container are individually sorted into the wells of a polypropylene-fritted 96-well plate according to their bead and cap color, and subsequently treated with a cleavage reagent. The cleavage reagent was then collected by filtration under a slight vacuum into a second nonporous 96-well plate. The individual removable wells of this plate were preweighed before collection of the cleavage solution. Alternatively, we also utilized glass test tubes for this procedure. The tubes were preweighed, and a single porous container was added to each tube followed by the cleavage solution (1 mL). After approximately 20 minutes the porous container was removed above the liquid level and rinsed with a small aliquot of CH_2Cl_2. The volatile components were subsequently removed under vacuum, and the residue was treated with ether. The resulting solid products were isolated in a range of 9.1 – 15.6 mg with an overall average yield of 83.5 % for the six-step sequence. The purity of each sample is excellent, and the analytical data are consistent with the structures assigned for all samples.[12]

We have applied this inert two color encoding strategy for the rapid construction of moderately sized, discrete sample libraries. It presents a simple, cost-effective method for performing mix and sort combinatorial chemistry that does not rely upon robotics, computer monitoring controls, or spectroscopic techniques. The versatility of this technology may be applied not only for the identification of lead structures but also for their subsequent optimization.

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[11] A glass-fritted vessel with a screw cap or an amber jar with a screw cap is routinely used.

[12] HPLC analysis was performed on a Hewlett-Packard ODS Hypersil column (5 μm, 4 × 125 mm) with monitoring at 220 nm. Elution was carried out with a solvent mixture A/B (A = 0.1 % TFA in water, B = 0.1 % TFA in acetonitrile); the amount of A was increased from 20 to 80 % over 20 min. A mass spectrum in the positive-ionization mode was recorded for all samples on a Hewlett-Packard electrospray mass spectrometer; selected ES-MS data: *m*/*z*: **A1** 374 [373], **B2** 348 [347], **C3** 396 [395], **D4** 510, 512 [510], **E7** 464 [463], **E9** 480 [479], **F7** 480 [479], **F10** 499 [498], **G5** 424 [424], **G11** 460 [459], **H10** 492 [491], **C12** 364 [363].

Ligand Self-Recognition in the Self-Assembly of a $[\{Cu(L)\}_2]^{2+}$ Complex: The Role of Chirality**

M. Athar Masood, Eric J. Enemark, and
T. Daniel P. Stack*

A large interest in the assembly of discrete molecular architectures from smaller molecules has developed in recent years with the realization that these assemblies may show interesting chemical, physical, and mechanical properties.[1] Examples of metal-assisted self-assembly of independent ligands to form helices,[2–8] grids,[9] knots,[10, 11] cylinders,[12] platonic shapes,[13, 14] and circular helicates[15] quantitatively with labile metals represent impressive feats of molecular design and assembly.[3, 16–19] Many forms of supramolecular complexes are intrinsically chiral, even if the individual

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[*] Prof. T. D. P. Stack, Dr. M. A. Masood, E. J. Enemark
Department of Chemistry, Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0259
E-mail: stack@leland.stanford.edu

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ligands are achiral. Achiral ligands can yield a racemic mixture of complexes such as a mixture of left- and right-handed helices under equilibrium conditions. Appropriately designed, enantiopure, polynucleating ligands can stereospecifically form a single, homochiral isomer[20] through "chiral-directed self-assembly", in which the chirality of all metal centers is identical and is dictated by ligand chirality.[1] Helices of this type have been synthesized quantitatively in solution with labile metals.[4, 6, 21] The homochirality of these complexes results from the enantiomeric purity of the starting components.

A more complex and perhaps more interesting situation arises when a mixture of ligands is used. In such systems, more types of complexes are possible. The biasing of ligand components to form a specific structural motif at equilibrium requires selective ligand recognition. Conceptually, the simplest form of selectivity is one of self-recognition whereby a single ligand type from a mixture of ligands is incorporated into each complex. An example of ligand self-recognition from a mixture of ligands with different numbers of chelating groups has been reported.[22] An example based on differences in distance between metal-chelating groups of ligands has also been reported.[23] A system is presented here that exhibits ligand self-recognition based solely on chirality in which the reaction of a racemic ligand mixture with metal ions generates only homochiral complexes.

The design of the ligand L^{6R} (Figure 1), meets three objectives needed for this study: conformational rigidity, preclusion of tetradentate ligation of a single metal, and chirality. These objectives are all accomplished by the incorporation of *trans*-1,2-diaminocyclohexane into the ligand backbone. Both the racemic ligands ${}^{rac}L^{6R}$ (R = Br, H) and the enantiomerically pure ligands[24] ${}^{RR}L^{6R}$ (R = Br, H) are readily prepared by Schiff base condensation of the appropriate diamine and 6-R-2-pyridinecarboxyaldehyde (R = Br,[25, 26] H). These ligands have geometric constraints that preclude tetradentate chelation of a single, first-row transition metal,[27, 28] and have only two effective degrees of rotational freedom, each about a N–C single bond (Figure 1). Models suggest that a binuclear metal complex, $[(ML)_2]$ complex could be generated from metals that prefer tetrahedral coordination such as Cu^I.

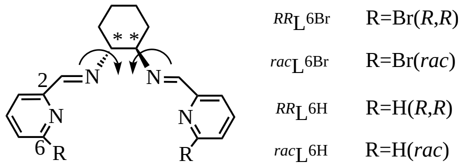

Figure 1. Nomenclature of the ligands used in this work.

In $[D_6]$DMSO ^1H NMR titrations of $[Cu^I(MeCN)_4]^+$ with ${}^{rac}L^{6R}$ show the formation of a single metal complex with D_2 symmetry at a metal:ligand ratio of 2:2. As an addition of more ligand to this 2:2 complex does not result in the formation of any new metal complex, a cooperative assembly process is indicated. The existence of a single metal species suggests that the enantiomeric forms of ${}^{rac}L^{6Br}$ sort to form exclusively either a heterochiral, binuclear complex, $[Cu2({}^{RR}L^{6Br})({}^{SS}L^{6Br})]^{2+}$, or a racemic mixture of stereospecific, homochiral[6, 20] binuclear complexes, Λ,Λ-$[\{Cu({}^{RR}L^{6Br})\}_2]^{2+}$ and Δ,Δ-$[\{Cu({}^{SS}L^{6Br})\}_2]^{2+}$ (vide infra). The identical ^1H NMR spectrum of the metal complex compared with that of a titration with enantiopure ligand ${}^{RR}L^{6Br}$ indicates that a racemic mixture of homochiral metal complexes is formed [Eq. (1)]. The bromine atom of L^{6Br} does not appear important for the stereoselectivity[20] of the assembly, because ${}^{RR}L^{6H}$ also forms a single D_2-symmetric species in solution [Eqs. (2) and (3)]. In contrast, the bromine atom plays an important role in ligand self-recognition; ${}^{rac}L^{6H}$ assembles to two diastereomeric species in solution while ${}^{rac}L^{6Br}$ exclusively forms one enantiomeric pair.[29]

$${}^{RR}L^{6Br} + {}^{SS}L^{6Br} + 2\,Cu^+ \longrightarrow \begin{matrix} 1/2\ \Lambda,\Lambda\text{-}[\{Cu({}^{RR}L^{6Br})\}_2]^{2+} \\ 1/2\ \Delta,\Delta\text{-}[\{Cu({}^{SS}L^{6Br})\}_2]^{2+} \end{matrix} \tag{1}$$

$$2\ {}^{RR}L^{6Br} + 2\,Cu^+ \longrightarrow \Lambda,\Lambda\text{-}[\{Cu({}^{RR}L^{6Br})\}_2]^{2+} \tag{2}$$

$$2\ {}^{RR}L^{6H} + 2\,Cu^+ \longrightarrow \Lambda,\Lambda\text{-}[\{Cu({}^{RR}L^{6H})\}_2]^{2+} \tag{3}$$

Crystal structures of the products of the equimolar reaction of Cu^I with either ${}^{RR}L^{6Br}$ or ${}^{rac}L^{6Br}$ support the interpretation of the behavior in solution. The enantiopure ligand generates a stereospecific binuclear species (Λ,Λ-$[\{Cu({}^{RR}L^{6Br})\}_2]^{2+}$, Figure 2),[26] while ${}^{rac}L^{6Br}$ leads to a racemic mixture of homochiral binuclear species (Λ,Λ-$[\{Cu({}^{RR}L^{6Br})\}_2]^{2+}$ and Δ,Δ-$[\{Cu({}^{SS}L^{6Br})\}_2]^{2+}$) in the unit cell.[26] Comparison of the structures of the two $[\{Cu({}^{RR}L^{6Br})\}_2]^{2+}$ entities indicates that they are nearly isostructural;[30] the greatest deviations occur in the positions of the pyridine rings. The complexes are effectively C_2-symmetric with a pseudo C_2 axis perpendicular to the Cu–Cu vector (Figure 2). The complex is significantly distorted from the idealized D_2 symmetry of a binuclear double helix; the pseudo twofold axes of the two metal

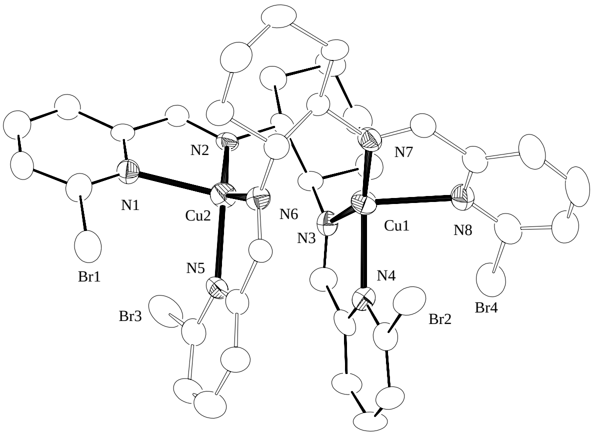

Figure 2. An ORTEP representation of the structure of Λ,Λ-$[\{Cu({}^{RR}L^{6Br})\}_2]^{2+}$ nearly perpendicular to the Cu–Cu vector (50% probability thermal ellipsoids). Shaded ellipsoids and atom labels for the trigonal monopyramidal coordination environment of each copper center are given. One ligand is drawn with solid bonds while the other is drawn with open bonds. Selected distances [Å]: N3–Cu1, 1.968(5); N3–Cu1, 1.968(5); N4–Cu1, 2.145(5); N7–Cu1, 1.966(5); N1–Cu2, 2.186(6); N2–Cu2, 1.966(5); N5–Cu2, 2.096(5); N6–Cu2, 1.993(5).

coordination spheres (bisecting N4-Cu1-N8 and N1-Cu2-N5) are not collinear.[31] This distortion makes the complex qualitatively different from a traditional helical or side-by-side binuclear structure.[4] However, the presence of identical chirality at each metal center within a given complex supports a helix designation. A clear relationship between ligand and metal chirality is found in these homochiral structures: the (R) and (S) configurations of the ligand stereocenters solely associate with the Λ and Δ metal configurations, respectively, which demonstrates the stereospecificity of the reaction.[32, 33]

The coordination geometry of each metal is best described as distorted trigonal monopyramidal rather than tetrahedral (Figure 2). The coordinated atoms in the trigonal plane (equatorial ligand atoms) consist of one pyridine (N4; N5) and two imine nitrogen atoms (N3, N7; N2, N6), while a pyridine nitrogen atom (N1; N8) occupies the axial position. The two monopyramidal coordination spheres are arranged in a antiparallel sense; the trigonal basal planes are oriented at 18° to each other. The Cu–Cu distance is short at 3.1 Å. One pyridine nitrogen atom of each ligand occupies an axial position at one copper center and an equatorial position at the other. The two pyridine–imine chelate planes within a single ligand are close to perpendicular at 80°. The equatorial pyridine rings of the two ligands are π-stacked and almost in van der Waals contact.

The D_2 symmetry suggested by the ^{1}H NMR spectrum of both $[\{Cu(^{rac}L^{6Br})\}_2]^{2+}$ and $[\{Cu(^{RR}L^{6Br})\}_2]^{2+}$ is not consistent with the distinct equatorial and axial arrangement of the pyridine rings displayed in the solid-state structures. Rapid interconversion of the axial and equatorial pyridine groups must occur in solution. While a rapid dissociative mechanism cannot be excluded, a nondissociative rearrangement is presumed. Within a single complex, simultaneous inward disrotatory motion of all 4 N–C single bonds by 90° not only maintains bonding to the metal centers while interconverting the axial and equatorial pyridine moieties, but also maintains the chirality at each metal center. The lack of broadening of the ^{1}H resonances at 200 K in [D$_6$]acetone indicates that this process must have a low energy barrier. Molecular dynamic calculations with $[\{Cu(^{RR}L^{6Br})\}_2]^{2+}$ support this interconversion mechanism with a D_2-symmetric helix-like transition state.[34]

The most interesting aspect of this system is the ligand self-recognition in the assembly process. The reaction of $^{rac}L^{6Br}$ with Cu^I ions leads to two discrete homochiral, stereospecific metal complexes: Λ,Λ-$[\{Cu(^{RR}L^{6Br})\}_2]^{2+}$ and Δ,Δ-$[\{Cu(^{SS}L^{6Br})\}_2]^{2+}$. Identification of the key structural features that promote such behavior is important for future design of other selective assembling systems. While stereospecifity and self-recognition are not required to occur simultaneously, assembling components that are rigid and project chirality almost assures a direct correlation. This is readily visualized by the construction of a cube (Figure 3) or by analogy to the classic example of "la coupe du roi".[35] Two rigid homochiral units combine to generate a compact structure (the cube in Figure 3) while two heterochiral units assemble to a structure that is less compact. As complexes generally adopt configurations that minimize the surface-to-volume ratio (maximizing intramolecular van der Waals interactions), rigid building components should preferentially assemble to homochiral, stereospecific complexes. Such is the case of the complex $[\{Cu(^{rac}L^{6Br})\}_2]^{2+}$, which has building components that possess both limited flexibility and spacially projected chirality analogous to the building components of the cube (Figure 3).

This analysis would suggest that all conformationally restricted ligands that project their chirality would exhibit ligand self-recognition and assemble in a homochiral fashion. This is not the case with $^{rac}L^{6H}$, a ligand with similar structural attributes to $^{rac}L^{6Br}$. This ligand forms both homo- and heterochiral complexes in solution in a ratio of approximately 3:1 [Eq. (4)]. The enhanced ligand selectivity exhibited by

$$^{RR}L^{6H} + {}^{SS}L^{6H} + 2\,Cu^{+} \longrightarrow \begin{array}{l} 3/8\ \Lambda,\Lambda\text{-}[\{Cu(^{RR}L^{6H})\}_2]^{2+} \\ 3/8\ \Delta,\Delta\text{-}[\{Cu(^{SS}L^{6H})\}_2]^{2+} \\ 2/8\ \Lambda,\Lambda\text{-}[Cu_2(^{RR}L^{6H})(^{SS}L^{6H})]^{2+} \end{array} \qquad (4)$$

$^{rac}L^{6Br}$ relative to $^{rac}L^{6H}$ probably does not arise from favorable nonbonded interactions of the bromine atoms within the complex formed, but rather through destabilization of unformed heterochiral complexes. With such energetics operative, such a system is not necessarily displaying "self-selective" behavior, but perhaps more accurately "opposite-deselective" behavior.

Experimental Section

The ligands $^{RR}L^{6H}$ and $^{rac}L^{6H}$ were prepared according to literature methods.[21] The ligands $^{RR}L^{6Br}$ and $^{rac}L^{6Br}$ were synthesized by reaction of

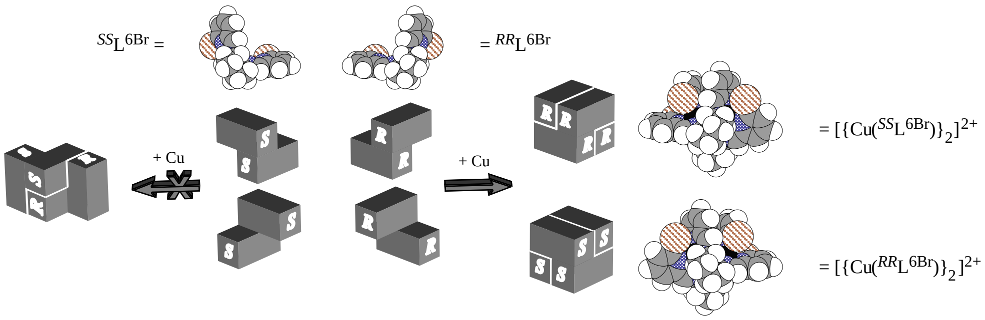

Figure 3. Self-assembly of a racemic mixture of rigid fragments to either a discrete heterochiral (Z-shaped) or homochiral (cube-shaped) species. The cube-shaped species is more compact. Space-filling drawings of the ligands ($^{RR}L^{6Br}$ and $^{SS}L^{6Br}$) and complexes (Λ,Λ-$[\{Cu(^{RR}L^{6Br})\}_2]^{2+}$ and Δ,Δ-$[\{Cu(^{SS}L^{6Br})\}_2]^{2+}$), are related to the appropriate rigid fragments and assembled products.

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6-bromo-2-pyridine-carboxyaldehyde[25] with enantiomerically pure[24] or racemic *trans*-(1,2)-diaminocyclohexane (0.5 equiv), respectively. The metal complexes were prepared by equimolar reaction of ligand with $[Cu(MeCN)_4]CF_3SO_3$ in 1:1 CH_2Cl_2:CH_3CN, followed by evaporation of the solvent.

Crystal data for $[\{Cu(^{RR}L^{6Br})\}_2](CF_3SO_3)_2 \cdot CH_3CN \cdot (C_2H_5)_2O$:[36] Crystals were grown by slow diffusion of ether into a CH_2Cl_2:MeCN solution of the complex. Space group $P2_12_12_1$ (no. 19) with cell constants based on 9999 reflections ($4.5° < 2\theta < 52.6°$): $a = 12.3865(2)$, $b = 13.9288(1)$, $c = 32.2188(3)$ Å, $V = 5558.68(9)$ Å^3, $Z = 4$. Of 27076 reflections collected at 155 K, ($4.5° < 2\theta < 52.6°$), 10026 were unique. Full matrix refinement of 667 variables based on 6964 reflections with $F_o^2 > 3\sigma F_o^2$ and σ weights converged with final residuals of $R(R_w) = 0.036(0.039)$. The absolute configuration of the molecule was assigned by the chirality of the ligand (*R,R*).

Crystal data for $[\{Cu(^{rac}L^{6Br})\}_2](CF_3SO_3)_2 \cdot CH_3OH$:[36] Crystals were grown by slow diffusion of ether into a methanol solution of the complex. Space group $P2_1/c$ (no. 14) with cell constants based on 5586 reflections ($4.5° < 2\theta < 47°$): $a = 11.702(1)$, $b = 20.898(1)$, $c = 20.015(1)$ Å, $\beta = 92.725(1)°$, $V = 4889.0(5)$ Å^3, $Z = 4$. Of 20478 reflections collected at 156 K ($4.5° < 2\theta < 47.0°$), 4795 were unique. Full matrix refinement of 613 variables based on 7227 reflections with $F_o^2 > 3\sigma F_o^2$ and σ weights converged with final residuals of $R(R_w) = 0.029(0.035)$. The $[\{Cu(^{RR}L^{6Br})\}_2]^{2+}$ and $[\{Cu(^{SS}L^{6Br})\}_2]^{2+}$ moieties are related by inversion.

Mass spectra were recorded at the University of California, San Francisco. ^{1}H NMR measurement conditions: 400 MHz, [D$_6$]DMSO, 25 °C, TMS (unless otherwise stated).

$^{rac}L^{6Br}$ and $^{RR}L^{6Br}$: ^{1}H NMR ($CDCl_3$): $\delta = 1.45$ (t, 2 H); 1.80 (s, 4 H); 1.90 (s, 2 H); 2.50 (s, 6 H); 2.75 (t, 4 H); 3.50 (t, 2 H); 7.45 (d, 2 H); 7.55 (t, 2 H); 7.90 (d, 2 H). UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 273 (10000), 232 nm (12500). Fast-atom-bombardment FABMS: $m/z = 451.0$ (found); 448.0 (calcd exact mass), 451.0 (calcd major isotope peak for $[C_{18}H_{19}Br_2N_4]^+$).

$^{rac}L^{6H}$ and $^{RR}L^{6H}$: ^{1}H NMR: $\delta = 1.48$ (m, 2 H); 1.80 (m, 6 H); 3.50 (m, 2 H); 7.38 (t, 2 H); 7.79 (t, 2 H); 7.85 (d, 2 H); 8.22 (s, 2 H; imine); 8.55 (d, 2 H). FABMS: $m/z = 293.1$ (found); 293.2 (calcd for $[C_{18}H_{21}N_4]^+$).

$[\{Cu(^{RR}L^{6Br})\}_2](CF_3SO_3)_2$ and $[\{Cu(^{rac}L^{6Br})\}_2](CF_3SO_3)_2$ ($M_r = 1325.6$): ^{1}H NMR: $\delta = 1.4$ (t, 1 H); 1.6–1.9 (pseudo dt, 2 H); 2.15 (d, 1 H); 4.05 (split s, 1 H); 7.75 (d, 1 H); 7.95 (t, 1 H); 8.9 (s, 1 H). LSIMS (LSI = liquid-secondary-ion): $m/z = 1176.7$ (found), 1177 (calcd for major isotope peak for $[(C_{18}H_{18}Br_2N_4)_2Cu_2(CF_3O_3S)]^+$); 512.9 (found), 513 (calcd major isotope peak for $[(C_{18}H_{18}Br_2N_4)Cu]^+$).

$[\{Cu(^{RR}L^{6H})\}_2](CF_3SO_3)_2$ and $[\{Cu(^{rac}L^{6H})\}_2](CF_3SO_3)_2$ ($M_r = 1010.0$): ^{1}H NMR: homochiral species: $\delta = 1.28$ (br.s, 2 H); 1.52 (br.s, 2 H); 1.75 (br.s, 2 H); 3.84 (br.s, 2 H); 7.54 (d, 2 H); 7.66 (d, 2 H); 7.97 (t, 2 H); 8.07 (d, 2 H); 8.75 (s, 2 H; imine). Heterochiral species for $^{rac}L^{6H}$ (only resonances distinguishable from the homochiral species are recorded): $\delta = 3.71$ (m, 1 H); 4.71 (m, 1 H); 7.88 (t, 2 H); 8.10 (m, 2 H); 8.30 (t, 2 H); 8.70 (s, 2 H); 9.12 (d, 2 H; imine). LSIMS: $m/z = 859.2$ (found), 859.3 (calcd major isotope peak for $[(C_{18}H_{20}N_4)_2Cu_2(CF_3O_3S)]^+$); 355.2 (found), 355.2 (calcd major isotope peak for $[(C_{18}H_{20}N_4)Cu]^+$).

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[36] General crystallographic details: data collected on a Siemens SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda =$

0.71069 Å). The structures were solved by direct methods (SHELX-86) and refined with teXsan (Crystal Structure Analysis Package, Molecular Structure Corporation). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned at an idealized geometry 0.95 Å from their parent atoms before the last cycle of refinement. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-406212 for $[\{\mathrm{Cu}({}^{RR}\mathrm{L}^{6\mathrm{Br}})\}_2](\mathrm{CF_3SO_3})_2 \cdot \mathrm{MeCN} \cdot \mathrm{Et_2O})$ and CSD-406213 for $[\{\mathrm{Cu}({}^{rac}\mathrm{L}^{6\mathrm{Br}})\}_2](\mathrm{CF_3SO_3})_2 \cdot \mathrm{MeOH})$.

Stereospecificity and Self-Selectivity in the Generation of a Chiral Molecular Tetrahedron by Metal-Assisted Self-Assembly**

Eric J. Enemark and T. Daniel P. Stack*

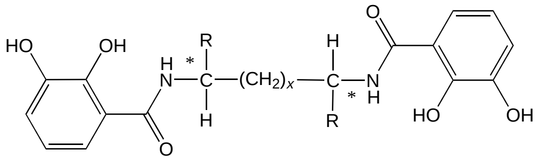

Figure 1. Structure of the bis-catecholamide ligands of this study (nomenclature given in Table 1).

Table 1. Nomenclature of the ligands and complexes.

x	R	*	Ligand	Product
0	H	–	$\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}}$	$\Lambda,\Lambda\text{-}[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}/\Delta,\Delta\text{-}[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}$
0	Me	*S*	${}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$	$\Lambda,\Lambda,\Lambda,\Lambda\text{-}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$
0	Me	*rac*	${}^{rac}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$	$\Lambda,\Lambda,\Lambda,\Lambda\text{-}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}/\Delta,\Delta,\Delta,\Delta\text{-}[\mathrm{Ga}_4({}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$
1	H	–	$\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}}$	$\Lambda,\Lambda\text{-}[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}})_3]^{6-}/\Delta,\Delta\text{-}[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}})_3]^{6-}$
1	Me	*R*	${}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$	$\Lambda,\Lambda\text{-}[\mathrm{Ga}_2({}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-}$
1	Me	*rac*	${}^{rac}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$	$[\mathrm{Ga}_2({}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-} + [\mathrm{Ga}_2({}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_2({}^{SS}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})]^{6-} +$ $[\mathrm{Ga}_2({}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})({}^{SS}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_2]^{6-} + [\mathrm{Ga}_2({}^{SS}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-}$

By design, a complex generated by metal-assisted self-assembly possesses a preconceived metal–ligand ratio (for example $\mathrm{M_nL_n}$). However, several stoichiometries satisfy this ratio ($\mathrm{M_2L_2}$, $\mathrm{M_3L_3}$, $\mathrm{M_4L_4}$,...), and recent results demonstrate that the actual stoichiometry of a supramolecular metal complex cannot be definitively predicted. A linear tris-bidentate ligand that forms a trinuclear triple helix with octahedrally coordinated metals ($\mathrm{M_3L_3}$)[1] also generates a circular helix ($\mathrm{M_5L_5}$) under different conditions.[2] More recently one bis-bidentate ligand generated a mixture of three rapidly equilibrating metal complexes $[(\mathrm{CuL})_n]^{n+}$ ($n = 1-3$).[3] Another ligand has been shown to generate both $[(\mathrm{FeL})_3]^{6+}$ and $[(\mathrm{FeL})_4]^{8+}$ complexes simultaneously.[4] In addition a binuclear $[(\mathrm{AgL_a})_2]^{2+}$ complex and a trinuclear $[(\mathrm{AgL_b})_3]^{3+}$ complex, where $\mathrm{L_a}$ and $\mathrm{L_b}$ are very similar bis-oxazoline ligands, have been crystallographically characterized.[5] The variety of stoichiometries observed with similar, or even identical ligands indicates that the factors discriminating such stoichiometries are rather subtle.

Supramolecular assemblies generated from octahedrally coordinated metals and bis-bidentate ligands include $[\mathrm{M}_{2n}\mathrm{L}_{3n}]$ complexes, where n can take the value 1,[6–17] 2,[18–22] and 4,[23] corresponding to 2:3, 4:6, and 8:12 complexes. Our previous investigations of the gallium complexes of a family of systematically varied bis(2,3-dihydroxybenzamide) ligands (Figure 1, Table 1, bis-catecholamide ligands) exclusively identified metal complexes of 2:3 stoichiometry: $[\mathrm{Ga_2L_3}]^{6-}$ ($\mathrm{L} = \mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}}$,[11, 24] $\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}}$,[9, 25] or ${}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$[9]). In contrast, our current work with ${}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ and ${}^{rac}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ (rac = racemic) ligands demonstrates a 4:6 stoichiometry [Eq. (1)], in a structure that has been described as an "adamantanoid"[19] or as a tetrahedral cluster.[22]

$$4\,\mathrm{Ga}^{3+} + 6\ {}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}} \rightarrow \Lambda,\Lambda,\Lambda,\Lambda\text{-}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-} \qquad (1)$$

The $[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$ complex has been characterized in the solid and in solution and is a stereoselectively formed tetrahedral cluster with T symmetry. More impressive is the exclusive assembly of an enantiomeric pair of homochiral tetrahedral clusters when the ligand is racemic rather than enantiopure [Eq. (2, 3)]. For a polynuclear species the term

$$\begin{gathered} 4\,(m+n)\ \mathrm{Ga}^{3+} + 6m\ {}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}} + 6n\ {}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}} \rightarrow \\ m\ \Lambda,\Lambda,\Lambda,\Lambda\text{-}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-} + n\ \Delta,\Delta,\Delta,\Delta\text{-}[\mathrm{Ga}_4({}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-} \end{gathered} \qquad (2)$$

$$\begin{gathered} 4\ \mathrm{Ga}^{3+} + 6\ {}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}} + 6\ {}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}} \not\twoheadrightarrow [\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_a({}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_{6-a}]^{12-} \\ (0 \leq \mathrm{a} \leq 6) \end{gathered} \qquad (3)$$

homochiral refers to a metal complex that meets two criteria: 1) each ligand has the same chirality, and 2) all metal centers are in identical configurations. Any metal complex that does not simultaneously satisfy both criteria is considered to be heterochiral.

Reaction of Ga^{3+} and enantiopure ${}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ in the ratio 2:3 generates a single, highly symmetric, metal complex as demonstrated by an ^{1}H NMR spectrum that contains a single set of resonances. The complex has a tetrahedral structure of 4:6 stoichiometry with a Λ configuration at each metal center: $\Lambda,\Lambda,\Lambda,\Lambda\text{-}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$. The crystal structure of $(\mathrm{Me_4N})_{12}[\mathrm{Ga}_4({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6] \cdot 42.5\,\mathrm{H_2O}$ (Figure 2) shows the metal complex to be on a site with T point symmetry. A threefold axis passes through each metal center, and a twofold axis bisects each ligand. One-third of a metal center and half of a ligand comprise the unique portion of the metal complex. All four metal centers possess identical Λ configurations defined by the configuration of the enantiopure ligand.[26, 27] An

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[*] Prof. T. D. P. Stack, E. J. Enemark
Department of Chemistry, Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1)650-725-0259
E-mail: stack@leland.stanford.edu

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