Triple-Stranded Helicates

A Self-Assembled Tetracopper Triple-Stranded Helicate: Towards the Controlled Synthesis of Finite One-Dimensional Magnetic Chains**

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The majority of self-assembled metallic helicates contain two metal centers, whilst those containing three or more remain quite rare.[1] The limitation to synthesizing high-nuclearity helicates appears to be the design of the organic ligand, since double- and quadruple-stranded helicates containing five[2] and nine[3] metal centers, respectively, have been reported. This is in contrast to triple-stranded helicates, which have not progressed beyond the inclusion of three metal centers.[4] The apparent lack of high-nuclearity helicates has undoubtedly limited the exploitation of these systems, which is currently driven towards the development of molecular devices having predetermined properties and functions such as chirality,[5] energy transfer,[6] metal–metal bonding,[7] and DNA groove binding.[8] Surprisingly, helicates exhibiting magnetic exchange remain scarce,[9] since the adjacent metal ions are often bridged by long spacers that preclude viable superexchange pathways. However the preparation of high-nuclearity helicates with adjacent metal centers bridged by a single atom, or groups of atoms, provide an ideal opportunity to study the magnetic exchange between fixed numbers of paramagnetic metal centers in an isolated finite one-dimensional (1D) system. These systems could serve as useful models to provide further insights into the magnetic properties of infinite 1D magnetic-chain compounds,[10] which occupy an intermediate position between zero-dimensional clusters and 3D extended lattices, and as building blocks for future supramolecular devices.[11] Consequently we have embarked upon a program to exploit the helical structural

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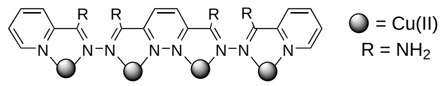
motif as a means of producing finite 1D magnetic chains in a controlled manner.

We now report the synthesis, structural characterization, and magnetic properties of the first triple-stranded helicate containing four metal centers $[Cu_4(L)_3](ClO_4)_8{\cdot}14\,H_2O$ (**1**) that exhibits intramolecular magnetic exchange between metal centers and is formed through the self-assembly of ligand L and $Cu(ClO_4)_2{\cdot}6\,H_2O$ (the preparation of ligand L is given in the Supporting Information). The design and synthesis of L was adapted from the pd2am ligand (pd2am = *N*-(bis(pyridine-2-amidine)pyridazine-3′,6′-dicaboxyamido)), which has produced a trinuclear nickel(II) triple-stranded helicate[9a] and a dodecanuclear copper(II) 4 × 4 gridlike assembly[12] that both suffer from incomplete metal-ion coordination. Replacement of the amide linkage within pd2am for a more innocuous amidrazone linkage through the reaction of the imidate ester of 3,6-dicyanopyridazine with pyridine-2-amidrazone in dry MeOH affords the ligand L in 91 % yield and presents it with a linear arrangement of alternating sequences of bridging $N{-}N_{diazine}$ and $N{-}N_{pyridazine}$ bidentate binding sites that are capable of coordinating four adjacent metal centers (Scheme 1). This sequencing of flexible and rigid N_2–azine binding sites within the ligand framework provides a route to propagate magnetic exchange between metal centers, as well as providing the subtle steric constraints to favor helical formation as opposed to other oligonuclear species when self-assembled with octahedral metal centers.



Scheme 1.

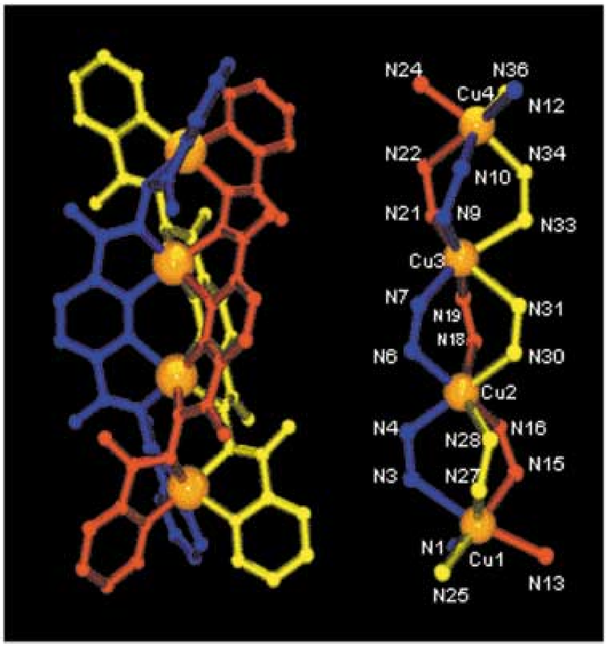


Figure 1. Left: POV-Ray structural representation of the $[Cu_4L_3]^{8+}$ cation in **1** (hydrogen atoms omitted for clarity). Right: tetranuclear core in **1**. Selected bond lengths [Å]. Cu1: N3 2.408(7), N13 2.203(7), N1 2.063(7), N27 2.045(7), N15 2.015(7), N25 1.997(8); Cu2: N18 2.267(8), N28 2.248(7), N30 2.089(7), N16 2.048(7), N6 2.000(6), N4 1.990(8); Cu3: N31 2.312(7), N33 2.178(8), N7 2.151(7), N21 2.045(7), N19 1.988(7), N9 1.974(7); Cu4: N10 2.212(8), N12 2.163(9), N22 2.225(7), N36 2.119(9), N24 2.019(7), N34 2.016(7).

Reaction of L with $Cu(ClO_4)_2{\cdot}6\,H_2O$ (3:4) in aqueous acetonitrile yielded dark-brown crystals (78 % yield), which upon standing for three weeks were found suitable for X-ray diffraction. The structure[13] of the cation in **1** (Figure 1) consists of three ligand strands that twist around a pseudolinear array of four six-coordinate Cu^{II} centers (Cu1-Cu2-Cu3 172.0°; Cu2-Cu3-Cu4 171.6°) that defines the helical axis. The bending of the Cu_4 chain is slight in comparison to the only other known tetranuclear copper(II) chain compound where a marked curvature is observed.[14] The long external dimension of the helicate is approximately 18 Å and the internal Cu1–Cu4 distance is 11.149(1) Å, with adjacent copper–copper separations of Cu1-Cu2 3.743(1), Cu2-Cu3 3.743(1), and Cu3-Cu4 3.730(1) Å. The ligands experience a significant degree of twisting about the flexible $N{-}N_{diazine}$ bonds, which is reflected by the disposition of the pyridine rings that point in approximately opposite directions. The twist experienced by each ligand between adjacent copper centers can be estimated by examining the angles between the least-squares planes of the pyridyl amidrazone (N_{py}-C-C-$N_{diazine}$) and the pyridazyl amidrazone ($N_{diazine}$-C-C-$N_{pyridazine}$) chelating subunits. Angles between adjacent $N{-}N_{diazine}$-bridged Cu centers fall in the range 75–89° and are consistent with the M_2L_3 pyridylimine-based helicates[9c,15] containing methyl or amine side chains, whereas adjacent $N{-}N_{pyridazine}$-bridged Cu centers are essentially coplanar (3–11°), which highlights the rigidity of this bridging group. The four copper centers (Figure 1) have distorted octahedral geometries, which becomes gradually more pronounced from Cu1 through to Cu4, and is manifested through the tapering of the ligands towards the Cu4 end of the helicate. The Cu1 center could be regarded as having a square-based pyramidal geometry (axial: Cu-N13 2.203(2); equatorial: Cu-N 1.997–2.063 Å, with an extremely long Cu-N3 contact of 2.408(7) Å occupying the sixth site. An elongated tetragonal geometry is observed for Cu2 (axial: Cu-N18 2.267(2) Å; Cu-N28 2.247(2) Å; equatorial: Cu-N 1.989–2.088 Å) in comparison to Cu3 and Cu4, which have no obvious axis of elongation but do have a substantial range of bond lengths (Cu3 1.974–2.313 Å; Cu4 2.019–2.225 Å). This type of coordination environment has been observed for a dicopper(II) double-stranded helicate and has been described as a dynamic Jahn–Teller effect.[16] It appears to have arisen in this case as a result of the stereoelectronic preference of the metal ion, rather than being imposed by the disposition of binding sites within the ligand. Examination of a solution of redissolved crystals of **1** in acetonitrile by electrospray mass spectroscopy at various cone voltages displayed four sets of peaks that correspond to the species $[Cu_4L_3(ClO_4)_n]^{8-n}$ ($n = 3$–6) together with their acetonitrile adducts. No other discernible peaks were observed, which indicates that the helical Cu_4L_3 motif is preserved in solution.

The magnetic susceptibility of a powdered sample of **1** was measured (Figure 2). The room temperature moment of 1.99(1) μ_B corresponds to an average g value of 2.29 per Cu^{II} center. The sample obeys a Curie–Weiss law over the entire measured thermal range with $C = 0.493(2)$ cm^{3}mol^{-1}K and $\theta = -4.6(6)$ K per Cu^{II} center, which suggests a lack of significant coupling. Alternatively, the small negative Weiss constant could be equated with a small antiferromagnetic exchange interaction between adjacent Cu^{II} ions. Attempts to extract values for the coupling constants by modeling the data as a tetranuclear system of interacting $S = 1/2$ ions were unsatisfactory. A successful fit of thermal susceptibility data relies on changes in the relative populations of the different states. In this case the very small size of the magnetic interactions (as inferred from the Curie–Weiss behavior) results in all eight magnetic states being closely spaced and at much lower energies, thus throughout the 5 to 280 K experimental range all states are almost equally populated.

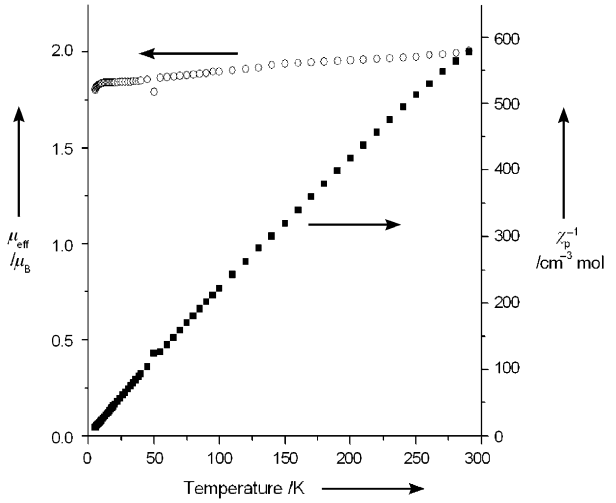


Figure 2. Reciprocal magnetic susceptibility and the effective magnetic moment as a function of temperature. The data reveals the weakness of the interactions between neighboring copper ions in the linear unit.

Structural considerations can help to explain why the coupling is so small in **1**. While diazine and pyridazine bridges can mediate a significant antiferromagnetic exchange interaction[9c,17] the value of this coupling is very dependant on the copper coordination geometry. This is because the magnetic orbitals are normally $d_{x^2-y^2}$, and the relative geometry of these orbitals on neighboring copper ions is crucial to the sign and magnitude of the coupling constant. In **1** the local xy plane of the Cu1 and Cu2 ions is tilted from one metal ion to the next; more significantly the helical structure of the complex imposes a twist between the local crystal-field x and y axes of neighboring copper ions. The effect of this twist is to reduce the overlap integral responsible for the antiferromagnetic exchange contribution. A twist of 45° between the x and y axes in neighboring copper ions results in strictly orthogonal orbitals and a value of zero for the overlap integral. The corresponding reduction in the antiferromagnetic component to the coupling often allows an underlying ferromagnetic exchange interaction to become dominant. In our case it is likely that the twisted structure results in a near balance between antiferromagnetic and ferromagnetic components to the exchange coupling. The Cu–N bond-length distribution for Cu3 and Cu4 makes it difficult to be sure of the magnetic orbitals on these ions.

In conclusion, this report has demonstrated that a tetranuclear "magnetic" helicate can be generated through a strict self-assembly process between the single octadentate ligand L and Cu^{II} ions. The helicate can be classed as being saturated and homotopic as the coordination algorithm of the four octahedral Cu^{II} centers is exactly matched by the three symmetrical ligands. Efforts are currently being driven in several directions that are centered on examining the coordination properties of L with other metals and increasing the number of metal centers by incorporating additional or alternative diazine-chelating subunits within the ligand framework.

Experimental Section

1: Elemental analysis (%) calcd for $[Cu_4(C_{18}H_{18}N_{12})_3](ClO_4)_8\cdot 14\,H_2O$: C 25.9, H 3.3, N 20.1; found (vacuum-dried sample): C 26.1, H 2.9, N 19.8; IR (nujol mull): $\tilde{\nu} = 3584$ (sh; ν_{H_2O}), 3331 (ν_{NH/H_2O}), 1659 (ν_{CN}), 1074 cm^{-1} (ν_{ClO_4}); UV/Vis (nujol mull): $\tilde{\nu} = 785$ nm; (MeCN): 785 nm (60).

Field-cooled magnetization studies were performed on a Quantum Design SQUID magnetometer operating at 0.02 T between 5 and 280 K. The powdered sample was held in an eicosane matrix to prevent reorientational effects. Corrections were made for diamagnetism including the samples inherent contribution estimated from Pascal's constants[10] to be -293×10^{-6} cm^{3}mol^{-1} (all molar quantities are given per Cu ion).

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Keywords: copper · helical structures · magnetism · N ligands · self-assembly

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[13] Crystal data for **1**: $C_{54}H_{82}N_{36}O_{46}Cl_9Cu_4$, brown plate, $0.10 \times 0.30 \times 0.39$ mm, triclinic, $P\bar{1}$, $a = 12.0630(14)$, $b = 17.4593(20)$, $c = 22.9083(26)$ Å, $\alpha = 89.095(2)$, $\beta = 82.266(2)$, $\gamma = 88.020(2)^\circ$, $V = 4777.7(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.769\ g\,cm^{-1}$, $2\theta_{max} = 46.74^\circ$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 1.243\ mm^{-1}$ (no absorption correction applied), 39524 reflections were recorded of which 13771 were unique ($R_{int} = 0.0663$) and 8394 had $F > 2\sigma(F)$. The structure was solved by direct methods, all hydrogen atoms were placed in idealized positions, all other atoms were refined anisotropically by a full-matrix least-squares method on F^2 to give $R1 = 0.0691$ (2σ data), $wR2 = 0.2090$, $S = 1.036$ (all data), max./min. residual electron density $+1.578/-1.678$ e Å^{-3}. CCDC-207896 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). A number of restraints were applied to the model. In particular the bond lengths, bond angles, and thermal parameters of the perchlorate counterions were restrained to be similar. Orientational and positional disorder was observed for many of these anions. In addition, the anisotropic thermal parameters of the terminal pyridyl rings in the ligand have been restrained to a rigid group model.

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