

Helicate Extension as a Route to Molecular Wires

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Dedicated to Professor Jeremy K. M. Sanders on the occasion of his 60th birthday

Abstract: We describe the preparation of a helicate containing four closely spaced, linearly arrayed copper(I) ions. This product may be prepared either directly by mixing copper(I) with a set of precursor amine and aldehyde sub-components, or indirectly through the dimerization of a dicopper(I) helicate upon addition of 1,2-phenylenediamine. A notable feature of this heli-

cate is that its length is not limited by the lengths of its precursor sub-components: each of the two ligands wrapped around the four copper(I) centers contains one diamine, two dialdehyde, and

two monoamine residues. This work thus paves the way for the preparation of longer oligo- and polymeric structures. DFT calculations and electrochemical measurements indicate a high degree of electronic delocalization among the metal ions forming the cores of the structures described herein, which may therefore be described as “molecular wires”.

Keywords: conducting materials · coordination chemistry · dynamic covalent chemistry · self-assembly

Introduction

The study of infinite linear one-dimensional chains of metal ions,^[1] starting with the partially oxidized tetracyanoplatinate polymers known as Krogmann salts,^[2] has long been of interest in the context of conductive molecular wires.^[3,4] These chains conduct electricity through the delocalization of electrons between linearly arrayed metal centers, but have escaped technological utility because they are neither ductile, like metal wires, nor can conducting fibers be generated from solution or the melt, as with many polymers. More recently, oligomeric chains of metal atoms sandwiched between parallel ligand strands have been investigated as potential molecular wires.^[5] These are soluble in many cases, but their lengths are necessarily fixed by the lengths of the ligand strands.

Herein we demonstrate a self-assembly process for generating chains of copper(I) ions surrounded by helical ligand strands the lengths of which are not limited by the lengths of the precursor sub-components. The ligand strands contain copper-bound imine (C=N) linkages that are generated from diamine and dialdehyde sub-components^[6] by metal-ion templation.^[7] A pair of ligands twist around a linear array of copper(I) template ions in a double-helical fashion.^[8] This report details the full characterization of a structure containing four copper ions; longer arrays also appear to have been generated, although their negligible solubility presented limited opportunities for characterization. Density-functional

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200800503>. It contains electrochemical data for **1** and **2**, the ¹H NMR spectrum of **2**, predicted TD B3LYP vertical excitation energies and oscillator strengths for the electronic transitions of ¹**2a**⁺⁺, and Cartesian coordinates for all computed species.

calculations and electrochemical measurements indicate that the highest-energy electrons of our four-copper chain are delocalized across all four copper ions, which suggests that previous reports^[9,10] of electronic delocalization between partially oxidized pairs of copper ions (Cu_2^{3+} centers) are likely to form the basis of a more general class of electronically delocalized $\text{Cu}_n^{[n+1]+}$ chains. Such structures may thus be of use as electrically conductive materials.

Results and Discussion

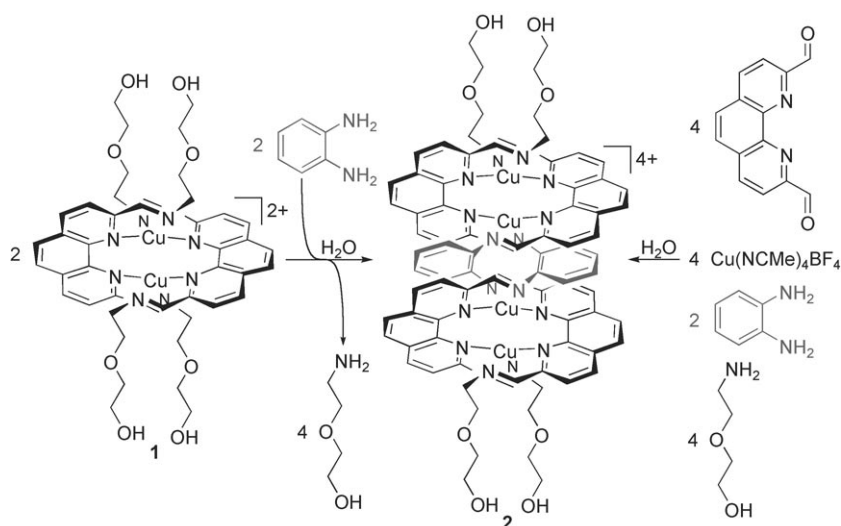
The reaction between equimolar amounts of dicopper double-helicate^[11] **1**^[12] and 1,2-diaminobenzene gave tetracopper double-helicate **2** in 54% yield (Scheme 1, left). This product was also directly accessible in 27% yield by subcomponent self-assembly^[6] starting from the compounds shown in Scheme 1, right. The identity of **2** was confirmed by NMR spectroscopy, electrospray mass spectrometry, and X-ray crystallography (see below).

Diamines and dialdehydes are known to come together with metal ions to form metal-templated macrocycles,^[7,13,14] as shown in Scheme 2a.^[15] Two factors allowed us to avoid

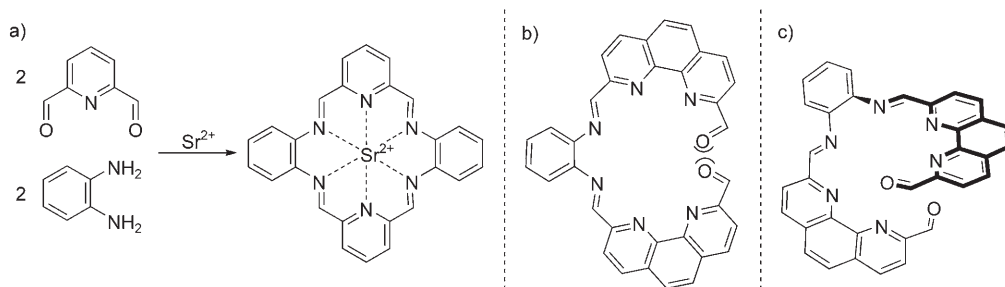
this outcome during the formation of **2**. First, our chosen diamine–dialdehyde pair cannot readily form an unstrained cycle. An entirely flat, conjugated product would result in the eclipse of two formyl groups (Scheme 2b), straining the bond angles of such a product away from their preferred value of around 120° . Models suggest that the cyclization of these two formyl groups with a single bridging diaminobenzene would result in a highly strained buckled or saddle-shaped product. In contrast, a helical conformation (Scheme 2c) could avoid much of this strain. The second factor, the preference of copper(I) ions to adopt a tetrahedral coordination geometry, would also reinforce the helical configuration shown in Scheme 2c. Two such helical ligands, capped with monoamine residues, thread neatly around four pseudotetrahedral copper ions in the structure of **2** (Figure 1), minimizing the strain of the system. The geometries and modes of linking of our system's subcomponents thus provide a program^[16] for the self-assembly process to follow,^[14,17] which selects a linear array of copper(I) ions surrounded by two helical polyimine ligands as the product.

In addition to product **2**, both of the self-assembly reactions of Scheme 1 resulted in the precipitation of a brown material; free 2-(2-aminoethoxy)ethanol was also observed in solution even when the correct stoichiometry of subcomponents was employed (Scheme 1, right). Elemental analysis of the insoluble brown product was broadly consistent with a poly- or oligomeric material with a repeat unit of two diaminobenzene and two diformylphenanthroline residues together with two copper(I) ions. Further characterization of this material was hampered by its lack of solubility in all solvents tested.

Between the insoluble coproduct, 2-(2-aminoethoxy)ethanol, and **2**, all starting materials appear to be accounted for. No evidence of free copper(I) or copper(II) was ob-



Scheme 1. Preparation of tetracopper(I) double-helicate **2** either through the reaction of dicopper double-helicate **1** with 1,2-diaminobenzene (left) or through the self-assembly of subcomponents (right)



Scheme 2. a) The strontium-templated^[7] hexaazamacrocycle reported by Bell et al.^[15] b) Steric clash should prevent the formation of a similar planar macrocycle from the subcomponents of Scheme 1; the adoption of a helical conformation (c) avoids this strain.

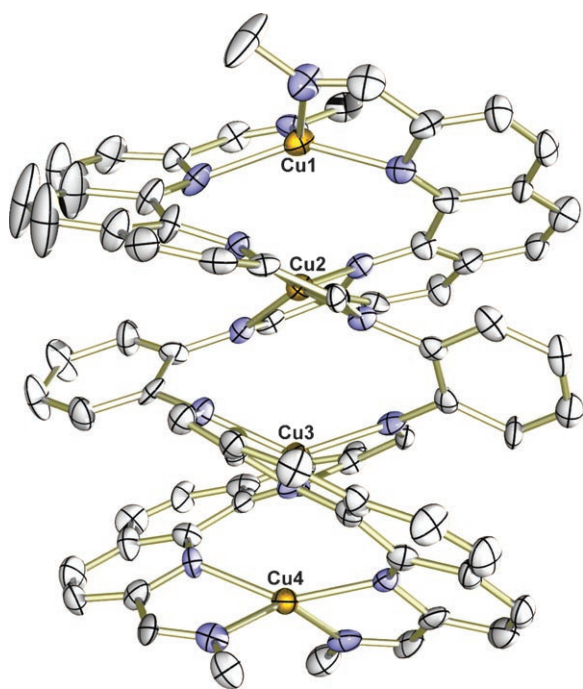


Figure 1. ORTEP^[24] view of **2**; the alkoxy side chains, hydrogen atoms, counterions, and solvent molecules of crystallization are not shown for clarity. Cu1...Cu2=2.768(2), Cu2...Cu3=3.212(2), and Cu3...Cu4=2.800(2) Å.

served by either NMR spectroscopy (broadening or shifting of amine or solvent peaks) or ESIMS (as copper-bound organic molecules), and no evidence was observed of other diaminobenzene- or diformylphenanthroline-containing products.

Examination of the mass balance of this reaction thus suggests that the self-assembly process is robust, generating only **2** and its coproduct, which we infer to be oligomeric in nature. The reactions in Scheme 1 are thus good candidates to generate polymeric materials. Following solubility optimization, mixtures of oligomers might be obtained, with the length distribution depending upon the ratio of capping amine to bridging phenylenediamine present in the starting mixture of subcomponents.^[18]

Crystals of **2** suitable for X-ray diffraction were grown by diffusion of an aqueous solution of **2** into an aqueous solution of barium perchlorate. A view of the structure is shown in Figure 1. Although the distance between the central two copper ions (Cu2 and Cu3 in Figure 1) was longer than the distance between the exterior pairs of copper ions, we reasoned that the distances involved were sufficiently short in all cases to allow for electronic delocalization between the copper centers.^[4]

Electronic structure calculations were thus carried out to investigate the possibility of electronic communication within wirelike structures similar to **2**. To facilitate calculation, the terminal -CH₂CH₂OCH₂CH₂OH chains of **2** were replaced with methyl groups in the computer model; this simplified version is referred to as **2a** below. The geometry

for **2a** was optimized both in the ground state (tetracationic singlet, ¹**2a**⁴⁺) and mono-oxidized (pentacationic doublet, ²**2a**⁵⁺) at the DFT level of theory by using the generalized gradient approximation (GGA) functional TPSS^[19] with the MIDI! basis set^[20] for hydrogen, carbon, and nitrogen, and a pseudopotential basis set^[21] for copper. The TPSS functional has previously been shown to provide quantitatively accurate predictions for electronic interactions between copper atoms in various bridged dicopper species.^[22] Aqueous solvation effects on energies and geometries were included by using the conductorlike polarized continuum model (CPCM).^[23]

The calculated Cu1...Cu2 and Cu2...Cu3 distances for ¹**2a**⁴⁺ were 2.754 and 3.218 Å, respectively; the corresponding distances for ²**2a**⁵⁺ were 2.618 and 3.190 Å, respectively. Both calculations converged to a structure of *D*₂ point symmetry, rendering the Cu1...Cu2 and Cu3...Cu4 distances equivalent. The calculated ground state Cu...Cu distances matched the crystallographic distances very well, which indicated that the chosen theoretical treatment was well adapted to this system. We note that in the absence of including solvation effects, the large positive charges on the gas-phase molecules lead to severe internal electrostatic repulsion and optimized geometries that show very poor agreement with experimental metrics. The prediction that oxidation of **2a** should lead to shorter Cu...Cu distances indicates that Cu...Cu electronic communication should be enhanced in the oxidized form, in keeping with the experimental results of Jeffery et al.^[10]

To assess and quantify the impact of chain lengthening upon electronic delocalization in dicopper **1** and tetracopper **2**, their oxidation potentials were measured and relevant calculations were undertaken. Aqueous oxidation potentials for **1a** (the analogue of **1** with methyl groups in place of the terminal -CH₂CH₂OCH₂CH₂OH chains) and **2a** were computed^[25] using Gaussian 03^[26] at the CPCM/TPSS level by first computing the one molar standard-state energy change Δ*G* (electronic energy plus electrostatic component of the free energy of solvation) for the processes shown in Equations (1) and (2):



in which *n*=1 or 2. For *n*=2, triplet ground states were found to be 6–9 kcal mol⁻¹ lower in energy than the corresponding closed-shell singlet states. Absolute oxidation potentials were then computed from Equation (3):

$$E^\circ = -\frac{\Delta G^\circ}{nF} \quad (3)$$

in which *F* is the Faraday constant. Potentials relative to the standard calomel electrode (SCE) were determined by subtracting 4.53 V from the absolute potential (4.53 V is the sum of the absolute potential of the normal hydrogen elec-

trode (NHE), 4.28 V,^[27] and the potential of the SCE relative to the NHE, 0.248 V).

The computed one- and two-electron oxidation potentials for both **1a** and **2a** are well separated, with $E_{1/2}$ values (V/SCE) of $\mathbf{1a}^{2+} \rightarrow \mathbf{1a}^{3+}$, 0.45; $\mathbf{1a}^{3+} \rightarrow \mathbf{1a}^{4+}$, 1.13; $\mathbf{2a}^{4+} \rightarrow \mathbf{2a}^{5+}$, 0.49; and $\mathbf{2a}^{5+} \rightarrow \mathbf{2a}^{6+}$, 0.75. These data indicate a strong interaction between the copper atoms in each case (such a strong interaction is also consistent with the large singlet-triplet energy difference noted above for the doubly oxidized states). The predicted potentials for **1a** are in good qualitative agreement with the cyclic voltammogram (CV) for **1** in CH_2Cl_2 , which exhibits a quasi-reversible wave at $E_{1/2} = 0.64$ V/SCE ($\Delta E = E_{\text{pa}} - E_{\text{pc}} = 0.16$ V) and an irreversible wave at 1.00 V. The direct comparison of theory and experiment when the latter indicates the occurrence of an irreversible process should not necessarily be expected to be quantitatively accurate. Nevertheless, the quantitative agreement between theory and experiment is also quite reasonable given the large charges (and thus large solvation-free energies, ranging from 5 to 35 eV) involved.^[28] This suggests that the theoretical predictions for **2a** may also be interpreted to support coupling between the copper atoms in this molecule; the experimental electrochemistry was more technically challenging in this case, but the CV of **2** does indeed exhibit four irreversible oxidation waves at 0.43, 0.59, 0.82, and 1.02 V versus SCE in CH_2Cl_2 . The very large positive charges for the triply and quadruply oxidized species made the calculated wave functions too unstable to be interpreted, but the first two computed oxidation potentials are again in fair agreement with the observed (irreversible) waves. CVs are presented in the Supporting Information.

Delocalization of the unpaired electron(s) in the oxidized states is evident from inspection of the excess spin density in the computed doublet and triplet species. As shown in Figure 2, there is complete delocalization over all of the copper atoms with some delocalization onto coordinating nitrogen atoms as well.

To better understand the electronic structure of **2a** and its implications for the band gap in an infinite wire, vertical electronic excitation energies were computed at the time-dependent (TD) DFT level for $\mathbf{1a}^{2+}$ ^[29] and $\mathbf{2a}^{4+}$ using the B3LYP functional,^[30] a polarized valence-double-zeta basis set^[31] on hydrogen, carbon, and nitrogen, and a Stuttgart pseudopotential^[21] on copper.^[32] Both systems are predicted to have long wavelength metal-to-ligand charge-transfer (MLCT) excitations; exact values are provided in the Supporting Information. Extrapolation of a plot of the HOMO–LUMO separation versus $1/n$ in which n is the oligomer length (in this case $n=1$ and 2) leads to a predicted band gap of 0.85 eV for a polymer. We note that the TD-B3LYP level has been shown previously to predict UV/Vis spectral transitions for $\mathbf{1a}^{2+}$ in good agreement with those measured experimentally for **1**.^[29]

The longest wavelength transitions in $\mathbf{2a}^{4+}$ are well described as being one-electron excitations from the HOMO and HOMO–1 to the LUMO, LUMO+1, and LUMO+2. The HOMO is dominated by a combination of d orbitals on

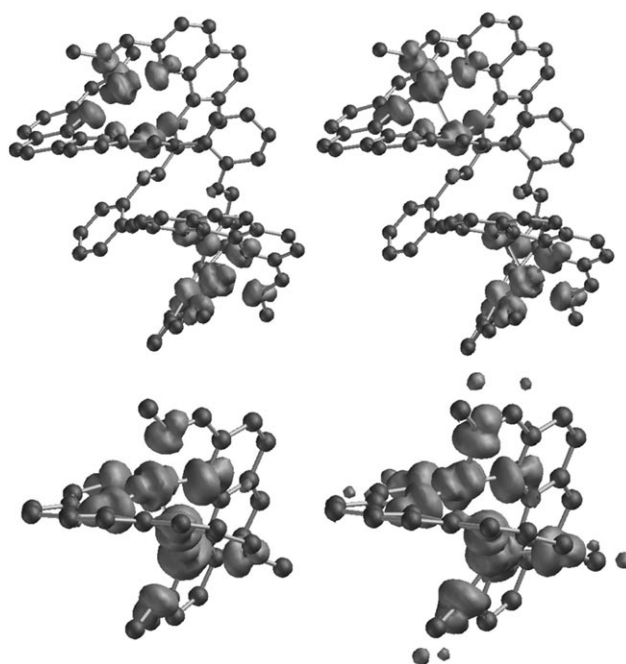


Figure 2. Excess spin densities at the 0.00075 (doublets) and 0.0015 (triplets) a.u. contour levels for $\mathbf{1a}^{3+}$ (lower left), $\mathbf{1a}^{4+}$ (lower right), $\mathbf{2a}^{5+}$ (upper left), and $\mathbf{2a}^{6+}$ (upper right). Hydrogen atoms have been removed for clarity.

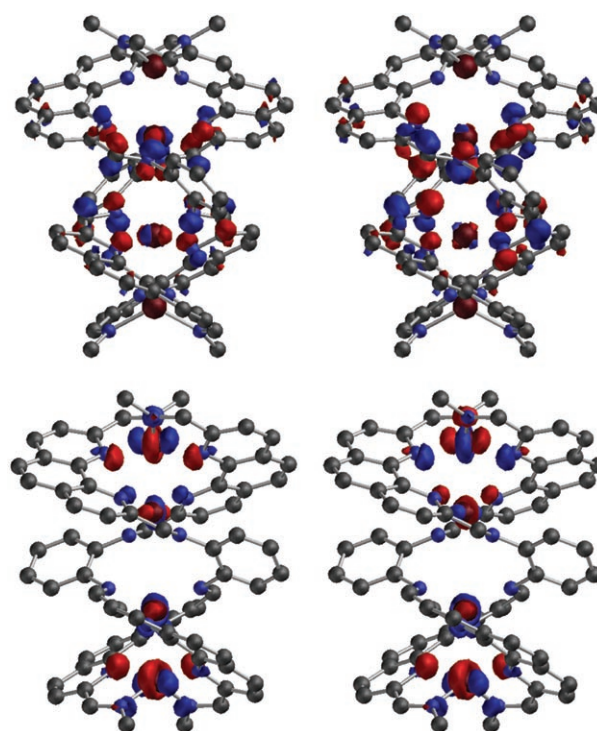


Figure 3. HOMO–1 (lower left), HOMO (lower right), LUMO (upper left), and LUMO+1 (upper right) orbitals of $\mathbf{1a}^{4+}$ at the 0.04 a.u. contour level. For clarity, hydrogen atoms have been removed and the viewing angle for the virtual orbitals is different from that for the occupied orbitals.

all four copper atoms, with somewhat larger amplitude on the outermost two compared with the innermost (Figure 3). The HOMO–1 is essentially identical to the HOMO except for a phase difference. The first two virtual orbitals are combinations of ligand π^* orbitals with minor contributions from innermost copper d orbitals; the LUMO+2 is another low-energy π^* orbital delocalized over the ligands.

DFT results, which mirror both structural and electrochemical experimental measurements, thus suggest strongly that tetracopper helicate **2** may form the basis of a new kind of self-assembled electrically conductive molecular wire. The electronic delocalization between copper ions, predicted to underlie the conductivity of these structures, could thus be considered as a generalization of the mixed-valence behavior previously observed in dicopper structures (originally by McKee and Nelson in cryptands,^[9] and more recently by Jeffery et al.^[10] in helicates). The aqueous self-assembly technique used to prepare **2** could therefore lead to a novel means of creating electrical connections within electronic devices. The “self-healing” potential of such dynamically self-assembled polymers^[33] is also worthy of note. Further studies are focusing upon the construction of soluble polymers based on analogues of **2** containing more soluble sub-components, as well as the growth of such polymers from surfaces.

Experimental Section

Preparative synthesis of 2: 1,10-Phenanthroline-2,9-dicarboxaldehyde (0.368 g, 1.56 mmol), 1,2-phenylenediamine (0.084 g, 0.78 mmol), 2-(2-aminoethoxy)ethanol (0.164 g, 1.56 mmol), copper(I) tetrakis(acetonitrile) tetrafluoroborate (0.490 g, 1.56 mmol), and deuterium oxide (10 mL) were added to a 25 mL Schlenk flask. A magnetic stirrer bar was added and the flask was sealed. The atmosphere was purified of dioxygen by three evacuation/argon fill cycles. The reaction was allowed to stir for 10 d at 50 °C, after which time no more **1** was noted in the reaction mixture by NMR spectroscopic monitoring. The 27% yield for the formation of **2** was determined by ¹H NMR spectroscopy by comparing the integrations of the free and incorporated amines. The mixture was then filtered and the filtered solution was frozen at –25 °C. Water was then sublimed under dynamic vacuum at 0 °C. The residue was dissolved in a minimum of methanol and precipitated by addition of diethyl ether. After filtration, a dark green-brown solid was isolated. ¹H NMR (400 MHz, 300 K, D₂O, referenced to 2-methyl-2-propanol at 1.24 ppm as internal standard; peak assignments are consistent with COSY and NOESY spectra): δ = 8.88 (d, J = 8.08 Hz, 4H; 4-phenanthroline), 8.48 (s, 4H; imine), 8.42 (d, J = 8.32 Hz, 4H; 7-phenanthroline), 8.16 (d, J = 8.08 Hz, 4H; 3-phenanthroline), 7.99 (m, 8H; 5,6-phenanthroline), 7.81 (d, J = 9.08 Hz, 4H; 8-phenanthroline), 7.53 (s, 4H; imine), 6.80 (m, 4H; 4,5-phenylene), 5.75 (m, 4H; 3,6-phenylene) 3.06 (m, 12H; NCHHCH₂OCH₂CH₂OH), 2.60 (m, 8H; NCH₂CH₂OCH₂CH₂OH), 2.39 (m, 8H; NCH₂CH₂OCH₂CH₂OH), 1.56 ppm (m, 4H, NCHHCH₂OCH₂CH₂OH); ¹³C NMR (100.62 MHz, 300 K, D₂O, referenced to 2-methyl-2-propanol at 30.29 ppm as internal standard): δ = 163.1, 155.9, 148.6, 146.9, 141.17, 141.11, 139.0, 138.6, 137.7, 132.9, 132.5, 131.7, 129.8, 129.2, 128.3, 126.8, 119.8, 71.7, 69.2, 60.3, 57.6 ppm; ESIMS: m/z : 422.1 [**2**⁺], 542.8 [**2**⁺–Cu⁺], 593.5 [**2**–BF₄]⁺, 932.5 [**2**–2BF₄]⁺. The brown material that precipitated during the reaction was subjected to elemental analysis: elemental analysis calcd (%) for polymeric [C₄₁H₂₇B₂Cu₂F₈N₈]_n: C 52.81, H 2.92, N 12.02; found: C 53.03, H 3.36, N 11.91. Slightly better agreement may be obtained for material assumed to

contain some 2-(2-aminoethoxy)ethanol: elemental analysis calcd (%) for [C₄₁H₂₇B₂Cu₂F₈N₈(C₄H₁₁NO₂)_{0.14}]_n: C 52.71, H 3.03, N 12.04.

X-ray analysis of 2: Brown crystals of **2** for single crystal X-ray diffraction analysis were obtained following counterdiffusion of an aqueous solution of **2** into an aqueous solution of barium perchlorate. A moderate-quality crystal, 0.30 × 0.15 × 0.05 mm in size, was mounted on a Nylon loop sample holder with perfluoro polyether and the data collected at 153.0(1) K using a Bruker Kappa Apex II diffractometer with graphite-monochromatized MoK α (λ = 0.71073 Å) radiation. Collect^[34] software was used for the data collection and DENZO-SMN^[35] was used for the processing. The structure was solved by direct methods with SIR97^[36] and refined by full-matrix least-squares methods with WinGX-software,^[37] which utilizes the SHELXL-97 module.^[38] Crystal data: C₈₄H_{75.5}Cl₄Cu₄N₁₆O_{29.5}; M_r = 2177.06; monoclinic; space group *C2/c* (no. 15); a = 46.803(2), b = 18.4037(6), c = 24.1872(7) Å; β = 120.863(2)°; V = 17884(1) Å³; Z = 8; ρ_{calcd} = 1.617 mg m^{–3}; μ = 1.150 mm^{–1}; $F(000)$ = 8892; 28678 collected reflections of which 15511 were independent ($R(\text{int})$ = 0.0995); no absorption correction; full-matrix least-squares on F^2 with 13 restraints and 1303 parameters; GOF = 1.124; $R1$ = 0.1236; $wR2$ = 0.2500 [$I > 2 \sigma(I)$]; $R1$ = 0.1958; $wR2$ = 0.2955 (all data); largest peak/hole = 1.374/–1.355 e[–] Å^{–3}. All C–H and O–H hydrogen positions were calculated and refined as riding atom model with 1.2 and 1.5 times of the thermal parameter of the carbon and oxygen atoms, respectively. The ethylene glycol chains of the helicate were found to be severely disordered, the disorder was modeled by assigning partial occupancy for some atoms within these chains. Residual electron density of the tetracation and the four perchlorate anions contained numerous separated peaks. All of these peaks were treated as disordered water molecules with partial occupancy (the hydrogen atoms could not be located).

CCDC-664077 contains the supplementary crystallographic data for **2**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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