with increasing numbers of metal centers, Colquhoun and co-workers prepared chiral cages containing 9, 10, or 12 palladium ions through reaction of the chloro-bridged dimer [Pd{*N*,*N*-dimethylbenzylamine(-H)}-μ-Cl]$_2$ with the 3-fold symmetric cyanuric acid.[13] The new cages have been characterized by single-crystal X-ray diffraction, NMR spectroscopy, and mass spectrometry. These cages contain relatively small cavities, but the possibility of entrapment of noble gas atoms is under investigation.

Returning to the tetrahedral hosts, Custelcean and co-workers developed a variant of the M_4L_6 receptors with zinc or nickel as the metals and bridging ligands (L-urea) that contain urea components as hydrogen-bond donors.[14] The bridging ligands have been specifically modified to facilitate binding of anions to the interior of the cage through hydrogen bonding to the N−H groups of the urea portion. A tetrahedral Ni_4(L-urea)$_6$ receptor with nitrate bound to the interior has been isolated and characterized by X-ray diffraction, as has a Zn_4(L-urea)$_6$ complex with sulfate bound to the interior. The presence of these urea-based segments allows these receptors to bind a variety of oxoanions with a selectivity trend: $PO_4^{3-} \gg CrO_4^{2-} > SO_4^{2-} > SeO_4^{2-} > MoO_4^{2-} > WO_4^{2-}$. However, these empty cages themselves are unstable, and the M_4(L-urea)$_6$ cages can only be characterized when stabilized by the presence of various interior ions.

In a related vein, Würthner and co-workers have modified the M_4L_6 receptors both to be redox-active and to strongly absorb through the 300−625 nm region.[15] To do this, they utilized a redox-active metal, iron(II), and introduced a perylene bisimide (PBI) dye into the bridging ligand to form the bridging ligand, L-PBI. The resulting cationic $[Fe^{II}_4(\text{L-PBI})_6]^{8+}$ host showed seven reversible redox waves (two oxidations and five reductions) in its cyclic voltammogram. Additionally, the cavity within cationic $[Fe^{II}_4(\text{L-PBI})_6]^{8+}$ is quite large (vide infra) .

Fullerenes, closed cages of carbon atoms, offer attractive molecules that can function either as guests within larger cage structures or as hosts for smaller molecules.[16] In the latter case, endohedral fullerenes are formed.[17] The readily available fullerene, C_{60}, has a molecular diameter of ∼7 Å and provides an attractive guest.

The large cavity within cationic $[Fe^{II}_4(\text{L-PBI})_6]^{8+}$, described above, provides sufficient internal space to encapsulate C_{60}, which has a molecular diameter of ∼7 Å.[13] Mass spectrometry, UV/vis spectroscopy, and ^{13}C NMR spectroscopic data substantiate the binding of C_{60} inside the cage of $[Fe^{II}_4(\text{L-PBI})_6]^{8+}$. Remarkably, the spectroscopic data indicated that one or two molecules of C_{60} bind within this large cage. Computational studies suggest that the C_{60} molecule resides at the center of the cavity when only one molecule is trapped within the cage, while with two trapped C_{60} molecules, the fullerenes move toward the corners of the tetrahedron.

Another type of host for the binding of C_{60} has been obtained by Lelj, MacLachlan, and co-workers by complexing zinc acetate with a giant Schiff base macrocycle to form a heptazinc cluster.[18] This metallocavitand provides a curved surface that includes six benzene rings, which is situated on the opposite side of the macrocycle from the Zn_7 cluster. Three of these metallocavitands can combine to effectively surround a single C_{60} molecule. However, the C_{60}/metallocavitand interactions are observed only in solvents that promote entropy-driven association.

In addition to C_{60}, fullerenes of other sizes are also known and can act as hosts for a variety of atoms and molecules. Fullerene cages that are larger than C_{60} are capable of binding one, two, or three metal atoms as well as small clusters such as M_3N and M_2C_2 units.[15] The largest clusters encountered so far involve the Sc_4O_2 and Sc_4O_3 units that are found in $Sc_4O_2@I_h\text{-}C_{80}$[19] and $Sc_4O_3@I_h\text{-}C_{80}$.[20] The redox activity of the Sc_4O_2 cluster inside I_h-C_{80} has recently been probed by Popov, Stevenson, Echegoyen, Dunsch, and co-workers through a series of electrochemical and electron-spin resonance experiments on $Sc_4O_2@I_h\text{-}C_{80}$.[21] These studies reveal that one-electron reduction and one-electron oxidation produce free-radical clusters with hyperfine splitting in their electron-spin resonance spectra that originate from the two different types of scandium ions within the Sc_4O_2 cluster. In particular, in the cation, the scandium hyperfine was unusually large for two of the scandium centers. Computations of the spin density for both the cation and anion showed that the odd electron was located on the cluster, not on the carbon cage.

Fullerene formation is a process that has been difficult to probe experimentally. Usually fullerenes are formed through the vaporization of graphite by either a laser or an electric arc in a low-pressure helium atmosphere. To form endohedral fullerenes, the graphite is doped with an appropriate metal oxide. Both bottom-up and top-down mechanisms of fullerene formation have been proposed.[22−24] Recent work by Poblet, Marshall, Kroto, and co-workers focuses upon the formation of the smallest stable endohedral fullerenes: $M@C_{28}$ where M may be Ti, Zr, or U.[25] The formation of these small and highly reactive endohedrals has been probed in the gas phase by Fourier transform ion cyclotron resonance mass spectrometry. The process of formation of $U@C_{28}$ has been carefully monitored under conditions of increasing helium gas pressure. The results show that $U@C_{28}$ forms before any other higher fullerenes appear. However, as the gas pressure increases, amounts of the larger endohedrals, $U@C_{36}$ and $U@C_{44}$, appear because of the addition of C and C_2 fragments to $U@C_{28}$.

The polyoxometalates form another class of building blocks that can be used to form truly inorganic clusters, some of which have a core−shell geometry.[26] Thus, Burns and co-workers have assembled gigantic clusters from uranium in which each uranyl ion is coordinated in hexagonal-bipyramidal fashion by two bidentate peroxo ligands and a side-on oxalate group.[27] One such cluster ($U_{50}Ox_{20}$) consists of 50 uranyl ions with the composition $K_{16}Li_8(H_2O)_6[(UO_2)_{50}(O_2)_{43}(OH)_4(C_2O_4)_{20}]$-$(H_2O)_n$. Another related cluster ($U_{120}Ox_{90}$) involves 120 uranyl groups and has the composition $K_{134}Li_{46}[(UO_2)_{120}(O_2)_{120}(C_2O_4)_{90}](H_2O)_n$. This cluster consists of an inner core of 60 uranyl ions and 30 oxalate groups with a fullerene topology. The outer shell involves 12 identical units that include 5 uranyl ions that form a pentagonal unit. The $U_{50}Ox_{20}$ cluster retains its structure when dissolved in water, while the $U_{120}Ox_{90}$ cluster dissociates to leave the inner $U_{60}Ox_{30}$ core intact.

Weinstock and co-workers have synthesized another remarkably large cluster that contains 60 molybdenum ions in a truncated icosahedral array.[28] This mixed-oxidation-state anionic cluster, which involves both Mo^{VI} and Mo^{V}, has the composition $[\{Mo^{VI}{}_6O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(\text{acetate})\}_{30}]^{42-}$. This large ion is porous, water-soluble, and catalytically active. The anion catalyzes the reversible cleavage and reformation of methyl *tert*-butyl ether in an aqueous solution. Experimental observations show that this reaction occurs within the cavity in the anion. Moreover, the availability of active sites within the cavity can be controlled by modulating the number of internally bound acetate groups, and the catalytic activity occurs specifically at Mo^{V} sites.

Another type of polyoxometalate cage has been synthesized by Dalal, Kortz, and co-workers and provides a coordination site for a central metal ion with strictly cubic coordination, a coordination geometry that is rare for some of the late-transition-metal cations that can be incorporated into this capsule.[29] A rather simple synthetic procedure leads to cages with the stoichiometry $[MO_8Pd^{II}{}_{12}L_8]^{n-}$ where M may be Sc^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Lu^{3+} and L can be $PhAsO_3{}^{2-}$, $PhPO_3{}^{2-}$, or $SeO_3{}^{2-}$. While polyoxometalates are well-known for early transition metals like V^{5+}, Nb^{5+}, Mo^{6+}, Ta^{5+}, and W^{6+},[24] the formation and study of late-transition-metal polyoxometalates such as those of palladium is a rather recent development.[30]

The magnetocaloric effect (MCE) occurs when a sample undergoes a change in temperature as a result of exposure to a changing magnetic field.[31] In the search for molecules that might serve as magnetic refrigerants through the use of the MCE, Winpenny, McInnes, and co-workers have examined the synthesis and magnetic properties of novel mixed-metal clusters of the type $[Ni_6Gd_6(\mu_3\text{-}OH)_2(\mu_2\text{-}OAc)_2(O_3PR)_6(O_2C\text{-}{}^tBu)_{16}]$, where the R group can be varied.[32] These new clusters have geometries similar to that of the well-known Wells–Dawson polyoxometalate[26] but also serve as a molecular container for a variety of magnetic interactions between Ni···Gd and Gd···Gd. These clusters are novel examples of the incorporation of late-transition-metal ions and f-block elements into a polyoxometalate-type cage.

As with the fullerenes where the carbon cage could act as both a host to form endohedral fullerenes and a guest that larger molecules could encapsulate, polyoxometalates can also function as hosts, as preceding examples have demonstrated, and as guests. To demonstrate the latter, Shionoya, Clever, and co-workers report that four concave ligands and two palladium(II) ions with planar coordination self-assemble to encapsulate a hexamolybdate dianion, $[Mo_6O_{19}]^{2-}$, in solution.[33] However, all attempts to crystallize this assembly resulted in the loss of the palladium ions and the crystallization of a capsule in which the four ligands alone surrounded the $[Mo_6O_{19}]^{2-}$ anion. The authors speculate that the ability to encapsulate polyoxometalates in organometallic cages can lead to improved electronic and optical properties and better control of the catalytic reactivity through controlled access to the active site.

Finally, we conclude this section on oxide-based capsules with a review article devoted to ferritin.[34] This molecule is important for iron storage and release in a wide variety of marine and terrestrial organisms, including the author of this editorial and you, its reader. In ferritin, the inorganic component is the core, a ferrihydrite-like ($Fe_2O_3\cdot 9H_2O$) nanomineral with 20% tetrahedral and 80% octahedral iron(III) sites. The container is a protein shell that contains channels that allow iron ions to enter and leave the interior. The transport activity involves iron(II), while redox processes allow the storage of iron(III) within the protein. Understanding ferritin activity is important to human disease and human health.

This virtual issue is largely focused on molecular containers, both large and small. However, the extended arrays known as metal–organic frameworks (MOFs) can involve permanent porosity and can trap many different molecules.[35,36] It seems appropriate to include two examples of MOFs in this virtual issue to demonstrate two types of encapsulation. One of these involves the trapping of reactive molecules that would otherwise be difficult to detect. In that regard, Kawano and co-workers have managed to trap neutral S_3 molecules in a crystalline network solid, $[ZnI_2(2,4,6\text{-tris}(4\text{-pyridyl})\text{triazine})_3]_n$, that has suitably sized (~8.3 Å × 10.5 Å) pores.[37] The solid was treated with sulfur vapor at 533 K for 6 h to obtain the bright-yellow encapsulate. Rietveld refinement of the powder diffraction data for this bright-yellow powder revealed the presence of disordered, bent S_3 molecules, which are analogues of ozone. Note that the S_3 molecule encapsulated here is distinctly different from the radical anion $S_3{}^{\bullet-}$, which is blue and responsible for the color of the gemstone lapis lazuli.[38,39] In addition to trapping neutral S_3 with the zinc framework material, Kawano and co-workers were also able to obtain evidence for trapping another example of the small allotropes of sulfur, S_6, within the same polymeric framework.

In another development in MOF-based capsules, Xu and co-workers synthesized another family of zinc-containing MOFs utilizing a tetrahedral organic core ligand that contained eight pendant carboxylate groups. Combining this ligand with zinc nitrate produced five MOFs with different architectures. The solvent employed determined which of the five different structures formed.[40] The luminescent chelate tris(8-hydroxyquinolinato)aluminum, which is a component in many light-emitting organic diodes, could be incorporated into the preformed network solids to produce new luminescent materials with prolonged lifetimes and modulated luminescence.

The next three articles we will consider involve molecules built around a core–shell model. In a sense, they are similar to endohedral fullerenes with one layer of atoms inside another. They differ from many of the other capsules and cages considered here because there may be strong chemical binding between the layers.

Silver acetylides, $AgC{\equiv}CR^+$, can be utilized to build up an extensive array of novel clusters.[41] In a recent article, Mak and co-workers have observed conversion of a silver cluster into one of higher nuclearity via an inner-core transformation.[42] Thus, the reaction of $[Cl@Ag_{14}({}^tBuC{\equiv}C)_{12}]OH$ with $AgClO_4$ leads to the formation of $[Cl_6Ag_8@Ag_{30}({}^tBuC{\equiv}C)_{20}(ClO_4)_{12}]\cdot Et_2O$, which has been characterized by single-crystal X-ray diffraction. The interior of the molecule consists of eight silver ions at the corners of a cube, with six chloride ions sitting at the centers of the faces of the cube. Each of the six Ag_4Cl faces of the cube is then capped by a square pyramid of five other silver ions to form the $Cl_6Ag_8@Ag_{30}$ core. The peripheral acetylide ligands are then bound to three or four of the 30 silver ions in the outer shell.

Other such core–shell molecules can be constructed from transition-metal carbonyl groups (as seen in the next two papers that we will consider) or from combinations of transition metals and Zintl ions in the form of clusters like $Pt_2@Sn_{17}{}^{4-}$ and Pt@

Sn_9H^{3-}.[43] The nanosized cluster $Au_2Pd_{28}(CO)_{26}(PEt_3)_{10}$ recently reported by Mednikov, Ivanov, and Dahl is an interesting example of the former type of cluster.[44] This molecule consists of a central pair of gold atoms that are surrounded by 18 nearest-neighbor palladium atoms. An additional six palladium atoms bridge groups of four palladium ions in the Pd_{18} core, while four other palladium atoms lie over pairs of palladium atoms around the Pd_{18} core. The study of such complex core−shell molecules is significant not only for understanding the complexities of multicentered chemical bonding but also for understanding bimetallic synergistic effects in catalysts.

The bimetallic carbide carbonyl cluster $Ni_6C(CO)_9(AuPPh_3)_4$, prepared by Zacchini and co-workers, also has a core−shell structure with a central carbide ion surrounded by six nickel atoms with an additional set of four $Au(PPh_3)$ groups attached to triangular sets of nickel atoms.[45] This carbonyl cluster was obtained from the reaction of $[Ni_9C(CO)_{17}]^{2-}$ with $Au(PPh_3)Cl$ through the elimination of nickel atoms and carbonyl groups. Weak aurophilic interactions at the periphery of the cagelike structure lead to the existence of two isomers of this cluster. These isomers differ in the set of Au···Au interactions present in each of the two forms. The presence of different solvate molecules in the crystalline forms of $Ni_6C(CO)_9(AuPPh_3)_4$ appears to be the influence that favors one set of Au···Au interactions over the other.

We conclude the virtual issue with an article by Therrien and co-workers that describes the use of a water-soluble organometallic cage that is able to transport hydrophobic porphyrin to cancer cells where photodynamic therapy can be used to kill the cancer cells.[46] The empty organometallic cage consists of two parallel flat surfaces that are connected by two ruthenium centers, which are bridged by 2,5-dioxido-1,4-benzoquinonato groups. The flat surfaces are provided by either 1,2,4,5-tetrakis[2-(4-pyridyl)vinyl]benzene or 2,4,6-tris(4-pyridyl)-1,3,5-triazine. Both cages bind the flat porphyrin between the two large planar surfaces of the cage. However, the two different cages deliver the encapsulated porphyrin in two different fashions. In one case, the cage is disrupted and the porphyrin is freed, while in the other case, the cage remains intact and the porphyrin simply diffuses from the cage to enter the target cancer cell. These are promising new means of improving cancer treatment through photodynamic therapy.

The articles collected here give only a small glimpse of the ongoing creative efforts to utilize the concept of a molecular container as a means of developing new chemical structures. Certainly, these cages present us with molecules that challenge the prevailing concepts of chemical bonding and add mechanical entrapment as a component in molecular design. The potential for the trapping, release, and delivery of the guest molecules offers intriguing opportunities in applications, particularly in the biomedical field. I encourage the submission of breakthough papers in the area of inorganic cages and containers to our journal, *Inorganic Chemistry*.

Alan L. Balch, Associate Editor

■ AUTHOR INFORMATION

Notes

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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