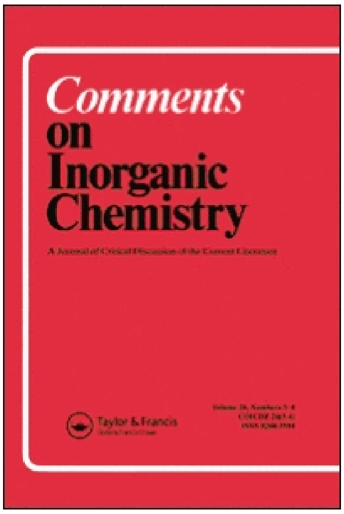

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Multinuclear Metal Complexes and their Assembly into Cage Molecules

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Multinuclear Metal Complexes and their Assembly into Cage Molecules

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Current research efforts focus on using metal ions to bring organic molecules together and in so doing form structures that resemble large common materials, such as boxes, cages, grids, and channels. These metal-organic supramolecular structures are at the interface between molecular and macromolecular chemistry. As a contribution to this field of chemistry, we have focused on binding metal ions to cupped-shaped template molecules, which can be appended with functional groups. These resorcinarene-based molecules have four phenyl groups linked together into a ring and various functional groups attached to their upper rim. Some of the functional groups, bispyridylmethylamine (bpa) and iminodiacetic acid, are able to coordinate to metal ions. In the case of the bispyridylmethylamine resorcinarene, **2**, a tetranuclear metal complex is formed when it is allowed to coordinate to copper(II). The copper centers surround the resorcinarene cavity and are not electronically coupled. In contrast to the Cu_42^{8+} complex, when cobalt(II) or iron(II) are allowed to coordinate to an iminodiacetic acid resorcinarene, **3**, two resorcinarenes are bought together. The $M_43_2^{8-}$ (M = Co or Fe) complexes are tetranuclear metal(II) cage compounds that assemble in aqueous solutions above pH 4 and have a cavity. These molecules are capable of encapsulating a variety of organic guest molecules, for example, nonpolar hydrocarbons, substituted phenyls, alcohols, halogen containing hydrocarbons, and polar organic molecules. The cages act as NMR shift reagents and cause substantial up-field iso-

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tropic hydrogen shifts (-30 to −40 ppm for Co^{2+} and −5 to −15 ppm for Fe^{2+}) in the guest molecule and separation of the guest hydrogen chemical shifts. The solid state structures of $Ba_4[M_4 3_2 \cdot \mathrm{guest}]$ (guest = 6 H_2O, bromobenzene, or ethylbenzene) show bond angles independent of whether the metal ion is cobalt or iron, and bond lengths typical of metal oxygen and nitrogen bonds. The encapsulated guest does not noticeably effect the cavity dimensions, bond lengths, and bond angles.

Keywords: *metal-assembled cages; resorcinarene-based ligands; host-guest; small molecule encapsulation; supramolecular*

INTRODUCTION

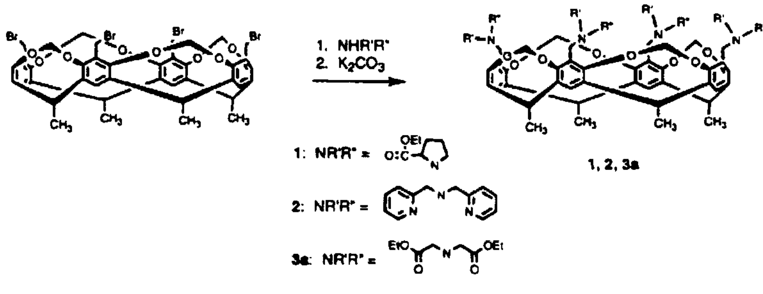
Although materials are routinely assembled into buildings, cars, and computers, it is much less common to assemble individual molecules into structures that have physical three-dimensional properties. There is probably not a need for molecular chairs, desks, or roads, but there are applications for cages, channels, and switches. This supramolecular field of molecular devices is growing in part due to our increasing ability to assemble molecules into molecular structures via organized processes. Transition metal ions are playing a large role in the assembly of supramolecular structures, due to their ability to make 2 to 6 bonds in a predictable arrangement, which bonds can be made and broken without the destruction of the organic or metal components.

The area of metal-assembled structures is gaining interest due to their application in catalysis and seperations.[1] Important in this area are metal-assembled grids, ladders, rings, interlocking grids, and two- and three-dimensional lattices.[2] Our understanding is progressing on how to make ordered one, two, and three dimension materials that are based on metal ions and that might be useful as molecular magnets, separations materials, or ion sensors. Some of these grids and structures have units that are shaped like boxes and therefore prove capable of encapsulating guest molecules. Along with these grid-type materials are the metal-assemble cages.[3]These cages have cavities that can house one to several molecules and can be composed of a few metal ions or many metal ions. The structure and chelation properties of the ligand as well as the preferred metal coordination geometry, are important in the formation of the cages.

The research efforts of our group have focused on coordinating metal ions to molecules, which have preformed cavities and multiple metal binding sites. We have relied on resorcinarenes, which have four phenyl groups in a ring, to act as template molecules for the attachment of metal chelating ligands.[4] Various functional groups may be attached to resorcinarenes, several of which bind metal ions. When copper(II) ions are allowed to coordinate to a pyridine-functionalized resorcinarene, a tetranuclear metal complex is formed. In contrast to copper, cobalt(II) and iron(II) ions form a novel cage complex when allowed to coordinate to an iminodiacetate-functionalized resorcinarene. This type of cage formation is very different from what is commonly seen when metals coordinate to resorcinarenes and calixarenes, which usually results in metal ions coordinated to one calixarene and no cavity formation.[5] Unlike cage complexes linked by nometal covalent bonds,[6] our cages can be opened and closed by changing pH. And, different from cages assembled by hydrogen bonds,[7] our cages are stable in water. Interestingly, the cavities of the cages can house guest molecules and trap organic molecules preferentially to water.

RESORCINARENES AS TEMPLATES

Resorcinarenes and the closely related calixarenes are two classes of molecules that possess a cavity suitable for molecular recognition. They, along with other molecules such as crown ethers and cyclodextrins, act as host molecules for small molecules. Resorcinarenes have this capability because of four phenyl groups, which are linked, together into a cup shaped molecule. One intriguing property of resorcinarenes is that functional groups can be attached to their upper and lower rims. One easy way to attach groups to the upper rim is by starting with the bromine derivative and then aminating it with the desired amine (Scheme 1).[8] Amino acid esters, in particular L-proline, are one of several groups of amines, which can be attached to the upper rim (Figure 1).[9] When L-proline is attached to a resorcinarene, the tetra(proline)resorcinarene molecule (**1**) has helical chirality and one diasteriomer is crystallized in preference to the other. Resorcinarenes with chiral groups attached to them have potential to recognize chiral molecules. Alkyl chains are often incorporated into the lower rim of the resorcinarene to help improve solubility in organic solvents. We have chose to make resorcinarenes with methyl groups on the lower rim to increase the solubility of the molecules in water.



SCHEME 1

In an attempt to make molecules that are able to coordinate metal ions and act as host molecules, we have attached nitrogen containing functional groups on to resorcinarenes. One of which is bispyridylmethylamine (bpa), which has two pyridines and an amine group and is known to strongly coordinate transition metal ions. The attachment of bpa to resorcinarene results in a ligand that has four sites for metal binding, **2**, and is soluble in organic solvents.[10]

Along with purely nitrogen containing ligands, oxygen containing ligands may also be attached to resorcinarenes. Iminodiacetate ethyl ester readily attaches to resorcinarene and forms a molecule with eight ethyl acetate groups (**3a**, Figure 2).[11] It is of interest to note that in the solid state the acetate groups run parallel to the upper rim or down toward the lower rim and not upward. They thus do not make the cavity deeper than it is without them. Once the ester groups are hydrolyzed, the alkali or alkaline earth metal salts of the resorcinarene are formed (**3**), which salts are solids and insoluble in organic solvents. However, the alkaline earth metal salts are soluble in acidic aqueous solutions and the alkali metal salts are soluble in neutral as well as acidic aqueous solutions. Thus, compound **3**, with its four iminodiacetic acid groups, is a water-soluble ligand capable of metal coordination at neutral pH.

TETRANUCLEAR COPPER COMPLEXES

Various catalysis, most notably metalloenzymes, use several metal centers in concert with each other to perform their reactivity, whether it be

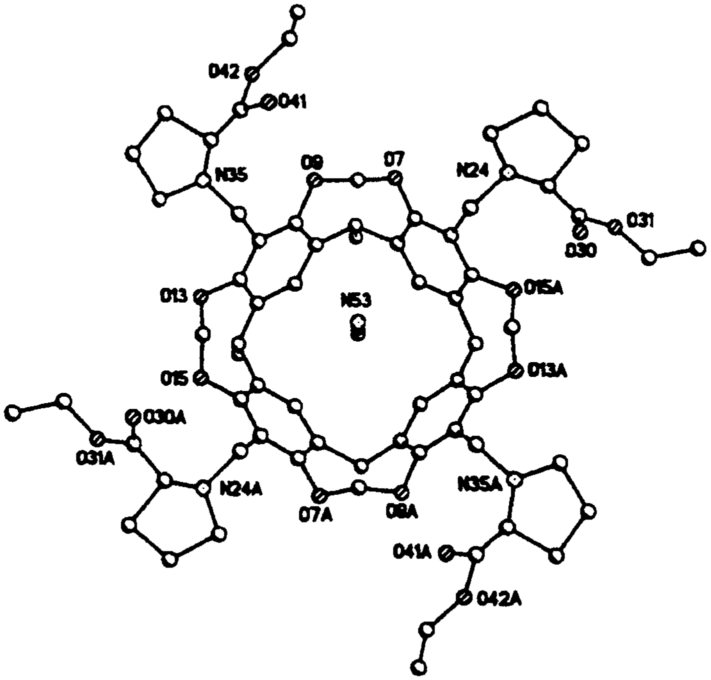


FIGURE 1 Solid state structure of the L-proline resorcinarene, 1. The prolines lie in a clockwise arrangement around the cavity and a acetonitrile occupies the cavity. Hydrogens removed for clarity

hydrolysis, alkane oxidation, or electron transfer.[12] Thus it is attractive to make complexes with metal centers in close proximately to each other so that the metal ions can function in a cooperative manner. The resorcinarene molecules we synthesized with four functional groups attached to their upper rims would seem to be ideal for bring four metal ions together. Indeed this is the case. When copper(II) ions are allowed to coordinate to **2**, four coppers coordinate to the bpa moieties (Figure 3).[10] In the solid state each copper has a similar coordination geometry but a different coordination environment. The coppers have a distorted octahedral geometry with two long bonds opposite each other and four short bonds lying in a plane. One of the long axial bonds for three of the coppers is to an ether oxygen of the resorcinarene. As shown by a magnetic moment of 1.87 μ_B at 300 K, the four copper atoms have isolated spins. Each copper atom has labile ligands in axial and equatorial bonding positions. These sites are available for substrate binding, which substrate may also be attracted to the resorcinarene cavity. Therefore, these complexes have potential as substrate selective catalysts.

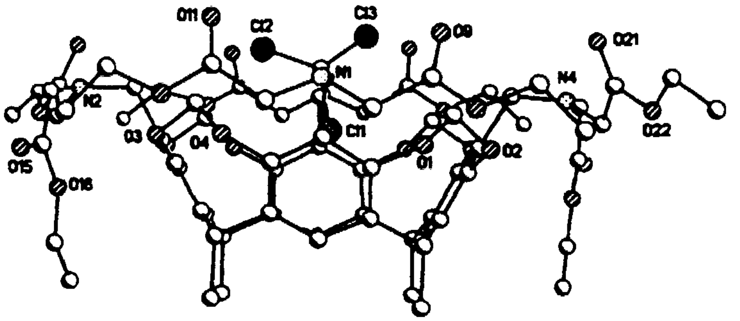


FIGURE 2 Side view of the iminodiacetate ethyl ester resorcinarene, 3a. The iminodiacetate groups extend outward and downward around the cavity. A chloroform resides within the cavity

COBALT- AND IRON-ASSEMBLED CAGE COMPLEXES

Given that cobalt(II) and iron(II) are stable in an octahedral geometry without major distortions, it is expected that they will form different compounds with functionalized resorcinarenes than what is observed with copper(II). When cobalt(II) is added to a neutral aqueous solution of 3, the proton NMR signals for the resorcinarene broaden and become shifted; the original 7 proton signals split into 15 and range from 160 ppm to −50 ppm (Table I).[13] X-ray crystallography on a single crystal of $Ba_4Co_4\mathbf{3}_2$, shows a molecule which has four cobalt ions between two resorcinarene molecules (Figure 4). Remarkably, a cage molecule, possessing an elliptical cavity of 9 by 10 Å, is assembled by four cobalt ions. Six water molecules hydrogen-bonded together in an octahedron reside within the cavity. The cage molecule is stable in water at neutral

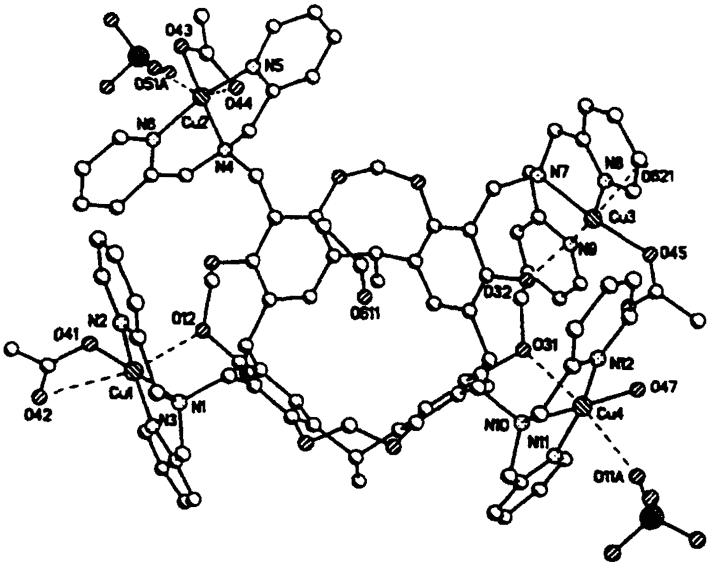


FIGURE 3 Top view of the bispyridylmethylamine functionalized resorcinarene coordinated to four copper ions, $Cu_4 2^{8+}$. The copper ions are positioned around the cavity and a ethanol resides within the cavity. Hydrogens, three perchlorate ions, and water molecules are not shown

pH but readily disassembles at pH below 4 because the acetate groups become protonated. Two resorcinarene molecules composing a cage compound is similar to the carcerands and hemicarcerands that are made of two resorcinarenes attached by organic linking molecules.[6] This metal-assembled cage also resembles the cage complexes assembled by hydrogen bonds.[7] Although the structure of the metal-assembled cages is similar to other cages they have two very important differences, they are easily opened and closed by changing pH and are stable in water.

Synthesis of an iron-assembled cage complex is done in a similar manner to how the cobalt-assembled cages are made, except care must be taken to keep the iron(II) from being oxidized. Thus, to obtain the iron cage, $Fe_4 3_2$·guest[8] (Figure 5), iron(II) is added to an aqueous solution of **3** under an inert atmosphere or in the presence ascorbic acid (which acts as a reducing agent).[14]The ^1H NMR signals for the iron

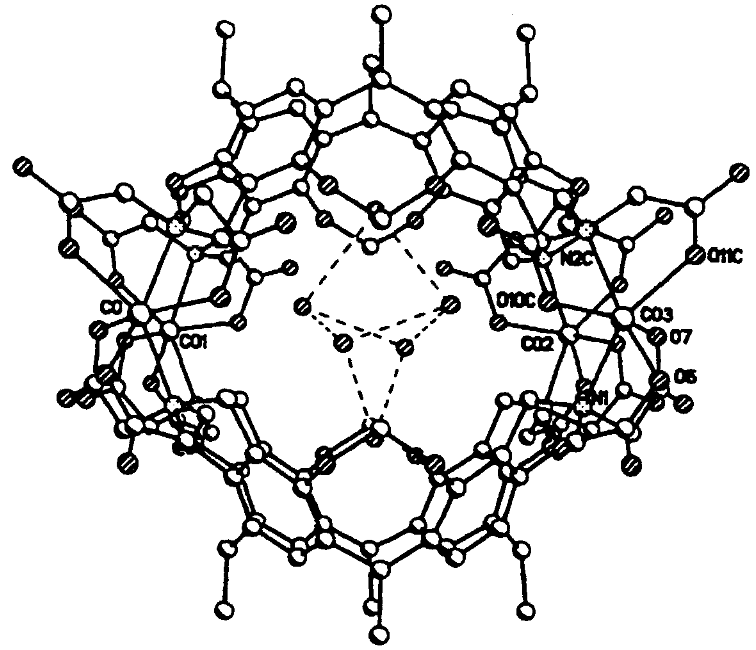


FIGURE 4 Crystal structure of the cobalt cage complex, $Co_4 3_2^{8-}$. Six water molecules hydrogen-bonded together occupy the cavity. The counter cations, water molecules outside of the cavity, and hydrogen atoms have been removed for clarity

cage are broader and less shifted from the diamagnetic region when compared to the cobalt cage resonances.

In the solid state, the four metal centers of $M_4 3_2^{8-}$ (M = Co, Fe) have a pseudo octahedral geometry and form a belt around the middle of the elliptical cavity. The metal centers are in a ΔΛΔΛ arrangement. The nitrogen atoms from two resorcinarenes are *cis* to each other, however with a larger angle (N-M-N = 120°), and the oxygen atoms from carboxylates of the two different resorcinarene are *cis* and *trans*. Two iminodicarboxylate groups per each metal ion results in an overall charge on the complex of negative eight. The cages are therefore soluble as alkali metal salts in water and insoluble in organic solvents.

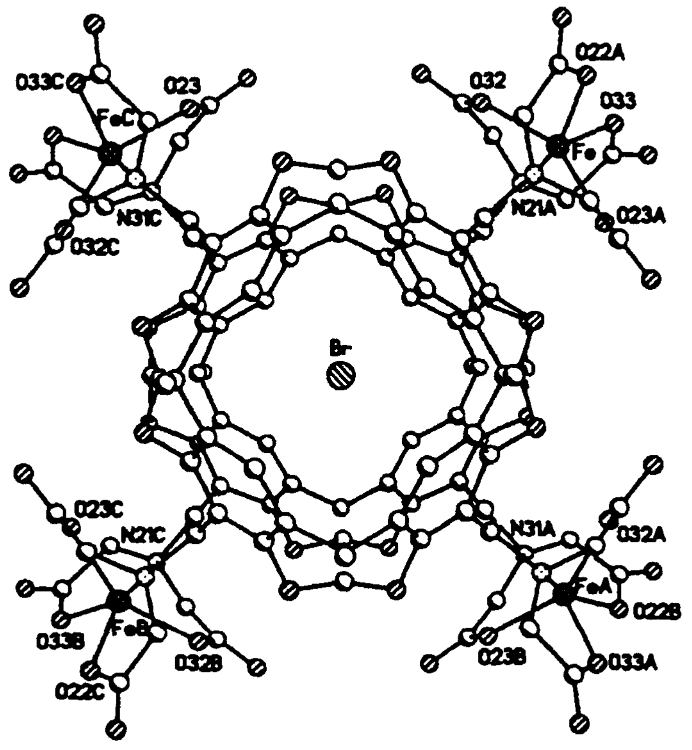


FIGURE 5 Top view down the C_4 axis of the iron cage complex, $Fe_4 3_2^{8-}$. Note how the metal centers are appendages to the elliptical cage. A disordered encapsulated bromobenzene resides within the cage. The counter cations, water molecules, and hydrogen atoms have been removed for clarity

It is not necessary to perform X-ray crystallography on the cages to know metal ions have coordinated to 3 or that cages have formed.[11] As stated previously, when cobalt(II) or iron(II) are added to an aqueous solution of 3, the ^1H NMR signals of the resorcinarene shift and indicate the paramagnetic metal ions have coordinated. When the cages were first synthesized, there seemed to be no good reason why the metal-coordinated resorcinarene produced 15 ^1H NMR resonances. It is not until the symmetry of the molecule is accounted for that the resonances can be explained. Reviewing the solid state structure of the cage shows that it belongings to the D_{2d} point group and therefore all of the hydrogen containing groups on the top resorcinarene are in the same chemical environment as their like groups on the bottom resorcinarene. Also, some of the groups, though not all, on an individual resorcinarene are in the same chemical environment as like groups on the same resorcinarene; these are the hydrogens on the aryl, benzyl, and acetate groups. Those groups that are not in the same chemically equivalent environments are the methyl, methylene, inner ether, and outer ether groups. These last four groups thus give two sets of resonances. Therefore the 15 ^1H NMR resonances arise from four acetate protons, two benzylic protons, one aryl proton, a set of two methyl protons, a set of two methyne protons, a set of two inner etheryl protons, and a set of two outer etheryl protons.

TABLE I Comparison of the proton NMR chemical shifts (ppm, HDO = 4.80 ppm) for K_83, $K_8Co_43_2 \cdot 6H_2O$, and $K_8Co_43_2 \cdot benzene$ in D_2O. Peak description and integrationare in parenthesis

K_83	$K_8Co_43_2 \cdot 6H_2O$	$K_8Co_43_2 \cdot benzene$
	166 (broad)	159 (broad)
	132 (broad)	120 (broad)
	93 (broad)	96 (broad)
7.71 (s, 4H)	15.8 (4H)	12.8 (4H)
5.83 (d, 4H)	12.4 (4H)	11.8 (4H)
4.89 (q, 4H)	4.6 (12H)	4.5 (12H)
4.36 (s, 8H)	1.7 (8H)	2.2 (8H)
4.21 (d, 4H)	−1.4 (12H)	−1.0 (12H)
4.04 (s, 16H)	−7.6 (4H)	−4 (broad)
1.79 (d, 12H)	−9 (broad)	−6.4 (4H)
	−11.7 (4H)	−12.4 (4H)
	−21 (broad)	−22 (broad)
	−28.4 (4H)	−23.9 (4H)
	−32.5 (4H)	−30.2 (4H)
	−68 (broad)	−60 (broad)

ENCAPSULATION OF SMALL MOLECULES BY COBALT AND IRON-ASSEMBLED CAGES

Noticing that $M_4\mathbf{3}_2^{8-}$ (M = Co, Fe) cages possessed cavities with volumes of approximately 300 Å^3 and realizing that the cavities were surround by phenyl groups, motivated us to attempt to encapsulate small organic molecules. We did not worry about the solvent water being preferentially encapsulated over the guest, but we did worry about the guests being soluble enough in water to be in close proximity to the complexes to be encapsulated. However, this proved to not be a problem. When neutral aqueous solutions of **3** are stirred in the presence of a small organic molecules and either cobalt(II) or iron(II) is added, the ^{1}H NMR signals of $Co_4\mathbf{3}_2^{8-}$ or $Fe_4\mathbf{3}_2^{8-}$ shift from where they are when the cages are assembled without organic guest present (Table I).[11] However, there are still fifteen resonances. The new resonances of $Co_4\mathbf{3}_2^{8-}$ and $Fe_4\mathbf{3}_2^{8-}$ are consistently close to the same chemical shift over a wide range of guest molecules. Most of the resonances with positive ppm values move upfield, while those with negative ppm values move downfield. In other words, the hydrogen resonances move slightly to the diamagnetic region.

Along with changes in the ^{1}H NMR chemical shifts of $M_4\mathbf{3}_2^{8-}$ (M = Co, Fe), new resonances appear which correlate to the protons on the added guest. In the cobalt-assembled cages the guest resonances are seen between −15 and −35 ppm, while those for the iron-assembled cages are observed between −10 and −20. In both cases, the guest resonances are close to two host resonances. As Table II and III show, these cages encapsulate a variety of organic molecules, such as aromatic molecules, alkanes, haloalkanes, alcohols, and nitrogen and oxygen containing molecules. The magnetic coupling from the cobalt and iron ions to the organic guests is through space. This is unique, in almost all examples of paramagnetically shifted NMR signals of compounds, the compounds are bonded to the paramagnetic metal center. Also noteworthy, is that these cages trap organic molecules from water, which organic molecules are only sparingly soluble in water. The cages bring organic molecules into water and are only fully occupied with guests when more guests are present than what are soluble in water. Even though there are thousands more water molecules present, the cages selectively extract the organic molecules from the water.

TABLE II ^1H NMR chemical shifts[a] and percent occupancy for a representative group of encapsulated guest molecules in $Co_43_2^{8-}$

Guest	*^1H Chemical shift (integration)[b]*				*% occupied*
Aromatics and Alkanes					
benzene	−26.8				100
toluene	−20.0 (1)	−23.4 (3)	−29.2 (2)	−32.2 (2)	100
chlorobenzene	−19.26 (1)	−28.3 (2)	−31.8 (2)		100
phenol	−19.2 (1)	−25.8 (2)	−30.8 (2)		100
p-xylene	−22.1 (3)	−32.0 (2)			100
ethylbenzene	−23.4 (2)	−23.9 (5)	−30.7 (2)	−32.5 (2)	100
anisol	−18.7 (1)	−20.7 (3)	−26.7 (2)	−32.1 (2)	100
pentane	−26.7 (3)	−33.9 (2)	−37.1 (1)		80
hexane (2 sets, 9:1)[c]	−25.0 (3)	−34.7 (2)	−37.8 (2)		100
heptane	−24.7 (3)	−32.5 (2)	−34.2 (2)	−39.9 (1)	90
	−40.4 (1)				
Alcohols and heteroatom containing molecules					
ethanol	−30.7 (2)	−32.7 (3)			40
propanol	−26.8 (3)	−32.4 (2)	−32.8 (2)		90
butanol	−27.1 (3)	−32.6 (2)	−35.6 (2)	−36.6 (2)	80
pentanol	−26.2 (3)	−32.7 (4)	−36.1 (2)	−37.2 (2)	65
isopropanol	−32.6				60
acetone	−30.1 (1)	−32.6 (1)			50
diethyl ether	−26.9 (3)	−32.5 (2)			95
tetrahydrofuran	−30.3 (1)	−32.2 (1)			90
ethyl acetate	−24.8 (3)	−28.6 (2)	−30.6 (3)		95
acetonitrile	−24.8				100
chloroform	−27.3				100
methylenechloride	−22.5				90
1,2-dichloroethane	−26.0				90

[a] D_2O solutions at ambient temperature, ppm, referenced to DHO = 4.80 ppm.

[b] Integral values are relative to other guest resonances.

[c] Two sets of peaks are observed and the least intense set are one to two ppm upfield from the most intense set of peaks. Only the chemical shifts for the most intense set of peaks are given.

TABLE III NMR chemical shift (ppm, HDO = 4.80 ppm) data for encapsulated guest molecules in $Fe_4 3_2{}^{8-}$[a]

Guest	*^1H (integration[b])*	*Other nuclei*
benzene	−15.5	
benzene-d_6		−16 (^2H)
fluorobenzene	−15.0	−139 (^{19}F)
chlorobenzene	−14.4(2), −16.0(1), −17.9(2)	
bromobenzene	−14.2(2), −15.4(1), −18.1(2)	
1,4-difluorobenzene	−15.3	−145 (^{19}F)
1,2-dichloroethane	−15.7	
1,2-dichloroethane-d_4		−16 (^2H)
diethyl ether	−16.9(3), −20.2(2)	
THF	−18.4(1), −21.3(1)	
ethyl acetate	−15.3(3), −18.1(2), −18.8(3)	
pentane	−16.8(3), −21.9(2), −24.0(1)	
hexane	−14.9(3), −21.2(2), −23.1(2)	
cyclohexane	−22.3	
tetramethylsilane	−23.7	

[a] Two sets of peaks exist for each guest. Only the most intense set of peaks is given.

[b] Integral values are relative to other guest resonances within each set of peaks and some are tentative due to the broadness of the peaks.

Once most of the organic guests are encapsulated by a cobalt-assembled cage they remain encapsulated, unless the pH is lowered causing cage opening. Lowering the pH of the solution is an efficient means of releasing the guest, while raising the pH allows cage assembly and guest encapsulation. Large guests are not encapsulated, as they do not fit within the cavity. Small guests are encapsulated if they are not strongly held by the water however they do escape from the cavity if they are polar and thus attracted by water. Thus, for most of the guests there is not equilibrium between being bound within the cage and being unbound. They are either in or out. Where the equilibrium probably does exist is before or during cage closure. Guest encapsulation includes several steps, some of which are:

$$\text{guest} + \mathbf{3} \rightarrow \mathbf{3}\cdot\text{guest},$$
$$4\text{M}^{2+} + \mathbf{3}\cdot\text{guest} \rightarrow \text{M}_4\mathbf{3}\cdot\text{guest},$$
$$2\text{M}_4\mathbf{3}\cdot\text{guest} \rightarrow \text{M}_4\mathbf{3}_2\cdot\text{guest}^{8-} + \text{guest} + 4\text{M}^{2+}.$$

All the steps but the last one have some degree of reversibility. In competition with the first step is water association with **3**, which leads to encapsulation of water through a series of similar steps.

In an attempted to know the conformation of the organic guest inside of the cage, X-ray crystallography was perform on $\text{M}_4\mathbf{3}_2\cdot\text{guest}^{8-}$ (M = Co, Fe) complexes.[11,14] Due to the highly symmetric space group of crystallization and ability of the guest to freely move within the cavity, only disrobed electron density was observed for encapsulated guest molecules. The dimensions of the cavity, however, are very close, within 0.05 Å, and fairly independent of what guest is encapsulated. Bond distances and angles in the $\text{Co}_4\mathbf{3}_2\cdot\text{guest}^{8-}$ (guest = $6\text{H}_2\text{O}$ or ethylbenzene) and $\text{Fe}_4\mathbf{3}_2\cdot\text{guest}^{8-}$ (guest = $6\text{H}_2\text{O}$ or bromobenzene) are also very similar and within 0.05 Å and 1 degree of each other. Thus, the guests in these complexes do not impose significant structural changes upon the complexes.

CONCLUSION

Resorcinarenes may have metal coordinating functional groups attached to their upper rims. When copper(II) coordinates to the bpa functionalized resorcinarene **2**, a tetra nuclear complex forms which has four copper ions surrounding a cup of phenyl groups. This is different from when cobalt(II) or iron(II) ions are added to the iminodiacetic acid functionalized resorcinarene **3**, which results in metal-assembled cages that are able to bind and release guest molecules in water as a function of pH. Facile encapsulation of a wide range of organic molecules demonstrates the encapsulation capabilities and versatility of $\text{Co}_4\mathbf{3}_2^{8-}$ and $\text{Fe}_4\mathbf{3}_2^{8-}$. As shown by the failure to encapsulate large and branched molecules, the cavity dimensions impose guest size and shape selectivity. Both NMR and X-ray crystallographic studies are consistent in indicating that guest resides within the cavities of $\text{Co}_4\mathbf{3}_2^{8-}$ and $\text{Fe}_4\mathbf{3}_2^{8-}$. Large up-field shifts in the proton resonances of the guest molecules are observed when guest is encapsulated. Thus, complexes $\mathrm{Co_4}\mathbf{3}_2^{8-}$ and $\mathrm{Fe_4}\mathbf{3}_2^{8-}$ function as NMR shift reagents for the encapsulated guest.

Acknowledgements

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