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 CB21EZ, 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 ^{1}H 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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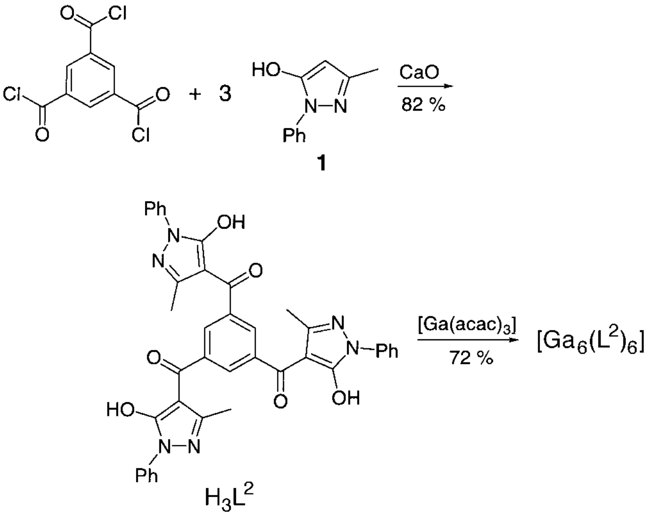
[17] Heating the [M_2L_3] complex in the presence of excess ligand did not result in the exchange of "free" and bound ligand, as determined by ^{1}H NMR spectroscopy.

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 ^{1}H 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 ^{1}H and ^{13}C NMR spectra (Figure 1). This implies

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that each arm of the ligand is inequivalent and thus the C_3 symmetry of the ligand $(L^2)^{3-}$ is disrupted upon metal complexation. None of the isomers of a tetrahedron (i.e. S_4 or C_3 symmetry) would generate a spectrum of this type.[21, 22] Additionally, the parent ion in the positive-ion FAB mass spectrum of the complex corresponds to $[Ga_6(L^2)_6]$ (*m/z* 4472.4).[23]

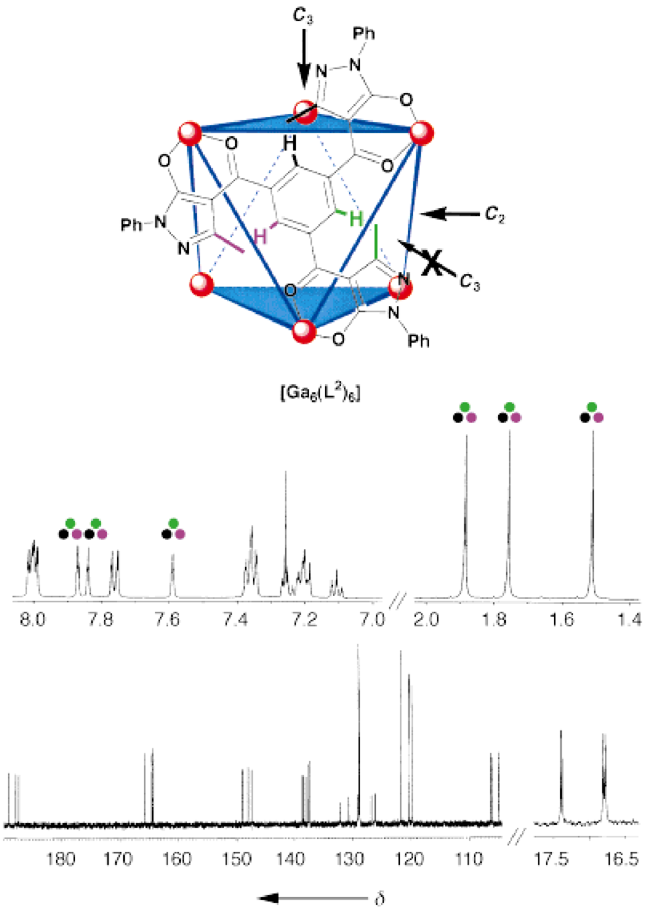

Figure 1. ^1H (top) and ^{13}C NMR spectra (bottom) of $[Ga_6(L^2)_6]$ in $CDCl_3$ showing the tripling of all ligand resonances upon complexation. The three inequivalent methyl protons and phenyl protons are labeled in color on the spectra to highlight these well-resolved signals.

The hexanuclear structure (Figure 1) justifies both the surprising stoichiometry elucidated by FAB-MS and the complicated NMR spectra. The ^1H and ^{13}C NMR spectra in $CDCl_3$ show a tripling of all ligand signals in the complex with respect to the free ligand. In particular, the three singlets in this portion of the spectrum correspond to the phenyl protons (Figure 1, shown in black, purple, and green) of the 1,3,5-trisubstituted phenyl backbone. In the putative $[Ga_6(L^2)_6]$ structure (Figure 1) the threefold axis and perpendicular twofold axes of the D_3 point group relate all six ligands by symmetry. However, there is no C_3 axis passing through the ligand backbone, therefore each arm of the ligand is inequivalent.

Single-crystal X-ray diffraction was used to confirm unequivocally this cylindrical geometry. Indeed, $[Ga_6(L^2)_6]$ crystallizes as a metal–ligand cylinder (Figure 2) in the space group $P2_1/n$ with four molecules per unit cell.[24] While the molecule has no crystallographic symmetry it can be described as having idealized D_3 molecular symmetry.[25] The gallium atoms define a distorted trigonal antiprism in which six ligands make up the equatorial faces of the cylinder with a hole at the top and the bottom. The antiprism is compressed along the pseudo C_3 axis, with average gallium $\cdots$ gallium distances of 9.82 Å (ranging from 9.71 to 9.95 Å) at the top and bottom, while the average gallium $\cdots$ gallium distance around the equator of the structure is 8.78 Å (ranging from 8.62 to 8.94 Å). Thus the pseudo threefold faces of the “holes” are larger than those occupied by the (equatorial) ligands. Due to this, the distance from the top of the prism to the bottom (Figure 3), as measured from the center of the top hole to the center of the bottom hole is 6.70 Å, whereas the average face-to-face distance between opposite equatorial sides of the antiprism is 7.88 Å. The average twist angle of the trigonal antiprism is 36.2°; a perfect trigonal antiprism would have a twist angle of 60° and a trigonal prism would have a twist angle of 0°.

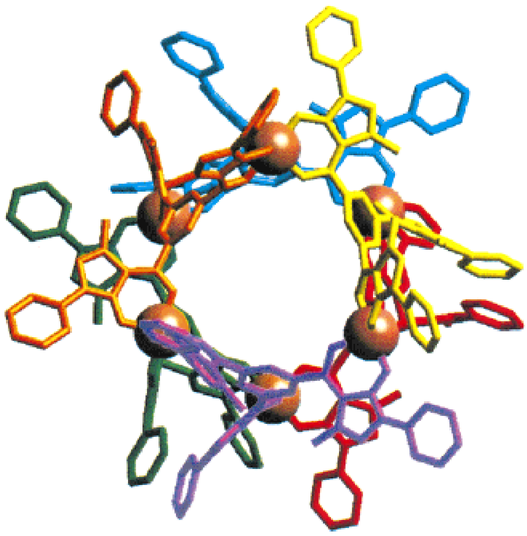

Figure 2. Wire frame and sphere representation of the crystal structure of $[Ga_6(L^2)_6]$ as viewed down the pseudo threefold axis of the cluster. For clarity each ligand is represented in a different color, with gallium ions represented by tan spheres.

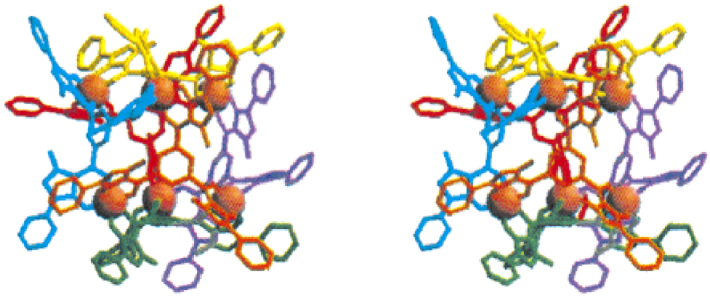

Figure 3. A stereo representation of the crystal structure of $[Ga_6(L^2)_6]$ viewed down the pseudo twofold axis of the cluster. For clarity each ligand is represented in a different color, with gallium ions represented by tan spheres.

The molecule exists as a racemic mixture of homochiral, hexanuclear clusters ($\Delta\Delta\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda\Lambda\Lambda$) in the solid state and in solution. There is no interconversion of the various possible isomers on the NMR time scale between −40 °C and 120 °C. Probably the interconversion of these species is slow due to strong chiral coupling between the metal centers. This is under investigation in this and related systems.[22, 26, 27]

Molecular modeling[28] indicates that an $[M_4L_4]$ tetrahedron could also form with $(L^2)^{3-}$, although the metal ions would be closer to one another in the tetrahedron (8.5 Å) than in the cylinder (9.82 Å) causing the methyl group of the pyrazolone functionality to be in close proximity to the phenyl backbone. Hence ΔH favors the cylinder, while ΔS favors the tetrahedron. We are currently investigating analogous compounds to try to make larger rings, and perhaps tetrahedra, in order to determine the relative magnitude of these thermodynamic forces.

In summary, we have presented the succesful formation of a new geometry of metal – ligand clusters, which we describe as cylinders. The $[Ga_6(L^2)_6]$ molecule was discovered while attempting to synthesize a $[M_4L_4]$ tetrahedron and has been unequivocally characterized by various techniques, including X-ray crystallography. This molecule has a pocket size similar to that of the cyclodextrins and could thus exhibit interesting host – guest chemistry, similar to that seen in compounds we have previously reported.[20, 29-31]

Experimental Section

General**:** All chemicals were used as received from Aldrich unless otherwise noted. The synthesis of H_3L^2 is given in the Supporting Information. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer. Mass spectra and elemental (C,H,N) analyses were performed at the Elemental Analysis Facility, College of Chemistry, UC Berkeley.

$[Ga_6(L^2)_6]$: A solution of gallium(III) acetylacetonate (0.37 g, 1 mmol) in DMSO (10 mL) was added to a suspension of $H_3L^2 \cdot H_2O$ (0.73 g, 1.05 mmol) in DMSO (30 mL). The reaction mixture was stirred under nitrogen at 90 °C for 16 h. The microcrystalline product precipitated during the reaction was collected by filtration, washed with DMSO, and dried in vacuo at 80 °C overnight. X-ray quality red block crystals were grown from a solution of the comopound in DMF in the course of two days (yield 72 %): ^{1}H NMR ($CDCl_3$): $\delta = 1.51$ (s, 3 H), 1.76 (s, 3 H), 1.89 (s, 3 H), 7.12 (t, $J = 7.4$ Hz, 1 H), 7.22 (t, $J = 8.0$ Hz, 2 H), 7.22 (t, $J = 8.0$ Hz, 1 H), 7.27 (t, $J = 7.4$ Hz, 1 H), 7.37 (t, $J = 7.7$ Hz, 2 H), 7.38 (t, $J = 7.9$ Hz, 2 H), 7.61 (s, 1 H), 7.78 (d, $J = 7.8$ Hz, 2 H), 7.86 (s, 1 H), 7.89 (s, 1 H), 8.02 (d, $J = 7.6$ Hz, 2 H), 8.03 (d, $J = 7.6$ Hz, 2 H); ^{13}C NMR ($CDCl_3$): $\delta = 16.77$, 16.80, 17.38, 104.89, 106.02, 106.30, 119.87, 120.34, 121.68, 126.10, 126.21, 126.76, 128.78, 128.91, 128.92, 129.09, 130.67, 132.06, 137.39, 137.42, 137.55, 137.99, 138.37, 138.60, 147.40, 148.02, 148.91, 164.22, 164.47, 165.66, 187.30, 187.92, 189.12; poisitve-ion FAB-MS: *m/z* (nitrobenzyl alcohol (NBA) matrix): calcd for $[Ga_6(L^2)_6H]^+$: 4472.4, found 4474; calcd for $[Ga_6(L^2)_6H_2]^{2+}$: 2236.7, found 2237; elemental analysis (%, crystals grown out of $CHCl_3$/pentane): calcd for $[Ga_6(L^2)_6] \cdot 4(C_5H_{12})$: C 64.64, H 4.81, N 10.28; found: C 64.55, H 4.82, N 10.21.

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[19] Various clusters have been synthesized containing V, Fe, Ga, In, Th, and La. For brevity we only describe the first fully characterized of these systems, $[Ga_6(L^2)_6]$, in this communication. For details on the corresponding lanthanum and thorium containing clusters see: J. Xu, K. N. Raymond, **1999**, unpublished results.

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[24] Crystal data for $[Ga_6(C_{39}H_{27}N_6O_6)_6] \cdot 13.5\,DMF \cdot 3.5H_2O \cdot x$(solvent) were collected using a Siemens SMART diffractometer equipped with a CCD area detector;[32] crystal size 0.30 × 0.10 × 0.08 mm; $T = -132\,°C$; graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); monoclinic, $P2_1/n$ (no. 14), $a = 24.8178(3)$, $b = 39.0554(7)$, $c = 31.3024(5)$ Å, $\beta = 93.721$, $V = 30277(1)$ Å^3, $Z = 4$, $\mu = 0.601\ mm^{-1}$, $F(000) = 11146$, $\rho_{calcd} = 1.192\ Mg\,m^{-3}$, $2\theta_{max} = 37.9°$. Of the 79 223 reflections collected, 23 948 were unique ($R_{int} = 0.1412$). Final $R_1 = 0.139$ for 12 941 reflections with $F_o > 4\sigma(F_o)$ (12 941 Friedel unique data, 2070 parameters, 1706 restraints, $2.04° < 2\theta < 37.9°$); for all 23 948 data, $wR_2 = 0.3613$, $GOF = 1.768$; max./min. residual density +1.176/−0.663 e Å^{-3}. (The largest difference peaks correspond to noise near severely disordered solvent). Details of the disorder in the structure are contained in the Supporting Information. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-117432. 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; email: deposit@ccdc.cam.ac.uk).

[25] Crystal data for the analogous $[In_6L^2)_6]$ cluster have been collected. The molecule crystallizes in space group $P3$ and has crystallographically imposed C_3 symmetry. The details of this structure will be contained in a future report.

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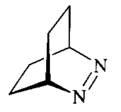
"Inverted" Solvent Effect on Charge Transfer in the Excited State**

Werner M. Nau* and Uwe Pischel

The mechanism of charge-transfer (CT) processes[1, 2] is vital to the understanding of many photochemical[3] and photobiological[4] reactions. It is paradigmatic for CT-induced photoreactions that their rates increase with solvent polarity, a phenomenon which has been most extensively examined through the fluorescence quenching of singlet-excited states.[5–7] The faster quenching in polar solvents is attributed to a stabilization of the primary reaction intermediates resulting from CT.[8] When free ions are formed, this stabilization derives from the reduced Coulombic attraction between ions in polar solvents which decreases with the inverse of the dielectric constant (ε) according to the Born formula.[8–10] When excited CT complexes or exciplexes are involved, the stabilization is related to the large induced dipole moment[11–14] and follows a $(\varepsilon\text{-}1)/(2\varepsilon+1)$ dependence according to the Kirkwood–Onsager continuum model.[5, 8–10, 15, 16]

The quenching of n,π*-excited ketones by amines and sulfides is a well-examined case of a CT-induced photoreaction,[17, 18] which displays the expected solvent effect. Herein, we have examined the fluorescence quenching of the n,π*-excited azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO)[19] by amines and sulfides, which presents a closely related example of a CT-induced photoreaction. This photoreaction is slowed down in polar solvents. To the best of our knowledge, this is the first observation of an "inverted" solvent effect on the rate constants for CT-induced quenching. It is presumed that the initial reaction step involves the formation of an exciplex with partial CT character. Counterintuitively, the exciplex is stabilized to a lesser degree by polar solvents than the reactants.



DBO

The rate constants for fluorescence quenching of DBO by triethylamine and diisopropyl sulfide in different solvents (Table 1) were on the order of 10^6–$10^8\,\mathrm{M^{-1}\,s^{-1}}$ and varied over one order of magnitude for each quencher. Linear Stern–Volmer behavior was observed in the steady-state experiments, and time-resolved measurements (for benzene and acetonitrile) gave consistent results. Most interesting, the quenching rates decreased with increasing solvent polarity (cf. Reichardt's E_T parameter[20] in Table 1), that is, they were *highest* in perfluorohexane and cyclohexane and *lowest* in acetonitrile.[21] The peculiar solvent effect of singlet-excited DBO is opposite to that established in the literature, both for n,π*-excited ketones (cf. data for triplet-excited benzophenone in Table 1) and π,π*-excited aromatic molecules as acceptors.[5–7]

Table 1. Rate constants k_q for the quenching of singlet-excited DBO and triplet-excited benzophenone by amines and sulfides in different solvents.

		k_q $[10^7\,\mathrm{M^{-1}\,s^{-1}}]$			
		NEt_3		$SiPr_2$	
Solvent	E_T[a]	$^1DBO^*$[b]	$^3Ph_2CO^*$[c]	$^1DBO^*$[b]	$^3Ph_2CO^*$[d]
perfluorohexane	30.4	24		23	
cyclohexane	33.2	14	14	6.7	9.0
Freon-113	33.2	18		5.0	14
benzene	34.8	7.2	170	1.8	19
ethyl acetate	38.1	5.6		1.4	
1,4-dioxane	36.0	6.1		1.3	
acetone	42.2	6.2		1.0	
acetonitrile	46.0	4.4	380	0.67	59

[a] Data from: C. Reichardt, E. Harbusch-Görnert, *Lieb. Ann. Chem.* **1983**, 721–743 except for Freon-113 (C. Laurence, P. Nicolet, M. Lucon, T. Dalati, C. Reichardt, *J. Chem. Soc. Perkin Trans. 2* **1989**, 873–876) and perfluorohexane (estimated from Equation (4) of the latter reference). [b] Determined from steady-state or time-resolved fluorescence quenching; error in data is 10%. [c] From: A. A. Gorman, C. T. Parekh, M. A. J. Rodgers, P. G. Smith, *J. Photochem.* **1978**, *9*, 11–17. [d] From: S. Inbar, H. Linschitz, S. G. Cohen, *J. Am. Chem. Soc.* **1982**, *104*, 1679–1682.

A mechanistic interpretation of the "inverted" solvent effect must take three pertinent features into account: a) The fluorescence quenching involves CT from the donor molecule to the excited DBO, as evidenced by the dependence of the quenching rate constant on the ionization potential of the donor (Table 2). The CT nature of the fluorescence quenching of DBO has also been firmly established for the weaker olefin donors.[22–24] Incidentally, a first indication for the unusual solvent effect (isooctane and acetonitrile) was noted by Engel et al. for olefin quenching,[23] but the underlying reasons were not discussed. b) Ion pair formation is unlikely to occur with

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