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[14] With the 6-31G(d) basis, we have used five pure d functions rather than the usual six cartesian functions. Detailed calculations on model systems (methane, neopentane, and spiropentane) indicate that the binding at the central $C(C)_4$ substructure is not well described by small basis sets.[10] In particular, we find that diffuse functions on the central atom significantly lower the relative energies of the planar versus the tetrahedral species. The 6-311+G(2d,p) basis was found to be the smallest basis set which adequately approaches the basis set limit for this energy difference. As might have been expected, calculations on alkaplanes indicate that the full 6-311+G(2d,p) basis can be well approximated by using a 6-31G(d) basis which is enhanced to 6-311+G(2d) level at the central carbon atom and to the 6-311+G(d) level at the four α-carbon atoms, thus significantly reducing the size of the calculations. Optimization in the full 6-311+G(2d,p) basis (765 basis functions for **3**) is beyond our current computational resources.

[15] Energies for the potential functions were calculated at the MP2/6-311+G(2d,p) level using the full 6-311+G(2d,p) basis on all atoms. Geometries were optimized at the HF/6-31G(d) level.

[16] Calculations at the B3-LYP/6-311+G(3df,2p) level predict a double-well potential for **3**, but with a barrier of just 0.1 kJ mol^{-1}.

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[22] Ionization energies for the alkaplanes **1**–**3** were obtained at the RMP2/6-31G(d)//RHF/6-31G(d) level and found to be 4.6, 4.3, and 4.2 eV, respectively. Test calculations on molecules where experimental data are available suggest that ionization energies calculated at this level of theory are generally underestimated by about 0.3–0.7 eV.[11b]

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meso Myths: What Drives Assembly of Helical versus *meso*-[M_2L_3] Clusters?**

Jide Xu, Tatjana N. Parac, and Kenneth N. Raymond*

Metallohelicates are the simplest supramolecular structures formed by the self-assembly of metal centers and bridging ligands.[1, 2] With each metal center viewed as a polyhedral vertex, metallohelicates [M_2L_3] are two-vertex structures. Currently the scope and power of the supramolecular chemistry of metal coordination compounds is being explored, particularly with regard to the selective preparation of more complex architectures based on the structures containing multiple vertices.[3]

Triple helicates of M_2L_3 stoichiometry may be formed by bridging bis-bidentate ligands bound to two octahedral metal centers. This generates chiral (Λ or Δ) metal centers.[2] If there is mechanical coupling between the two centers, the chirality at one can be transmitted to the second, thereby generating the homochiral ($\Lambda\Lambda$ or $\Delta\Delta$) helicate. The magnitude of this coupling has been measured in one case.[4] In contrast, the

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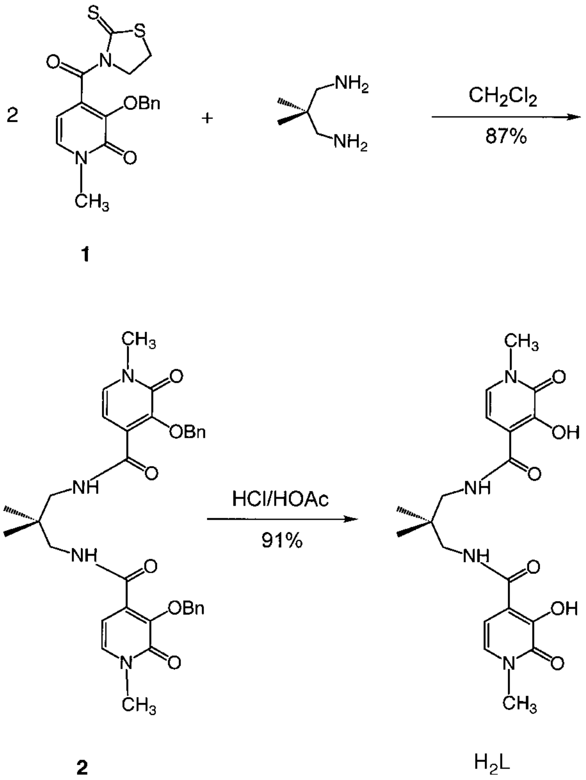
heterochiral (*ΛΔ*) complex is an achiral *meso* structure.[5] What determines the formation of either the helical or *meso* forms?

In one case it has been proposed that the length of the alkyl spacer between two bidentate chelating units of the bridging ligand can determine whether the resulting complex will have a helical or *meso* structure. Based on the principle that the most favorable conformation of a linear alkyl chain has a zigzag structure, it was suggested that a chain with an even number of atoms would favor a helix, while a chain with an odd number of atoms would favor a *meso* structure.[6] An alternative hypothesis came from a recent study in which an enantiomerically pure catecholate-based tetradentate ligand led exclusively to the formation of a *ΛΛ* triple helicate. It was suggested that a chiral ligand backbone will force the formation of a helicate and disfavor the formation of a *meso* complex.[7] Here we contradict the generality of any such hypothesis with an example of *both* helical and *meso* complexes formed from the same ligand. We further demonstrate that in this complex the interconversion of helicate to mesocate is driven by formation of a host–guest solvate.

The bis-hydroxypyridinone ligand H_2L was synthesized in an overall 79% yield according to established general synthetic methods (Scheme 1).[8] The two methyl groups in its symmetric spacer were designed as spectroscopic tags to allow monitoring of the solution structure of the metal complexes by NMR spectroscopy. In the helical complex, both metal centers have the same chirality and the two methyl groups are equivalent, related by C_2 symmetry. In the case of the *meso* complex the two methyl groups are symmetrically inequivalent. Remarkably, the solution NMR results are confirmed by the single-crystal structure analyses, which show that in the solid state the $[Al_2L_3]$ complex is a helicate, while $[Ga_2L_3]$ forms a mesocate. The crystal structures of the $[Al_2L_3]$[9] and $[Ga_2L_3]$[10] complexes (Figure 1) are markedly different: the distance between the two metal centers in the helicate $[Al_2L_3]$ is 7.13 Å, while in the mesocate $[Ga_2L_3]$ it is 9.74 Å. In addition, the helicate encapsulates a water molecule within its cavity, while no encapsulated guest is found in the mesocate $[Ga_2L_3]$, which has no significant void volume within the cluster.



Scheme 1. Synthesis of the ligand H_2L.

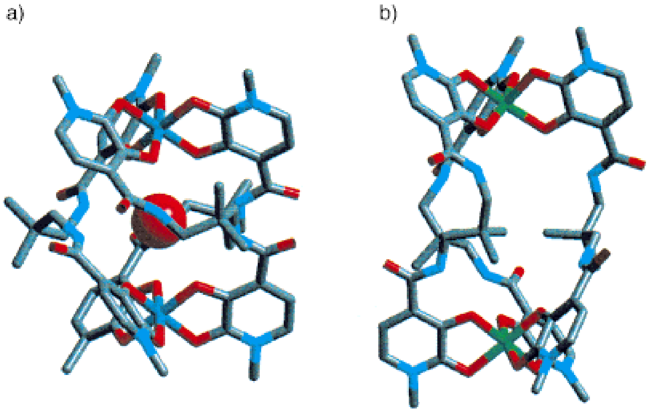


Figure 1. Crystal structures of a) $H_2O \subset (\Delta\Delta,\Lambda\Lambda)$-$[Al_2L_3]$ and b)$(\Delta\Lambda)$-$[Ga_2L_3]$ (hydrogen atoms are omitted for clarity). The $[Al_2L_3]$ helicate has a guest molecule of water in the cluster cavity. The red sphere represents the guest water oxygen atom. The wireframes represent the complexes with carbon atoms shown in gray, nitrogen atoms in deep blue, oxygen atoms in red, aluminium atoms in pale blue, and gallium atoms in green.

The water guest in $[Al_2L_3]$ is located in the center of the helicate and is close (2.9–3.0 Å) to the six phenolic oxygen donor atoms of the ligands.[11] The host–guest interaction brings the two Al^{III} centers closer and stabilizes the helicate structure. Indeed, the $[Al_2L_3]$ complex synthesized from wet methanol (containing ca. 1% water) solution yielded the pure helicate form;[12] the helical host–guest complex is the favored thermodynamic product.

While the solid-state structure of $[Ga_2L_3]$ contains only the *meso* form, ^1H NMR spectra of $[Ga_2L_3]$ in $[D_6]$DMSO show the presence of both helical and *meso* forms. The two singlets for the methyl groups at $\delta = 0.40$ and 0.85 are assigned as the resonances of the two diastereotopic methyl groups of the *meso* complex, while an additional singlet at $\delta = 0.50$ indicates that the helical form of this complex is also present in solution. The variable temperature NMR spectra (Figure 2) display the dynamic behavior of the $[Ga_2L_3]$ complex: at higher temperatures the amount of the mesocate decreases relative to the helicate. Cooling the solution to room temperature restores the original ratio of *meso* to helical complexes, indicating that these two structures are in thermodynamic equilibrium. The relative concentrations of mesocate and helicate of the $[Ga_2L_3]$ complex were determined by integrating the intensities of their methyl resonances.[13, 14] The data show that

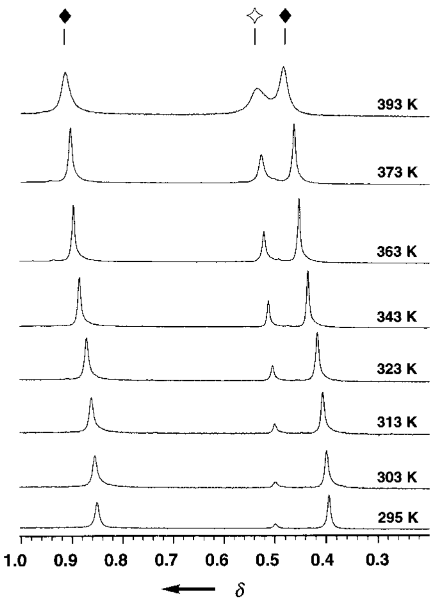


Figure 2. Variable temperature NMR spectra of $[Ga_2L_3]$ in $[D_6]$DMSO (◆: resonaces of *meso* form, ◇: resonance of helix form).

there are two temperature-dependent equilibria (1 a), one of which shows a first-order dependence on D_2O concentration. Our interpretation is that the helicate complex encapsulates either water or DMSO as a guest (G).

$$\underset{\text{mesocate}}{[M_2L_3]} \overset{K}{\rightleftharpoons} \underset{\text{helicate}}{[M_2L_3] \subset G} \tag{1a}$$

$$K = \frac{[\text{helicate}]}{[\text{mesocate}][G]} \tag{1b}$$

For G = DMSO the equilibrium constant according to Equation (1 b) will be called K_{DMSO}, for G = D_2O the constant will be called K_{water}. The ratios of helicate to mesocate are shown in Figure 3 as a function of both D_2O concentration and temperature. Since the model has two equilibrium constants, K_{DMSO} and K_{water}, there are four thermodynamic parameters, ΔH_{DMSO}, ΔH_{water}, ΔS_{DMSO}, and ΔS_{water} that define the system. A weighted least-squares fit[14] to the helicate/mesocate ratios, with the relationship shown in Equation (2), gave the following values: $\Delta H_{DMSO} = 18(3)$ kJ, $\Delta S_{DMSO} = 19(9)$ J K^{-1}, $\Delta H_{water} = 18(3)$ kJ, $\Delta S_{water} = 25(9)$ J K^{-1}. The lines

$$[\text{helicate}]/[\text{mesocate}] = [\text{DMSO}]\,e^{-(\Delta H_{DMSO}/RT + \Delta S_{DMSO}/R)} + [D_2O]\,e^{-(\Delta H_{water}/RT + \Delta S_{water}/R)} \tag{2}$$

in Figure 4 are calculated from these parameters. Like other host–guest interactions,[3f] this is entropy driven. We interpret the relatively low helicate/mesocate ratio found in DMSO to be due to the poor fit of the large guest inside the host.

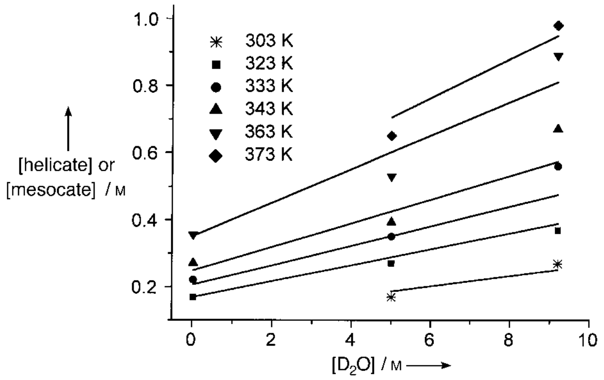


Figure 3. Plots of the helicate/mesocate ratio of $[Ga_2L_3]$ in $[D_6]$DMSO as a function of temperature and D_2O concentration. There are two temperature-dependent equilibria: one dependent on $[D_2O]$ and one independent. Both are interpreted as due to a host–guest complex formed by the helicate.

The ^1H NMR spectra of the $[Al_2L_3]$ complex in $[D_6]$DMSO also indicates dynamic behavior, although markedly slower than that of the corresponding $[Ga_2L_3]$ complex. The singlet at $\delta = 0.39$, which corresponds to two equivalent methyl groups in the helicate, slowly converts into two singlets at $\delta = 0.36$ and 0.82, which correspond to the two diastereotopically inequivalent methyl groups on the mesocate. This conversion is very slow at ambient temperature, requiring about ten days to reach equilibrium. Figure 4 shows the proton NMR spectra of the $[Al_2L_3]$ helicate in $[D_6]$DMSO immediately after dissolution (a) and the same solution after 10 days (b). After this period of time there is a new set of resonances, due to the mesocate, in addition to those of the helicate. At 295 K the ratio of helicate to mesocate is 0.62.

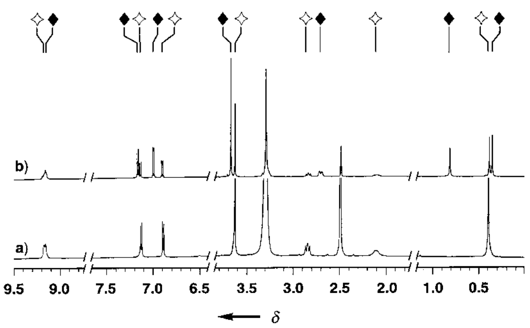


Figure 4. ^1H NMR spectra of $[Al_2L_3]$ helix in $[D_6]$DMSO solution immediately after dissolution (a), and the same solution after 10 days (b). (◆: resonaces of *meso* form, ◇: resonance of helix form).

The helicate to mesocate isomerization requires inversion at only one metal center. We have previously shown that inversion of Ga^{III}-catecholamide helicates is fast on the NMR time scale and proceeds through an intramolecular Bailar twist.[4] In general, coordination isomerization in mononuclear Al^{III} and Ga^{III} complexes proceeds through the same mechanism.[15] We therefore assume that inversion of the $[Al_2L_3]$ helicate also proceeds through an intramolecular Bailar twist. Furthermore, it is known that the rearrangement rates are consistently faster for Ga^{III}-tris-chelates than for the corresponding Al^{III} complexes. Most Ga^{III} complexes reach the fast NMR exchange limit below 273 K, while fast inversion of Al^{III} complexes sometimes requires temperatures of up to 373 K.[16] Indeed, when the $[Al_2L_3]$ complex is held above 333 K the equilibrium between the helicate and mesocate is established within a few minutes.

In summary, we have shown that the ligand H_2L forms both helicate and mesocate complexes: the $[Ga_2L_3]$ complex crystallizes as a mesocate, the $[Al_2L_3]$ complex as a helicate hydrate. Both the Ga and Al complexes form helicate–mesocate equilibria in $[D_6]$DMSO with the mesocate enthalpically favored. The helicate structure is markedly stabilized by forming a host–guest complex in which solvent is encapsulated. In both the Ga and Al complexes the inversion at the metal centers proceeds by a nondissociative mechanism.[17] The mechanical coupling between metal centers, which determines the degree to which a homochiral (helicate) or heterochiral (mesocate) complex forms, will generally require full molecular modeling for a quantitative prediction. Even then, the formation of host–guest complexes, as occurs here within the large cavity of the helicate complex, can drive the equilibrium to the otherwise less stable structure.

Experimental Section

General: All NMR spectra were measured on a 500 MHz Bruker DRX-500 spectrometer (TMS as standard). All compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

2: To a solution of 3-benzyloxy-4-(2-thioxothiazolidin-1-yl)carbonyl-2(*1*H)-pyridinone[8] (**1**, 1.44 g, 4 mmol) in CH_2Cl_2 was added neat 2,2-dimethyl-1,3-propanediamine (184 mg, 1.8 mmol). The mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was purified by flash column chromatography (SiO_2, eluent CH_2Cl_2 with 2–6% CH_3OH) to give **2** as white foam (0.92 g, 87%). ^{1}H NMR(300 MHz, $CDCl_3$): $\delta = 0.876$ (s, 6H), 3.127 (d, br, 4H), 3.565 (s, 6H), 5.301 (s, 4H), 6.507 (dd, 2H), 7.135 (d, 2H), 7.246 (d, 2H), 7.21–7.50 (m, 6H), 7.850 (t, 2H, $J = 6.6$ Hz); ^{13}C NMR(300 MHz, $CDCl_3$): $\delta = 23.0$, 36.2, 37.5, 46.4, 74.1, 104.7, 128.4, 128.7, 130.5, 131.8, 136.2, 146.0, 159.4, 163.7.

H_2L: Compound **2** (587 mg, 1 mmol) was dissolved in a 1:1 mixture of 12 M HCl and glacial acetic acid (20 mL) and stirred at room temperature for two days. Filtration followed by removal of the solvent gave a beige residue which was recrystallized from methanol/diethyl ether solution to give H_2L as a white powder in 91% yield. ^{1}H NMR (500 MHz, $[D_6]$DMSO): $\delta = 0.88$ (s, 6H); 3.17 (d, $J = 6.3$ Hz, 4H); 5.6 (s, 6H); 6.53 (d, $J = 7.3$ Hz, 2H, ArH) 7.21 (d, $J = 7.3$ Hz, 2H, ArH); 8.53 (t, $J = 6.5$ Hz, 2H, NH);.11.40 (s, 2H, phenol OH); ^{13}C NMR (500 MHz, $[D_6]$DMSO): $\delta = 23.30$, 36.84, 36.85, 46.10, 102.87, 117.65, 127.84, 147.17, 158,09, 165.70; elemental analysis (%) calcd. for $C_{19}H_{24}N_4O_6 \cdot H_2O$ (422.445): C 54.02, H 6.20, N 13.26; found: C 54.14, H 6.11, N 12.99.

$[Al_2L_3] \cdot 3H_2O$: A solution of aluminum acetylacetonate complex (0.1 mmol) in CH_3OH was added to a stirring solution of H_2L (0.16 mmol) in CH_3OH. The resulting mixture was heated under reflux overnight under an atmosphere of nitrogen. The beige microcrystalline solid that precipitated from the solution was collected by filtration, washed with methanol, and dried in a vacuum oven (yield 87%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.476$ (s, 18H), 2.115 (d, $^2J = 14$ Hz, 6H), 3.041 (dd, $^2J = 14$ Hz, $^3J = 10$ Hz, 6H), 3.683 (s, 18H), 6.774 (d, $J = 7.2$ Hz, 6H, ArH), 7.164 (d, $J = 7.2$ Hz, 6H, ArH), 9.311 (d, $J = 10$ Hz, 6H, NH); elemental analysis (%) calcd. for $Al_2C_{57}H_{66}N_{12}O_{18} \cdot 3H_2O$: C 52.05, H 5.51, N 12.78; found: C 51.84, H 5.61, N 12.52. Crystals of $[Al_2L_3] \cdot 2CHCl_3 \cdot CH_3OH \cdot 2H_2O \cdot 2C_6H_{12}$ suitable for analysis by X-ray diffraction were obtained by diffusion of cyclohexane into a 3:1 chloroform/wet methanol (with ca. 1% water) solution.

$[Ga_2L_3] \cdot H_2O$: This complex was prepared by a procedure similar to that for $[Al_2L_3] \cdot 3H_2O$, except $[Ga(acac)_3]$ was used instead of $[Al(acac)_3]$. Separation and purification were performed similarly. Yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.529$ (s, 9H), 1.002 (s, 9H), 2.938 (d, $^2J = 14$ Hz, 6H), 3.577 (dd, $^2J = 14$ Hz, $^3J = 7$ Hz, 6H), 3.757 (s, 18H), 6.743 (d, $J = 7.2$ Hz, 6H, ArH), 7.284 (d, $J = 7.2$ Hz, 6H, ArH), 9.294 (s,br, 6H, NH); elemental analysis (%) calcd for $Ga_2C_{57}H_{66}N_{12}O_{18} \cdot H_2O$: C 50.16, H 5.02, N 12.32; found: C 49.94, H 5.16, N 12.12. X ray-quality crystals of $[Ga_2L_3] \cdot 4CHCl_3 \cdot 2CH_3OH \cdot 0.5C_6H_{12}$ were obtained by diffusion of cyclohexane into a 3:1 chloroform/wet methanol (with ca. 1% water) solution.

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[5] Since a helix is by definition chiral "*meso* helicate" is an oxymoron and will not be used. Instead we will use the term "*meso* complex" or "mesocate".

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[9] Crystal data for $[Al_2L_3] \cdot 2CHCl_3 \cdot CH_3OH \cdot 2H_2O \cdot 2C_6H_{12}$ ($Al_2C_{57}H_{66}N_{12}O_{18} \cdot 2CHCl_3 \cdot CH_3OH \cdot 2H_2O \cdot 2C_6H_{12}$): $M_r = 1736.36$, monoclinic, $C2/c$ (no. 15), $a = 17.2348(1)$, $b = 20.7011(3)$, $c = 21.4044(3)$ Å, $\beta = 91.742(1)^\circ$, $V = 7633.1(1)$ Å^3, $Z = 4$, $T = 132$ K, $\rho_{calcd} = 1.305$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.317$ mm^{-1}, $F(000) = 3112.00$. Data for the crystal of dimensions $0.30 \times 0.25 \times 0.17$ mm^3 were collected on a Siemens SMART diffractometer equipped with a CCD area detector ($2\theta = 46.5^\circ$), ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Of the 15974 reflections collected, 5458 were unique ($R_{int} = 0.026$). The structure was solved by direct methods (SHELXL-97) and was refined on F^2. Data were corrected for Lorentz and polarization effects and anomalous dispersion. An empirical absorption correction was applied using XPREP (ellipsoidal model, $T_{max} = 0.909$ and $T_{min} = 0.847$). All non-hydrogen atoms except the disordered solvent (chloroform and cyclohexane) were refined anisotropically. Hydrogen atoms were assigned to idealized positions. The convensional $R_1 = 0.0526$, $wR_2 = 0.1361$ for 5458 observations ($I > 2.00\sigma(I)$) 526 parameters; maximum and minimum residual electron density in the final difference Fourier map were $+0.433$ and -0.375 e Å^{-3}.[10b]

[10] a) Crystal data for $[Ga_2L_3] \cdot 4CHCl_3 \cdot 2CH_3OH \cdot 0.5C_6H_{12}$ ($Ga_2C_{57}H_{66}N_{12}O_{18} \cdot 4CHCl_3 \cdot 2CH_3OH \cdot 0.5C_6H_{12}$): $M_r = 1930.36$, triclinic, $P\bar{1}$ (no. 2), $a = 13.6579(2)$, $b = 17.1346(3)$, $c = 18.5746(1)$ Å, $\alpha = 81.992(1)$, $\beta = 78.198(1)$, $\gamma = 78.201(1)^\circ$, $V = 4143.47(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.581$ g cm^3, $T = 143$ K, $F(000) = 2028.00$, $\mu(Mo_{K\alpha}) = 1.114$ mm^{-1}. Data for the crystal of dimensions $0.30 \times 0.25 \times 0.10$ mm^3 were collected on a Siemens SMART diffractometer equipped with a CCD area detector ($2\theta = 46.5^\circ$), ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Of the 17438 reflections collected, 11616 were unique ($R_{int} = 0.024$). The structure was solved by direct methods (SHELXL-97) and was refined on F^2. Data were corrected for Lorentz and polarization effects and anomalous dispersion. An empirical absorption was applied using XPREP (ellipsoidal model, $T_{max} = 0.868$ and $T_{min} = 0.757$). All non-hydrogen atoms except the disordered solvent (chloroform and cyclohexane) were refined anisotropically. Hydrogen atoms were assigned to idealized positions. Final $R_1 = 0.0599$, $wR_2 =$

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0.1557 for 11596 observations ($I > 2.00\sigma(I)$) 1066 parameters; maximum and minimum residual electron density in the final difference Fourier map were +0.878 and −1.123 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118969 and -118970. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The distances from the encapsulated water oxygen atom to the six endohedral oxygen atoms of the hydroxypyridinonate binding units in [Al_2L_3] are: 2.905(6), 2.905(6), 2.915(3), 2.915(3), 2.996(6), 2.996(6) Å.

[12] A quantity of 1 % of H_2O in [D_6]DMSO solution corresponds to about 0.5 M, which is a large excess of water compared to the concentration of the complex. The hydrated complex, which requires one water molecule as the guest, can be easily formed in this wet [D_6]DMSO solution.

[13] The equilibrium ratios of helicate to mesocate were determined by integration of the ^1H NMR spectra (500 MHz) of 1.0 mM [M_2L_3] complex in [D_6]DMSO solution.

[14] A nonlinear least-squares refinement minimized the function (3), where $w_i = 1/\sigma_i^2 = (1/0.06\,y_i)^2$, $y_{calcd} = K_{DMSO}[DMSO] + K_{water}[D_2O]$.

$$R = \sum_{i=1}^{n} w_i (y_{obs} - y_{calcd})_i^2 \qquad (3)$$

K_{DMSO} and K_{water} are functions of their respective ΔH and ΔS values as described in the text. The weighted R_w factor which is equal to $[R/(\Sigma w_i y_{obs}^2)]^{1/2}$ is 0.0855. The reported standard deviations are from the variance-covariance matrix.

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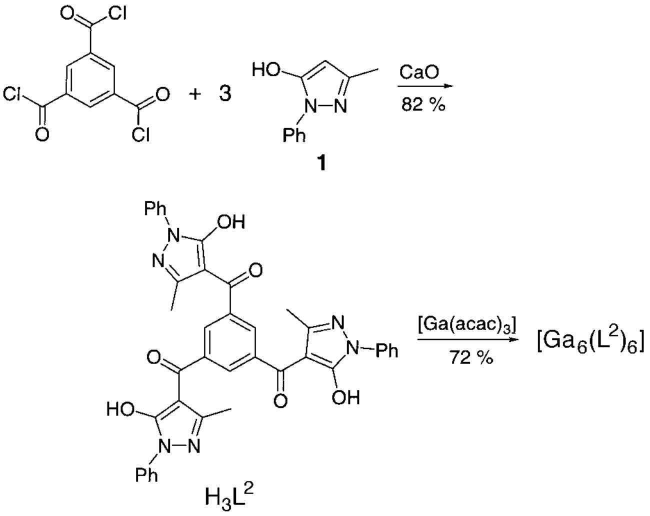
[17] Heating the [M_2L_3] complex in the presence of excess ligand did not result in the exchange of "free" and bound ligand, as determined by ^1H NMR spectroscopy.

Self-Assembly of a Three-Dimensional [$Ga_6(L^2)_6$] Metal–Ligand "Cylinder"[**]

Darren W. Johnson, Jide Xu, Rolf W. Saalfrank,[*] and Kenneth N. Raymond[*]

There are many lovely examples of supramolecular high-symmetry metal–ligand clusters.[1–5] Typically these have resulted from the self-assembly of a twofold symmetric ligand and a carefully chosen metal ion. However, there are far fewer examples of T symmetry [M_xL_y] clusters containing a threefold symmetric ligand.[6–10] [M_6L_6] and higher stoichiometry rings have been assembled from triethanolamine,[11] and Fujita and co-workers have synthesized [M_6L_4] metallamacrotricycles,[12] as well as a [M_3L_2] cagelike complex,[13] from rigid, C_3-symmetry ligands.

A rational design for the synthesis of high-symmetry, metal–ligand clusters has been reported;[14] one example is a $(HNEt_3)_8[Ti_4(L^1)_4]$ tetrahedral cluster comprising a threefold symmetric, tris-bidentate catecholamide ligand.[6] In an attempt to generalize this methodology for assembling [M_4L_4] tetrahedra, we prepared H_3L^2 (Scheme 1), a rigid, threefold symmetric, tris-bidentate, pyrazolone-based ligand. Here we describe the serendipitous formation of a [$Ga_6(L^2)_6$] "cylinder" having idealized D_3 symmetry, a new geometry for metal–ligand clusters comprising threefold symmetric ligands.



Scheme 1. Synthesis of the metal–ligand "cylinder" [$Ga_6(L^2)_6$].

The venerable class of pyrazolone ligands has recently been used in the self-assembly of M_2L_3 helicates containing lanthanum(III) ions.[15–18] Scheme 1 depicts the synthesis of the threefold symmetric, tris-β-diketone ligand H_3L^2. Treatment of 3-methyl-1-phenyl-2-pyrazoline-5-one (**1**) with 1,3,5-benzenetricarbonyl trichloride and calcium oxide in dioxane at 85 °C under an inert atmosphere affords the C_3-symmetric ligand H_3L^2 in high yield. This ligand reacts with a variety of metal acetylacetonate salts to generate high-symmetry, three-dimensional metal–ligand clusters.[19]

In particular, a microcrystalline material precipitated out of a DMSO solution of H_3L^2 and [$Ga(acac)_3$] (acac = acetylacetonate) during a period of 16 h at 90 °C. This compound analyzed as a cluster with the composition [$Ga_n(L^2)_n$] and gave, at first glance, a confusing ^1H NMR spectrum for a high-symmetry molecule. In a metal–ligand cluster with T molecular symmetry (i.e. [$Ga_4(L^2)_4$] stoichiometry), all four ligands are equivalent and one would expect to see only one set of signals shifted with respect to the free ligand.[6, 20] Surprisingly, a tripling in the number of signals was observed in both the ^1H and ^{13}C NMR spectra (Figure 1). This implies

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