(5.0 mL) were added, the purple solution was heated at 80 °C for 24 h. The solution was allowed to cool to room temperature, and then diluted with water (10 mL). The solution was poured into acetone (300 mL) to precipitate a solid, which was collected by filtration, and redissolved in water (50 mL). After the solution was neutralized with triethylamine, the solvent was removed under reduced pressure. The remaining solid was suspended in CH_3CN (20 mL) and the suspension filtered. The filter cake contains CB*[5] as a major product whereas the filtrate contains mostly CB*[6]. Recrystallization of the crude products from water produced colorless crystalline products CB*[5] (356.7 mg, 16 %) and CB*[6] (47.8 mg, 2 %). CB*[5]: ^1H NMR (300 MHz, D_2O): $\delta = 5.64$ (d, $J = 15.6$ Hz, 10 H), 4.33 (d, $J = 15.8$ Hz, 10 H), 2.20 (s, 20 H), 1.46 (s, 20 H); ^{13}C NMR (75 MHz, D_2O): $\delta = 156.33$, 76.45, 43.51, 23.56, 14.0; IR (KBr): $\tilde{\nu}_{CO}$ 1745 cm^{-1}; MS (ESI): m/z (%): 1123.5 (100) $[M+Na]^+$. CB*[6]: ^1H NMR (300 MHz, D_2O): $\delta = 5.73$ (d, $J = 15.9$ Hz, 12 H), 4.32 (d, $J = 16.0$ Hz, 12 H), 2.26 (s, 24 H), 1.49 (s, 24 H); ^{13}C NMR (75 MHz, D_2O): $\delta = 156.43$, 76.51, 44.1, 23.37, 14.07; IR (KBr): $\tilde{\nu}_{CO}$ 1734 cm^{-1}; MS (ESI): m/z (%): 1361.6 (100) $[M+Na+H_2O]^+$. Satisfactory elemental analyses were obtained for CB*[5] and CB*[6].

Received: June 12, 2001
Revised: September 10, 2001 [Z 17272]

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[8] Crystals of CB*[*n*] ($n = 5, 6$) suitable for X-ray work were grown from aqueous solution in a refrigerator. Crystal data of CB*[5]: $[(C_{50}H_{60}N_{20}O_{10}) \cdot 25\,H_2O]$, $M_r = 1551.58$, triclinic, $P\bar{1}$ (No. 2), $a = 15.0886(2)$, $b = 15.7065(1)$, $c = 17.8902(3)$ Å, $\alpha = 101.802(1)$, $\beta = 109.337(1)$, $\gamma = 108.471(1)°$, $V = 3560.49(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.447$ g cm^{-3}, $T = 223$ K, $\mu = 1.22$ cm^{-1}. Siemens SMART diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), all non-hydrogen atoms were refined anisotropically (SHELXL-93). Final refinement on F^2 with all 10 651 reflections and 955 variables converged to $R1\,(>2\sigma(I)) = 0.0925$, $wR2$(all data) $= 0.2557$, and GOF $= 1.094$. Crystal data of CB*[6]: $[(C_{60}H_{72}N_{24}O_{12}) \cdot 18\,H_2O]$, $M_r = 1645.70$, $P\bar{1}$ (No. 2), $a = 12.7505(1)$, $b = 15.1302(3)$, $c = 19.3353(4)$ Å, $\alpha = 91.2977(8)$, $\beta = 92.8870(8)$, $\gamma = 92.9115(1)°$, $V = 3719.39(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.469$ g cm^{-3}, $T = 223$ K, $\mu = 1.18$ cm^{-1}. Final refinement on F^2 with all 11 157 reflections and 1045 variables converged to $R1\,(I > 2\sigma(I)) = 0.0826$, $wR2$(all data) $= 0.2235$, and GOF $= 1.126$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164887 (CB*[5]), and -164888 (CB*[6]). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] The solubility of CB*[*n*] ($n = 5, 6$) in a solvent was determined by ^1H NMR spectroscopy with an internal standard (see Supporting Information). Solubility (mol L^{-1}) of CB*[5] (CB*[6]): 2.6×10^{-1} (1.7×10^{-1}) in D_2O, 3.1×10^{-2} (4.3×10^{-2}) in [D$_4$]methanol, 1.8×10^{-2} (3.9×10^{-2}) in [D$_6$]DMSO, 1.3×10^{-3} (6.5×10^{-4}) in [D$_6$]ethanol, 2.5×10^{-3} (3.4×10^{-3}) in [D$_7$]DMF, 6.7×10^{-4} (2.1×10^{-3}) in [D$_3$]acetonitrile.

[10] $\Delta H_1 = -1.49 \pm 0.01$ kcal mol^{-1}, $\Delta S_1 = 13.89$ cal mol^{-1} K^{-1}; $\Delta H_2 = -1.49 \pm 0.04$ kcal mol^{-1}, $\Delta S_2 = 4.98$ cal mol^{-1} K^{-1}.

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Self-Assembly of a Mixed-Valence Copper(II)/Copper(III) Dithiocarbamate Catenane[**]

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During the past few decades the design and high-yielding syntheses of interlocked macrocyclic molecules, the catenanes,[1] have evolved mainly as a result of the elegant and inspirational transition metal and organic templated synthetic

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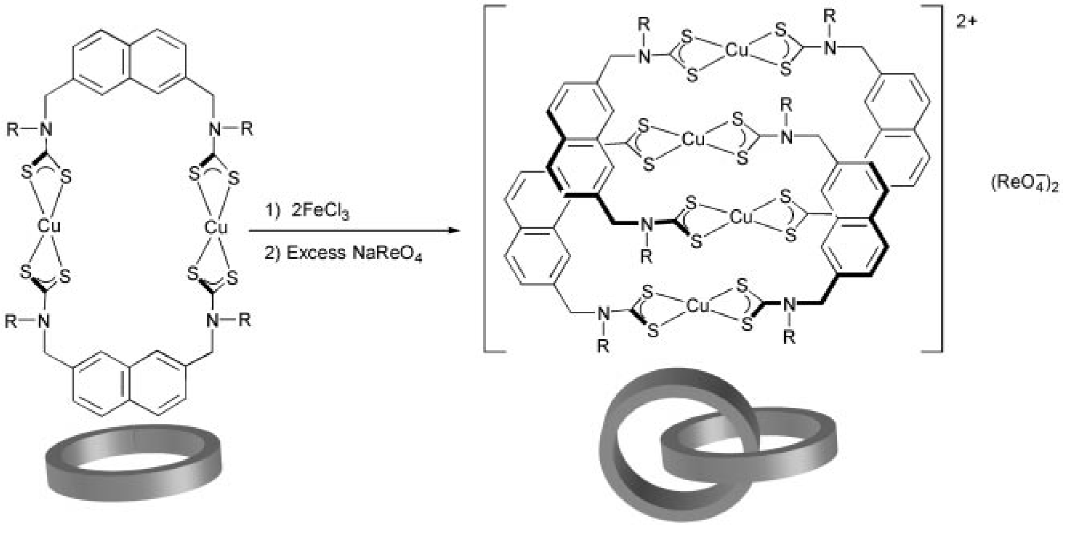
[**] We thank the EPSRC for a postdoctoral fellowship (O.D.F.) and the EPSRC and University of Reading for funds for the crystallographic image plate system.

strategies pioneered by the research groups of Sauvage,[2] Stoddart,[3] and Fujita.[4] In particular, Fujita et al. have demonstrated the quantitative metal-directed self-assembly of [2]catenanes from preformed molecular boxes by using the lability of the palladium(II)/platinum(II) – pyridine coordinate bond in combination with efficient hydrophobic aromatic stacking interactions in aqueous media.[5]

We recently reported on the utility of the dithiocarbamate (dtc) moiety as a coordinating group in the zinc(II), cadmium(II), and copper(II) transition metal directed construction of nanosized resorcarene-based assemblies[6] and macrocycles.[7] The incorporation of redox-active metal – ligand units into the macrocyclic framework of a host introduces the possibility of using the host as an electrochemical sensor for guest substrates,[8] and indeed we have demonstrated the use of the copper(II)/(III) – dtc redox couple as an electrochemical anion-sensing unit in self-assembled dinuclear copper(II) dithiocarbamate macrocycles.[7] The presence of such redox-active metal – ligand moieties also provides an opportunity for switching the lability or inertness of the metal – ligand coordinate bond through a controlled chemical or electrochemically induced redox reaction. We report here the serendipitous synthesis of a novel mixed-valence tetranuclear copper(II)/copper(III) dithiocarbamate [2]catenane by the selective oxidation of two preformed copper(II) dithiocarbamate macrocycles in remarkably high yield.

The addition of two equivalents of iron(III) chloride in MeCN to a solution of the naphthyl-spaced dinuclear copper(II) dithiocarbamate macrocycle (**1a**)[7] in CH_2Cl_2:MeCN (12:1) gave a reaction mixture that was allowed to stand for 12 h at room temperature open to the atmosphere. The addition of excess sodium perrhenate produced crystals of a novel catenane suitable for X-ray structural determination (Scheme 1).



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a: R = butyl

b: R = hexyl

Scheme 1.

The structure[9] contains discrete cations and ReO_4^- ions and that of the tetranuclear copper catenane $(\mathbf{1a})_2^{2+}$ is shown in Figure 1. All four independent copper atoms have four-coordinate square-planar environments and are bonded to four sulfur atoms from two dithiocarbamate ligands. A search of the Cambridge Crystallographic Database shows a clear distinction between Cu^{II}–S and Cu^{III}–S bond lengths in these types of complexes, with mean distances of 2.306 Å (76 examples) and 2.210 Å (36 examples), respectively, although both types of copper centers provide square-planar coordination spheres. The bond lengths found in the present structure do not fall clearly into either category (mean bond lengths: Cu(1): 2.233, Cu(2): 2.258, Cu(3): 2.286, Cu(4): 2.300 Å), although it should be noted that the mean bond length of 2.269 Å is intermediate between the mean values for Cu^{II}–S and Cu^{III}–S bonds. It is likely that there is some disorder between the Cu^{II} and Cu^{III} centers, though it is apparent that Cu(1) and Cu(2) have more Cu^{II} character than Cu(3) and Cu(4). Hence, successive copper atoms in the catenane are alternately Cu^{II} and Cu^{III}.

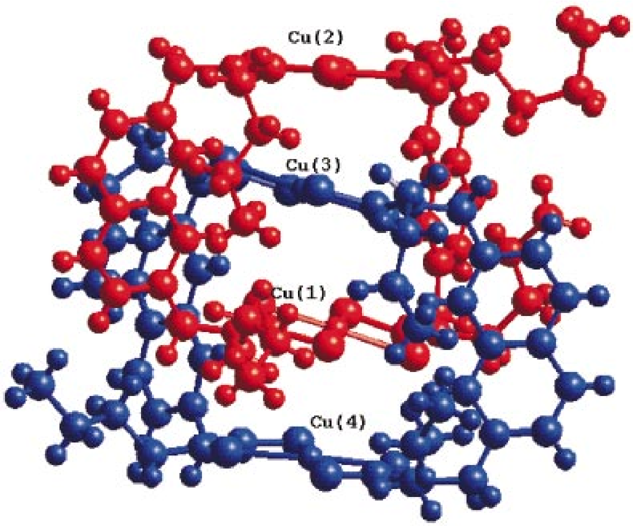

Figure 1. The structure of $(\mathbf{1a})_2^{2+}$ showing the layering of the metal coordination spheres. One link is shown in blue, the other in red.

Although each copper center is four coordinate, there are axial contacts, either intra- or intermolecular, from all four copper atoms to two sulfur atoms in adjacent thiocarbamate ligands; thus the two central copper atoms Cu(1) and Cu(3) in each catenane have two intramolecular Cu ⋯ S contacts in the range 3.34 to 3.36 Å, while the two outer copper atoms Cu(2) and Cu(4) have only one such contact with distances of 3.18 and 3.27 Å. However, these outer atoms also form axial intermolecular contacts of 3.15 and 3.16 Å to sulfur atoms in adjacent catenanes. Indeed inspection of the crystal packing of the [2]catenane reveals a stacking of catenane units along the b direction that is held together through these intermolecular and intramolecular weak Cu⋯S interactions (Figure 2). Successive coordination spheres of the [Cu(dtc)$_2$] units, both intra- and intermolecular, are rotated approximately 90° to each other in the chain along the b direction, thus the N-Cu-Cu-N torsion angles range from 90.2 to 100.8° (Figure 1). The adjacent CuS$_4$ planes within each catenane intersect at angles of 15.4, 16.0, and 15.2°.

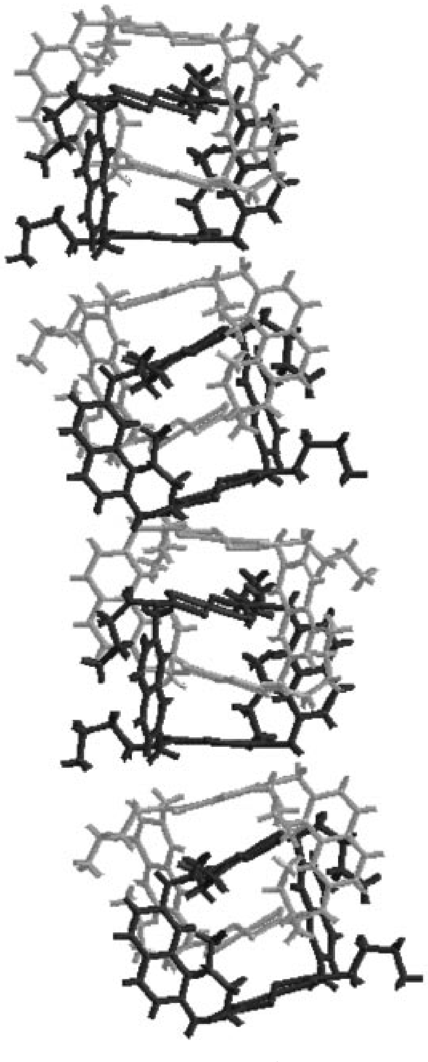

Figure 2. The structure of $(\mathbf{1a})_2^{2+}$ showing the packing of catenanes along the b glide plane. The links are depicted in two shades of gray.

The magnetic susceptibility of **1a** and the catenane was investigated over the temperature range 5–300 K. The magnetic susceptibility of **1a** obeys the Curie Law and exhibits a room temperature magnetic moment of 1.76 B.M., which is consistent with the presence of two non-interacting copper(II) ions. The catenane's magnetic susceptibility data also obeys the Curie Law and displays a room temperature magnetic moment (calculated on the basis of two copper(II) d^9 and two low-spin copper(III) d^8 ions) of 2.09 B.M. per copper(II) center. The magnetic moment of the catenane decreases gradually from 2.09 to 1.86 B.M. over the range 75–300 K. This magnetic susceptibility data is consistent with the catenane's mixed valency of Cu^{II}Cu^{III}Cu^{II}Cu^{III}, and with the copper(II) centers being effectively magnetically isolated at room temperature.[10] The small fall in magnetic moment at lower temperatures is indicative of a weak antiferromagnetic interaction.

Evidence for the existence of the catenane in solution came from electrospray mass spectrometry (ES-MS). Ions corresponding to the dication $\mathbf{1a}^{2+}$ were observed (Figure 3a) following chemical oxidation (using excess NOBF$_4$) of the parent copper(II)–dtc complex. The formation of the catenane was followed by treating a solution of the copper(II) macrocycle in dichloromethane with one equivalent of anhydrous iron(III) chloride, with the solution being allowed to stand (3 h) before being injected into the spectrometer shortly after a small injection of NOBF$_4$. This addition of NOBF$_4$ causes further oxidation of the catenane within the spectrometer and allows for the observation of the trication $(\mathbf{1a})_2^{3+}$ (Figure 3b).[11] Finally, a solution of crystals of $(\mathbf{1})_2(\mathrm{FeCl_4})_2$, synthesized in near quantitative yield, in methanol gave intense ion peaks corresponding to the dication catenanes at *m*/*z*: 1024.4 $(\mathbf{1a})_2^{2+}$ and 1136.3 $(\mathbf{1b})_2^{2+}$ together with weaker ion peaks for the mono-charged catenanes at *m*/*z*: 2048.8 $(\mathbf{1a})_2^{+}$ and 2273.6 $(\mathbf{1b})_2^{+}$ (Figure 3c).

The electrochemical properties of **1a** and the [2]catenane were investigated in CH$_2$Cl$_2$:MeCN (4:1) by using cyclic and square-wave voltammetry with NBu$_4$BF$_4$ as the supporting electrolyte. The catenane exhibits two quasi-reversible oxidation waves at 0.07 and 0.25 V (reference Ag/AgCl) whilst, in contrast, the macrocycle (**1a**) displays a single broad quasi-reversible oxidation wave at 0.19 V which is indicative of overlapping waves.[7] It is noteworthy that the first catenane oxidation occurs at a significantly less anodic potential ($\Delta E =$ 120 mV) than that of the macrocycle. This observation suggests that the stabilization of the copper(III) oxidation state is a direct consequence of the unique topological arrangement of the [2]catenane.

In summary a novel mixed-valence tetranuclear copper(II)/copper(III) dithiocarbamate catenane has been prepared by chemical oxidation of two preformed dinuclear copper(II) dithiocarbamate macrocycles. Structural, magnetic susceptibility, electrospray mass spectrometry, and electrochemical studies all support the tetranuclear catenane dication formulation Cu^{II}Cu^{III}Cu^{II}Cu^{III}. The mechanism of the catenane's formation may be attributed to the kinetic lability of the copper(III) dithiocarbamate oxidation state[12] which enables the preformed dinuclear copper macrocycle to dissociate on oxidation. By virture of favorable copper(II)-dithiocarbamate-copper(III)-dithiocarbamate donor–acceptor charge-transfer effects, self-assembly of interlocked macrocycles can then occur to produce the mixed-valence tetranuclear [2]catenane in near quantitative yield.

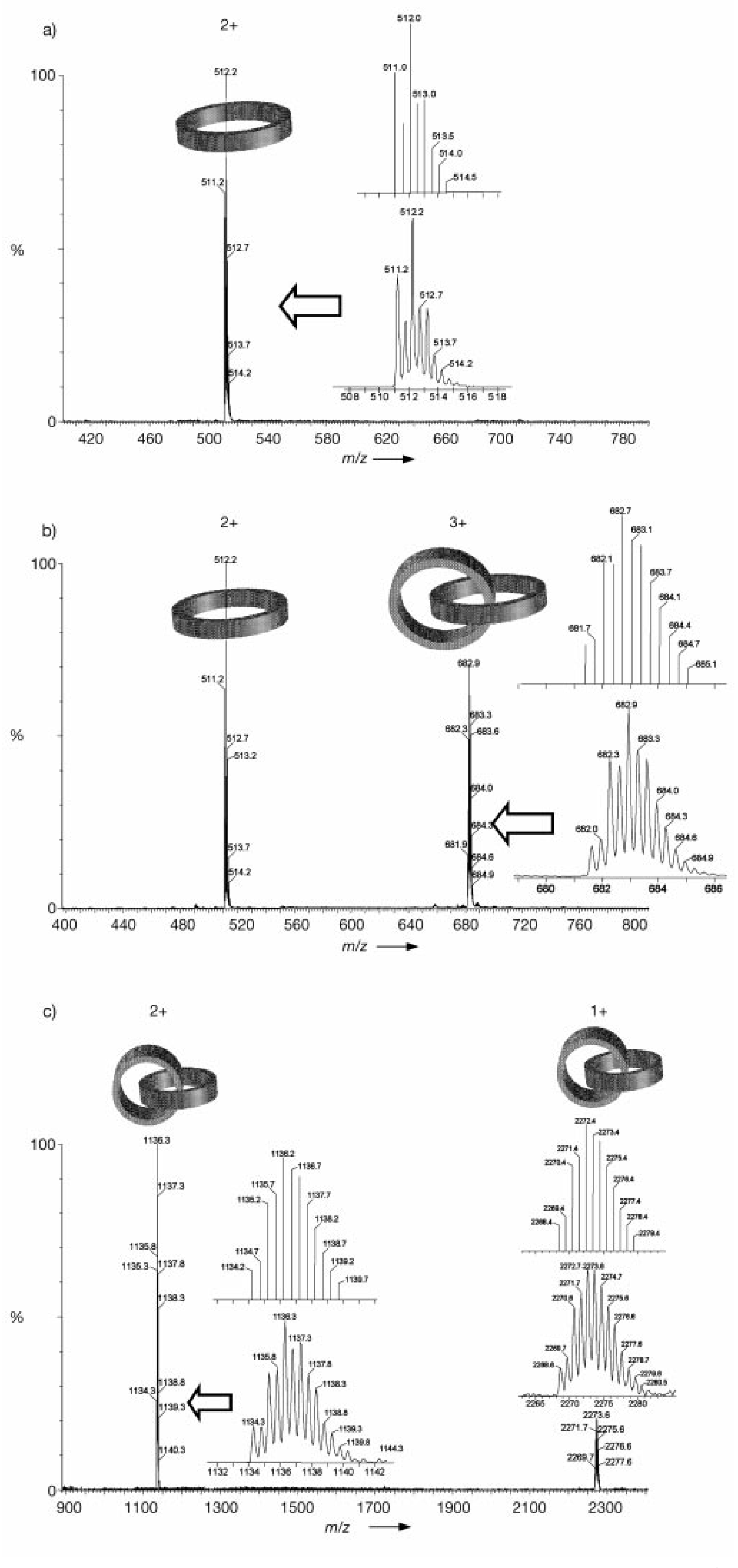

Figure 3. Electrospray mass spectra showing catenane formation. a) Freshly prepared $(\mathbf{1a})^{2+}$. b) Solution of **1a** partially oxidized with $FeCl_3$ after 3 h in the presence of excess $NOBF_4$. c) Crystals of $(\mathbf{1b})_2(FeCl_4)_2$ redissolved in dichloromethane.

Experimental Section

[2]Catenane $(\mathbf{1a})_2(FeCl_4)_2$: A solution of iron (III) chloride (0.049 g, 0.30 mmol) in acetonitrile (3 mL) was added to a solution of **1a**[7] (0.153 g, 0.15 mmol) in dichloromethane (50 mL) and acetonitrile (4 mL). The resulting mixture was allowed to stand at room temperature for 12 h. Removal of the solvent in vacuo and recrystallization from dichloromethane/diethyl ether gave the catenane (0.17 g, 93 %). Elemental analysis calcd for $C_{88}H_{112}N_8S_{16}Cu_4Fe_2Cl_8$: C 43.25, H 4.6, N 4.6 %; found: C 43.3, H 4.5, N 4.8 %. An analogous synthetic procedure was used to prepare $(\mathbf{1b})_2(FeCl_4)_2$ in 94 % yield. Elemental analysis calcd for $C_{104}H_{144}N_8S_{16}Cu_4Fe_2Cl_8$: C 46.8, H 5.4, N 4.2 %; found: C 46.7, H 5.2, N 4.3 %.

Received: July 27, 2001 [Z17618]

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[9] Crystal structure data for $(\mathbf{1a})_2(\mathrm{ReO_4})_2$: $\mathrm{C_{88}H_{112}Cu_4N_8O_8Re_2S_{16}}$, $M_r = 2549.37$, monoclinic, space group $P2_1/c$, $a = 16.096(23)$, $b = 26.620(35)$, $c = 32.039(41)$ Å, $\beta = 90.89(1)°$, $V = 13726$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.234$ gm cm^{-3}. Data were measured on a Marresearch Image Plate system using $\mathrm{Mo_{K\alpha}}$ radiation with the crystal positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 10 mins. 12787 reflections were measured to give 8069 independent reflections (R(int) = 0.0327). Data analysis was carried out with the XDS program.[13] The structure was solved using direct methods with the SHELX86 program.[14] The Re, Cu, and S atoms were refined with anisotropic thermal parameters. The $\mathrm{ReO_4}$ anions had high thermal motion, but no disordered model proved satisfactory. The crystal was twinned (hkl, $hk-l$) with a refined factor of 0.23(2). An absorption correction was introduced using DIFABS.[15] Distance and thermal constraints were used particularly for the alkyl chains. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using SHELXL.[16] The final R values were $R1 = 0.1094$ and $wR2 = 0.3018$ for 4572 data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166825. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] The observation of a room temperature magnetic moment a little higher than that usually observed for a free copper(II) ion (1.7–1.9 B.M.) may be attributed to either a small quantity of $\mathrm{FeCl_4^-}$ co-crystallizing and occupying $\mathrm{ReO_4^-}$ sites in the unit cell or incomplete oxidation of the catenane.

[11] We chose to follow the emergence of the tricationic peak because ions arising from the dication catenane (for example, $(\mathbf{1a})_2^{2+}$) overlap with the monocation of the ring (for example, $(\mathbf{1a})^+$), and similarly, the tetracation of the catenane (for example, $(\mathbf{1a})_2^{4+}$) overlaps with the signal for the dication of the ring (for example, $(\mathbf{1a})^{2+}$).

[12] Evidence for the lability of the copper(III) oxidation state in the dithiocarbamate complex comes from the mixing of simple copper(III) alkyldithiocarbamates which leads to global exchange of the alkyldithiocarbamate ligands, as evidenced by electrospray mass spectrometry, see A. M. Bond, R. Colton, A. D. Agostino, J. Harvey, J. C. Traeger, *Inorg. Chem.* **1993**, *32*, 3952.

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Artificial Enzymes Formed through Directed Assembly of Molecular Square Encapsulated Epoxidation Catalysts[**]

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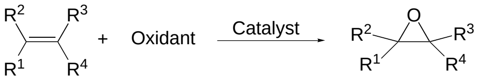
SonBinh T. Nguyen,[*] and Joseph T. Hupp[*]

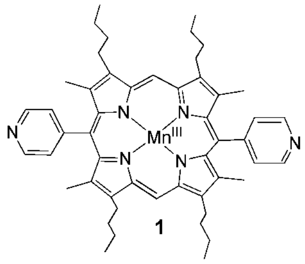
Enzymes are exquisite catalysts for chemical and biochemical reactions: They typically display excellent stability and are highly selective both with respect to the substrates used and the products produced. Most enzymes are comprised of a highly potent catalytic center and a surrounding protein superstructure. In contrast to many, or most man-made, catalysts, naturally occurring enzymes tend to rely upon the superstructure, rather than the catalytic site itself, to achieve substrate selectivity. In addition, the superstructure serves to isolate the catalytic center from other reactive centers, thereby enhancing the center's stability and extending its functional lifetime. Here we describe the artificial enzyme-like induction of stability and selectivity for a simple epoxidation catalyst by a supramolecular coordination chemistry approach. We further show that the selectivity is tailorable through the supramolecular approach. The tailorability permits, in principle, the rapid and systematic optimization of catalytic selectivity for specific substrates.

To demonstrate the utility of the encapsulation concept we targeted the epoxidation of olefins [Eq. (1)] because of its relevancy in biooxidation.[1] We stress that our goal here is to demonstrate the utility of directed supramolecular complex formation in manipulating the properties of conventional catalysts rather than to create a competitive analogue of existing epoxidation catalysts.



(1)

The baseline for comparing catalyst stability was established by using **1**



1

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[**] This work was supported by the National Science Foundation's Partnership in Nanotechnology initiative (NSF grant CHE-9811334) as well as by the EMSI program of the National Science Foundation and the Department of Energy (NSF grant CHE-9810378) at the Northwestern University Institute for Environmental Catalysis. S.T.N. thanks the Alfred P. Sloan Foundation, the Dreyfus Foundation, the DuPont Company, the Beckman Foundation, and the Packard Foundation for support.

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