

A neutral self-assembled coordination cage organized for inclusion of aromatic guests†

Amir H. Mahmoudkhani, Adrien P. Côté and George K. H. Shimizu*

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada.
E-mail: gshimizu@ucalgary.ca; Fax: 1 403 289 9488; Tel: 1 403 220 5347

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Jahn–Teller distorted Cu^{2+} centers, axially ligated by RSO_3^- groups, act as spacers to form a cage molecule with ligands organized at a distance well-suited for inclusion of aromatics.

Cage and container molecules remain a fundamental interest in the realm of supramolecular chemistry owing both to the application of such assemblies as selective hosts and molecular reaction vessels.¹ A wide range of hosts have been reported employing both coordinate covalent bonding as the primary assembly tool as well as purely non-covalent interactions. Specifically for uptake of aromatic molecules,² an efficient arrangement for the host would place two aromatic rings roughly 7.5 Å apart to enable entrapment of the guest *via* π interactions. Several groups have found effective spacers to orient host aromatic units at or near this desirable value. From a purely organic standpoint, spacing two bipyridinium units with *p*-xylene gives the preorganized “blue box” pioneered by Stoddart *et al.*³ An inorganic coordination counterpart to this structure could be envisioned with 4,4'-bipyridine, in lieu of the bipyridinium, and a pyrazine, replacing the *p*-xylene and frameworks using these units which absorb aromatics have been reported.⁴ Similarly, a layered structure pillared by coordinated pyridine has been shown to be very selective for aromatic inclusion.⁵ Spacers that offer a ~ 7.5 Å ligand separation and could readily be incorporated into different systems would be valuable in the design of host systems for aromatic molecules.

This work concerns the use of copper(II) and a trisulfonated aromatic ligand to form discrete trimetallic assemblies which are organized to include aromatic guests. The complex, $[\text{Cu}_3\text{L}_2(\text{py})_{12}]$ -pyridine, **1**, where L = the trianion of 1,3,5-tris(4-sulfophenyl)benzene, forms a self-assembled cage where three Cu centers bridge two molecules of L and trap a molecule of pyridine. The desired spacing is obtained by bis-axial coordination of the SO_3^- groups to the Jahn–Teller distorted Cu^{2+} centers. Additional H-bonding interactions augment the stability of the cage considerably. This structure represents the first report of a discrete assembly of any kind sustained exclusively by metal sulfonate interactions.

Ligand L was made by sulfonating triphenylbenzene with chlorosulfonic acid. Complex **1** was synthesized by combining $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and Na_3L in aqueous solution then diffusing in pyridine. Dark blue cube-shaped crystals of **1** were obtained by this method in 4 days in 60% yield. Single crystal X-ray analysis revealed the structure to be that of a self-assembled cage as shown in Fig. 1. The cage is composed of two molecules of L bridged by three Jahn–Teller distorted $[\text{Cu}(\text{py})_4]^{2+}$ units. The pyridine ligands occupy the equatorial sites on the Cu^{2+} ions (Cu–N1 2.023(3), Cu–N2 2.033(3) Å) with the sulfonate oxygen atoms coordinated axially (Cu–O2 2.461(3) Å). This sulfonate coordination anchors the periphery of the two molecules of L at an inter-ligand S–S distance of 7.679 Å. The cage is a neutral species which removes the need for potentially cage-filling counterions. Most coordination cages are cationic but excellent examples of neutral cages are known.⁶

The molecules of L which form the top and bottom of the cage

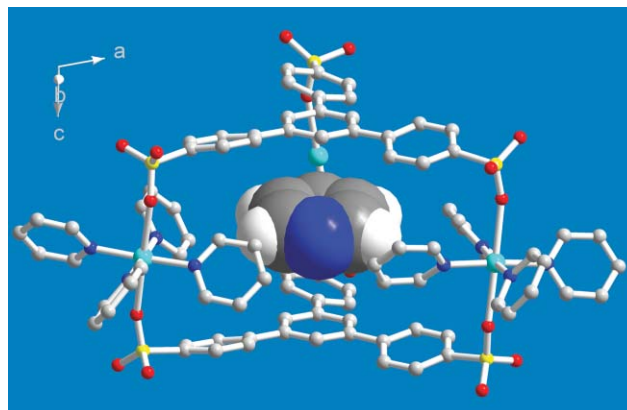


Fig. 1 Single-crystal X-ray structure of the cage formed by three Jahn–Teller distorted Cu^{2+} ions and two molecules of the trisulfonate L. Included pyridine is shown in a space-filling representation. Pyridine ligands on the Cu center at the rear are deleted for clarity.

are perfectly eclipsed as shown in Fig. 2. Trapped between the ligands is a three-fold disordered pyridine molecule. Vertically, the guest pyridine forms weak face-to-face π interactions with the two ligand molecules (mean plane distance = $2 \times 4.059 = 8.118$ Å). Laterally, there are no significant edge-to-face π interactions with the six inward-directed pyridine ligands as the shortest intermolecular C–C distance is > 3.9 Å.

Cu^{2+} is uniquely suited as a spacer for this assembly. With most transition metals, sulfonate anions do not coordinate directly to the metal center. Rather they form second-sphere hydrogen bonded

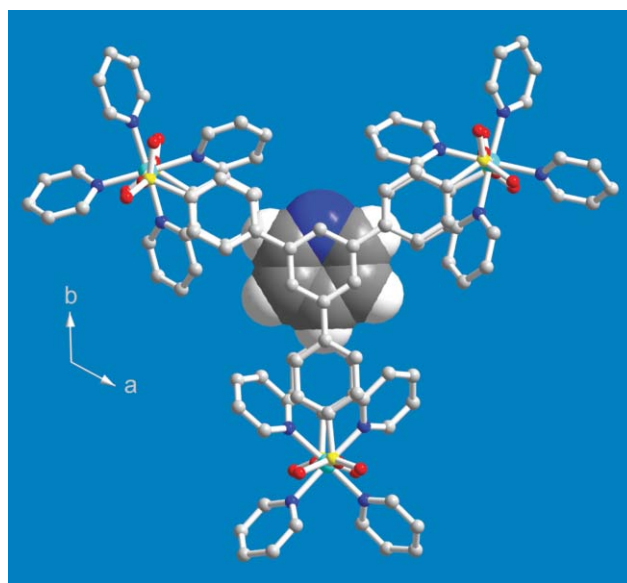


Fig. 2 View onto a self-assembled cage showing the eclipsed trisulfonate ligands and the framing of the cavity by pyridine ligands on the Cu centers. The guest pyridine is shown in a space-filling representation.

† Electronic supplementary information (ESI) available: Preparation and characterization of L and **1**. See <http://www.rsc.org/suppdata/cc/b4/b412325e/>

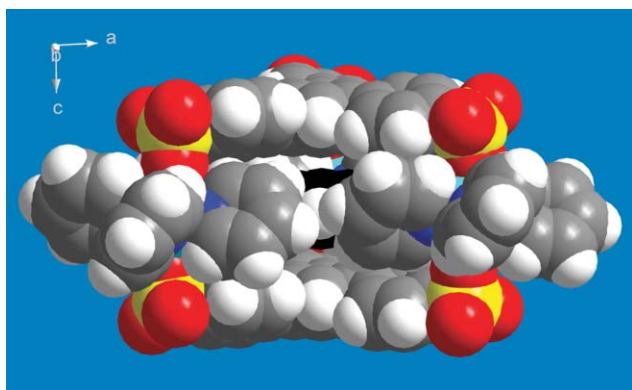


Fig. 3 Space-filling representation of complex **1** which shows the virtual complete encapsulation of the guest (C atoms shown in black). The guest in this cage is found to be inexchangeable.

complexes.⁷ Cai has studied the coordination chemistry of various sulfonate ligands with Cu^{2+} and a frequent feature is ligation by two sulfonate groups to the axial sites in a tetragonally distorted complex.⁸ The Jahn–Teller distortion is very important as, with axial ligation to a perfect octahedron, the SO_3 groups, and hence the ligands, would lie 0.8–0.9 Å closer together. This decrease in the interligand distance is more than sufficient to preclude any inclusion of aromatic guests.

The stability of this solid and the exchangeability of the guest in this complex were examined. TGA data revealed stability to 125 °C from which point to 325 °C the pyridine ligands and guest are lost in three steps. More interesting is the resistance of the guest to exchange. After heating crystals of **1** in toluene- d_7 at 100 °C for 20 h, the ^1H NMR spectrum showed no trace of either pyridine or ligand **L** in solution. Fig. 3 shows a space filling model of the structure which clearly demonstrates the degree to which the guest pyridine is contained.

The steric encapsulation of the guest on its own seems insufficient to explain the inertness of the guest to exchange when, at the elevated temperatures, the Cu–pyridine bonds would be expected to be more labile. Indeed, additional stabilizing interactions exist between the acidic α -hydrogen atoms of the coordinated pyridine molecules and the axially ligated sulfonate oxygen atom ($\text{O}\cdots\text{H}$ 2.567–2.940 Å, $\text{C}\cdots\text{H}\cdots\text{O}$ 104.6–119.6°) as shown in Fig. 4. While the individual interactions are not so strong, two H-bonding interactions from each pyridine molecule function cooperatively with the M–N coordinate bond.

Individual cages do not align in the extended solid. Rather, the packing optimizes C–H \cdots O interactions between the two non-coordinating sulfonate oxygen atoms and the ligated pyridine molecules of adjacent cages ($\text{H}\cdots\text{O}$ 2.320–2.378 Å, $\text{C}\cdots\text{H}\cdots\text{O}$ 160.9–174.2°). Twelve such interactions are formed between each cage and its neighbors. Undoubtedly, these interactions play a role in augmenting the stability of both the coordinated, and hence guest, pyridine molecules.

As mentioned, the search for suitable spacers for cages suitable for aromatic inclusion is ongoing. A versatile spacer applicable to different ligands would be of considerable interest. In this regard, the coupling of $[\text{Cu}(\text{py})_4]^{2+}$ units with sulfonate ligands is promising as one can envision readily changing the size and symmetry of the polysulfonated organic core to afford larger cages of different size while retaining an interligand separation suited for aromatic molecules. Larger cages could afford exchangeable guest species as the pyridine ligands would be further dispersed. Work along this vein as well as varying the peripheral pyridine ligands is currently in progress.

Notes and references

‡ Crystal data for **1**, $[\{\text{Cu}(\text{py})_4\}_2\text{L}_2]\cdot\text{pyridine}$: $\text{C}_{113}\text{H}_{95}\text{Cu}_3\text{N}_{13}\text{O}_{18}\text{S}_6$, $M = 2306.00$, trigonal, space group $R\bar{3}c$ (no. 167), $a = b = 20.324(5)$,

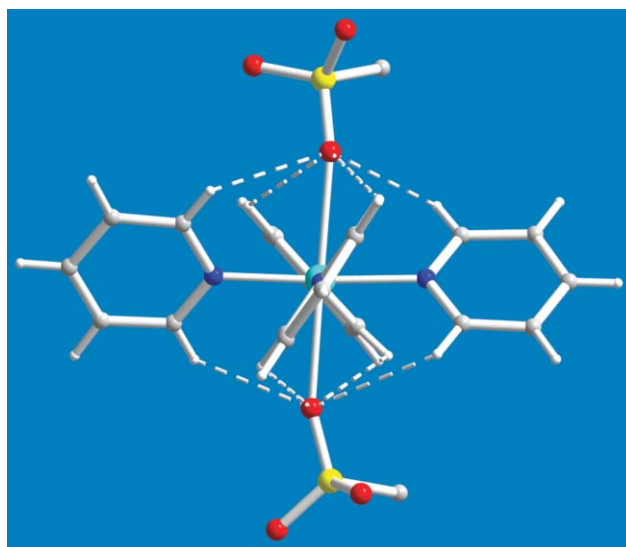


Fig. 4 The H-bond interactions formed between the acidic α -hydrogen atoms of the pyridine ligands and the axially coordinated sulfonate O atoms. Two pyridine ligands are directed in and out of the page.

$c = 47.623(5)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 17036(6)$ Å³, $Z = 6$, $D_c = 1.349$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.737$ mm⁻¹, crystal size 0.22 × 0.22 × 0.20 mm. Data were collected on a Nonius Kappa CCD diffractometer using Mo-K α radiation. A total of 6602 reflections ($1.44 < \theta < 25.35^\circ$) were processed of which 3462 were unique and significant with $I_{\text{net}} > 2\sigma(I_{\text{net}})$. Structure solution and refinement were carried out with the SHELXS-97 software package, release 5.1.⁹ Final residuals for $I_{\text{net}} > 2\sigma(I_{\text{net}})$ were $R = 0.1090$ and $R_w = 0.3113$ (GoF = 1.170) for 226 parameters. CCDC 247011. See <http://www.rsc.org/suppdata/cc/b4/b412325e/> for crystallographic data in .cif or other electronic format.

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