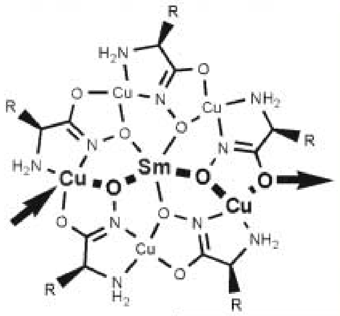
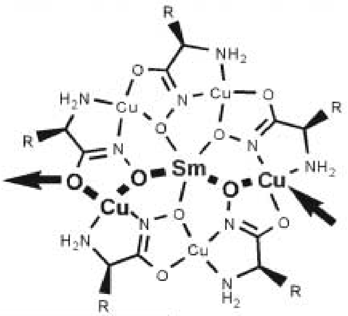
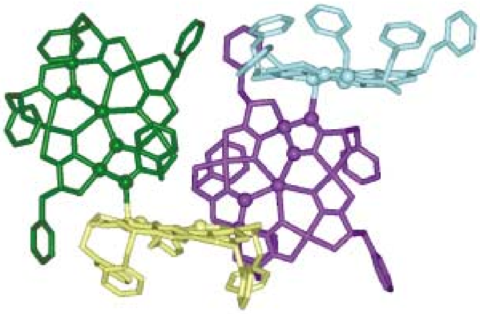
$[(\mathrm{Sm^{III}})\{[15]\text{-}\mathrm{MC_{Cu^{II}N(PheHA)}}\text{-}5\}]^{3+}$ complexes are chiral building blocks for making metallahelices

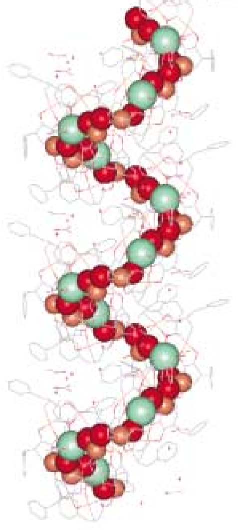


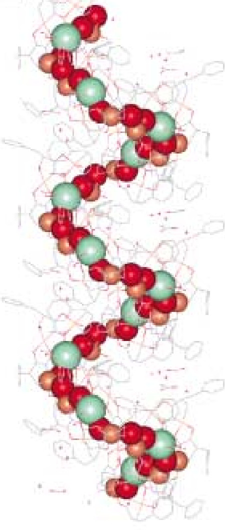




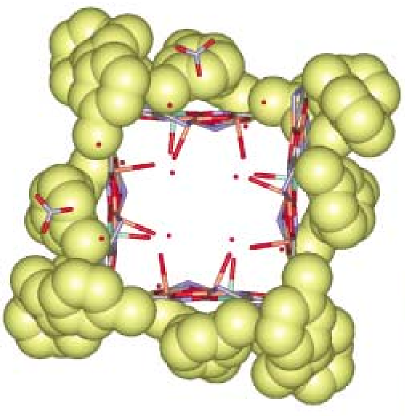
Amphiphilic metallacrowns coordinate in a chain...

...to make a helix based on a $P4_1$ axis





P **or** ***M*** **helix? This is determined by the enantiomer of the metallacrown**



The helix is amphiphilic with a hydrophobic exterior

A hydrophilic pore is formed in the interior of the helix

For more information see the following pages

Preparation of Resolved Fourfold Symmetric Amphiphilic Helices Using Chiral Metallacrown Building Blocks

Annabel D. Cutland-Van Noord, Jeff W. Kampf, and Vincent L. Pecoraro*

Helical structures are critical motifs in molecular biology and biochemistry, and are also generating interest in the field of materials science. The field of metallahelicates and metal-containing helical chains has attracted attention as a result of interest in building macromolecular structures with chiral and nonlinear optical properties and for the development of molecules with host–guest interactions.[1] An important goal is to form resolved *P* or *M* helices in noncentrosymmetric solids. Unresolved helicates or infinite helices existing as racemates are usually recovered.[2]

Current development of metallahelicates involves the use of polydentate ligands such as oligopyridines and oligocatechols that "wrap around" and coordinate to transition-metal ions.[2] These systems typically yield double- and triple-stranded molecular helicates rather than extended/infinite coordination polymers. Strategies that have been used to obtain a single enantiomer of a helix include the use of ligands that incorporate bulky chiral side chains[3] and the use of chiral anions that are cocrystallized with the helicate.[4] Infinite helical chains have also been made, frequently through the use of a "twisted" ligand that bridges metal ions. Infinite helices prepared with achiral starting materials form a mixture of both enantiomers.[5] Single enantiomers of helical chains are realized through the use of resolved chiral "bridging" ligands.[6] Chiral metal complexes can make twofold symmetric helical chains through the coordination of a peripheral group of one molecule to a central Cu^{II} ion of the next molecule.[7]

An attractive strategy for obtaining resolved, helical solids is by assembling chiral metallacrowns into extended structures. Metallacrowns were first recognized in 1989, when we reported a metallamacrocyclic complex analogous to a crown ether.[8a] Different ligands and transition metals may be used to form metallacrowns in a variety of structure types, including [9]metallacrown-3 (9-MC-3), 12-MC-4, 15-MC-5, and larger rings up to 30-MC-10.[8b–d] Metallacrowns have been made with ligands derived from α-amino acids that provide side chains at the periphery of the disk-shaped complex.[8e,f] The use of such chiral ligands results in face-differentiated molecules that include resolved chiral centers and which may be amphiphilic. Cationic [15]metallacrown-5 complexes made from α-aminohydroximates can form chiral cavities showing selective anion recognition.[8g] Such planar [15]metallcrown-5 complexes are prepared in high yield from simple precursors in a one-step reaction, and are stable to ligand exchange in solution. We now show that metallacrowns can be easily linked to form resolved fourfold symmetric, amphiphilic metallahelices by using chiral [15]metallacrown-5 building blocks.

The metallacrown $[\{Sm(NO_3)\}\{15\text{-}MC_{Cu^{II}N(\text{L-pheHA})}\text{-}5\}](NO_3)_2$ (**1**, Figure 1) is prepared using L-phenylalanine hydroxamic acid (L-H_2pheHA).[9] The complex is planar, with five peripheral benzyl groups that are oriented to the same "hydrophobic" face. These side chains come from five pheHA ligands that coordinate in a cyclic fashion to five Cu^{II} ions. A Sm^{III} ion is encapsulated in the center of the complex through ligation of the oxime oxygen atoms, which gives a formula of $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm]^{3+}$. The metallacrown is pseudo-fivefold symmetric as a consequence of the $\{Cu^{II}pheHA\}$ repeat unit that rotates around the central Sm^{III} ion.

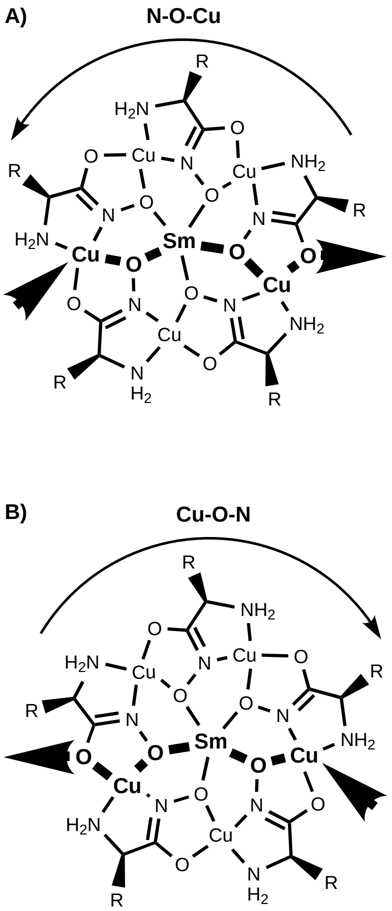


Figure 1. Schematic representation of the metallacrowns **1** and **1a**. The Cu-O-Sm-O-Cu-O path through the metallacrown between the coordination points to and from adjacent metallacrowns is highlighted. A) Metallacrown **1** has an anticlockwise Cu-O-N rotational sense. B) **1a** has a clockwise Cu-O-N rotational sense. Benzyl side chains are indicated by "R" for clarity.

A *P*-type helical chain is generated by the linkage of adjacent metallacrowns. There is one unique metallacrown in the crystal structure[10] (space group $P4_1$), which is related to its nearest neighbors by an S_4 screw axis that runs parallel to the face of the complex. Each metallacrown interacts with a neighboring molecule through their edges, by providing a peripheral carbonyl oxygen atom as an axial ligand to a

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Cu^{II} ion in the next complex (Cu–O = 2.791 Å). This arrangement places the metallacrowns at 90° to each other, with the hydrophilic faces forming the interior of this angle. The second metallacrown provides an oxygen donor, in the same way, to a Cu^{II} ion in a third complex, and so forth. The result is a chain of metallacrowns as shown in Figure 2.

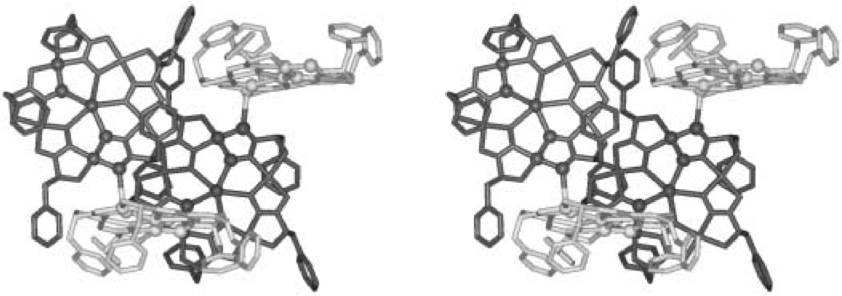

Figure 2. Stereoview of **1** from the X-ray crystal structure. A chain of four linked metallacrowns is shown. Solvents and anions have been removed for clarity.

The pseudo-fivefold symmetry displayed by the planar [15]metallacrown-5 complex $[Sm\{15\text{-}MC_{Cu^{II}N(L\text{-}pheHA)}\text{-}5\}]^{3+}$ is integrally related to the formation of the helix. The positioning of the Cu ions in each complex forces the metallacrowns to be staggered to allow the $O_{(carbonyl)}$–Cu interaction. The noncommensurate nature of this interaction prevents the formation of a "molecular box" and an infinite helical chain of metallacrowns is formed instead. The bulky benzyl side chains, directed to the same face of the metallacrown by the chiral α-carbon atom, are also critical as they prevent a "zig-zag" chain orientation of metallacrowns. Even more importantly, they induce the right-handed (*P*) form of the helix. Combining these factors yields a resolved fourfold-symmetric metallohelix using self-associating chiral building blocks.

The helix of metallacrowns form the walls of a hydrophilic "square pore", which contains water solvent molecules, with a face-to-face distance of approximately 11 Å (including the van der Waal radii). As shown in Figure 3, a solvent water is coordinated to the samarium ion on the hydrophilic face and points into the channel. There are also two water molecules that axially ligate copper(II) ions on the hydrophilic face. Additional hydrogen-bonded solvents fill the channel. The hydrophobic faces of the metallacrowns are oriented toward the outside of the helix, with the benzyl groups of adjacent helices being well-packed. The resulting structure is an amphiphilic helix with a hydrophilic interior and hydrophobic exterior.

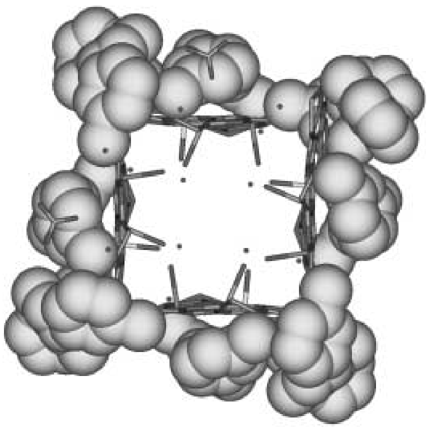

Figure 3. View of **1** down the *z*-axis. The ligand benzyl groups are shown as a CPK representation.

We predicted that a metallacrown made with D-pheHA would form a helix that was the mirror image of **1** (**1** uses L-pheHA which yields the opposite enantiomer of the metallacrown). The metallacrown $[\{Sm(NO_3)\}\{15\text{-}MC_{Cu^{II}N(D\text{-}pheHA)}\text{-}5\}](NO_3)_2$ (**1a**) crystallized in the space group $P4_3$.[11,12] As shown in Figure 4, the helices in **1** and **1a** are indeed mirror images. The Cu-O-N linkage of the metallacrown defines the rotational symmetry of the molecule.[8b] The metallacrown, when oriented with the side chains directed out of the page, forms the clockwise (C) isomer or the anticlockwise (A) isomer depending on the rotational sense of the Cu-O-N linkage (Figure 1). The thick lines illustrate the Cu-O-Sm-O-Cu-O pathway that links adjacent metallacrowns of the helix. This pathway has a positive (*P*) rotational sense for the A isomer and a minus (*M*) sense for the C isomer. Thus, the ligand chirality defines the *P* or *M* helix because the benzyl groups must be oriented toward the helix exterior.

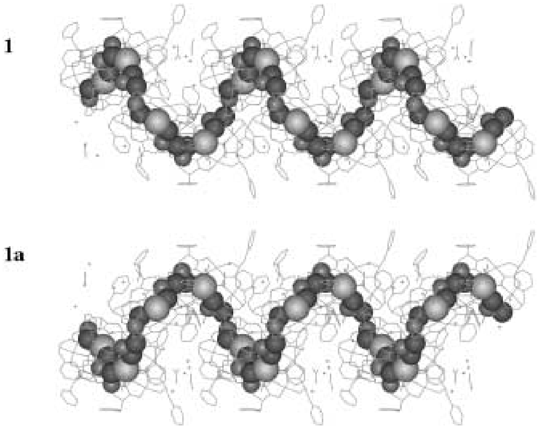

Figure 4. Comparison of the structures of **1** and **1a**. The continuous chain of Cu-O-Sm-O-Cu-O through the metallacrowns is highlighted as CPK models.

In conclusion, we have prepared enantiomerically pure helical solids (either *P* or *M*) through the use of an appropriate chiral metallacrown building block. To the best of our knowledge this is a novel technique for the formation of helical chains based on a *4*$_1$ screw axis that provides a channel through the amphiphilic helix.

Experimental Section

1: L-phenylalanine hydroxamic acid (L-H_2pheHA, 0.180 g, 1.00 mmol) was treated with $Cu(OAc)_2{\cdot}H_2O$ (0.200 g, 1 mmol) and $Sm(NO_3)_3{\cdot}6\,H_2O$ (0.090 g, 0.20 mmol) in methanol (20 mL) and water (2 mL). The reaction mixture was filtered after 2 h. Blue-violet crystals were obtained by slow

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evaporation of the solvent. A similar procedure was used to prepare X-ray quality crystals of **1a** that contain D-H_2pheHA.

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[9] Elemental analysis calcd for $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{2.5}$ (**1**): C 33.99, H 3.49, N 11.45, Cu 19.98; found: C 33.97, H 3.53, N 11.30, Cu 18.9. ESMS (methanol): *m*/*z*: 1482.8 $[M{\cdot}2NO_3]^+$.

[10] Crystal data for **1**: $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_8$, $M_r = 1689.18$, tetragonal, space group $P4_1$ (no. 76), $a = 19.310(2)$, $b = 19.310(2)$, $c = 18.330(3)$, $\alpha = 90.000$, $\beta = 90.000$, $\gamma = 90.000°$, $V = 6835.0(15)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.641$ g cm^{-1}; $2.98 < \theta < 26.50°$; crystal dimensions, $0.24 \times 0.34 \times 0.40$ mm; $\mu = 24.52$ cm^{-1}; $T = 133(2)$ K; 14015 unique of 60540 reflections collected. 14015 reflections and 784 parameters were used for the full-matrix, least-squares refinement on F^2, $R1 = 0.0560$, and $wR2 = 0.1543$. A PLATON/SQUEEZE subroutine (Spek, A. L. Platon, *Acta Crystallogr. Sect. A* **1990**, *46*, C-34) was used to handle solvent and anion disorder. Further details are given in the Supporting Information.

[11] Elemental analysis calcd for **1a** $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{4.5}$: C 33.24, H 3.66, N 11.20, Cu 19.54; found: C 33.19, H 3.69, N 11.04, Cu 19.2. ESMS (methanol): *m*/*z*: 1482.8 $[M{\cdot}2NO_3]^+$.

[12] Crystal data for **1a**: $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{12}$, $M_r = 1761.22$, tetragonal, space group $P4_3$ (no. 78), $a = 19.253(3)$, $b = 19.253(3)$, $c = 18.313(4)$, $\alpha = 90.000$, $\beta = 90.000$, $\gamma = 90.000°$, $V = 6788(2)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.723$ g cm^{-1}; $2.99 < \theta < 28.35°$; crystal dimensions(mm), $0.20 \times 0.24 \times 0.42$; $\mu = 24.82$ cm^{-1}; $T = 133(2)$ K; 16835 unique of 77985 reflections collected. 16835 reflections and 784 parameters were used for the full-matrix, least-squares refinement on F^2, $R1 = 0.0387$, $wR2 = 0.1025$. A PLATON/SQUEEZE subroutine (Spek) was used to handle solvent and anion disorder. Further details are given in the Supporting Information. CCDC-192390 (**1**) and CCDC-192391 (**1a**) contain 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).

Novel Synthetic Approach to Trinuclear 3d-4f Complexes: Specific Exchange of the Central Metal of a Trinuclear Zinc(II) Complex of a Tetraoxime Ligand with a Lanthanide(III) Ion**

Shigehisa Akine, Takanori Taniguchi, and Tatsuya Nabeshima*

Salen (*N*,*N*′-disalicylideneethylenediamine) and its analogues are fascinating and versatile ligands because their metal complexes are known to serve as catalysts of organic reactions,[1] models of catalytic centers of metalloenzymes,[2] and nonlinear optical materials.[3] The negatively charged oxygen atoms of the transition-metal complexes of the salen-type ligands can coordinate to a different cation such as an alkali metal,[4] an alkaline-earth metal,[5] a d-block transition metal,[6] or an f-block transition metal[7] to provide a number of attractive heteronuclear complexes. In particular, synthesis and characterization of heterodinuclear complexes bearing 3d and 4f transition metals are interesting and important because magnetic superexchange interactions between the bridged metal atoms may exist in the complexes.[8,9]

A variety of acyclic and cyclic "compartmental ligands" bearing two different sites have also been designed to synthesize such a heteronuclear complex.[10] However, preparation of the complexes is limited mostly to stepwise reactions using a readily available mononuclear complex. The method of the strategy can be regarded as an "addition reaction". In recent years, advanced synthetic methodology for these types of heteronuclear complexes has been developed. For example, the metal initially bound to one site of some ligands migrates to another site during the second metalation step.[11] Metal exchange between two "coordination-position isomers" of a heterodinuclear complex has also been reported.[12] Here we describe a new method—a "substitution reaction"—to synthesize a $(3d)_2(4f)$ trinuclear complex. A $(3d)_3$ homotrinuclear complex generated in a cooperative manner from three zinc(II) ions and acyclic tetraoxime ligand **1** bearing two salen-type chelating moieties[13] under-

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