

Rational Design of a Double-Walled Tetrahedron Containing Two Different C_3 -Symmetric Ligands**

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The rapidly growing field of supramolecular coordination chemistry can be divided into two classes. Polymers are already well-known because of their possible applications as new materials, heterogeneous catalysts, and ion exchangers.^[1] The rational design of the second class, discrete cage molecules, can be carried out using the molecular library method,^[2] in which the stoichiometry and symmetry elements of the product are predetermined by the molecular starting fragments, as illustrated by tetrahedral cages. In the oldest and most common system $[M_4L_6]$, the metal centers form the corners, which are linked by doubly bridging ligands along the edges.^[3] Building blocks that cover the faces of the cage have been reported far less often and result in the formation of $[M_4L_4]$ or $[M_6L_4]$ systems.^[4,5] Nearly all examples for the last case can be seen as truncated tetrahedra or adamantanoid cages with wide openings at their corners, allowing guest-exchange reactions.^[5]

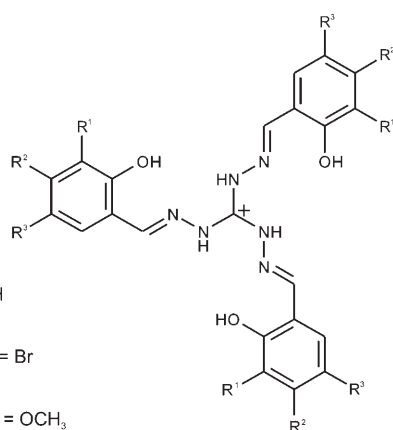
We are interested in C_3 -symmetric ligands such as $[H_6L^1]^+$, $[H_6L^2]^+$, and $[H_6L^3]^+$, which cover the faces of a cage nearly completely. We were able to construct tetrahedral coordination cages,^[6] for which an exact match of the ligands to the steric requirements of the metal centers was shown to be essential. The supramolecular reaction then leads to products

formed in high purity and yield. This design principle can be used for the construction of even more complex coordination compounds with additional ligands, such as octahedral or trigonal-bipyramidal cages.^[7,8] However, we are just starting to understand the reactions that take place when the ligands and metal centers do not match exactly, and a prediction of the products is not usually possible. Herein, we report the rational design of the first double-walled tetrahedron containing a ligand–metal pair that is not perfectly matched.

Coordination cages with tetrahedral shapes have been prepared using tris(2-hydroxybenzylidene)triaminoguanidinium $[H_6L^1]^+$ and tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium $[H_6L^2]^+$, in which the triangular faces are linked by $(CdO)_2$ four-membered rings (O stands for a phenolate oxygen atom), resulting in $[(CdCl)_3L^1]_4^{8-}$ and $[(CdCl)_3L^2]_4^{8-}$, respectively.^[6] The formation of a comparable discrete single-walled tetrahedron containing Zn^{2+} was impossible owing to the much smaller size of the Zn^{2+} ion compared to the Cd^{2+} ion (Zn^{2+} : 0.74 Å, Cd^{2+} : 0.97 Å^[9]). Because of this size difference, the faces would come in closer contact in a Zn^{2+} compound, which is sterically unfavorable.

On the other hand, it has been demonstrated that $[H_6L^1]^+$ and $[H_6L^2]^+$ are able to bind the smaller Zn^{2+} ions, resulting in cationic, neutral, or anionic coordination compounds with one or two ligands, for example $[[Zn(NH_3)(H_2O)]_3L^1]^+$,^[10] $[Zn[Zn_2(H_2O)_3(NH_3)L^2]_2]$, and $[[Zn(NH_3)]_3L^2]_2[\mu-(OH)]_3]^-$.^[11] In these structures, the metal ions are not located at ideal positions within the plane of the ligand but are up to 0.87(1) Å above or below this plane. Especially the last, dimeric compound (Figure 1) suggested that it might be possible to obtain a novel tetrahedral cage containing Zn^{2+} ions instead of Cd^{2+} . With the Zn^{2+} centers twisted out of the ligand plane, it should be possible to link these ions through the phenolate oxygen atoms to form a double-walled tetrahedron. Moreover, the overall charge would be reduced from 8– to 4–, as each building block carries only one negative charge. This charge reduction should have an additional stabilizing effect. However, the reaction of $[H_6L^2]Cl$ with even a large excess of $ZnCl_2$ leads only to the formation of the known dimeric compound.

This result is likely due to a missing stabilization at the corners, which can be changed by the introduction of additional side chains on the aromatic ring. As depicted in Figure 1, the proton bound to C(4) in each dimer is in close contact with the Br atom at C(5) in the neighboring ligand. If this proton at C(4) is exchanged for a stabilizing group (e.g. a methoxy group), the corner of the cage should be closed more tightly and stabilized by weak $O-CH_3 \cdots Br$ interactions. Comparable stabilizing effects have been described.^[12]



$[H_6L^1]^+$: $R^1 = R^2 = R^3 = H$

$[H_6L^2]^+$: $R^1 = R^2 = H$; $R^3 = Br$

$[H_6L^3]^+$: $R^1 = R^2 = Br$; $R^3 = OCH_3$

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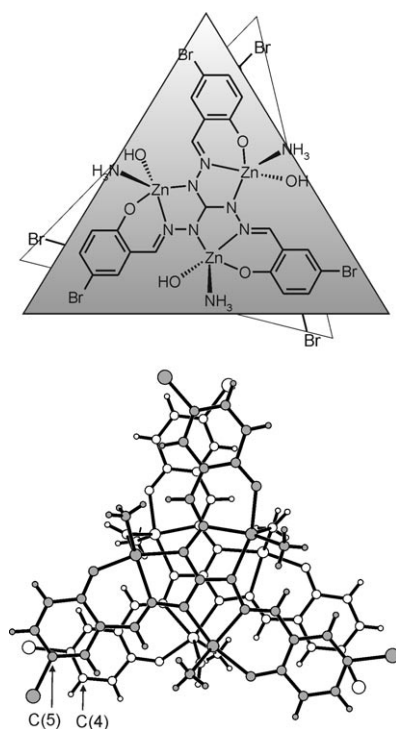


Figure 1. Triangular faces (top) and molecular structure (bottom) of $[\{Zn(NH_3)_3\}L^2]_2[\mu-(OH)]_3^-$. The gray and white atoms in the molecular structure correspond to the gray and white faces in the top depiction.

Therefore, we synthesized tris(3,5-dibromo-2-hydroxy-4-methoxy-benzylidene)triaminoguanidinium chloride ($[H_6L^3]Cl$) as an additional ligand. Both $[H_6L^2]Cl$ and $[H_6L^3]Cl$ were then treated with six equivalents of $ZnCl_2$ in a methanol–triethylamine mixture, resulting in the formation of orange-brown crystals with a large unit cell (cubic, $a = 41.829(1)$ Å, $V = 73189(4)$ Å³). The diffraction pattern was weak, but using $Cu_{K\alpha}$ radiation, we were able to record a satisfactory intensity data set. The structure was solved by direct methods and reveals the expected double-walled tetrahedron with the formula $(C_6H_{16}N)_4(H_2O)-[\{Zn_3(\{\mu-(OCH_3)\}_3\{Zn_3(solvent)_3L^3\})L^2\}_4]$ (**1**).^[13]

The cage is formed by four dimeric units that each contain both ligands. Each ligand binds three Zn^{2+} centers linked by three bridging methanolate ligands (Figure 2a,b). The inner walls of the tetrahedron are formed by the four $\{Zn_3L^2\}$ units, and the phenolate oxygen atoms bridge the neighboring faces, as expected. One of the $\{Zn_3L^2\}$ units is located on the C_3 axis; as a result, the asymmetric unit contains only a third of the cage (Figure 2c), the remaining parts of which are symmetry-related. Each outer $\{Zn_3(solvent)_3L^3\}$ face is formed by a ligand bound to three Zn^{2+} centers, which adopt trigonal-bipyramidal coordination geometry. Two equatorial positions are occupied by the bridging methanolate ligand and a solvent molecule (water for the ligand located on the C_3 axis and methanol for the others). In the four inner $[L^2]^{5-}$ units, the central CN_6 cores show the same screw direction, making the cage chiral. In the outer $[L^3]^{5-}$ units, the same situation is observed, but the screw goes the opposite way. As shown in Figure 2b, the Zn^{2+} centers are located below the plane of the

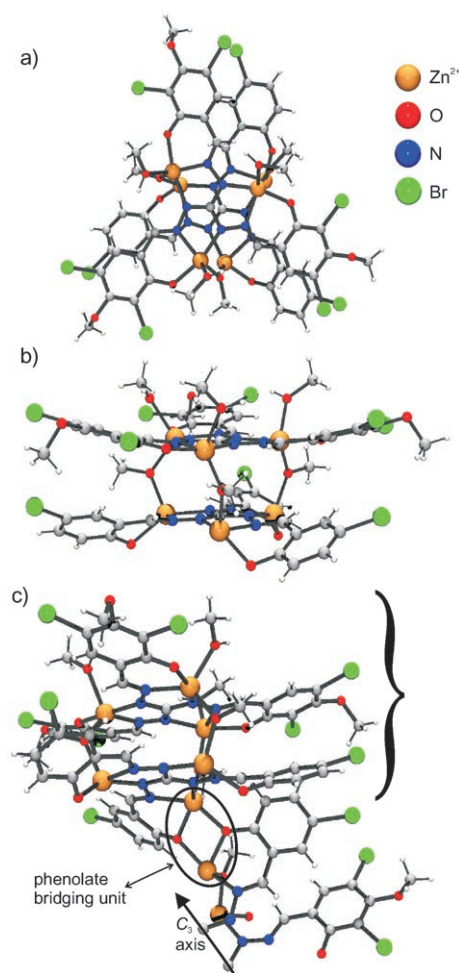


Figure 2. a, b) Double-walled triangular faces, comparable to the dimeric complex in Figure 1. c) The asymmetric unit of **1**. The connection of the double-walled units by phenolate O atoms, resulting in a $(ZnO)_2$ four-membered ring, is highlighted by an oval. Counter-cations and solvent molecules have been omitted for clarity. The part of the asymmetric unit marked by the curly bracket corresponds to the triangular face in (b).

$[L^2]^{5-}$ ligand, with distances of 0.12(1) to 0.15(1) Å. These values are larger than those observed in the Cd tetrahedra (0.02(1)–0.08(2) Å). The phenyl rings are also twisted out of the plane of the central CN_6 core, and all dihedral angles adopt values of 29(1)°. In this way, the phenolate oxygen atom can reach the Zn^{2+} center of the neighboring face. These values are comparable to those found in the Cd cages (16(1)–36(1)°). Because of the bridging methanolate ligands, the Zn^{2+} ions bound by the outer $[L^3]^{5-}$ ligands point inside the dimeric building blocks, with average distances to the central CN_6 plane of 0.11(2) Å. These ligands show much less distortion, as can be seen by the average dihedral angle between the central CN_6 core and the phenyl rings (14(2)°). Furthermore, the expected weak $O-CH_3\cdots Br$ interactions, three at each corner, can be observed (3.05(1) to 3.17(1) Å, 119(1)° to 133(1)° at the Br atoms, Figure 3).

The complete double-walled tetrahedron **1** is depicted in Figure 4. The overall charge of 4– is compensated by four triethylammonium ions, one of which is located inside the

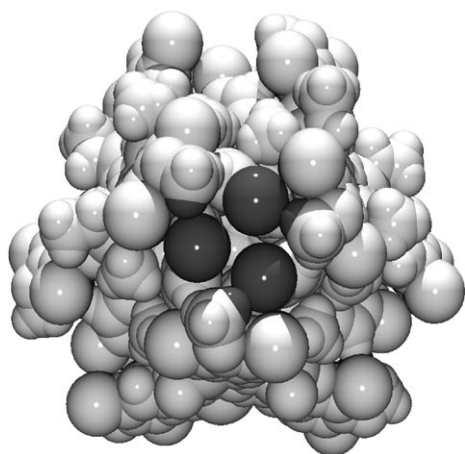


Figure 3. Corner of the double-walled tetrahedron; the $\text{OCH}_3\cdots\text{Br}$ interactions of **1** are depicted in dark gray.

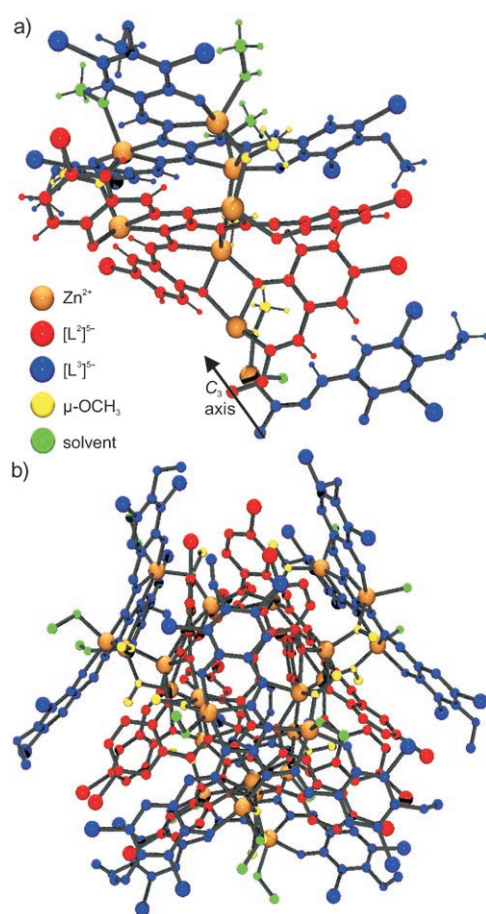


Figure 4. a) The same asymmetric unit as in Figure 2c, but with the same color code as in Figure 4b. b) Crystal structure of **1**. Protons (for (b)), counteranions, and solvent molecules have been omitted for clarity.

cage. It is disordered with an additional water molecule that is fixed to the NH group by a hydrogen bond ($d(\text{N}\cdots\text{H}\cdots\text{O}) = 1.57(8)$ Å). Owing to the large degree of disorder outside the cage (about 24650 Å³ or 34% of the overall cell volume is occupied by counteranions and solvent molecules), only the

central N atoms of the counteranions could be found in the Fourier difference synthesis. Nevertheless, the data could be satisfactorily corrected by employing the SQUEEZE routine in the program Platon (see the Experimental Section), resulting in an electron count of 4220 e per unit cell or about 527 e per cage. This value, minus the electrons from the three counteranions, corresponds to approximately 35 water molecules (or a comparable number of methanol molecules) per cage; this number can be confirmed by elemental analysis.

Compound **1** is very poorly soluble in most common NMR solvents. Nevertheless, we were able to dissolve sufficient substance in hot $[\text{D}_6]$ acetone to obtain a ^1H NMR spectrum. A broad, poorly defined multiplet in the aromatic region was observed, as is expected for the two different ligands. The most important information is that only one signal set could be observed for the triethylammonium ions, thus indicating that under such harsh conditions the cage is not stable on the NMR timescale.

In conclusion, we have successfully carried out the rational synthesis of a coordination cage with the outer shape of a tetrahedron by employing a metal–ligand pair that does not exhibit a perfect match. With the help of a ligand tailored for this purpose, we were able to isolate and characterize the first example of a double-walled coordination cage.

Experimental Section

$[\text{H}_6\text{L}^2]\text{Cl}$ was prepared according to literature methods.^[14]

$[\text{H}_6\text{L}^3]\text{Cl}$: 3,5-Dibromo-2-hydroxy-4-methoxybenzaldehyde (2.00 g, 6.45 mmol) in ethanol (30 mL) was slowly added to triaminoguanidinium chloride (303.6 mg, 2.16 mmol) dissolved in a hot mixture of ethanol (10 mL) and water (5 mL). After adjusting to pH 3 with $\text{HCl}_{(\text{aq})}$, the suspension was allowed to cool to room temperature. The precipitate was collected, washed with diethyl ether and dried under reduced pressure. Yield: 1.8738 g (1.84 mmol, 85.37%). Elemental analysis calcd for $\text{C}_{25}\text{H}_{21}\text{N}_6\text{O}_6\text{Br}_6\text{Cl}\cdot\text{H}_2\text{O}$, (1034.36): C 29.03, H 2.24, N 8.12, found: C 29.12, H 2.42, N 8.14. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 22°C): $\delta = 12.09$ (s, 1H; NH), 10.67 (s, 1H; OH), 8.86 (s, 1H; HC=N), 8.32 (s, 1H; HC(6)), 3.84 ppm (s, 3H; OCH_3).

1: ZnCl_2 (10.2 mg, 0.0748 mmol) was combined with $[\text{H}_6\text{L}^2]\text{Cl}$ (8.7 mg, 0.0141 mmol) and $[\text{H}_6\text{L}^3]\text{Cl}$ (12.7 mg, 0.0125 mmol). A mixture of methanol (2 mL) and triethylamine (41.76 μL) was added. After a few days, orange-brown cubes of **1** were formed in a yield of 22.1 mg (2.3×10^{-3} mmol, 73.6%). Elemental analysis calcd for $\text{C}_{233}\text{H}_{252}\text{N}_{52}\text{O}_{61}\text{Br}_{36}\text{Zn}_{24}\cdot 20\text{H}_2\text{O}\cdot 4\text{MeOH}$, **1** (9691.18): C 29.37, H 3.20, N 7.52, found: C 29.01, H 3.04, N 8.02.

X-ray analysis: Intensity data for **1** were collected on an Oxford Diffraction Xcalibur2 CCD ($\text{CuK}\alpha$ radiation, ω scan). The data were corrected for Lorentz, polarization, and absorption (Gauss method) effects. The structure was solved by direct methods (SHELXS-97)^[15] and refined using a full-matrix least-squares procedure (SHELXL-97).^[16] All hydrogen atoms were placed at geometrically estimated positions. Owing to the large number of disordered counteranions and solvent molecules outside the cage and the resulting low data-to-parameter ratio, we decided to correct the X-ray data for their influence employing the SQUEEZE routine in PLATON.^[17] Nevertheless, the triethylammonium ion as well as the water molecule inside the cage were located in the difference synthesis and refined isotropically. They are both disordered but could be modeled with the bond lengths fixed to literature values. CCDC-657925 contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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