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Facile Preparation of Face Differentiated, Chiral 15-Metallacrown-5 Complexes

Ann J. Stemmler, Almut Barwinski, Michael J. Baldwin, Victor Young,[†] and Vincent L. Pecoraro*

Departments of Chemistry
The University of Michigan
Ann Arbor, Michigan 48109-1055
University of Minnesota
Minneapolis, Minnesota 55455

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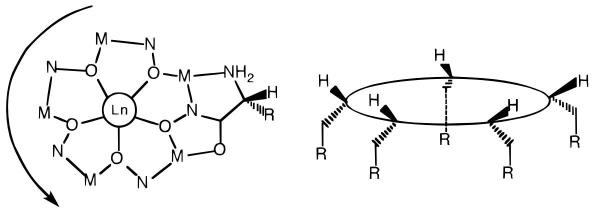
The controlled assembly of chiral transition metal clusters is a difficult task.[1] It is also synthetically challenging to differentiate two sides of a planar molecule, especially when forming hydrophobic and hydrophilic faces of a porphyrin or phthalocyanine. Porphyrins have been altered to distinguish one face of a complex in order to append mesogenic moieties.[2] Similarly, carceplexes with long alkyl chains are differentiated on one side when appended as a monolayer to a gold surface.[3] Both of these examples of site-differentiated molecules require multistep syntheses and molecular separation techniques that result in low product yields.

The metallacrowns are a new class of inorganic molecule[4] that offers a solution to the problem of face differentiation. The chiral induction of the cluster can be driven by the ring connectivity and closure of the metallacrown. As shown in Scheme 1, a 15-metallacrown-5 formed with L-α-amino hydroximates (hydroximate derivatives of the corresponding amino acids) should position each side chain upon a single face of the planar metallacrown. The side chain orientation is enforced by the directionality of the metal−nitrogen−oxygen bonds, indicated by the arrow in Scheme 1. If this connectivity is altered, ring closure is less likely to occur. Using this design concept, we have prepared and characterized the first chiral, face-differentiated metallacrown. These 15-metallacrown-5 complexes can be synthesized in methanol or water in one step and at room temperature with yields as high as 68%.

A planar 15-metallacrown-5 complex was synthesized by the addition of 0.0877 g (0.2 mmol) of $Nd(NO_3)_3$ to a solution of 0.1041 g (1 mmol) of L-α-alanine hydroxamic acid (alaha), and 0.1997 g (1 mmol) of $Cu(OAc)_2 \cdot H_2O$ in methanol. The solution was stirred for 1 h. Purple crystals grew in the saturated solution after evaporation of solvent.[5]

Scheme 1



An X-ray crystal structure of $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu(II)\ N(L\text{-}alaha)}\text{-}5]$ (**1**) was obtained, and the ORTEP diagram is shown in Figure 1.[6] As was predicted, the methyl groups of the L-alanine hydroxamic acid are all present on only one face of the metallacrown. In addition to the five ring oxygens, the Nd(III) ion is coordinated by one oxygen atom on one face and three oxygens on the other face, each from solvent water molecules. This results in a Nd(III) ion that is nine-coordinate. Four Cu(II) ions in the ring (all except Cu4) have weak interactions with one water molecule each, with an average Cu−O distance of 2.57 Å. Two independent nitrate anions are present in the lattice. As a result, charge balance requires that one water in the lattice is deprotonated as hydroxide. However, the position of this hydroxide has not been established. The reported ionic radius of nine-coordinate neodymium(III) is 1.16 Å.[7] The calculated cavity radius of the 15-metallacrown-5 is 1.17 Å. Despite the agreement between cavity and ionic radii, the Nd(III) ion is significantly displaced from the ring (by 0.64 Å) toward three bound solvent atoms on the same face as the methyl groups. This suggests that solvation of the cation can be more important in determining the displacement of the encapsulated ion than a hole−size relationship.

This synthetic strategy to isolate face differentiated 15-metallacrown-5 structures can be generally applied to generate metallacrowns using other amino hydroximates, ring metals, and lanthanide ions. Planar 15-metallacrown-5 complexes have been isolated with the ligands H_2-L-pheha, H_2-D-alaha, H_2-L-tyrha, H_2-L-metha, and H_2-L-leuha with gadolinium(III), neodymium(III), and europium(III) in various combinations. These metallacrowns are listed in Table S1 (Supporting Information). Incorporation of functionalized appendages off the metallacrown ring may be achieved by the use of other amino hydroximates. Since several forms of amino acids with various functional groups and protected sites are commercially available, this approach to complex supermolecular design can be rapidly and easily achieved.

The stability in water of mononuclear and dinuclear copper complexes with amino hydroximate ligands has been well-

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* Author to whom correspondence should be addressed.

[†] University of Minnesota.

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(5) Anal. Calcd for $Cu_5C_{45}H_{55}N_{18}O_{24}Nd$: C, 14.02; H, 3.97; N, 13.28; Cu, 23.2. Found: C, 14.11; H, 3.40; N, 12.66; Cu, 23.0. FAB+MS gave $[M]^+$ of 1095 *m/z*, $[M]^{2+}$ of 1033 *m/z* in methanol in a (3-nitrobenzyl)-alcohol matrix.

(6) X-ray parameters for **1**: orthorhombic ($P2_12_12_1$, No. 19); purple crystals, $a = 13.5774(1)$ Å, $b = 16.9867(2)$ Å, $c = 21.3471(3)$ Å, $\alpha = \beta = \gamma = 90°$; $V = 4923.4(1)$ Å^3; $Z = 4$; $R_1 = 0.0350$, $wR_2 = 0.0962$; goodness of fit on $F^2 = 1.080$. Thirteen water molecules and a single methanol solvent molecule were located in the crystal lattice. The hydrogen atoms were not located on the water molecules or hydroxide in determining the crystal structure. This molecule also has an interesting network of hydrogen bonds that surround the metallacrown. Hydrogen bonds link the water molecules that are bound to ring metal−encapsulated metal−ring metal. This linkage of hydrogen bonding is found on both faces of the metallacrown. Three of the L-alaha ligands in the metallacrown have a hydrogen bond from a water molecule to the amine nitrogen.

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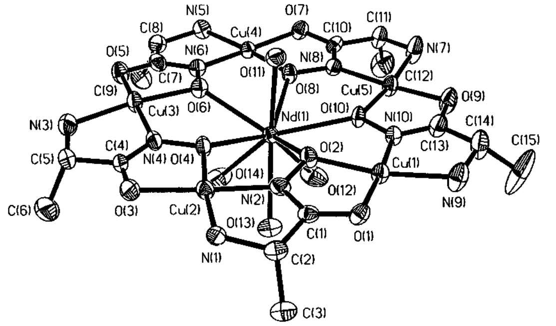

Figure 1. ORTEP representation of $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ (**1**) with 50% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd−O4, 2.494(5); Nd−O8, 2.549(4); Nd−O6, 2.538(4); Nd−O2, 2.568(4); Cu1−O2, 1.926(5); Cu1−O1, 1.968(4); Cu1−N9, 2.025(6); Cu1−N10, 1.907(5); O4−Nd−O6, 70.40(14); O4−Nd−O(water), 76.7(2), O2−Cu1−O1, 84.8(2); N10−Cu1−N9, 82.7(2); O1−Cu1−N9, 101.4(2); N10−Cu1−O2, 91.0(2).

documented.[4d,8] The solution stability of the higher nuclearity copper complexes **1** and **2** was studied in water by ESI-MS$^+$ and NMR and UV-vis spectroscopies. All of the amino hydroximate complexes that were studied by ESI-MS$^+$ show intact ions (M^{2+} and M^{3+}) and molecular ions (M^+).[9] In particular, the ESI-MS$^+$ of $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ (**1**) and $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{D}-alaha)}\text{-}5]$ (**2**) in water are identical. These two complexes are expected to have identical solution molecular weights because they only differ in the chirality of the ligand. These spectra show intact ions for $\{Nd(NO_3)[15\text{-}MC_{Cu^{II}N(ligand)}\text{-}5]\}^{2+}$ and $\{Nd[15\text{-}MC_{Cu^{II}N(ligand)}\text{-}5]\}^{3+}$. The observation of molecular ions for **1** and **2** implies that these metallacrowns retain their structure when dissolved in methanol or water. The NMR spectrum of $Nd(NO_3)_3[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ in D_2O has broad resonances at 35.92 and 9.59 ppm.[10] By peak integration, the resonance at 35.92 ppm is assigned to the α proton and the resonance at 9.59 ppm to the β protons. This observation is consistent with the proton in closest proximity to the paramagnetic center being shifted the farthest and showing the greatest line broadening.[11] All of the NMR spectra of the amino hydroximate metallacrowns that are listed in Table S1 (Supporting Information) have a resonance in the 30−45 ppm range that can be assigned to the α proton of the ligand.

The two metallacrowns **1** and **2**, were also studied in water and methanol by UV-vis spectroscopy. A titration of $Nd(NO_3)_3$ in methanol into a solution of equal amounts of $Cu(OAc)_2$ and H_2-L-alaha in methanol was followed by UV-vis spectroscopy. A well-defined endpoint in the titration curve is observed after the addition of 0.2 equiv of $Nd(NO_3)_3$. The endpoint with a lanthanide:copper ratio of 1:5 is consistent with the structure of $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ ($\lambda_{max} = 612$ nm, $\epsilon = 65\ M^{-1}\ cm^{-1}$ per Cu(II) in methanol).[12] The addition of excess Nd(III) does not affect the copper(II) ligand field spectrum, indicating that **1** is stable to the addition of excess lanthanide in methanol. A plot of concentration versus absorption of a serial dilution of **1** exhibits linear behavior in solution from 1.5 mM to 0.09 mM with the slope of the line giving the extinction coefficient. The UV-vis, mass spectrometry, and NMR spectral data lead to the conclusion that the amino hydroximate metallacrowns generally retain their integrity in water or methanol over a range of concentration of 2 orders of magnitude.

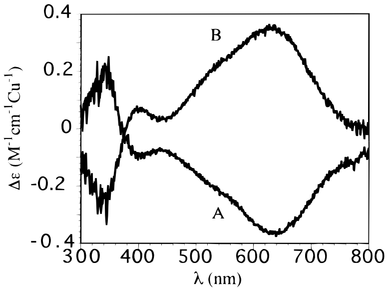

Figure 2. Circular dichroism spectra of **1** (A) and **2** (B) in water.

The chirality of the metallacrowns formed with precursor L-amino hydroximates has been explored by circular dichroism (CD) in water. The crystal structure has shown that one face of the metallacrown is differentiated when L-amino hydroximates are used. As shown in Figure 2, the CD spectra of **1** and **2** in water show equal and opposite polarization of light. If the M−N−O−M connectivity for the molecules is given the same directionality, then the opposite face of the metallacrown has been differentiated when H_2-D-alaha is used instead of H_2-L-alaha.

The bands in the CD and UV-vis spectra have been assigned assuming an idealized D_{4h} symmetry about the copper(II) ions with weak axial ligand field. The d−d bands present in the UV-vis spectra of **1** in water are at 648 nm ($\epsilon = 35\ M^{-1}\ cm^{-1}$ per metallacrown), 585 nm ($\epsilon = 20\ M^{-1}\ cm^{-1}$ per metallacrown), and 564 ($\epsilon = 185\ M^{-1}\ cm^{-1}$ per metallacrown). Two or more charge transfer bands are present at lower wavelengths, but have not been assigned. The CD spectrum revealed ligand field bands with $\Delta\epsilon$ of $-0.23\ M^{-1}\ cm^{-1}$ at 648 nm and $-0.23\ M^{-1}\ cm^{-1}$ at 556 nm. The UV-vis band at 585 nm had no resolvable CD intensity. The bands at 648, 585, and 564 nm can be assigned to the ligand field transitions $B_{1g} \rightarrow B_{2g}$, $B_{1g} \rightarrow A_{1g}$ and $B_{1g} \rightarrow E_g$, respectively, assuming a slight distortion from D_{4h} symmetry based on the significant CD intensity for two of the three transitions. Similar results were obtained for **2**, $Eu(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$, and $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-pheha)}\text{-}5]$.[13]

In summary, the 15-metallacrown-5 structure class offers a facile synthetic approach to prepare chiral clusters that can form face differentiated structures. The method is general, allowing for incorporation of a wide range of organic functional groups and different metals. The compounds are soluble and stable in water and methanol. Both solid state and solution data show the chirality of the metal cluster **1**. The face differentiation of planar 15-metallacrown-5 structures can be achieved with a variety of amino hydroximate ligands and lanthanide ions. In the future, functionalized amino hydroximates (e.g., cysteine hydroxamic acid) could be used to form metallacrowns that may be appended to a surface or converted into chiral mesophases.

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Supporting Information Available: Text, tables, and CD, UV-vis, and X-ray data (tables of crystal structure data collection parameters, bond lengths and angles, position coordinates and structure factors) (31 pages). See any current masthead page for ordering and Internet access instructions.

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(10) The NMR spectra of the $Nd(NO_3)_3[15\text{-}MC_{Cu^{II}N(\text{L}-pheha)}\text{-}5]$ and $Nd(NO_3)_3[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ in D_2O and $Nd(NO_3)_3[15\text{-}MC_{Cu^{II}N(glyha)}\text{-}5]$ in methanol-d_4 are shown in Supporting Information. Two proton resonances are predicted for glycine hydroxamic acid for the two inequivalent α protons. However, we observe only one broad peak.

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(12) The plot of [Nd]/[Cu] versus molar absorptivity at 612 nm is shown in the Supporting Information.

(13) $Eu(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-alaha)}\text{-}5]$ has nearly identical ligand field transitions and charge transfer bands. The $Nd(NO_3)_2(OH)[15\text{-}MC_{Cu^{II}N(\text{L}-pheha)}\text{-}5]$ complex shows some differences, especially in the charge transfer region and possible reversal of the order of the $B_{1g} \rightarrow B_{2g}$ and $B_{1g} \rightarrow A_{1g}$ transitions, with no observable intensity for the latter in the ligand field region. There are also significant changes in the CD intensities which are not observed in the UV-vis spectra.