Jahn–Teller Distortion

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Second-Order Jahn–Teller Effect in a Host–Guest Complex**

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The original Jahn–Teller theorem applied to specific types of degenerate electronic systems.[1] Chemists are generally familiar with the first-order Jahn–Teller effect, which explains, for example, the elongated axial bond lengths in pseudooctahedral copper(II) complexes.[2] An often cited example of a dynamic second-order Jahn–Teller distortion is XeF_6 in the gas phase.[3] Its sterically active lone pair distorts one face of the octahedron to yield a C_{3v} ground state, yet it is in dynamical exchange through an essentially octahedral intermediate on its way to the other seven degenerate C_{3v} structures, in which the lone pair occupies the other seven faces of the octahedron.[4] Most studies concerning second-order Jahn–Teller effects involve bond distortions or ruptures within a single covalent network.[5] Herein, we report a macromolecular host–guest complex with a fluxional structure caused by the dynamic second-order Jahn–Teller effect.

The earliest example of an M_4L_6 coordination tetrahedron was reported by Saalfrank and co-workers; its time-averaged T_d symmetry in solution was readily apparent from its simple ^{1}H NMR spectrum.[6] We have described supramolecular metal–ligand assemblies of M_4L_6 stoichiometry in which the directionality, lability, and coordination strength of the metal–ligand bond drives the formation of a unique, highly symmetric molecular cluster (Figure 1 a, $M = Al^{III}$, Fe^{III}, Ga^{III}, Ti^{IV}, Ge^{IV}; L = 1,5-bis(2,3-dihydroxybenzamido)naphthalene).[7,8] Four pseudooctahedral metal ions are located at the vertices of the tetrahedron, linked by six bis(bidentate) catechol amide ligands spanning the edges. Although the cluster is constructed from achiral subunits, each tris(bidentate) coordination environment has helical chirality, and coupling by the rigid ligands forces all vertices to be homochiral; thus, the assembly has pure rotation point group T symmetry. When prepared with trivalent metal ions such as gallium(III), the anionic cluster has an overall −12 charge, which makes complexes such as $K_{12}[Ga_4L_6]$ very water soluble. The interior of the tetrahedron is surrounded by six naphthalene rings from the ligands to form a 300–500-Å^3 hydrophobic cavity that preferentially binds lipophilic monocations as guests. The amazing variety of guests encapsulated by $[Ga_4L_6]^{12-}$ continues to demonstrate its versatility as a host.[7]

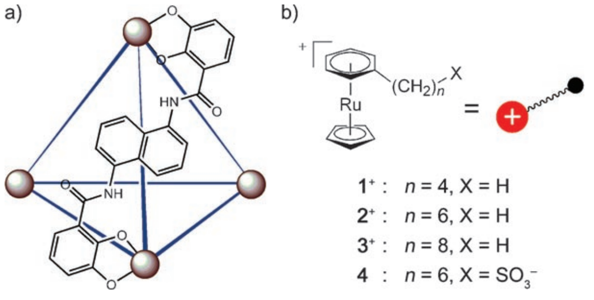

Figure 1. a) Schematic illustration of $[M_4L_6]$ showing the structure of the ligand L^{4-}. b) General structural formula for guests with *n* carbon atoms in the side chain, terminated by substituent X.

Guest ingress and egress into and out of the host cavity has been demonstrated to occur through expandable apertures in each of the four identical triangular faces of the host, centered along the three-fold rotation axis passing through the opposite vertex.[9] When a strongly bound cationic guest is tethered to a repulsive anion by a linear alkane (e.g., **4**; Figure 1 b), encapsulation of the cation by $[Ga_4L_6]^{12-}$ leads to permanent penetration of the chain through one face of the tetrahedron, allowing the anion to remain solvated outside the cavity.[10] The protruding chain is collinear with, and freely rotates about, one of the threefold axes of the tetrahedron, thus breaking the T symmetry and reducing the symmetry of the host–guest complex to C_3.

Spurred on by this result, we prepared a series of cationic analogues ($[CpRu(\eta_6\text{-}C_6H_5(CH_2)_{n-1}CH_3)]^+$; $n = 4, 6, 8$; Cp = cyclopentadienyl), which feature a neutral linear alkyl chain terminated by a methyl group (Figure 1 b, X = H). In all cases, the cationic ruthenium sandwich complex is encapsulated within the $[Ga_4L_6]^{12-}$ cluster. For a long side chain ($\mathbf{3}^+$, $n = 8$), the entire alkane cannot fit inside the cavity and remains extruded through one of the faces of the host. With a short chain ($\mathbf{1}^+$, $n = 4$), the entire guest is completely encapsulated by the host, and rapid tumbling of the guest within the cavity leads to overall T symmetry for the host–guest complex. With an intermediate chain length ($\mathbf{2}^+$, $n = 6$), the side chain rapidly extends and retracts at room temperature such that it dynamically protrudes through all four triangular faces of $[Ga_4L_6]^{12-}$ on the NMR timescale (Figure 2). During this dynamic process, the side chain retracts such that $\mathbf{2}^+$ is fully encapsulated for long enough that its tumbling averages out to T symmetry for the host–guest complex. Lowering the temperature reveals that the ground-state configuration has

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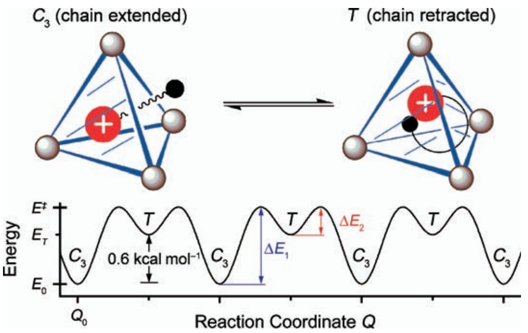

Figure 2. While the cationic Ru^{II} sandwich complex of $\mathbf{2}^+$ (red ball at top) remains within the $[Ga_4L_6]^{12-}$ cluster, the pendant alkyl chain rapidly retracts and extends at room temperature, moving the terminal methyl group (black ball) inside and outside the host cavity. The higher energy retracted state exhibits T symmetry, and the four degenerate C_3-symmetric states are lower in energy.

C_3 symmetry with the alkyl chain fully extended and protruding through one of the four triangular faces of the host. As all four apertures are identical in the retracted, T-symmetric state, there are four degenerate C_3 states. Rapid interconversion between C_3 states on the NMR timescale leads to time-averaged T symmetry at higher temperatures.

When equimolar amounts of solid **2**-PF_6 and $K_{12}[Ga_4L_6]$ are combined in D_2O, a homogeneous solution is obtained despite the very low water solubility of **2**-PF_6 on its own. This enhanced solubility is due to encapsulation of the cationic ruthenium center by the water-soluble $[Ga_4L_6]^{12-}$ host; formation of $[\mathbf{2}\subset Ga_4L_6]^{11-}$ is clearly indicated by the large upfield shifts of the ^1H NMR resonances of the Cp and phenyl rings of the guest.[10,11] At room temperature, six signals—two broad and four sharp—integrating to 12H each are observed for the 72 aromatic host protons, which is consistent with T point group symmetry (Figure 3). However, the terminal methyl resonance shows only a modest upfield shift upon encapsulation, which suggests that the methyl group does not always reside inside the magnetically shielded environment of the host cavity. At low temperature ($T < -40$ °C), the host resonances split into 24 overlapping signals integrating to 3H each, and the 2D COSY spectrum is consistent with a C_3-symmetric host–guest complex whose guest side chain protrudes from one of the face apertures. At high temperature ($T \geq 50$ °C), the host signals coalesce into six sharp peaks.

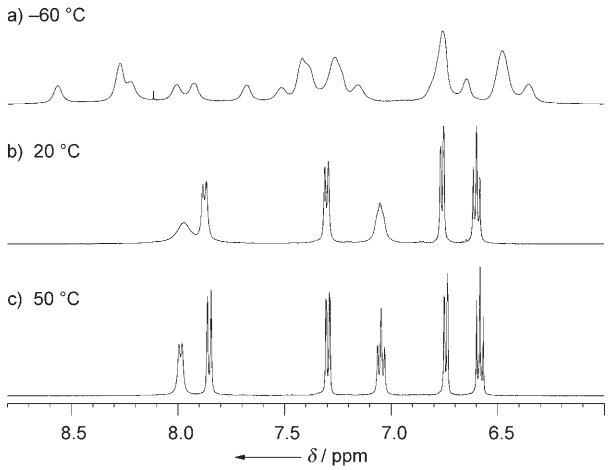

Figure 3. Aromatic region of the ^1H NMR spectra of $[\mathbf{2}\subset Ga_4L_6]^{11-}$ showing the signals for the 72 aromatic protons of the host at a) −60 °C in MeOD, b) room temperature in D_2O, and c) 50 °C in D_2O.

The 2D NOESY spectrum of $[\mathbf{2}\subset Ga_4L_6]^{11-}$ at 27 °C shows a cross-peak between the terminal methyl group of the guest and one of the catechol protons of the host. This peak indicates that, on average, the methyl group is located outside the host cavity, because the catechol protons point away from the interior of $[Ga_4L_6]^{12-}$. Similar NOE interactions were observed with related zwitterionic guests such as **4**, for which a host catechol resonance showed cross-peaks with signals from the unencapsulated portion of the alkanesulfonate chain of the guest.[10] In contrast, fully encapsulated guests such as $\mathbf{1}^+$ and Et_4N^+ only show NOE cross-peaks with the three naphthalene signals.[11]

Under the fast-exchange conditions at room temperature, the chemical shift observed for the CH_3 signal at $\delta_{obs} = 0.74$ ppm in the ^1H NMR spectrum of $[\mathbf{2}\subset Ga_4L_6]^{11-}$ is a population average of the chemical shifts for the C_3 and T states (δ_{C_3} and δ_T, respectively). From estimates of $\delta_{C_3} = 1.01$ ppm and $\delta_T = -0.12$ ppm from the CH_3 signals observed for $[\mathbf{3}\subset Ga_4L_6]^{11-}$ and $[\mathbf{1}\subset Ga_4L_6]^{11-}$, respectively, one can calculate that the methyl group is located inside the capsule about 24 % of the time (T state), and extended outside the rest of the time (C_3 state). This corresponds to an equilibrium constant $K = [T]/[C_3] = 1/3$, which means the energy difference between the T and C_3 states is about 0.6 kcal mol^{-1} (Figure 2).

The reaction-mechanism consequences of such a dynamical process were described by Pearson as based on the second-order Jahn–Teller effect.[12] Following the description of Pearson, after a displacement $q = Q - Q_0$, the Hamiltonian may be expanded as a Taylor–Maclaurin series as a function of the reaction coordinate Q, and the energy E is given by Equation (1),[12] in which E_0 is the original energy at point Q_0 ($q = 0$), U is the potential energy of the system, and ψ_k is the electronic wave function for the k^{th} energy level ($k = 0, 1, 2, \ldots$).

$$E = E_0 + \langle\psi_0|\frac{\partial U}{\partial Q}|\psi_0\rangle q + \langle\psi_0|\frac{\partial^2 U}{\partial Q^2}|\psi_0\rangle \frac{q^2}{2} + \sum_{k<0} \frac{\langle\psi_0|\frac{\partial U}{\partial Q}|\psi_k\rangle^2 q^2}{E_0 - E_k} \tag{1}$$

Although Figure 2 is a cartoon diagram of the energy of the host–guest complex, it serves to illustrate Equation (1). At maxima or minima, the slope $(\partial U/\partial Q) = 0$, and the term linear in q vanishes. For Q_0 defined as the C_3 ground state with a fully extended chain, $E = E_0$, and the force constant $(\partial^2 U/\partial Q^2) > 0$. When Q is at the transition state, with the chain partially retracted, $E > E_0$, and the force constant $(\partial^2 U/\partial Q^2) < 0$. When Q is at T, with the chain fully retracted inside the cavity, $E_T > E_0$, but now $(\partial^2 U/\partial Q^2) > 0$ because the system is at a local minimum. The last term in Equation (1) is negative, and mixing of excited states with ψ_0 lowers the energy when Q approaches T from the C_3 transition state. These are the descriptors of a second-order Jahn–Teller distortion.

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At low temperatures, the system does not have enough thermal energy to populate the appropriate excited states sufficiently to overcome the activation energy ΔE_1, and the alkyl chain of the guest remains extruded through a single face. At higher temperatures, there is a greater statistical population of excited electronic states ψ_k, permitting distortion to the transition state towards the T-symmetric intermediate. The system can easily overcome the smaller activation barrier ΔE_2 to return to one of the C_3 ground states. At 50°C, this distortion is very fast, allowing the system to interconvert rapidly between the four degenerate C_3 states through the T intermediate state, leading to the T time-averaged symmetry on the NMR timescale. This apparently represents the first reported example of a second-order Jahn–Teller distortion in a supramolecular host–guest system.

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