

Construction of an $M_3L_2A_6$ Cage with Small Windows from a Flexible Tripodal Ligand and $Cu(hfac)_3$

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Supporting Information

ABSTRACT: An $M_3L_2A_6$ cage has been prepared with small windows from a tripodal ligand, **L**, and $Cu(hfac)_2$. Cold spray ionization mass spectrometry of a mixture of **L** and $Cu(hfac)_2$ revealed the formation of a $Cu_3L_2hfac_6$ cage in solution. X-ray crystallography showed that the $Cu_3L_2hfac_6$ cage included neutral molecules such as THF and $CHCl_3$. Furthermore, the six *hfac* anions have been shown to play an important role in holding neutral guest molecules securely in place.

The formation of molecular cages by self-assembly has attracted considerable attention from many researchers,¹ and various tripodal ligands have been reported in the literature in this particular context.² For example, Fujita et al.^{2a} reported that the combination of 1,3,5-tris(4-pyridylmethyl)benzene and $enPd(NO_3)_2$ led to the formation of a cagelike complex, and Kaim et al.^{2b} reported that different combinations of $AgBF_4$ or CuI and 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene led to the formation of metallocages containing BF_4^- or CuI_3^- anions in their cavity. In these cases, the counteranions of the metal salts (e.g., NO_3^- , BF_4^- , and I^-) did not participate in the formation of cage structures, indicating that these cages contained large windows through which the anions could readily pass.

Hexafluoroacetylacetonate (*hfac*) salts have been used in a number of studies to form supramolecular systems such as coordination polymers,³ metallomacrocycles,⁴ and clusters.⁵ In these supramolecular structures, the *hfac* anions bind tightly to the metal cations, and $Cu(hfac)_2$ is about 280 \AA^3 .⁶ On the basis of these observations, it was envisaged that the combination of *hfac* salts with a tripodal ligand would lead to the formation of a new type of cage with small windows, where the *hfac* anions would effectively form a barrier, preventing escape of the guest molecules and leading to enhanced binding properties (Figure 1a). Herein, we report the combination of a flexible tripodal ligand and $Cu(hfac)_2$ to construct a new type of three-dimensional cage structure with small windows.

A new tripodal ligand (Figure 1b, **L**) was prepared in 45% yield by the reaction of tris(4-bromobenzyl)amine (**2**) with 3-pyridineboronic acid.

Single crystals of the $Cu(hfac)_2$ complex with **L** were obtained as follows. A solution of **L** in $CHCl_3$ was mixed with a solution of $Cu(hfac)_2$ in CH_3OH to give a green powder, which was recrystallized from a mixture of tetrahydrofuran (THF)/hexane (1:1, v/v) to give single crystals of the desired material.

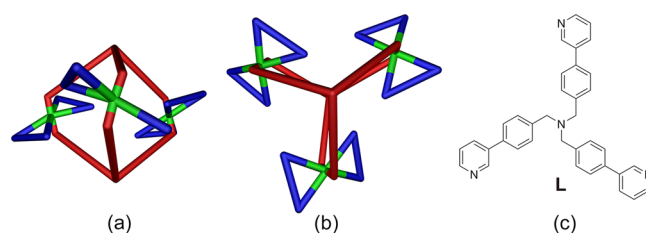


Figure 1. Side view (a) and top view (b) of a cage structure with small windows and our new flexible tripodal ligand (c). Red, green, and blue tubes mean **L**, Cu^{2+} , and *hfac* anions, respectively.

Recrystallization of the green powder from a mixture of $CHCl_3$ and hexane (1:1, v/v) gave the $[CHCl_3 \cdot Cu_3L_2hfac_6]$ complex. The X-ray crystal structure of the $[CHCl_3 \cdot Cu_3L_2hfac_6]$ complex is shown in Figure S3 in the Supporting Information (SI).

Elemental analysis of the complex indicated that it was 2:3 **L**/ $Cu(hfac)_2$. Figure 2 shows the crystal structure of the $Cu(hfac)_2$ complex with **L**. The complex formed an $M_3L_2A_6$ -type cage containing two THF molecules in its cavity. Each Cu^{2+} ion is six-coordinated by four O atoms of the *hfac* anions and two N atoms of the pyridines of **L**. The four O atoms and the Cu^{2+} ion lie in the same plane, and the N–Cu–N angles are in the range 174.7 – 178.5° . The mean N(pyridine)–Cu distance was found to be 2.000 \AA and therefore comparable to that of a pyridine/ $Cu(hfac)_2$ complex.^{3k} The void volume of the $Cu_3L_2hfac_6$ cage was estimated to be 285 \AA^3 .⁷ Lindoy et al.⁸ reported that the two di- β -diketone ligands 1,10-(1,4-phenylene)dihexane-1,3-dione (**L**¹) and 1,1'-biphenyl-4,4'-diylbis(4,4,4-trifluorobutane-1,3-dione) (**L**²) formed large neutral open-faced Fe_4L_6 tetrahedral cage complexes. The $Fe_4L_1^6$ cage had a small cavity (void volume = 174 \AA^3), whereas the $Fe_4L_2^6$ cage had a larger cavity (void volume = 844 \AA^3). The $Fe_4L_1^6$ and $Fe_4L_2^6$ cages contained one and four THF molecules, respectively. It is therefore important to note that the $Cu_3L_2hfac_6$ cage with a small void volume (285 \AA^3) and small windows held on tightly to two molecules of THF (total 163.5 \AA^3)⁹ using its ligand framework and the six *hfac* anions (Figure 2b). Two atropisomers (Δ and Λ forms) existed for the conformation of **L** (Figure 2c), and the $[2THF \cdot Cu_3L_2hfac_6]$ complex existed in its racemic form in the solid state.

The $[2THF \cdot Cu_3L_2hfac_6]$ complex was subjected to thermogravimetric–differential thermal analysis (TG-DTA). As shown in Figure 3, the weight losses at 93 and 176°C were 2.7 and 5.5% ,

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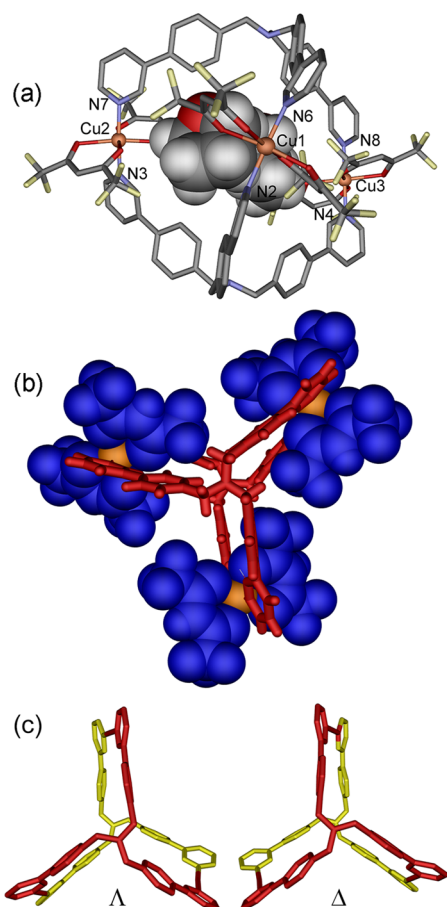


Figure 2. Side view (a), top view without the THF molecules (b), and atropisomers without the THF molecules and hfac anions (c) of the $[2\text{THFCCu}_3\text{L}_2\text{hfac}_6]$ complex. The hfac anions are colored blue in part b.

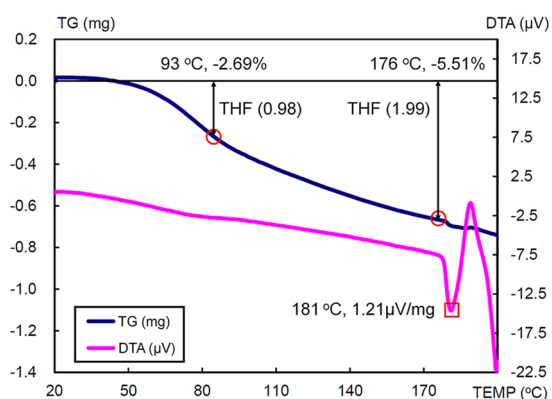


Figure 3. TG-DTA of the $[2\text{THFCCu}_3\text{L}_2\text{hfac}_6]$ complex.

respectively. These weight losses were attributed to the sequential loss of two molecules of THF (0.98 and 1.01 molecules in the first and second steps, respectively). TG-DTA also indicated that the $\text{Cu}_3\text{L}_2\text{hfac}_6$ cage retained some of its THF molecules up to a temperature of 176 °C. Ananchenko et al.¹⁰ reported that a capsule composed of two molecules of *p*-alkanoylcalix[4]arene encapsulates four molecules of THF in its cavity. In this case, all of the THF molecules remained within the inclusion complex until the temperature reached 140 °C. Beyond this temperature, the THF molecules left the complex. This

example indicated that the $\text{Cu}_3\text{L}_2\text{hfac}_6$ cage was holding onto its THF molecules tightly.

Cold spray ionization mass spectrometry (CSI-MS) was used to determine whether L formed a cage structure with $\text{Cu}(\text{hfac})_2$ in a solution at 298 K, using a mixture of THF and CH_3OH (1:1, v/v). As shown in Figure 4, a base peak corresponding to $[\text{L} +$

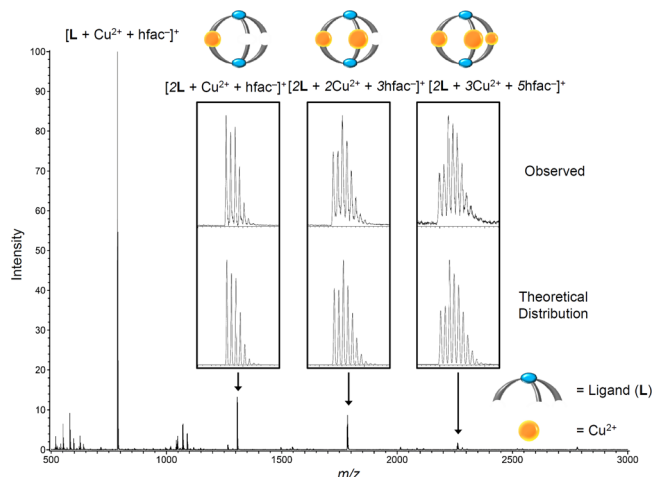


Figure 4. CSI-MS of the $\text{Cu}_3\text{L}_2\text{hfac}_6$ cage in THF/ CH_3OH (1:1, v/v) at 298 K. The hfac anions are omitted in the cage models.

$\text{Cu}^{2+} + \text{hfac}^{-}]^+$ was observed at m/z 788. Fragment-ion peaks corresponding to $[2\text{L} + \text{Cu}^{2+} + \text{hfac}^{-}]^+$ and $[2\text{L} + 2\text{Cu}^{2+} + 3\text{hfac}^{-}]^+$ were also observed at m/z 1306 and 1785, respectively. Furthermore, a fragment-ion peak corresponding to $[2\text{L} + 3\text{Cu}^{2+} + 5\text{hfac}^{-}]^+$ was observed at m/z 2262. These CSI-MS data strongly supported the idea that the $\text{Cu}(\text{hfac})_2$ complex with L formed a cage structure in solution. These fragment-ion peaks, however, did not include THF molecules because the lack of hfac anions effectively opened the cage windows and allowed the THF molecules to readily escape from the complex.

The binding constant between L and $\text{Cu}(\text{hfac})_2$ was estimated by $\text{Cu}(\text{hfac})_2$ -induced titration experiments using UV-vis in CH_3OH (Figure 5 and the associated multimedia file in the SI). $\log K$ for the 2:3 $2/\text{Cu}(\text{hfac})_2$ complex in CH_3OH was estimated to be 18.1 based on nonlinear least-squares curve fitting.¹¹ Walker and Li¹² reported that $\log \beta_2$ for a 2:1 4-methylpyridine/ $\text{Cu}(\text{hfac})_2$ complex was much less than that of the current complex at 2.7. The lower $\log \beta_2$ value of the 4-methylpyridine/

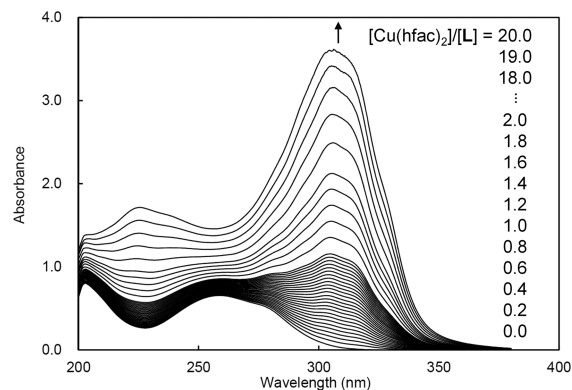


Figure 5. Changes in the UV-vis spectra of L upon the addition of $\text{Cu}(\text{hfac})_2$ in CH_3OH .

Cu(hfac)₂ system suggested that the Cu₃L₂hfac₆ cage would be stabilized by the synergistic coordination of six pyridines.

In conclusion, we have demonstrated that the new tripodal ligand, L, forms an M₃L₂A₆ cage with Cu(hfac)₂. This is the first reported example of a cage compound with small windows composed of hfac anions. TG-DTA indicated that the hfac anions played an important role in holding the guest molecules tightly. The application of this system to enhance the circular dichroism (CD) intensity of chiral molecules with small CD molecular ellipticity is now underway in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

Crystallographic data in CIF format, ¹H and ¹³C NMR spectra of compounds, conditions for the titration experiments, X-ray structure of the [CHCl₃·Cu₃L₂hfac₆] complex, crystal data, and UV-vis spectra and speciation analyses, which are also available as a multimedia file (habata.avi). 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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