Host–Guest Systems

DOI: 10.1002/anie.200804225

Template and pH-Mediated Synthesis of Tetrahedral Indium Complexes $[Cs\subset\{In_4(L)_4\}]^+$ and $[In_4(H^NL)_4]^{4+}$: Breaking the Symmetry of *N*-Centered C_3 $(L)^{3-}$ To Give Neutral $[In_4(L)_4]$**

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Dedicated to Professor Bernt Krebs on the occasion of his 70th birthday

There are two classes of well known *T*-symmetric complexes, in which four octahedrally coordinated metal ions are located in the apices of a tetrahedron, and each of the six edges are bridged by linear C_2-symmetric bis(bidentate) chelators $(L^1)^{2-}$ and $(L^2)^{4-}$. In $[Cs\subset\{Fe^{II}Fe^{III}_3(L^1)_6\}]$ (**1**),[1] $[M^1\subset\{Fe^{III}_4(L^1)_6\}]^+$ (**2**; $M^1 = NH_4^+$, K^+, Cs^+),[1] and $[R_4N\subset\{M^2_4(L^2)_6\}]^{11-}$ (**3**; $M^2 = Fe^{3+}$, Ga^{3+}),[2] a cation is endohedrally encapsulated in the center of the tetrahedron, whereas in the complexes $[M^1_4\cap\{M^3_4(L^1)_6\}]$ (**4**) ($M^1 = NH_4^+$, RNH_3^+: empty, K^+, Cs^+: H_2O as guest; $M^3 = Mg^{2+}$, Co^{2+}, Ni^{2+}, Mn^{2+}),[3] four cations are exohedrally centered above the four tetrahedral triangular faces (Figure 1).

However, there are far fewer examples known of *T*-symmetric complexes,[2b,4–7] in which the octahedrally coordinated metal centers in the vertices of the tetrahedra are linked by C_3-symmetric tris(bidentate) chelators $(L^3)^{3-}$ or $(L^{4,5})^{6-}$, which occupy the faces of the tetrahedra. Examples thereof are the complexes $[Fe_4(L^3)_4]$ (**5**)[4] and $[Ti_4(L^4)_4]^{8-}$ (**6**)[2b,5] with a phenyl ring at the center of the tripodal ligand, or complex $[Ti_4(L^5)_4]^{8-}$ (**7**)[6] with nitrogen at the center of the tripodal ligand (Figure 1).

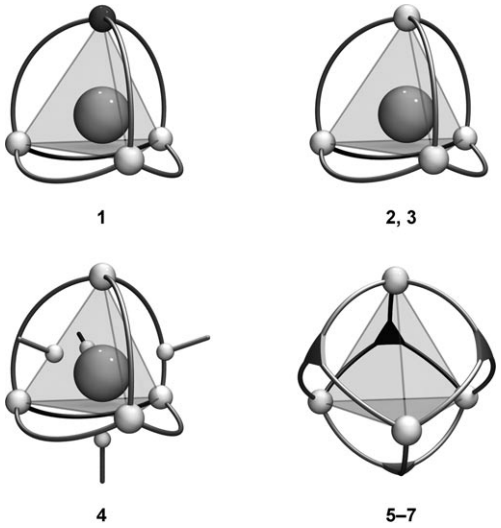

Figure 1. Schematic presentation of the complexes **1**–**7**, with the charges given as superscripts: $\mathbf{1}^0$, $\mathbf{2}^+$, $\mathbf{3}^{11-}$, $\mathbf{4}^0$, $\mathbf{5}^0$, $\mathbf{6}^{8-}$, $\mathbf{7}^{8-}$.

Recently, we reported the intermediate generation of tris(5,5-dimethyl-2,4-dioxohexyl)amine (**8**) and its isomerization in a domino cascade (aldol addition/hemiketal formation/hemiketal formation/epimerization) to dioxaazaadamantane (**9**) (Scheme 1).[8] Threefold-symmetric H_3L (**8**) is now accessible by Claisen condensation from triethyl nitrilotriacetate with pinacolone and potassium hydride in tetrahydrofuran, and isomerizes to **9** simply by adding a catalytic amount of potassium hydroxide to a solution of **8** in methanol. In addition, the *N*-centered tripodal heptadentate tris(1,3-diketonate) $(L)^{3-}$ of **8** should also be suitable for complexation of appropriate metal ions, leading to higher aggregated complexes.[9]

In the following, starting from **8**, we describe the one-pot synthesis of three new tetrahedral cages **10**–**12** by self-assembly[10] (Scheme 1). The most important parameter affecting the formation of **10** is the presence of guest cesium ions, and for **11** and **12** the pH value. Therefore, when H_3L (**8**) was first treated with cesium carbonate, and then a solution of indium(III) perchlorate in methanol was added to tris(1,3-

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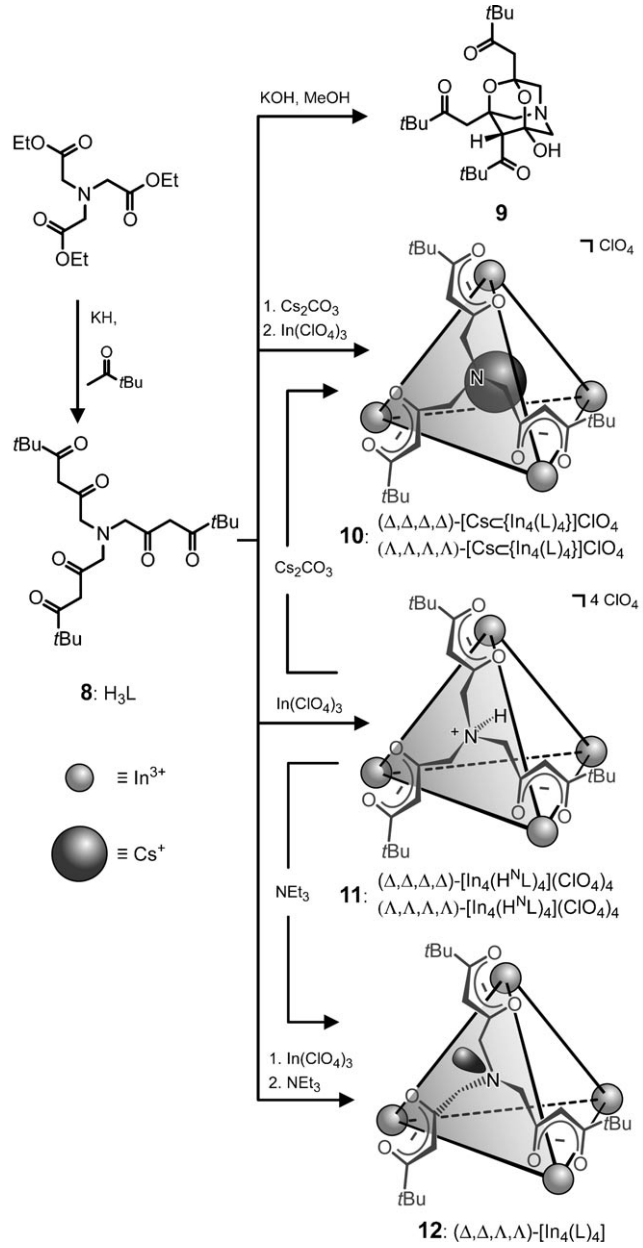
[**] Chelate Complexes, Part 39. This work was supported by the Deutsche Forschungsgemeinschaft SPP 1137 "Molecular Magnetism" (SA 276/26-1–3), SA 276/29-1, SFB 583, GK 312, SPP 1178 "Experimental Charge Density" (STA 334/14-1 and 2), the Bayerisches Langzeitprogrammm Neue Werkstoffe, and the Fonds der Chemischen Industrie. The generous allocation of premises by Prof. Dr. K. Meyer at the Institut für Anorganische Chemie (Universität Erlangen-Nürnberg) is gratefully acknowledged. We also thank Dr. M. Engeser, Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität, Bonn, for recording ESI spectra. Bruker AXS, Karlsruhe, and INCOATEC, Geesthacht, is acknowledged for continuous support. Part 38: Ref. [9a].

Supporting information for this article, including experimental details, is available on the WWW under http://dx.doi.org/10.1002/anie.200804225.



Scheme 1. Isomerization of tripodal **8** to give heteroadamantane **9**, and synthesis and representation of tetrahedra **10**–**12**.

diketonate) $(L)^{3-}$, $[Cs\subset\{In_4(L)_4\}]ClO_4$ (**10**) was isolated, whereas reaction of indium(III) perchlorate with a solution of hexaketone H_3L (**8**) in chloroform yielded $[In_4(H^NL)_4](ClO_4)_4$ (**11**). Complex **10** is also accessible from **11** by deprotonation with cesium carbonate. However, reaction of indium(III) perchlorate with H_3L (**8**) in methanol followed by triethylamine afforded $[In_4(L)_4]$ (**12**). Complex **12** is also accessible from **11** by deprotonation with triethylamine (Scheme 1).

The ^1H NMR spectrum of the cationic cesium complex $[Cs\subset\{In_4(L)_4\}]^+$ ($\mathbf{10}^+$) is compatible with *T* molecular symmetry. All four ligands are equivalent, and thus for the olefinic hydrogens and the *t*Bu groups only two singlets at $\delta =$ 5.34 and 1.09 ppm, respectively, were observed. The diastereotopic CH_2 protons appear as a simple AB pattern ($\delta =$ 3.41 ppm and 2.84 ppm, $|^2J_{H,H}| = 17.5$ Hz). The solid-state structural analysis shows that the pentanuclear monocation $[Cs\subset\{In_4(L)_4\}]^+$ ($\mathbf{10}^+$) adopts non-crystallographic T_d symmetry (Figure 2, top).[11–14] It crystallizes in the orthorhombic

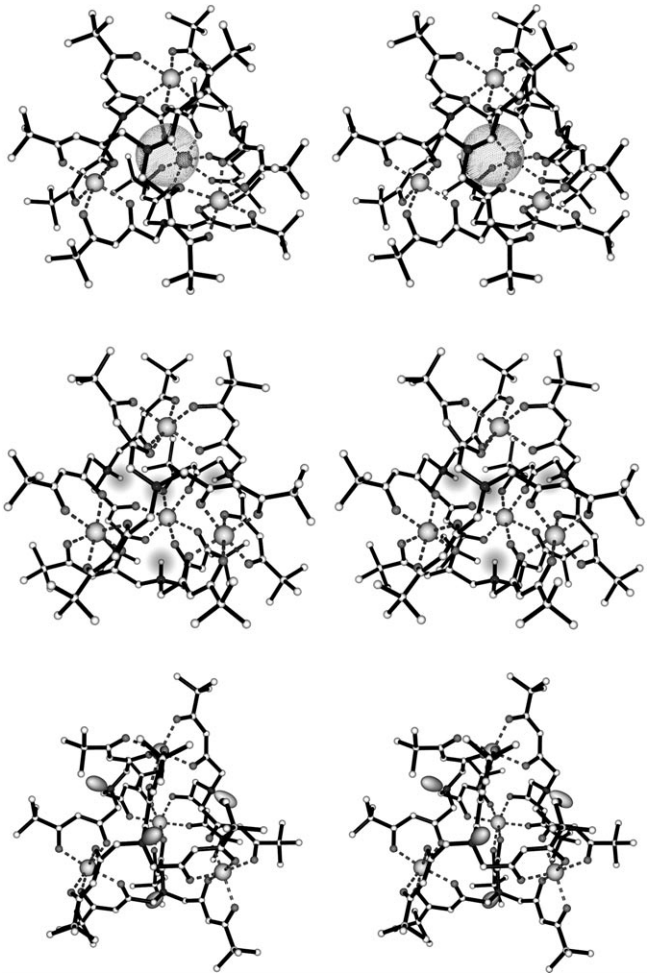


Figure 2. Stereoviews of the molecular structures of monocation (Δ,Δ,Δ,Δ)-[Cs⊂{$In_4(L)_4$}]$^+$ ($\mathbf{10}^+$, top), tetracation (Λ,Λ,Λ,Λ)-[In_4-$(H^NL)_4]^{4+}$ ($\mathbf{11}^{4+}$, center), and neutral (Δ,Δ,Λ,Λ)-[$In_4(L)_4$] (**12**, bottom) in the crystal. In gray, Cs gray (small dots), C white, O gray (small), N black. Disorder, non-coordinating solvent molecules, counterions, and hydrogen atoms are omitted for clarity, except hydrogen atoms at nitrogen in $\mathbf{11}^{4+}$ (white small, pointed out by grey clouds). The lone pairs at nitrogen in **12** are highlighted (gray sp^3 orbital).

space group $C222_1$ with half an In_4 tetrahedron in the asymmetric unit. Each indium atom is octahedrally coordinated by the six oxygen atoms of three different ligands. The endohedral cesium cation resides in the middle of the four In^{3+} cations. The charge is counterbalanced by a single exohedral chloride anion, which is not in close contact with the supramolecular core.[14] Six exohedral chloroform solvent molecules are present per ion pair, located between two adjacent In_3 triangles. The higher symmetrical space group *Cmcm* is prevented by the chiral molecule, which crystallizes

as a racemic mixture of homoconfigurational (Δ,Δ,Δ,Δ)/(Λ,Λ,Λ,Λ)-*fac* stereoisomers.

In the ^{1}H NMR spectrum of racemic (ΔΔΔΔ/ΛΛΛΛ)-*fac* $[In_4(H^NL)_4](ClO_4)_4$ (**11**), the protons within each CH_2 group of the ligand are inherently diastereotopic (geminal coupling $|^2J_{H,H}| = 17.0$ Hz), and resonate at $\delta = 4.57$ ppm and $\delta =$ 3.28 ppm, respectively. The signal at $\delta = 4.57$ ppm has additional coupling ($^3J_{H,H} = 9.5$ Hz) to the H^{N+} proton ($\delta =$ 9.11 ppm). By contrast, no coupling to the H^{N+} proton is detected for the upfield CH_2 signal at $\delta = 3.28$ ppm, as confirmed by a COSY spectrum. The lack of $^3J_{H,H}$ coupling for this proton is attributed to a near 90° dihedral angle (Karplus equation). Thus, the prochiral CH_2 protons may be assigned. Compatible with these findings, the signal of the H^{N+} proton ($\delta = 9.11$ ppm) is split into a quartet (coupling with three equivalent CH^AH^B protons). The solid-state structural analysis of $[In_4(H^NL)_4](ClO_4)_4$ (**11**; Figure 2, center) shows a tetranuclear complex tetracation similar to **10**.[11–13] It crystallizes in the chiral space group $P6_522$ with half an In_4 tetrahedron in the asymmetric unit. Each trisubstituted nitrogen atom is protonated, and remarkably, all four hydrogen atoms face the midpoint of the tetrahedron rather than pointing to the outside, as steric considerations might suggest. Pairs of exohedral perchlorate anions are located between each of the two adjacent In_3 triangles. A single chloroform solvent molecule in proximity to the supramolecular core could be located and refined. **11** crystallizes as a racemic twin of homoconfigurational (Δ,Δ,Δ,Δ)/(Λ,Λ,Λ,Λ)-*fac* stereoisomers.

At first glance, **12** gave a confusing ^{1}H NMR spectrum for a highly symmetrical molecule. Whereas in complexes **10** and **11**, with *T* molecular symmetry, all four ligands are equivalent, surprisingly, a tripling of the signals in both the ^{1}H and ^{13}C NMR spectra of **12** was observed. The ^{1}H NMR spectrum displays three different sets for the signals for the olefinic protons and *t*Bu groups ($\delta = 6.19$, 6.14, 5.53 ppm and $\delta = 1.18$, 1.16, 1.06 ppm, respectively). The three different sets of a total of twenty-four hydrogen atoms for each of the diastereotopic CH_2 protons appear as three simple, but different, AB systems ($\delta = 4.02$ ppm and 3.05 ppm, $|^2J_{H,H}| = 19.3$ Hz; $\delta = 3.48$ ppm and 3.25 ppm, $|^2J_{H,H}| = 14.7$ Hz; $\delta = 3.23$ ppm and 3.13 ppm, $|^2J_{H,H}| = 14.4$ Hz; confirmed by a COSY spectrum, see the Supporting Information). This pattern would be the case for a trigonal antiprismatic complex $[In_6(L)_6]$ of D_3 molecular symmetry, in which a threefold axis and three perpendicular twofold axes would relate all six ligands $(L)^{3-}$ by symmetry. However, there would be no C_3 axis passing through the center of the ligands, and as a result, each arm of the ligands would not be equivalent.[4,15] In contrast to these considerations, the exact mass of **12** (*m*/*z* 2196.6326) is in conflict with $[In_6(L)_6]$, but corresponds with $[In_4(L)_4]$. Furthermore, no tetrahedral system with C_3-symmetric ligands $(L)^{3-}$ would generate the ^{1}H NMR spectrum recorded. Suitable crystals for an X-ray structural analysis were obtained from solutions of **12** on standing in [D$_3$]acetonitrile.[13,16,17] Based on these data, the complex is composed of four indium ions, located in the apices of a tetrahedron linked by four C_1-symmetric ligands $(L)^{3-}$ across the tetrahedral faces (Figure 2, bottom). The C_3 symmetry of the ligands in $[In_4(L)_4]$ (**12**) is broken during deprotonation of **11**.[18] The distorted octahedrally coordinated indium ions have alternately Δ or Λ configuration, resulting in an idealized S_4 molecule symmetry for (Δ,Δ,Λ,Λ)-$[In_4(L)_4]$ (**12**). Detailed evaluation of the X-ray data of the homochiral crystals of chiral space group $P2_12_12_1$ of **12** indicates that, owing to the desymmetrized ligands $(L)^{3-}$, **12** is intrinsically chiral.

Quantum chemical calculations[19] on $[In_4(L')_4]$[20] rationalize the structural motives of **10**, **11**, and **12**. The gas-phase proton affinities for the mono inside and outside protonation $[In_4(L')_4]$ were estimated. The mono outside protonation of $[In_4(L')_4]$ showed a gas-phase proton affinity typical for amines such as $N(CH_3)_3$ or the outside protonation of cryptand [1.1.1][21,22] of -237.3 kcal mol^{-1}. In contrast, the mono inside protonation of $[In_4(L')_4]$ shows a significantly higher proton affinity of approximately -260 kcal mol^{-1}. This result impressively demonstrates the observed outside arrangement of the four nitrogen lone pairs in **12**, which clearly reduces the electron density in the cage, allowing isolation of the parent host. Therefore, protonation and ion complexation is favored inside the host, as the oxygen lone pairs act as extra donors and add further stabilization.

In summary, we have shown that tetrahedral complexes are accessible from *N*-centered tripodal heptadentate tris(1,3-diketonate) ions (L^{3-}) and indium ions. Slight changes of the reaction conditions determine whether pentanuclear complex $[Cs\subset\{In_4(L)_4\}]ClO_4$ (**10**) or the fourfold protonated complex $[In_4(H^NL)_4](ClO_4)_4$ (**11**) is generated. Most interesting, reaction of **11** with triethylamine to generate the empty cage compound $[In_4(L)_4]$ (**12**) comes with a break of the symmetry in the initial C_3-symmetric tripodal ligand. The structures of **10**–**12** were determined by the combination of mass spectrometry, NMR spectroscopy, single-crystal X-ray analyses, and DFT calculations. Reactions of the outward oriented lone pairs at nitrogen of **12** with electrophiles are in progress.

Received: August 26, 2008

Keywords: host–guest systems · indium · N,O ligands · self-assembly · X-ray diffraction

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[14] Suitable crystals for an X-ray structure analysis could only be obtained from solutions of **10** in chloroform. During the crystallization process of **10**, a counterion exchange from perchlorate to chloride occurred. This complex [Cs⊂{$In_4(L)_4$}]Cl is denoted as **10**-Cl.

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[16] Crystal data for **12**·6.25 CD_3CN: $C_{108.50}H_{144}D_{18.75}In_4N_{10.25}O_{24}$, $M_r = 2472.90$; crystal size $0.32 \times 0.23 \times 0.04$ mm^3; orthorhombic, space group $P2_12_12_1$, $a = 18.183(4)$, $b = 18.811(2)$, $c = 35.947(4)$ Å, $V = 12295(3)$ Å^3; $Z = 4$; $F(000) = 5094$, $\rho_{calcd} = 1.336$ g cm^{-3}; Nonius-KappaCCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 100(2)$ K; graphite monochromator; θ range $3.32 < \theta < 27.10°$; section of the reciprocal lattice: $-23 \le h \le 23$, $-24 \le k \le 24$, $-46 \le l \le 46$. A semiempirical absorption correction based on multiple scans was applied (SADABS 2.06;[25] $T_{min} = 0.831$, $T_{max} = 0.970$); of 172665 measured reflections, 26829 were independent and 25174 had $I > 2\sigma(I)$; linear absorption coefficient 0.808 mm^{-1}. The structure was solved by direct methods using SHELXTL NT 6.12, and refinement was performed with all data (1530 parameters) by blocked-matrix least-squares on F^2 using SHELXTL NT 6.12.[17] All non-hydrogen atoms were refined anisotropically; $R_1 = 0.0344$ for $I > 2\sigma(I)$ and $wR_2 = 0.0781$ (all data); absolute structure parameter $x = 0.006(12)$;[26] 0.985/−0.684 e Å^{-3} residual densities.[17,25] Hydrogen atoms were attached in idealized positions and

refined using the riding model; their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of 1.2 or 1.5. Two of the solvent molecules are disordered on two alternative sites. In addition, one CD_3CN site is only occupied by around 25%. Finally, five *t*Bu groups are disordered and could be located on two alternative sites. A number of restraints (657; SIMU, ISOR, SADI,) were applied in the treatment of the disorder.

[17] SHELXTL NT 6.12, Bruker AXS Inc., Madison, WI, USA, **2002**.

[18] C. Olivier, E. Solari, R. Scopelliti, K. Severin, *Inorg. Chem.* **2008**, *47*, 4454 – 4456.

[19] B3LYP/LANL2DZp + ZPE(HF/LANL2MB); see the Supporting Information for more details.

[20] The *t*Bu groups in H_3L (**8**) were replaced by methyl groups; in $[In_4(L')_4]$ all nitrogen lone pairs point inside.

[21] R. Puchta, M. Galle, N. J. R. van Eikema Hommes, *Z. Naturforsch. B* **2006**, *61*, 1327 – 1334.

[22] M. Klisch, P. Richter, R. Puchta, D.-P. Häder, W. Bauer, *Helv. Chim. Acta* **2007**, *90*, 488 – 511.

[23] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171 – 178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615 – 619.

[24] a) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194 – 201; b) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13.

[25] SADABS 2.06, Bruker AXS Inc., Madison, WI, USA, **2002**.

[26] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876 – 881.

