

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

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Supporting Information Placeholder

ABSTRACT: A rare discrete mixed-valent heterometallic Fe(III)/Cu(II) cage, [Cu₆Fe₈L₈](ClO₄)₁₂· χ solvent (H₃L = 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 phenomena⁶ 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,5e,8}

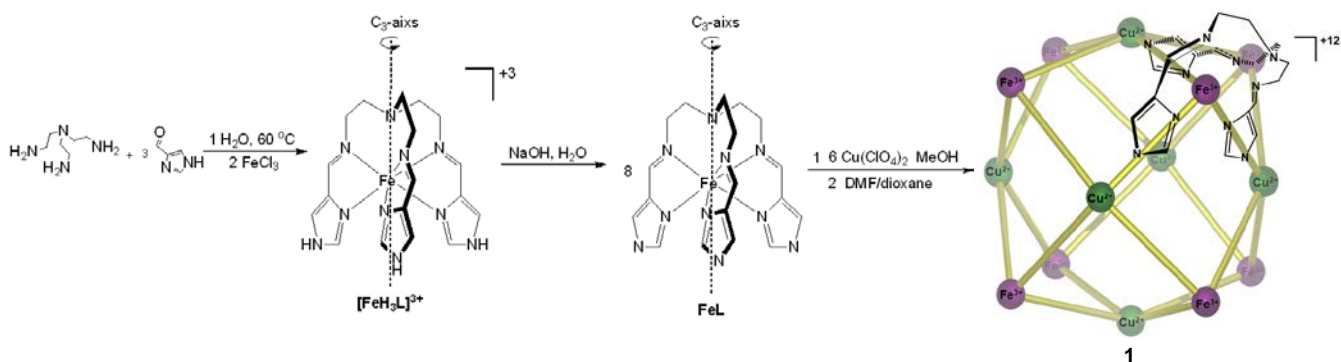
Three synthetic procedures have been successfully exploited for the construction of discrete heteronuclear coordination architectures: 1) exploitation of the inherent coordination properties between ligands and different metal ions for the metal-directed assembly of discrete metallo-supramolecular architectures;⁹ 2) formation of discrete metallo-assemblies preorganised for binding a second metal ion, or ions, to yield discrete heterometallic architectures;¹⁰ 3) employing preformed metalloligands functionalised for use as building blocks reacting with additional metal ions and sometimes extra ligands.^{2b,5c,5e,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 metal-locoronand structural motifs^{10b} and the preparation of a discrete heteronuclear metallomacrocyclic (Ag₃/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** [Cu₆Fe₈L₈](ClO₄)₁₂· χ solvent (H₃L = tris[[2-((imidazole-4-yl)methylidene)amino]ethyl]amine) enclosing a void space of 277 Å³.¹³ Thus, we have employed a suitable metalloligand together with an additional metal ion (Cu^{II}) that was anticipated to favour 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 C₃-symmetric metalloligand FeL¹⁴ and C₄-symmetric Cu^{II} centres (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 FeCl₃ in a 3:1:1 ratio in water with heating resulted in the protonated dark red species [FeH₃L]³⁺ from which a dark blue powder was obtained upon slow addition of aqueous base (Scheme 1). The precursor [FeH₃L]³⁺ of metalloligand FeL exists as two enantiomers in both the solid state and solution, with either a Δ (clockwise) or Λ (anti-clockwise) 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.



Scheme 1. A schematic representation of the synthesis of the heterometallic nanocage **1** through neutral metal-ligand self-assembly

Synthesis of the discrete heterometallic Fe^{III}Cu^{II} cage proceeds via metal-ion directed self-assembly of the neutral tripod metal-ligand FeL with Cu(ClO₄)₂ in methanol. Diffusion of dioxane vapour into the DMF solution of the 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 CH₃CN and the major peak in the corresponding ESI-MS occurred at *m/z* 908.5 {[Cu₆Fe₈L₈](ClO₄)₇}⁵⁺ (Figure S1) 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 {[Cu₆Fe₈L₈](ClO₄)₈}⁴⁺ at *m/z* 1160.5 and six anions {[Cu₆Fe₈L₈](ClO₄)₆}⁶⁺ at *m/z* 740.4. The expected isotope patterns for the various charged species (Figures S2 and S3) were observed and the isotopic distributions for both {[Cu₆Fe₈L₈](ClO₄)₇}⁵⁺ and {[Cu₆Fe₈L₈](ClO₄)₈}⁴⁺ are in excellent agreement with their calculated patterns. The FT-IR spectrum of **1** exhibits the characteristic absorption bands for DMF ν_{C=O} (1652 cm⁻¹), imine ν_{C=N} (1591 cm⁻¹)¹⁴ and perchlorate ν_{Cl-O} (~1055 and 621 cm⁻¹)¹⁶ (Figure S4). The UV-vis-NIR spectrum of **1** in CH₃CN for the region 2000-200 nm (Figure S5a and S5b), 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 π-π* 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 which are localised at both Fe^{III} and Cu^{II} centres.^{14,17}

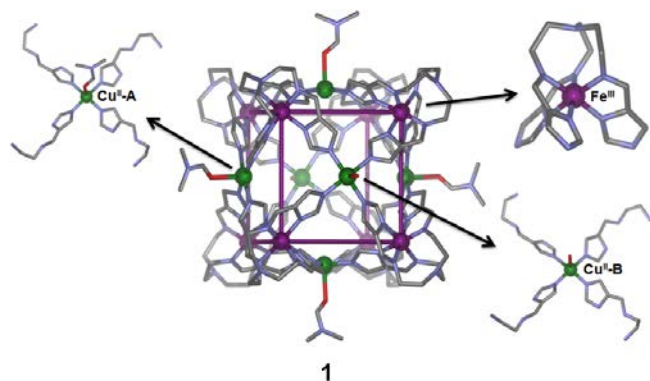


Figure 1. Single-crystal structure of the heterometallic nanocage **1** and the respective coordination environments of

the Fe^{III}, Cu^{II}-A and Cu^{II}-B sites, which include either bound DMF or water molecules. X-ray crystal structures: C, grey; O, red; N, blue; Fe, purple; Cu, green.

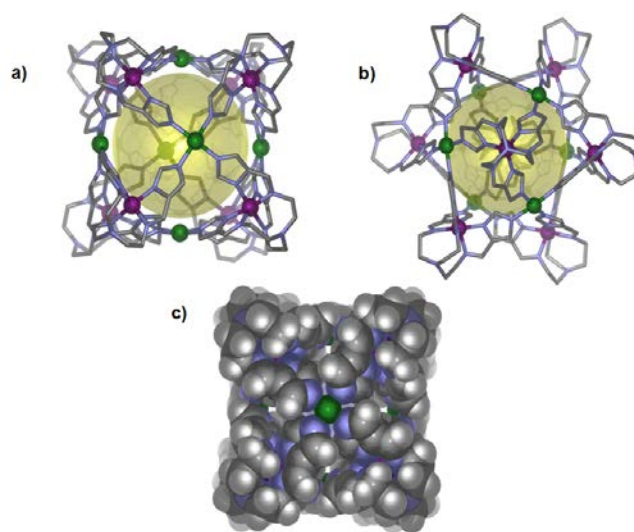


Figure 2. X-ray single-crystal structure of **1**. a) Perspective view emphasizing one of the C₄ symmetry axes; b) view down one of the C₃ axes; the large yellow sphere is added to indicate the size of the central cavity. c) Space-filling model of the structure. Solvent molecules, counter ions and hydrogen atoms (a and b) are omitted for clarity. X-ray crystal structures: C, grey; N, blue; Fe, purple; Cu, green; H, white.

In a relevant recent study, Li and his coworkers have reported high-symmetry homometallic polyhedral cages obtained by metal-ion directed self-assembly involving twenty four imidazolates bridging fourteen Ni^{II} ions.¹⁸ In our study, the formation of the related nanoscale cage **1** was confirmed by single crystal X-ray diffraction (Figures 1-2). Cage **1** crystallizes in the tetragonal space group *P*₄/*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 1.920-1.995 Å (Figure 1) suggesting it is low-spin at 150K; there are twenty four imidazolate bridges to six distorted square pyramidal Cu^{II} ions with different coordination environments, where the bound

axial DMF and water ligands are directed towards the exterior of **1** (Figure 1). Each complex is chiral, with either $\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda$ or $\Delta\Delta\Delta\Delta\Delta\Delta\Delta\Delta$ configuration at the Fe^{III} centres. Moreover, the chirality of the FeL centres is communicated through the 4-bladed Cu^{II} propellers, such that all Fe^{III} centres and all Cu^{II} centres 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 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} centres 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 calculated¹³ to have a volume of 277 Å³ 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, magnetic properties and as well as solvent or gas storage of **1** with other heterometallic cage species of this general type.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains 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 interests.

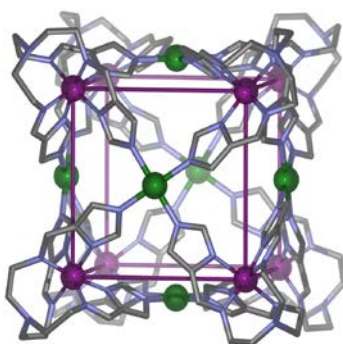
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TOC Graphic



An imidazolate-bridged Fe^{III}/Cu^{II} heterometallic nanocage has been synthesized by coordination-driven face-directed self-assembly using a suitable metalloligand.
