Supramolecular Chemistry

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Solvent-Dependent Host–Guest Chemistry of an Fe_8L_{12} Cubic Capsule**

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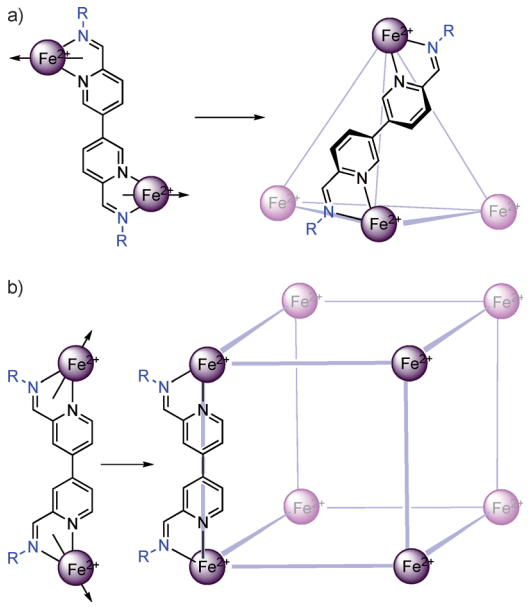
The applications of metal–organic polyhedral container molecules[1] include gas storage and separation,[2] nanoparticle templation,[3] catalysis,[4] and the protection of sensitive guests.[5] The promise of new functions and applications motivates much current interest in this class of compounds.[6] A well-studied subclass of such polyhedra is the M_4L_6 tetrahedral capsules,[7] the first example of which was published by Saalfrank and co-workers,[8] which consist of a hexacoordinate metal ion at each of the four vertices, linked by six organic bis(bidentate) ligands that form the tetrahedron's edges.

As shown in Scheme 1a, such M_4L_6 tetrahedral cage structures may be prepared from 4,4′-diimino-3,3′-bipyridines and octahedral Fe^{II} templates. The coordinate vectors of the bis(bidentate) ligand are parallel and point in opposite directions, which in combination with the rigidity of the 3,3′-bipyridine backbone, leads to the formation of a M_4L_6 tetrahedral framework, following the rules determined by Raymond and Caulder for the rational design of $M_nL_{(3n/2)}$ complexes.[9]

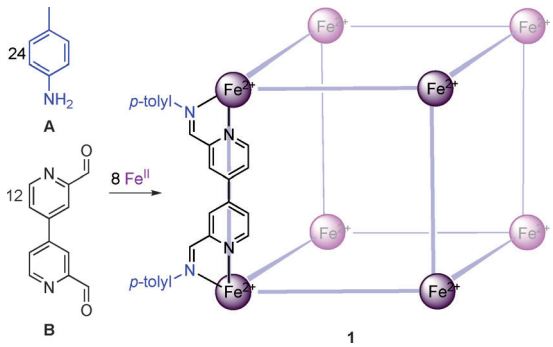
Such tetrahedral capsules are of use in guest binding[10] and the investigation of stereochemical amplification phenomena.[11] We reasoned, however, that the analogous larger, cube-shaped hosts shown in Scheme 1b might offer complementary guest-binding properties to the tetrahedra of Scheme 1a. M_8L_{12} cubes would offer a larger cavity volume compared to M_4L_6 tetrahedra for a given ligand length, thus potentially allowing larger and more complex guests to be bound.

The design principle used in the preparation of an edge-bridged M_8L_{12} cube[12] (Scheme 1b), in contrast with a face-capped M_8L_6 cube,[13] was to prepare a ditopic 3,3′-diimino-4,4′-bipyridine bridging ligand in which the coordinate vectors were forced into an obtuse orientation of no less than 120°.[12h]



Scheme 1. The differing orientations of the coordinate vectors[15] (arrows on the Fe^{II} centers) of isomeric bis(pyridylimine) ligands bring about different self-assembled architectures. a) A parallel orientation led to the formation of Fe_4L_6 tetrahedral assemblies.[10–11] b) The divergence of these vectors at 120° led to cubic Fe_8L_{12} assemblies.

In the antiparallel arrangement required to form an M_4L_6 tetrahedron (Scheme 1a), such a ligand would need to distort substantially in order to provide an octahedral coordination environment at the Fe^{II} vertices, whereas an M_8L_{12} cube would be comparatively strain-free. Such a ligand could be prepared through the subcomponent self-assembly[14] of 3,3′-diformyl-4,4′-bipyridine (**B**; Scheme 2) and primary amines around Fe^{II} ions, as was shown to work well for the



Scheme 2. Preparation of **1** from iron(II) triflimide, *p*-toluidine (**A**), and bis(formylpyridine) **B**.

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preparation of the structurally-related tetrahedra shown in Scheme 1 a.[10,11] The properties of the resulting assemblies could, we hypothesized, be tuned through the incorporation of different amine residues into the periphery.

Upon mixing iron(II) (trifluoromethylsulfonyl)imide (iron(II) triflimide, 2 equiv), dialdehyde **B** (3 equiv), and *p*-toluidine **A** (6 equiv) in acetonitrile, the formation of an intensely colored blue-green solution was observed. The ^{1}H NMR spectrum of this solution was indicative of multiple species being present, but upon heating at 50 °C overnight the spectrum simplified to show the formation of a single, symmetrical product. The use of iron(II) triflimide appeared essential to the preparation of a soluble product; when the trifluoromethanesulfonate, tetrafluoroborate, perchlorate or hexafluorophosphate salt of iron(II) was used, poorly soluble products were obtained.

The ^{1}H NMR spectrum of product **1** (Figure 1 a) reflects high symmetry. A single peak was observed for each proton of the ligand, with ^{1}H–^{1}H COSY and NOESY data allowing assignment of each signal. The presence of only a single species in solution was confirmed by DOSY NMR. ESI mass spectrometry revealed peaks corresponding to the +9, +8, +7, +6, and +5 peaks of an M_8L_{12} species associated with triflimide counterions (Figures S2 and S3 in the Supporting Information).

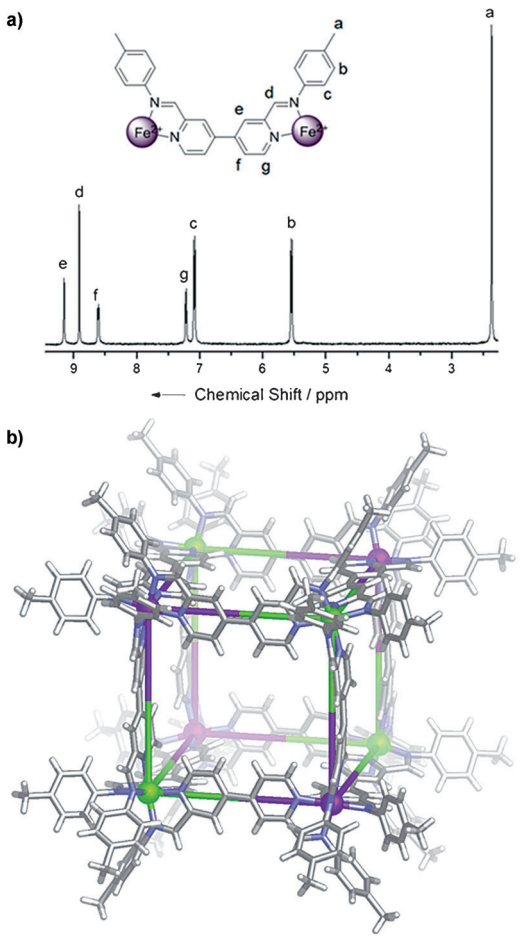


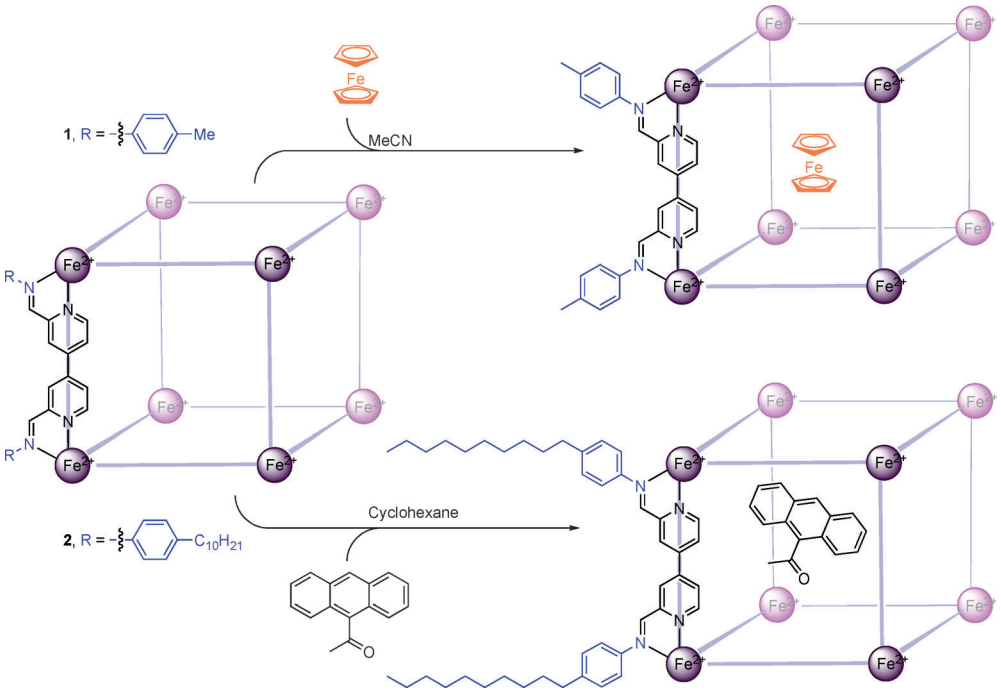
Figure 1. a) ^{1}H NMR spectrum of **1**. b) Crystal structure of **1**·16 ClO_4·16 MeCN·16 Et_2O.[23] Green spheres correspond to Fe^{II} ions of Λ stereochemistry and purple spheres depict Δ-Fe^{II} ions (Λ and Δ indicate left- and right-handed twists, respectively).

Single crystals of the perchlorate salt of **1** were obtained through vapor diffusion of Et_2O into a dilute, saturated acetonitrile solution. The structure of the $[Fe_8L_{12}]^{16+}$ cube, **1**·16 ClO_4·16 MeCN·16 Et_2O, was thus confirmed by single-crystal X-ray diffraction (Figure 1 b), performed at the Diamond Light Source.[16] Each metal center of Λ stereochemistry is adjacent to three Δ centers and vice versa, lending the capsule approximate T_h point symmetry. This is an uncommon point group; other M_8L_6[13] and M_8L_{12}[12] cube-like structures have possessed approximate *O* (chiral octahedral) symmetry, in which all metal centers have the same stereochemical configuration. M_4L_6 tetrahedral structures have in certain cases been observed to exhibit lower-symmetry diastereomeric configurations;[17] we observed no evidence for additional diastereomers in this study.

We had not anticipated that **1** would adopt a T_h-symmetrical configuration, which forces the bipyridine rings into an eclipsed coplanar configuration, and instead we predicted an *O*-symmetric configuration in which these rings would have been mutually orthogonal; either point group would have been consistent with the observed NMR spectra of **1**. We posit that the T_h-symmetrical arrangement allows the ligands to bow slightly away from the Fe–Fe vectors, thereby relieving strain more effectively than would be possible in an *O*-symmetric arrangement. This bowing also moves the eclipsed hydrogen atoms at positions e and f (Figure 1 a) away from each other, thereby alleviating transannular strain.

The metal–metal distances along the edges of **1** average 11 Å, and the structure encloses an interior volume exceeding 1000 Å^3. Although large pores lead into the cavity of **1** (the largest sphere that could freely pass through these pores would have a van der Waals radius of 6.7 Å), we reasoned that the aromatic surfaces lining the cavity of **1** might lead to binding of aromatic guests. The cage's charge of +16 also provided potential for the encapsulation of anionic guests. A variety of prospective guests, both neutral and anionic, were screened for binding within **1** (Table S1 in the Supporting Information), but no change in the ^{1}H NMR spectrum was observed upon addition of any of these (10 equiv) to a solution of **1** in acetonitrile (0.01 mM).

In contrast, ferrocene was observed to interact with **1** in a manner consistent with guest binding (Scheme 3, top). Upon addition of ferrocene (1 equiv) to a solution of **1** in acetonitrile (0.01 mM), no ^{1}H NMR signal corresponding to ferrocene was observed. When additional ferrocene was added, its characteristic singlet signal was observed to grow out of the baseline in both ^{1}H and ^{13}C NMR spectra (Figures S8 and S9 in the Supporting Information). When a solution containing equimolar amounts of ferrocene and **1** (0.01 mM) was cooled from room temperature to 233 K, a signal assigned to ferrocene was seen to grow from the baseline, sharpening as the temperature was decreased (Figure S7 in the Supporting Information). This observation is consistent with ferrocene exchange between cavity and solution occurring at a rate comparable to the NMR timescale at room temperature. Heating the sample to 333 K did not result in reappearance of the ferrocene peak in the ^{1}H NMR



Scheme 3. Solvent-dependent host–guest chemistry of **1** and **2**.

spectrum, but upon lowering the temperature the rate of exchange was slowed sufficiently so that the signal for ferrocene could be detected once again. The broadness of this signal, when it was observed, precluded quantification of the binding interaction between ferrocene and **1** by NMR titration; the UV/Vis spectrum of **1** also did not appear to be perturbed by the presence of ferrocene.

To further examine the nature of the interaction of ferrocene with **1**, cyclic voltammetry (CV) experiments were performed in acetonitrile at 2.5 mM concentration (Figure 2). A positive shift of 27 mV was seen in the peak potential of ferrocene upon addition of one equivalent of cage. This shift is in agreement with prior CV observations of ferrocene encapsulated within a cationic host.[18] Coulombic repulsion between ferrocinium and the positively charged host framework causes the guest's oxidation to occur at a higher potential.

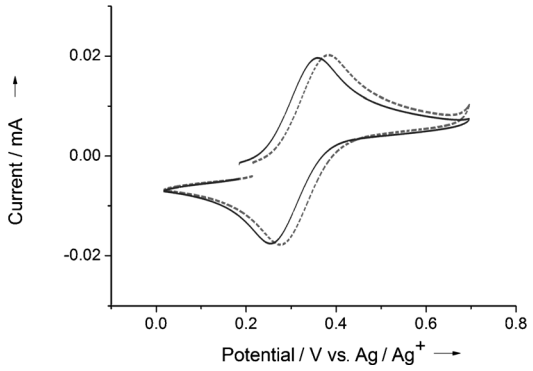


Figure 2. Cyclic voltammograms (scan rate of 50 mVs^{-1}) of ferrocene (2 mM; solid trace) and ferrocene with capsule **1** (both 2 mM; dashed trace) in acetonitrile solution containing NMe_4PF_6 (0.1 mM).

Under the same conditions wherein ferrocene was observed to bind, decamethylferrocene and acetylferrocene showed no evidence of binding by NMR spectroscopy or CV. Examination of models suggests that the additional steric bulk prevents the inclusion of these guests within **1**.

The modularity of the subcomponent self-assembly approach[14] allows for differently substituted aniline residues to be incorporated into the cubic framework of **1**. These anilines' substituents offer a straightforward means to alter the physicochemical properties of the resulting assemblies. We reasoned the incorporation of decylaniline residues into an analogous cubic structure **2** (Scheme 3, bottom) might increase solubility in hydrocarbon phases, thereby allowing access to such functions as gating ions across membranes.[19]

Cubic capsule **2** was thus synthesized as shown in Scheme 3, and was characterized by NMR spectroscopy and MALDI-TOF MS. Whereas **1** was observed to dissolve only in acetonitrile and nitromethane, the alkyl chains of **2** granted solubility in apolar solvents, such as chloroform and cyclohexane, as well.

In cyclohexane **2** displayed host–guest chemistry distinct from the guest binding observed for **1** in acetonitrile. Upon progressive addition of 9-acetylanthracene (1–20 equiv) to a solution of **2** (0.01 mM) in C_6D_{12}, shifts of the peaks of the aromatic protons of the capsule were observed, most notably the imine signal, as an increasing amount of guest was added. NOESY NMR experiments confirmed this interaction, with cross-peaks seen between the peaks of the guest and the host (Figure S12 in the Supporting Information). NMR titration allowed determination of the association constant, $K_a = (470 \pm 50)\,M^{-1}$ when a 1:1 binding model was employed (Figure S11 in the Supporting Information); attempts to use a 1:2 host/guest binding model resulted in a poorer fit.

This interaction between **2** and 9-acetylanthracene was observed in cyclohexane but not in acetonitrile, which we attribute to the increased importance of dipole–dipole and π–π quadrupolar interactions to drive binding in this apolar medium.[20] This binding was observed to occur only in the case of 9-acetylanthracene with no evidence of complexation seen for anthracene, pyrene, or 1-acetylpyrene.

In conclusion, a ligand was conceived to have the correct geometry for the synthesis of an edge-bridged M_8L_{12} metallosupramolecular cube with approximate T_h point symmetry.

Versions of this assembly could be prepared that enabled different guests to be bound in different solvents. Geometrical principles suggest that larger assemblies isostructural to **1** will be accessible from longer 3,3′-diimino-4,4′-bipyridine ligands,[6e,21] and prior studies[22] indicate that judicious subcomponent design can allow the pores of these assemblies to be closed, thus allowing for new functions associated with guest binding[1a,e,2–5] to be explored.

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[23] CCDC 907584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

