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Head-To-Tail and Heteroleptic Pentanuclear Circular Helicates

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The rational design of polynuclear helicates is one of the major achievements of metallosupramolecular chemistry.[1] These linear structures form by self-assembly and consist of two or more multidentate ligand strands that are helically wrapped about a central array of metal cations.[1] Not only can polynuclear double-, triple-, and quadruple-stranded helicates now be made in a predictable fashion,[1f] they can also be programmed to express certain structural features of higher-order complexity. This goal may be achieved by elaborating on the basic design principles that govern helicate formation itself (i.e., careful consideration of ligand topology and metal stereoelectronic preference) and, amongst others, can entail: 1) directional control over ligand alignment, 2) selective incorporation of different metal cations, and 3) selective incorporation of different ligand strands, within the helical array.[1]

The first two of these scenarios are intimately linked. They can be illustrated by considering a ditopic C_s-symmetric N-donor ligand with one bidentate and one tridentate donor site.[2] When combined with equal amounts of a five-coordinate metal cation, a double-stranded dinuclear C_2-symmetric head-to-tail (HT) helicate results, wherein each metal is coordinated by a "2+3" donor set comprising the tridentate head of one ligand and the bidentate tail of the other (Figure 1 a). Alternatively, combination of the same ligand with half an equivalent each of a four- and six-coordinate cation gives a hetero-bimetallic head-to-head (HH) helicate. In this case, one metal is octahedrally (3+3) coordinated by the two tridentate heads whilst the other is tetrahedrally (2+2) coordinated by the two bidentate tails (Figure 1 b).[2] Importantly, the two ligands are now co-aligned in a parallel fashion. The third scenario can likewise be realized by combining a five-coordinate cation with half an equivalent each of a C_{2v}-symmetric bis(bidentate) and bis(tridentate) ligand. The resulting structure is a C_2-symmetric heteroleptic (mixed ligand) helicate, wherein both cations have the required bi- and tridentate (2+3) donor sets (Figure 1 c).[3]

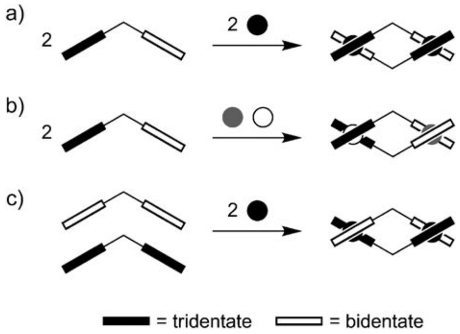
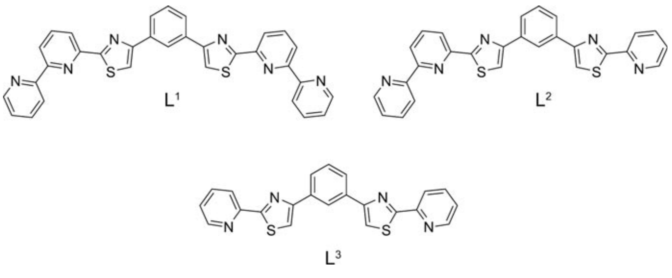


Figure 1. Formation of a double-stranded a) HT helicate, b) HH helicate, and c) heteroleptic helicate: black, grey, and open circles represent five-, four-, and six-coordinate metals, respectively.

More subtle effects, such as interligand interactions[4] and cation or binding-site size mismatch,[5] can also be used to fine-tune structural complexity in linear helicates. However, neither these effects nor the more intuitive principles described above have ever been applied to helicates that have a higher nuclearity, that is, circular helicates. Herein we describe how some of the basic rules that govern linear helicate assembly can also be applied to generate the first heteroleptic and head-to-tail circular helicates.

If the linear double-stranded helicates discussed above are denoted as $[M_2(L)_2]$, then circular helicates are cyclic oligomers that have the general formula $[M_n(L)_n]$ $(n>2)$ and retain the "over-and-under" ligand motif requisite of helical chirality.[6] Circular helicates can arise from intermolecular templating effects or intramolecular interactions that destabilize their more entropically favored linear counterparts.[6] In a recent report, we showed that bis(tridentate) ligand L^1 (Scheme 1) forms pentanuclear circular helicates with small transition-metal dications.[7] Formation of the observed structure was driven by repulsion between the central phenyl groups of L^1, which are brought too close to one another in the putative dimer. Since this appeared to be a



Scheme 1. Multidentate ligands L^1–L^3.

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robust approach for generating circular helicates, we decided to explore whether L^1, and its variants L^2 and L^3 (Scheme 1), could be used to further diversify structural complexity in circular helicates.

We first addressed the issue of ligand directionality (Figure 1 a). Reasoning that a five-coordinate ion would combine with a ditopic "3+2" dentate ligand to give a HT motif regardless of overall structural topology, we prepared C_s-symmetric L^2 by standard transformations (see the Supporting Information). As in other reports,[3] we chose Cu^{II} as the metal dication since, amongst its possible coordination geometries, five-coordinate Cu^{II} ions are frequently observed.

Reaction of L^2 with an equimolar amount of $Cu(ClO_4)_2{\cdot}6H_2O$ in MeCN gave a light green solution from which a crystalline solid was deposited in high yield (ca. 80 %) after slow diffusion of chloroform. The ESI-MS spectrum of this material showed a number of low-nuclearity fragments, for example, $\{[Cu_2(L^2)](ClO_4)_3\}^+$ (*m*/*z* 901, 3 %), $\{[Cu(L^2)_2](ClO_4)\}^+$ (*m*/*z* 1114, 50 %), $\{[Cu_2(L^2)_2](ClO_4)_3\}^+$ (*m*/*z* 1376, 100 %) and $\{[Cu_3(L^2)_3](ClO_4)_5\}^+$ (*m*/*z* 2114, 5 %), but also a peak at *m*/*z* 1745 corresponding to $\{[Cu_5(L^2)_5](ClO_4)_8\}^{2+}$, with the correct isotope pattern for a dicationic species (see Supporting Information). X-ray structural analysis confirmed the formation of a pentanuclear circular helicate $[Cu_5(L^1)_5](ClO_4)_{10}$ (Figure 2).[8] In the solid state, the ligands adopt the anticipated "3+2" binding mode, wherein the bidentate and tridentate N-donor domains span two different Cu^{II} centers. The ligands are furthermore arranged such that a given metal is coordinated by the bidentate domain of one ligand and the tridentate domain of the next. The resulting structure has approximate C_5 symmetry, with all Cu^{II} centers displaying distorted square-based pyramidal geometries (Cu–N bond lengths: 1.936(9)–2.327(9) Å). By analogy with the HT linear helicate, the complex cation $[Cu_5(L^2)_5]^{10+}$ may thus be considered a HT circular helicate.

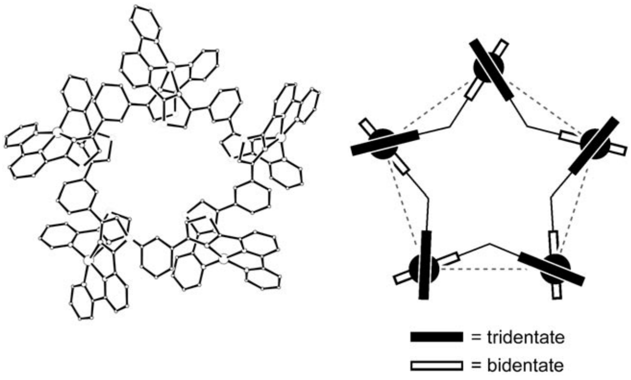

Figure 2. Left: crystal structure of the HT-$[Cu_5(L^2)_5]^{10+}$ circular helicate. Right: Schematic representation of HT-$[Cu_5(L^2)_5]^{10+}$ showing head-to-tail ligand arrangement (black circles represent five-coordinate Cu^{II} ions).

The distribution of species in the ESI-MS spectrum of $[Cu_5(L^2)_5](ClO_4)_{10}$ is strikingly similar to that observed for the previously reported zinc-based circular helicate $[Zn_5(L^1)_5](OTf)_{10}$,[7] the solid-state structure of which was shown to be quantitatively retained in solution. Nonetheless, we have conducted tandem MS experiments to ascertain whether the lower nuclearity species observed in the ESI-MS spectrum of $[Cu_5(L^2)_5](ClO_4)_{10}$ are present in solution or merely products of gas-phase fragmentation in the ion source. The results supported the latter scenario: selective collision-induced fragmentation of the ion at *m*/*z* 1745 gave rise to peaks at *m*/*z* 901, 1376, and 2114, thus indicating clear correlation between the pentanuclear parent ion and $\{[Cu_2(L^2)](ClO_4)_3\}^+$, $\{[Cu_2(L^2)_2](ClO_4)_3\}^+$, and $\{[Cu_3(L^2)_3](ClO_4)_5\}^+$, respectively. The peak at *m*/*z* 1114 that arises from $\{[Cu(L^2)_2](ClO_4)\}^+$ was not observed, though it is possible that this species is a fragment ion from further down the fragmentation cascade.

We next focused on forming the heteroleptic circular helicate (Figure 1 c). To this end, we chose C_{2v}-symmetric bis(tridentate) and bis(bidentate) ligands L^1 and L^3, respectively. Arrangement of these ligands in a pentameric circular array afforded any number of different structures, in which the occurrence and disposition of four-, five- and six-coordinate binding sites depends on the ratio and relative orientation of the ligand strands. The use of mixtures of metal ions with different stereoelectronic preference therefore represents one approach for selecting a desired heteroleptic species (i.e., a hybrid of the two cases outlined in Figure 1 b,c). However, preliminary attempts were unsuccessful and so we again opted for the use of Cu^{II} ions, in the hope that its (relatively) diverse coordination tendencies would permit the formation of a homo-pentametallic structure that features both five- and six-coordinate binding sites.

The diagram in Figure 3 represents one such possibility; Cu^{II}, L^1, and L^3 appear in a 5:3:2 ratio, respectively, and one of the metals occupies an octahedral binding site whilst the remaining four are five-coordinate. ESI-MS studies indicate that the reaction of Cu^{2+} with L^1 and L^3 in the ideal ratio (i.e., 5:3:2) indeed gives the desired pentanuclear heteroleptic complex $[Cu_5(L^1)_3(L^3)_2]^{10+}$, but other L^1-rich species such as $[Cu_5(L^1)_5]^{10+}$, $[Cu_5(L^1)_4(L^3)]^{10+}$, and related fragments are more abundant (see the Supporting Information). Attempts at crystallizing the putative heteroleptic complex

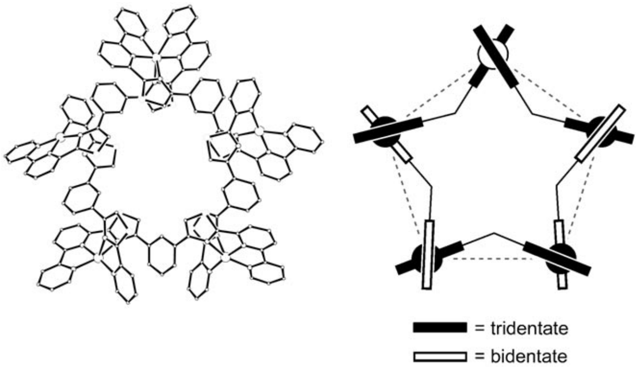

Figure 3. Left: Crystal structure of the heteroleptic $[Cu_5(L^1)_3(L^3)_2]^{10+}$ circular helicate. Right: Schematic diagram of $[Cu_5(L^1)_3(L^3)_2]^{10+}$ (black and open circles represent five- and six-coordinate Cu^{II} ions, respectively).

$[Cu_5(L^1)_3(L^3)_2]^{10+}$ were likewise unsuccessful. This result is perhaps not surprising since, like its previously reported Zn^{II} analogue $[Zn_5(L^1)_5]^{10+}$, the homoleptic circular helicate based on L^1 would furnish all five Cu^{II} centers with a more favorable six-coordinate donor set.[9] The relative L^1/L^3 ratio was therefore reduced in order to drive the equilibrium towards the desired heteroleptic species.[10] Combination of Cu^{II}, L^1, and L^3 in MeCN in a 2:1:1 ratio, respectively, gave a solution for which ESI-MS now showed virtually no traces of $[Cu_5(L^1)_5]^{10+}$ and $[Cu_5(L^1)_4(L^3)]^{10+}$. Peaks for heteroleptic ions $\{[Cu(L^3)(L^2)](OTf)\}^+$ (m/z 1164, 40%), $\{[Cu_2(L^3)(L^2)](OTf)_3\}^+$ (1525, 10%), $\{[Cu_5(L^3)_3(L^2)](OTf)_8\}^{2+}$ (1782, 5%) and in particular $\{[Cu_5(L^3)_3(L^2)_2](OTf)_8\}^{2+}$ (1982, 10%) were, however, retained.

Since the components were combined in nonstoichiometric quantities, the solution clearly contains a mixture of interconverting species. We are not able to estimate the extent to which the target heteroleptic pentanuclear complex dominates in solution as the ESI-MS response factors for the ions observed in the gas phase are unknown. Nonetheless, attempts at crystallization were successful. When ethyl acetate was diffused into a $MeNO_2$ solution containing $Cu(OTf)_2$, L^1, and L^3 in a 2:1:1 ratio, respectively, a homogenous crystalline material was deposited in high yield after several days.[11]

An X-ray analysis confirmed the formation of the target heteroleptic circular helicate $[Cu_5(L^3)_3(L^2)_2]^{10+}$ (Figure 3).[12] In the solid state, the complex features a cyclic array of five Cu^{II} ions, bound by three strands of L^1 and two strands of L^3. Since the structure has an odd number of ligands, one of the Cu^{II} centers is octahedrally coordinated by two tridentate thiazole–pyridyl–pyridyl domains from L^1. The remaining four Cu^{II} centers are bound by one tridentate domain from L^1 and one bidentate domain from L^3 to result in five-coordinate donor sets. As for $[Cu_5(L^2)_5]^{10+}$, the ligands bridge adjacent metals in an "over and under" conformation, thus giving the complex a circular helicate topology with approximate C_2 symmetry.

In summary, we have established that some of the basic algorithms for programming structural complexity in linear helicates can also be applied to related cyclic complexes. The pentanuclear circular helicates HT-$[Cu_5(L^2)_5]^{10+}$ and $[Cu_5(L^1)_3(L^3)_2]^{10+}$ are analogous to their linear counterparts shown in Figure 1 a,c by virtue of both their specific structural features and the design principles employed in their synthesis. The formation of these head-to-tail (in the case of L^2) and heteroleptic (in the case of L^1 and L^3) helicates is a result of two main factors. Firstly, the phenylene spacer units which connect the various N-donor chelates and which prevent the ligands from forming linear double-stranded assemblies (with small metal cations). Secondly, the stereoelectronic preferences of Cu^{II} ions, which are sufficiently versatile to enable both 1) all-five- or all-six-coordinate sites, or 2) a mixture of five- and six-coordinate sites to occur in the same polynuclear assembly.

It is not entirely clear to what extent the structures persist in solution since the systems were not amenable to NMR investigation. Isolation of the heteroleptic complex $[Cu_5(L^1)_3(L^3)_2]^{10+}$, in particular, is likely not a result of strict thermodynamic self-assembly,[13] but rather a dynamic combinatorial selection process,[14] the outcome of which is highly sensitive to the ratio of the two ligands. This factor differentiates the circular complex somewhat from the reported examples of its linear counterpart,[3] although it also opens up interesting avenues for the design of complex new architectures by targeted or template-based syntheses.

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[8] Crystal data for $[Cu_5(L^2)_5](ClO_4)_{10}\cdot 2\,CHCl_3\cdot 0.47\,MeCN\cdot 0.53\,H_2O$: $C_{137.93}H_{88.39}C_{116}Cu_5N_{25.47}O_{41.53}S_{10}$, 0.28 × 0.20 × 0.20 mm, $M_r = 3972.46$, Triclinic, $P\bar{1}$, $a = 17.2058(8)$, $b = 20.4431(10)$, $c = 25.9847(12)$ Å, $\alpha = 87.9110(10)$, $\beta = 85.8010(10)$, $\gamma = 81.7440(10)°$, $V = 9017.7(7)$ Å^3, $Z = 2$, $Z' = 1$, $\rho_c = 1.463$ Mg m^{-3}, $F(000) = 4007$, $\mu(Mo_{K\alpha}) = 1.010$ mm^{-1}, $T = 100(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å. 68 110 measured reflections, 17 769 unique reflections ($R_{int} = 0.0526$). The structure was refined on F^2 to $R_w = 0.0844$, $R = 0.2369$ (12 837 reflections with $I > 2\sigma(I)$) and GOF = 1.110 on F^2 for 1978 refined parameters and 1256 restraints. Largest difference peak and hole 1.813 and −1.463 e Å^{-3}. CCDC 778980 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] The ESI-MS spectrum for a solution containing only Cu^{II} and L^1 in equimolar amounts shows numerous peaks corresponding to the homoleptic pentanuclear helicate $[Cu_5(L^1)_5]^{10+}$ (see the Supporting Information).

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[11] $Cu_5(L^1)_3(L^3)_2](OTf)_{10}$ can be obtained in good yield (ca. 75 %) from either $MeNO_2$ or MeCN by diffusion of a variety of nonpolar solvents. Several batches of crystals were produced from both solvents and either a full data set or unit cell was collected. All data gave the same cell parameters as those observed for the structure reported.

[12] Crystal data for $[Cu_5(L^1)_3(L^3)_2](OTf)_{10}$: $C_{150}H_{88}Cu_5F_{30}N_{26}O_{30}S_{20}$, 0.08 × 0.06 × 0.04 mm, $M_r = 4263.36$, Triclinic, $P\bar{1}$, $a = 21.0573(13)$, $b = 21.0816(13)$, $c = 22.4884(14)$ Å, $\alpha = 92.2160(10)$, $\beta = 100.0820(10)$, $\gamma = 109.2860(10)°$, $V = 9227.2(10)$ Å^3, $Z = 2$, $Z' = 1$, $\rho_c = 1.534$ Mg m^{-3}, $F(000) = 4290$, $\mu(Mo_{K\alpha}) = 0.896$ mm^{-1}, $T = 100(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å. 68 246 measured reflections, 18 187 unique reflections ($R_{int} = 0.0506$). The structure was refined on F^2 to $R_w = 0.0919$, $R = 0.2619$ (11 972 reflections with $I > 2\sigma(I)$) and GOF = 1.108 on F^2 for 2282 refined parameters and 1113 restraints. Largest difference peak and hole 1.121 and −1.370 e Å^{-3}. CCDC 778979 contains the supplementary crystallographic data for this compound. These 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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