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*

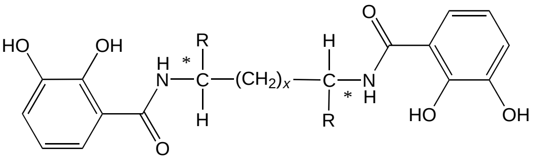

Figure 1. Structure of the bis-catecholamide ligands of this study (nomenclature given in Table 1).

Table 1. Nomenclature of the ligands and complexes.

x	R	*	Ligand	Product
0	H	–	$\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}}$	Λ,Λ-$[\mathrm{Ga_2}(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}$/$\Delta,\Delta$-$[\mathrm{Ga_2}(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}$
0	Me	*S*	${}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$	$\Lambda,\Lambda,\Lambda,\Lambda$-$[\mathrm{Ga_4}({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$
0	Me	*rac*	${}^{rac}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$	$\Lambda,\Lambda,\Lambda,\Lambda$-$[\mathrm{Ga_4}({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$/$\Delta,\Delta,\Delta,\Delta$-$[\mathrm{Ga_4}({}^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$
1	H	–	$\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}}$	Λ,Λ-$[\mathrm{Ga_2}(\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}})_3]^{6-}$/$\Delta,\Delta$-$[\mathrm{Ga_2}(\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}})_3]^{6-}$
1	Me	*R*	${}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$	Λ,Λ-$[\mathrm{Ga_2}({}^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-}$
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 M_nL_n). However, several stoichiometries satisfy this ratio (M_2L_2, M_3L_3, M_4L_4,...), and recent results demonstrate that the actual stoichiometry of a supramolecular metal complex cannot be definitively predicted. A linear trisbidentate ligand that forms a trinuclear triple helix with octahedrally coordinated metals (M_3L_3)[1] also generates a circular helix (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 L_a and 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 $[M_{2n}L_{3n}]$ 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: $\Lambda,\Lambda,\Lambda,\Lambda$-$[\mathrm{Ga_4}({}^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$. 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

---

[*] 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

[**] This research was supported by the Shell Foundation and the Stanford Office of Technology and Licensing. We thank Dr. Fred Hollander and Dr. Ryan Powers at the University of California (CHEXRAY Berkeley) for collection of the X-ray diffraction data, and the University of California Mass Spectrometry Facility (Department of Pharmaceutical Chemistry, San Francisco). Supporting information for this article is available on the www under http://www/wiley-vch.de/home/angewandte/ or from the author.

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1998
1433-7851/98/3707-0932 $ 17.50+.50/0

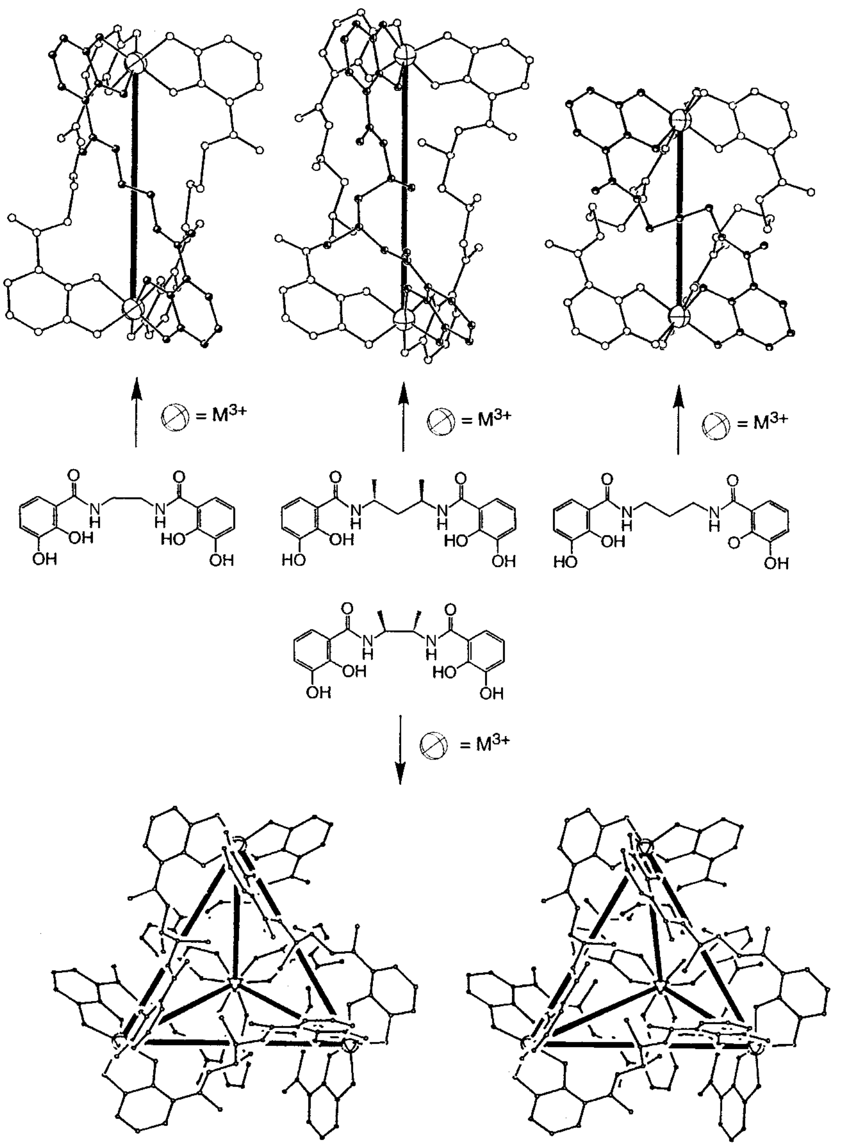

Figure 2. ORTEP representations of the structures of the complexes formed by each ligand. Atoms are represented as ideal spheres, and the metal–metal vectors are highlighted by thick lines. While $\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}}$, $\mathrm{L}_{\mathrm{pr}}^{\mathrm{H,H}}$, and $^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$ each generate a helical 2:3 metal complex (top), $^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ leads to a 4:6 tetrahedral cluster (bottom, shown as a stereoview).

identical configuration at each metal center produces a molecular topology with overall chirality. Such a tetrahedral topology has been observed previously in racemic mixtures with achiral ligands.[18, 19, 21] An achiral, S_4-symmetric, tetrahedral topology has also been demonstrated with two metals in a Λ configuration and two metals in a Δ configuration.[20, 22]

The highly symmetric, single set of ^{1}H NMR signals is consistent with the stereoselective formation in solution of the single T-symmetric tetrahedral cluster that is observed in the crystal structure analysis.[28] This stereoselectivity is analogous to that demonstrated in the formation of helical metal complexes.[5, 9, 13, 29–31] The enantiopure ligand $^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$ selectively discriminates between three potential diastereomers (Λ,Λ; Λ,Δ; Δ,Δ) to generate a 2:3 left-handed helix: Λ,Λ-$[\mathrm{Ga}_2(^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-}$.[9] Stereoselective generation of Λ,Λ,Λ,Λ-$[\mathrm{Ga}_4(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$ from enantiopure $^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ is statistically four times less probable. The observed isomer would comprise $^1/_{16}$ of a truly statistical mixture, while Λ,Λ-$[\mathrm{Ga}_2(^{RR}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}})_3]^{6-}$ would comprise $^1/_4$ of a purely statistical mixture of triply-bridged 2:3 complexes.

An impressive difference in specificity between the $\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ and $\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$ ligands is observed when the ligands are a racemic mixture rather than enantiopure. Racemic $^{rac}\mathrm{L}_{\mathrm{pr}}^{\mathrm{Me,Me}}$ generates a mixture of diastereomeric metal complexes (Table 1)[9] while $^{rac}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ produces only one enantiomeric pair of homochiral isomers in solution: Λ,Λ,Λ,Λ-$[\mathrm{Ga}_4(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$ and Δ,Δ,Δ,Δ-$[\mathrm{Ga}_4(^{RR}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$ [Table 1 and Eqs. (2) and (3)]. This result is supported by a ^{1}H NMR spectrum of the $^{rac}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ metal complex that is identical to the spectrum observed for enantiopure $[\mathrm{Ga}_4(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$. The ligands self-selectively sort based on their chirality in a stereospecific equilibrium. This process requires dramatic specificity since a total of 112 isomers are theoretically possible considering all combinations of four metal configurations with six ligand configurations and orientations.[32] The observed enantiomeric pair would comprise less than $^2/_{1024}$ of the hypothetical statistical mixture.[33]

Previous investigations of the Ga^{3+} complexes of simple alkyl-bridged bis-catechol and bis-catecholamide ligands have shown no evidence for the formation of a $[\mathrm{Ga}_{2n}\mathrm{L}_{3n}]^{6n-}$ complex where $n \neq 1$[9–11, 13–15] and prompts examination of the factors enhancing the stability of the larger $[\mathrm{M}_4\mathrm{L}_6]$ complex of $^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$. Conceptual modification of the known $[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})^3]^{6-}$ structure[24] allows a simple conformational analysis of the hypothetical 2:3 complex $[\mathrm{Ga}_2(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_3]^{6-}$, since $\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}}$ and $^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}}$ both have a two-carbon bridge between the catecholamide groups. This analysis predicts unfavorable steric interactions that are not present in the observed structure of $[\mathrm{Ga}_4(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_6]^{12-}$. Within the parent $[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}$ complex, rotational freedom about the bonds of the ligand backbone is severely restricted.[11] As a result, the torsional angles observed in the ligand backbone of $[\mathrm{Ga}_2(\mathrm{L}_{\mathrm{et}}^{\mathrm{H,H}})_3]^{6-}$ are expected to be essentially unchanged in the hypothetical $[\mathrm{Ga}_2(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_3]^{6-}$. These torsional angles are 180° ($\mathrm{N-C^1-C^2-N}$, Figure 3a), 120° ($\mathrm{C-N-C^1-C^2}$, Figure 3b), 240° ($\mathrm{C-N-C^1-H^1}$, Figure 3b), and 0° ($\mathrm{C-N-C^1-H^2}$, Figure 3b).

Given such constraints, the hypothetical helical complex $[\mathrm{Ga}_2(^{SS}\mathrm{L}_{\mathrm{et}}^{\mathrm{Me,Me}})_3]^{6-}$ is readily visualized by substituting two methyl groups for both H^1 atoms or both H^2 atoms. The substitution of both H^1 atoms (Figure 3c) generates the conformation that is sterically the most favorable for the $\mathrm{N-C^1}$ bond, whereas substituting methyl groups in the H^2

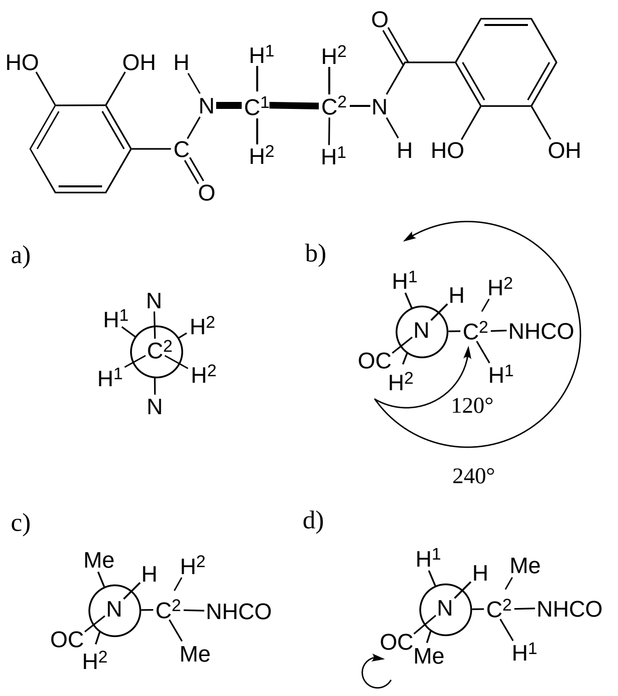

Figure 3. Newman projections of the ligand backbone (structure at the top) a) along the C^1–C^2 bond (highlighted in bold) and b), c), and d) along the N–C^1 bond (also highlighted). a, b) Representation of the ligand fragments in the $[Ga_2(L_{et}^{H,H})_3]^{6-}$ crystal structure. c, d) Modification of $[Ga_2(L_{et}^{H,H})_3]^{6-}$ to generate the hypothetical $[Ga_2({}^{SS}L_{et}^{Me,Me})_3]^{6-}$ complex. In c) H^1 has been substituted by Me to yield the lowest energy conformation, whereas in d) H^2 has been substitued to yield the highest energy conformation.

positions (Figure 3d) generates the highest energy conformation for this bond. The stability of each conformation correlates with the distances between the amide carbonyl oxygen group and C^2 and the methyl group. Calculations indicate that the difference in energy between the two conformations is 2.7 kcal mol^{-1}.[34] Because $[Ga_2L_3]^{6-}$ complexes contain six such N–C^1 units, an energetic stabilization of 16 kcal mol^{-1} in favor of the H^1-substituted metal complexes over the H^2-substituted complexes is predicted, enough to favor the former complex quantitatively. However, within the hypothetical 2:3 complex, the H^1 substitution is not possible because the methyl groups of different ligands would come into contact in the interior of the complex. As a result, the less stable conformation (H^2 substitution) would be adopted, resulting in a strained conformation that has a C-N-C^1-Me torsional angle near zero degrees (Figure 3d).

The larger internal volume of a 4:6 complex is sufficient to allow inward projection of the methyl groups without interligand contact. As a result, a favorable N–C^1 conformation is possible (two conformations were observed crystallographically with torsional angles of 250° and 300°). Projection of the methyl groups towards the interior provides additional stabilization for the $[Ga_4L_6]^{12-}$ complex over the hypothetical $[Ga_2L_3]^{6-}$ complex. In a 4:6 complex the hydrophobic methyl groups are all located within the cavity of the metal complex, whereas a 2:3 complex would direct these hydrophobic groups into the aqueous solvent. This simple analysis illustrates two important factors, namely, a favorable torsional conformation and good packing of the hydrophobic methyl groups of $L_{et}^{Me,Me}$, which result in the formation of a $[M_4L_6]$ complex rather than the $[M_2L_3]$ type of complex formed by $L_{et}^{H,H}$ that lacks methyl substituents.

An interesting difference between $\Lambda,\Lambda,\Lambda,\Lambda$-$[Ga_4({}^{SS}L_{et}^{Me,Me})_6]^{12-}$ and the previously characterized Λ,Λ-$[Ga_2({}^{RR}L_{pr}^{Me,Me})_3]^{6-}$ is that the correlation between the ligand configuration and the metal configuration is reversed ($S-\Lambda$ versus $R-\Lambda$). This reversal correlates with a reversal in the preferred projection of the methyl groups in the two compounds. The inward projection in the 4:6 complex contrasts with the external projection in the 2:3 helical complex[35] which results in opposite metal configurations.

Experimental Section

${}^{SS}L_{et}^{Me,Me}$ and ${}^{rac}L_{et}^{Me,Me}$: The ligands were synthesized as previously described,[36] from a reaction of an activated 2,3-dimethoxybenzoic acid derivative with diamine (0.5 equiv), followed by deprotection with BBr_3. The racemic and enantiomerically pure diamines used in the synthesis of ${}^{rac}L_{et}^{Me,Me}$ and ${}^{SS}L_{et}^{Me,Me}$ were prepared and resolved according to literature procedures.[26] ^{1}H NMR (400 MHz, $[D_6]$DMSO): $\delta = 12.48$ (s, 2 H; O*H*), 9.17 (s, 2 H; O*H*), 8.50 (d, $J = 8.1$ Hz, 2 H; N*H*), 7.28 (pseudo d, $J = 8.1$ Hz, 2 H; H_a), 6.90 (pseudo d, $J = 7.7$ Hz; H_c), 6.68 (pseudo t, $J = 7.9$ Hz, 2 H; H_b), 4.27 (m, 2 H; C*H*Me), 1.20 (d, $J = 6.3$ Hz, 6 H; CH*Me*). FABMS (FAB = fast-atom-bombardment): $m/z = 361.1$ calcd; 361.2 found.

$K_{12}[Ga_4({}^{SS}L_{et}^{Me,Me})_6]$ and $K_{12}[Ga_4({}^{rac}L_{et}^{Me,Me})_6]$: The metal complexes were synthesized by reaction of the ligand (6 equiv) with $[Ga(acac)_3]$ (4 equiv) and a base (KOH or $(R_4N)OH$, 12 equiv), followed by removal of the solvent and the resulting acacH under vacuum. The crude solid was dissolved in H_2O and equilibrated at 85 °C until a highly symmetric ^{1}H NMR spectrum was attained (≤ 3 hours). ^{1}H NMR (400 MHz, D_2O): $\delta = 6.87$ (pseudo d, $J = 8.2$ Hz, 2 H; H_a), 6.44 (pseudo d, $J = 7.4$ Hz; H_c), 6.30 (pseudo t, $J = 7.8$ Hz, 2 H; H_b), 3.53 (m, 2 H; C*H*Me), 0.91 (d, $J = 6.2$ Hz, 6 H; CH*Me*).

Crystal data for $(Me_4N)_{12}[Ga_4({}^{SS}L_{et}^{Me,Me})_6] \cdot 42.5\,H_2O$: the complex crystallized by diffusion of acetone into an acetonitrile/water solution in the F-centered cubic space group *F*23 (no. 196) or *F*432 (no. 209) with cell constants based on 8192 reflections ($3° < 2\theta < 46.5°$): $a = 35.3133(3)$ Å, $V = 44036.80$ Å^3, $Z = 8$. A total of 51272 reflections ($3° < 2\theta < 46.5°$) was collected at 117 K with ω scans on an Siemens SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) of which 5275 were unique to space group *F*23 (no. 196). The structure was solved by direct methods (SHELXS-86). Many of the atoms were disordered, and the structure was considered a 50:50 orthogonal twin in the space group *F*23, which was most conveniently modeled as space group *F*432 with disorder. This disorder was modeled with the aid of rigid groups at reduced occupancies. The gallium centers, coordinated oxygen atoms, amide nitrogen atoms, and bridging carbon atoms were refined anisotropically. The amide oxygen atoms and well-ordered solvent water atoms were also refined anisotropically. All other solvent atoms were refined isotropically, and rigid groups were each refined with a single isotropic parameter. Full matrix refinement of 137 variables based on all data unique to *F*23 ($3° < 2\theta < 46.5°$, 5275 reflections) converged with final residuals of $R_1 = 0.088$ ($I > 4\sigma(I)$), 1470 reflections, 912 unique to *F*432), $wR_2 = 0.213$. The absolute configuration of the space group was assigned by the chirality of the ligand (*S*,*S*).[26, 27] All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Further details on the crystal structure investigation 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-407967.

Received: September 29, 1997 [Z10982IE]
German version: *Angew. Chem.* **1998**, *110*, 977–981

Keywords: chirality · gallium · self-assembly · supramolecular chemistry

---

[1] R. Krämer, J.-M. Lehn, A. De Cian, J. Fischer, *Angew. Chem.* **1993**, *105*, 764 – 768; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703 – 706.

[2] B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987 – 1990; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838 – 1840.

[3] P. N. W. Baxter, J.-M. Lehn, K. Rissanen, *Chem. Commun.* **1997**, 1323 – 1324.

[4] F. M. Romero, R. Ziessel, A. Dupont-Gervais, A. Van Dorsselaer, *Chem. Commun.* **1996**, 551 – 553.

[5] C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonnière, A. F. Williams, *Angew. Chem.* **1997**, *109*, 1346 – 1348; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1287 – 1289.

[6] R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540 – 6546.

[7] A. F. Williams, C. Piguet, G. Bernardinelli, *Angew. Chem.* **1991**, *103*, 1530 – 1533; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1490 – 1492.

[8] D. Zurita, P. Baret, J.-L. Pierre, *New J. Chem.* **1994**, *18*, 1143 – 1146.

[9] E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1995**, *107*, 1082 – 1084; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996 – 998.

[10] M. Albrecht, S. Kotila, *Angew. Chem.* **1995**, *107*, 2285 – 2287; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2134 – 2137.

[11] E. J. Enemark, T. D. P. Stack, *Inorg. Chem.* **1996**, *35*, 2719 – 2720.

[12] B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 7221 – 7222.

[13] M. Albrecht, *Synlett* **1996**, 565 – 567.

[14] M. Albrecht, H. Röttele, P. Burger, *Chem. Eur. J.* **1996**, *2*, 1264 – 1268.

[15] M. Albrecht, S. Kotila, *Angew. Chem.* **1996**, *108*, 1299 – 1300; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1208 – 1210.

[16] V. A. Grillo, E. J. Seddon, C. M. Grant, G. Aromí, J. C. Bollinger, K. Folting, G. Christou, *Chem. Commun.* **1997**, 1561 – 1562.

[17] A. Williams, *Chem. Eur. J.* **1997**, *3*, 15 – 19.

[18] R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem.* **1988**, *100*, 878 – 880; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851 – 853.

[19] R. W. Saalfrank, A. Stark, M. Bremer, H.-U. Hummel, *Angew. Chem.* **1990**, *102*, 292 – 294; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 311 – 314.

[20] R. W. Saalfrank, B. Hörner, D. Stalke, J. Salbeck, *Angew. Chem.* **1993**, *105*, 1223 – 1225; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1179 – 1182.

[21] R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Müther, A. X. Trautwein, *Angew. Chem.* **1994**, *106*, 1697 – 1699; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1621 – 1623.

[22] T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166 – 1168; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084 – 1086.

[23] P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem. Commun.* **1997**, 1361 – 1362. A reviewer has pointed out that the reported 8:12 complex is a two-dimensional ring and that a three-dimensional 8:12 “molecular cube” is also possible.

[24] The crystal structure presented[11] is the structure of $(Et_4N)_6[Fe_2(L_{et}^{H,H})_3] \cdot 10\,H_2O$. The gallium structure is isomorphic. Crystal data for $(Et_4N)_6[Ga_2(L_{et}^{H,H})_3] \cdot 10\,H_2O$: $P3_221$ (no. 154) or $P3_121$ (no. 152), $a = 16.441(4)$, $c = 35.512(7)$ Å, $V = 8400(4)$ Å^3, $Z = 3$, $R(R_w) = 0.073(0.069)$.

[25] Since our initial report of this complex,[9] a crystal structure has been determined. Crystal data for $(TMI)_3[Ga_2(L_{pr}^{H,H})_3] \cdot 14\,H_2O$: $R\bar{3}c$ (no. 167), $a = 20.047(6)$, $c = 36.527(3)$ Å, $V = 12\,721(5)$ Å^3, $Z = 6$, $R(R_w) = 0.061(0.056)$. TMI = tetramethyldihydroimidazolinium.

[26] F. H. Dickey, W. Fickett, H. J. Lucas, *J. Am. Chem. Soc.* **1952**, *74*, 944 – 951.

[27] R. D. Gillard, *Tetrahedron* **1965**, *21*, 503 – 506.

[28] A single set of resonances is also consistent with a fluxional species or with a less symmetric species that has coinciding resonances. Fluxional behavior is highly unlikely given the lengthy equilibration time required to generate the complex and also the lack of fluxional behavior in $[Ga_2(L_{et}^{H,H})_3]^{6-}$ and $[Ga_2(L_{pr}^{H,H})_3]^{6-}$. This is demonstrated by diastereotopic signals in the ^1H NMR spectra of these complexes. Diastereotopic protons are not observed in $[Ga_4({}^{SS}L_{et}^{Me,Me})_6]^{12-}$ or in $[Ga_2({}^{RR}L_{pr}^{Me,Me})_3]^{6-}$, but none are anticipated for these complexes. A less symmetric species is also unlikely as it would be expected that the various methyl and methylene protons of the ligand backbone would have very different chemical environments.

[29] J. Libman, Y. Tor, A. Shanzer, *J. Am. Chem. Soc.* **1987**, *109*, 5880 – 5881.

[30] W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991**, *74*, 1843 – 1852.

[31] R. W. Saalfrank, M. Decker, F. Hampel, K. Peters, H. G. von Schnering, *Chem. Ber.* **1997**, *130*, 1309 – 1313.

[32] Several combinations of the two ligand enantiomers are possible: $[Ga_4({}^{SS}L_{et}^{Me,Me})_a({}^{RR}L_{et}^{Me,Me})_{6-a}]^{12-}$ $(0 \leq a \leq 6)$. If more than one of each enantiomer is present in a metal complex $(2 \leq a \leq 4)$, these ligands can be arranged in multiple orientations relative to each other. A list of all possible isomers is given in the supporting information on the WWW.

[33] Other examples of self-selectivity in self-assembly: R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394 – 5398; D. L. Caulder, K. N. Raymond, *Angew. Chem.* **1997**, *109*, 1508 – 1510; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1439 – 1442; M. A. Masood, E. J. Enemark, T. D. P. Stack, *ibid.* **1998**, *110*, 973 – 977 and **1998**, *37*, 928 – 932.

[34] AM1 calculations were performed with an idealized isopropylformamide unit.

[35] The additional carbon atom in the bridge of ${}^{RR}L_{pr}^{Me,Me}$ versus ${}^{SS}L_{et}^{Me,Me}$ provides one additional degree of rotational freedom in the ligand backbone. This degree of freedom allows an external projection of methyl groups while maintaining a favorable torsional conformation for C-N-C^1-Me. This degree of freedom is also likely to play an important role in the lack of selectivity in racemic $L_{pr}^{Me,Me}$.

[36] T. B. Karpishin, T. D. P. Stack, K. N. Raymond, *J. Am. Chem. Soc.* **1993**, *115*, 6115 – 6125.

B_4 Tetrahedra for Aluminum Atoms—A Surprising Substitution in τ-Borides $Ni_{20}Al_3B_6$ and $Ni_{20}AlB_{14}$**

Harald Hillebrecht* and Martin Ade

The solid-state chemistry of boron is remarakably diverse, which is attributed to the tendency of boron to form homonuclear interactions and numerous clusters.[1] Isolated boron atoms are usually observed for metal-rich borides with a ratio M:B > 2. Among this class of compounds, “τ-borides” of the cubic $Cr_{23}C_6$-type ($Fm3m$, $cF112$[2]) represent the largest group with about 80 examples.[3] Usually ternary

---

[*] Prof. Dr. H. Hillebrecht,[+] Dr. M. Ade
Institut für Anorganische und Analytische Chemie
Albertstrasse 21, D-79104 Freiburg (Germany)

[+] New address:
Institut für Anorganische Chemie
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228 735-660
E-mail: hille@snchemie2.chemie.uni-bonn.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (DFG). We thank Prof Dr. G. Thiele (Freiburg) for his generous support of our work.