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Self-Assembly of an Imidazolate-Bridged Fe^{III}/Cu^{II} Heterometallic Cage

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Supporting Information

ABSTRACT: A rare, discrete, mixed-valent, heterometallic Fe(III)/Cu(II) cage, [Cu$_6$Fe$_8$L$_8$](ClO$_4$)$_{12}$·χsolvent (H$_3$L = tris{[2-{(imidazole-4-yl)methylidene}amino]ethyl}amine), was designed and synthesized via metal-ion-directed self-assembly with neutral tripodal metalloligands. The formation of this coordination cage was demonstrated by X-ray crystallography, ESI mass spectrometry, FT-IR, and UV−vis-NIR spectroscopy.

The self-assembly of coordination cages has continued to receive considerable attention over the past decade[1] because of their many potential applications in gas adsorption,[2] drug delivery,[3] catalysis,[4] magnetic materials,[5] host−guest phenomena,[6] and synthetic membranes for ion channels.[7] Although a number of coordination cage types have been developed, the design and successful construction of these systems, particularly those with heteronuclear coordination motifs, still represents a significant challenge.[5d,e,8]

Three synthetic procedures have been successfully exploited for the construction of discrete heteronuclear coordination architectures: (1) exploitation of the inherent coordination properties between ligands and different metal ions for the metal-directed assembly of discrete metallo-supramolecular architectures,[9] (2) formation of discrete metallo-assemblies preorganized for binding a second metal ion, or ions, to yield discrete heterometallic architectures,[10] and (3) employing preformed metalloligands functionalized for use as building blocks reacting with additional metal ions and sometimes extra ligands.[2b,5c,e,8b,11]

In a recent review,[12] we discussed the employment of planar di-, tri-, and oligonuclear platforms, including both homo- and heteronuclear systems, as structural elements for the formation of both discrete and polymeric metallo-supramolecular assemblies. As part of our continuing efforts to prepare heterometallic coordination architectures, we reported the synthesis of predesigned hexanuclear Cu^{II}/Ni^{II} metallocycles featuring unprecedented six-node metallocoronand structural motifs[10b] and the preparation of a discrete heteronuclear metallomacrocycle (Ag$^{I}_3$/Fe^{II}) by metal-ion-directed self-assembly via a Fe^{II} template.[10a]

Herein, we report an extension of the above studies leading to the construction of a new discrete coordination heterometallic nanocage **1** [Cu$_6$Fe$_8$L$_8$] (ClO$_4$)$_{12}$·χsolvent (H$_3$L = tris{[2-{(imidazole-4-yl)methylidene}amino]ethyl}amine) enclosing a void space of 277 Å^3.[13] Thus, we have employed a suitable metalloligand together with an additional metal ion (Cu^{II}) that was anticipated to favor structure-specific self-assembly. A key feature of our design was to employ short organic components that would bridge the different metal ions in a way that would give the potential for magnetic exchange between metal centers. In addition, we have employed a cooperative effect to build a robust metalloligand, which can react with additional metal ions to yield a heterometallic cage. To this end, we demonstrated that a heterometallic polyhedral cage can be constructed by combining the C$_3$-symmetric metalloligand FeL[14] and C$_4$-symmetric Cu^{II} centers (with distorted square pyramidal coordination geometries) via metal-directed assembly (Scheme 1).

The metalloligand FeL was prepared as reported previously.[14] The one-pot reaction of 4-formylimidazole and tris(2-aminoethyl)amine with FeCl$_3$ in a 3:1:1 ratio in water with heating resulted in the protonated dark red species [FeH$_3$L]$^{3+}$ from which a dark blue powder was obtained upon slow addition of aqueous base (Scheme 1). The precursor [FeH$_3$L]$^{3+}$ of metalloligand FeL exists as two enantiomers in both the solid state and solution, with either a Δ (clockwise) or Λ (anticlockwise) configuration due to the screw coordination arrangement of the achiral tripodal ligand around Fe^{III}.[14,15] That is, the deprotonated metalloligands of type FeL act as chiral building blocks incorporating secondary binding sites for further reaction with additional metal ions.

Synthesis of the discrete heterometallic Fe^{III}Cu^{II} cage proceeds via metal-ion-directed self-assembly of the neutral tripodal metalloligand FeL with Cu(ClO$_4$)$_2$ in methanol. Diffusion of dioxane vapor into the DMF solution of the

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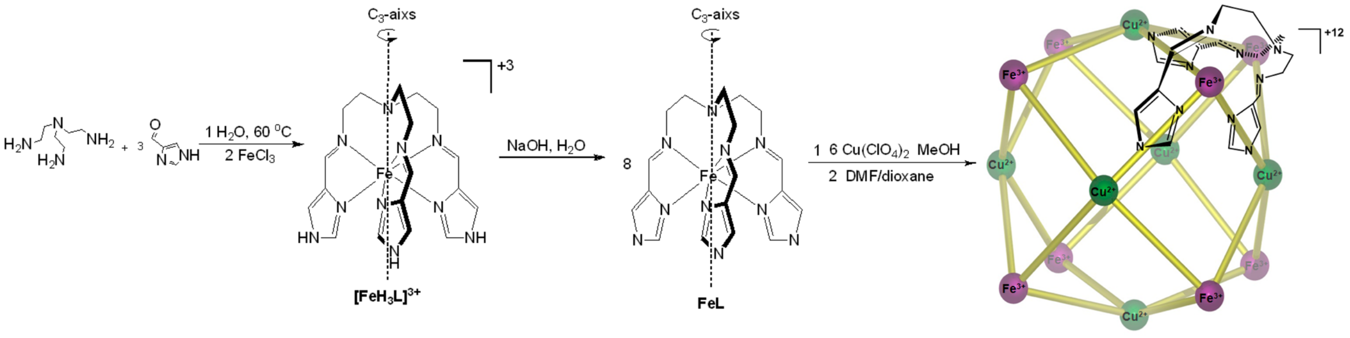
Scheme 1. Schematic Representation of Synthesis of Heterometallic Nanocage 1 through Neutral Metalloligand Self-Assembly



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crude product affords dark blue cube-shaped crystals of nanocage **1** in 73% yield. Electrospray ionization (ESI) mass spectrometry provided evidence that heterometallic **1** persists in solution. Cage **1** was dissolved in CH_3CN, and the major peak in the corresponding ESI-MS occurred at m/z 908.5 $\{[Cu_6Fe_8L_8](ClO_4)_7\}^{5+}$ (Figure S1, Supporting Information), which is consistent with the loss of five anions from the heterometallic cluster. A few minor fragments were also identified, for example, involving the loss of four anions $\{[Cu_6Fe_8L_8](ClO_4)_8\}^{4+}$ at m/z 1160.5 and six anions $\{[Cu_6Fe_8L_8](ClO_4)_6\}^{6+}$ at m/z 740.4. The expected isotope patterns for the various charged species (Figures S2 and S3, Supporting Information) were observed, and the isotopic distributions for both $\{[Cu_6Fe_8L_8](ClO_4)_7\}^{5+}$ and $\{[Cu_6Fe_8L_8](ClO_4)_8\}^{4+}$ are in excellent agreement with their calculated patterns. The FT-IR spectrum of **1** exhibits the characteristic absorption bands for DMF $\nu_{C=O}$ (1652 cm^{-1}), imine $\nu_{C=N}$ (1591 cm^{-1}),[14] and perchlorate ν_{Cl-O} (~1055 and 621 cm^{-1})[16] (Figure S4, Supporting Information). The UV−vis-NIR spectrum of **1** in CH_3CN for the region 2000−200 nm (Figure S5a and b, Supporting Information) at two different concentrations revealed two relatively low intensity absorption bands at 570 and 776 nm and an intense band at 279 nm. The latter is attributed to the $\pi-\pi^*$ transition of the bridged imidazolate ligand. The relatively low intensity bands at 776 and 570 nm are likely to be charge−transfer transitions and a combination of d−d bands that are localized at both Fe^{III} and Cu^{II} centers.[14,17]

In a relevant recent study, Li and his co-workers have reported high-symmetry homometallic polyhedral cages obtained by metal-ion-directed self-assembly involving 24 imidazolates bridging 14 Ni^{II} ions.[18] In our study, the formation of the related nanoscale cage **1** was confirmed by single-crystal X-ray diffraction (Figures 1 and 2). Cage **1** crystallizes in the tetragonal space group $P4/n$. It features a 14-nucleus heterometallic polyhedral structure in which the eight Fe^{III} ions are each chelated by a tris(imidazolateimine) ligand to yield an octahedral coordination environment, and each Fe−N bond length falls in the range of 1.920−1.995 Å (Figure 1), suggesting it is low-spin at 150 K. There are 24 imidazolate bridges to six distorted square pyramidal Cu^{II} ions with different coordination environments, where the bound axial DMF and water ligands are directed toward the exterior of **1** (Figure 1). Each complex is chiral, with either ΛΛΛΛΛΛΛΛ or ΔΔΔΔΔΔΔΔ configuration at the Fe^{III} centers. Moreover, the chirality of the FeL centers is communicated through the 4-bladed Cu^{II} propellers, such that all Fe^{III} centers and all Cu^{II} centers have the same handedness within an individual cage and that the crystal structure contains an equal ratio of each of the cage enantiomers. The $Fe^{III}-Cu^{II}$ distance through the

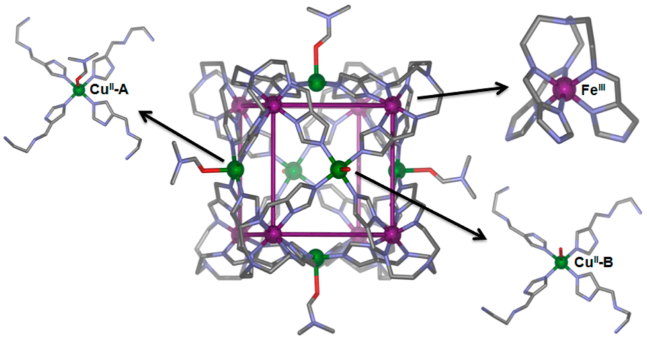

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Figure 1. Single-crystal structure of the heterometallic nanocage **1** and the respective coordination environments of the Fe^{III}, Cu^{II}−A, and Cu^{II}−B sites, which include either bound DMF or water molecules. X-ray crystal structures: C, gray; O, red; N, blue; Fe, purple; and Cu, green.

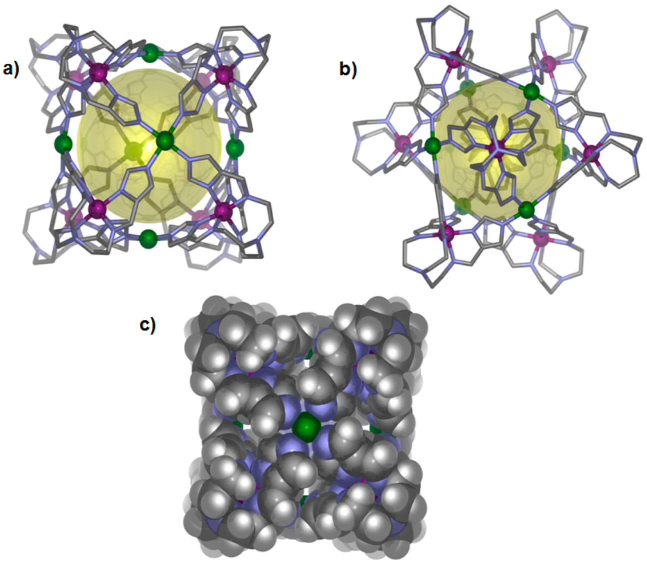

Figure 2. X-ray single-crystal structure of **1**. (a) Perspective view emphasizing one of the C_4 symmetry axes. (b) View down one of the C_3 axes. The large yellow sphere is added to indicate the size of the central cavity. (c) Space-filling model of the structure. Solvent molecules, counterions, and hydrogen atoms (a and b) are omitted for clarity. X-ray crystal structures: C, gray; N, blue; Fe, purple; Cu, green; and H, white.

imidazolate bridge is 6.1 Å, which is potentially close enough to facilitate electron transfer and magnetic exchange coupling between the different paramagnetic metal ions. The $Cu^{II}-Cu^{II}$ distance between pairs of opposite Cu^{II} centers is on average 11.3 Å, and the diagonal distance between two octahedral Fe^{III} ions is 14.4 Å. The central cavity in **1** was calculated[13] to have a volume of 277 $Å^3$, and examination of the space-filling model (Figure 2) suggests that the cavity is tightly closed off from the surrounding environment. In addition, the labile ligands (DMF and water) on the Cu^{II} sites can be readily removed without destruction of the cage as evidenced by the mass spectra. The coordinatively unsaturated Cu^{II} sites obtained by the desolvation are of interest because of their potential ability to store solvent or gas.

In conclusion, we describe the efficient synthesis of the first example of a new heterometallic mixed-valent cage category **1** incorporating a neutral metalloligand of type FeL, with the structure having been unambiguously characterized by X-ray crystallography, ESI mass spectrometry, FT-IR, and UV−vis-NIR spectroscopy. Further studies are underway to explore the electronic and magnetic properties and as well as solvent or gas storage of **1** together with other heterometallic cage species of this general type.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details of syntheses and characterization of cage **1** and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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