Isolation and Single X-ray Crystal Structure of a Flattened M_3L_2 Type Metallosupramolecular Cage Obtained by Self-Assembly of Tripodal Ligand with Zinc(II) Chloride

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A novel cake-like complex, $Zn_3(tbib)_2Cl_6 \cdot 3DMF \cdot 2H_2O$ [tbib = 1,3,5-tris(benzimidazol-2-ylmethyl)benzene], was synthesized by self-assembly of tripodal ligand tbib with zinc(II) chloride. The X-ray crystal structural analysis indicates that the framework is a flattened M_3L_2 type cage-like complex in which the tbib ligand has a *cis, trans, trans* conformation.

Construction of supramolecular frameworks with specific topologies is a subject of current interests.[1] Particularly architectures with internal cavities have attracted much attention of chemists because of their interesting structures and possible properties such as ion and molecular recognition, selective inclusion and catalysis for specific reactions.[2] From the previous studies, it can be seen that both metal ions and organic bridging ligands play important roles in controlling the self-assembly of multicomponent into metallosupramolecular cages.[3–5] Two ten-component M_6L_4 type cages were obtained by self-assembly of rational designed tripodal ligands and $Pd(en)(NO_3)_2$ (en = ethylenediamine) or $PdCl_2$, respectively.[3] Nanosized cages of $[Cu^{III}{}_8(dtc)_4]^{8+}$ (dtc = derivative of dithiocarbamate), $Cu^{II}{}_{12}(tapp)_8$ (H_3tapp = 2,4,6-tris(azophenyl)-1,3,5-trihydroxybenzene) and $Pd_{18}(tpb)_6$ [tpb = 1,3,5-tris(3,5-pyrimidyl)benzene] were reported most recently.[4] In these reported cases, all the metal ions of Pd(II), Pt(II), Cu(II) and Cu(III) have square planar configuration. Only in the Ward's and our previous studies, five-component molecular cages with tetrahedral metal ions, $[Cu^I{}_3(Tppy)_2][PF_6]$ [Tppy = tris(3-(2-pyridyl)pyrazol-1-yl)hydroborate] and $Zn_3(tib)_2(OAc)_6$ [tib = 1,3,5-tris(imidazol-1-ylmethyl)benzene; OAc = acetate anion], were obtained by self-assembly of the tripodal ligands with copper(I) and zinc(II) ions.[6,7]

In order to further investigate the influence of organic bridging ligand on formation of supramolecular metallocages, a tripodal ligand, 1,3,5-tris(benzimidazol-2-ylmethyl)benzene (tbib), was designed and synthesized, in which the arm of the ligand was changed from imidazol-1-yl in the tib to benzimidazol-2-yl in the tbib. Now a systemic study of the self-assembly of these tripodal ligands with various metal ions was initiated in our lab.[7,8] We herein report the isolation and single X-ray crystal structure of another M_3L_2 type metallocage, $Zn_3(tbib)_2Cl_6$, which has similar constitution with the $Zn_3(tib)_2(OAc)_6$, but the topologies of these two cages are different.

Assembly reaction of zinc(II) chloride with the tbib ligand in ethanol solution gives a neutral colorless product.[9] Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the *N,N*-dimethylformamide (DMF)/ethanol (1:1) solution of title complex. The crystallographic analysis revealed that the complex is a flattened M_3L_2 type cage as shown in Figure 1.[10] Each tbib ligand binds to three zinc(II) atoms and in turn each zinc(II) atom coordinates with two nitrogen atoms from two different tbib ligands. Two additional positions of each zinc(II) atom are occupied by two chloride ions. Thus the zinc(II) atoms are four-coordinated with N_2Cl_2 binding set. The coordination geometry of the zinc(II) atoms is distorted tetrahedral with coordination angles ranging from 101.4(3) to 118.7(3)° The intermetallic distances of Zn1···Zn2, Zn1···Zn3 and Zn2···Zn3 are 10.13, 8.28 and 8.37 Å, respectively, which are close to that of 9.10 Å observed in the $Zn_3(tib)_2(OAc)_6$ cage.[7] Two central benzene ring planes are near parallel with a dihedral angle of 8.7° (Figure 2) and the centroid–centroid distance between the two central benzene ring planes is 4.45 Å. There are no solvent molecules inside the cage, however, three DMF, one of which disordered in two positions (containing O1 and O2 as shown in Figure 1) with the site occupancy factors of 0.5, and two water molecules were found outside the cage. The presence of the solvent DMF and water molecules is also confirmed by thermogravimetric analysis. The TGA spectrum of the complex showed an initial

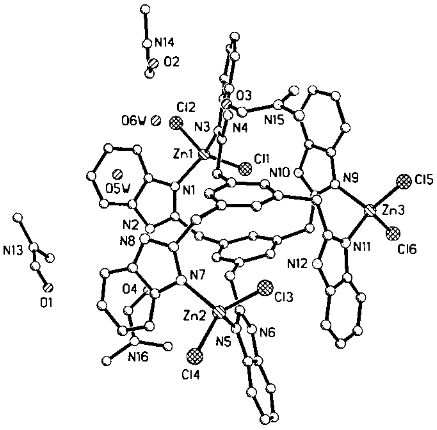

Figure 1. Crystal structure of $Zn_3(tbib)_2Cl_6 \cdot 3DMF \cdot 2H_2O$, hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-N(1) = 2.015(8), Zn(1)-N(3) = 2.026(7), Zn(1)-Cl(1) = 2.247(3), Zn(1)-Cl(2) = 2.251(3), Zn(2)-N(7) = 2.003(8), Zn(2)-N(5) = 2.023(8), Zn(2)-Cl(3) = 2.249(3), Zn(2)-Cl(4) = 2.252(3), Zn(3)-N(9) = 2.016(8), Zn(3)-N(11) = 2.034(8), Zn(3)-Cl(5) = 2.222(3), Zn(3)-Cl(6) = 2.234(3), N(1)-Zn(1)-N(3) = 105.8(3), N(1)-Zn(1)-Cl(1) = 118.7(3), N(3)-Zn(1)-Cl(1) = 106.3(2), N(1)-Zn(1)-Cl(2) = 105.3(3), N(3)-Zn(1)-Cl(2) = 106.4(2), Cl(1)-Zn(1)-Cl(2) = 113.50(10), N(7)-Zn(2)-N(5) = 101.4(3), N(7)-Zn(2)-Cl(3) = 116.4(3), N(5)-Zn(2)-Cl(3) = 108.7(2), N(7)-Zn(2)-Cl(4) = 107.9(2), N(5)-Zn(2)-Cl(4) = 112.7(2), Cl(3)-Zn(2)-Cl(4) = 109.64(12), N(9)-Zn(3)-N(11) = 104.8(3), N(9)-Zn(3)-Cl(5) = 113.4(3), N(11)-Zn(3)-Cl(5) = 106.1(2), N(9)-Zn(3)-Cl(6) = 103.2(3), N(11)-Zn(3)-Cl(6) = 113.5(3), Cl(5)-Zn(3)-Cl(6) = 115.50(12).

endotherm centered at 85 °C with a weight loss of 2.1% (calcd 2.2%), representing the loss of uncoordinated water molecule. The following weight loss of 13.0% (calcd 13.7%) centered at 230 °C indicates the presence of three DMF molecules in the title complex. There are total eleven hydrogen bonds of three N–H···Cl, three N–H···O, four C–H···O and one C–H···Cl formed among the cage, DMF and water molecules.

The tripodal ligands tbib as well as above mentioned tib are flexible since there is a methylene group between the appending group and central benzene ring. Thus there are two kinds of conformations adoptable for these flexible ligands when they interact with metal ions, one is *cis, cis, cis* and the other one is *cis, trans, trans*.[11] However up to now, to our knowledge, only the *cis, cis, cis* conformation was found in the reported metallosupramolecular cages.[3,6,7,12] In the present case, it is noteworthy that the two tbib ligands in the title complex are both *cis, trans, trans* conformations and joined together by three zinc(II) chloride moieties to form a flattened M_3L_2 cage (Figures 1 and 2). The formation of such flattened cage may be caused by steric effect of benzimidazole group which inhibits the *cis, cis, cis* conformation of the tbib ligand and by weak π–π interactions between the two central benzene ring planes with a distance of 4.45 Å as mentioned above.

The volumes available inside the cage for the complexes $Zn_3(tib)_2(OAc)_6$ and $Zn_3(tbib)_2Cl_6$ are different. The former one has a large cavity capable of accommodating guest molecules such as camphor.[7] While in the case of the present complex, the cavity is too small to include the camphor molecule. In order to further investigate the host–guest chemistry of the zinc(II) complexes of tbib and tib, smaller molecules such as cyclohexane, toluene were used as guest molecules. Large upfield shift of 2.0 ppm (in D_2O at 298 K) was observed in the ^1H NMR spectrum of cyclohexane when the $Zn_3(tib)_2(OAc)_6$ (2.0 mM) was added to the D_2O solution of cyclohexane (0.5 mM). Similar shifts (1.8–2.0 ppm) were also found in the toluene/$Zn_3(tib)_2(OAc)_6$ system under the same conditions. The observation of such large chemical shifts indicates the inclusion of guest molecules by the $Zn_3(tib)_2(OAc)_6$ cage complex as reported for the Pd(II) cage-like complex.[12] However, no such chemical shifts were observed in the ^1H NMR spectrum of cyclohexane or toluene by addition of $Zn_3(tbib)_2Cl_6$. This implies that the zinc(II) complex of tbib has no inclusion property for these small guest molecules. The results demonstrate that the nature of tripodal ligands has great influence on the formation of supramolecular complexes.

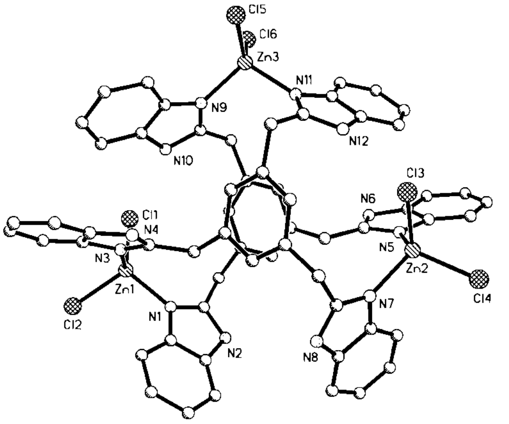

Figure 2. Top view of the cage-like complex $Zn_3(tbib)_2Cl_6$ through the central benzene rings.

In conclusion, this work provides an example of structurally characterized M_3L_2 cage with tetrahedral metal ions. This is also the first example of X-ray structural characterized metallosupramolecular cage with *cis, trans, trans* conformational tripodal ligand.

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9 Preparation of title compound. A solution of tbib (23.4 mg, 0.05 mmol) in ethanol (5 mL) was added to a ethanol (5 mL) solution of $ZnCl_2$ (10.5 mg, 0.075 mmol) to give colorless precipitate in ca. 50% yield. ^1H NMR (DMSO-d_6, 298 K): δ 7.54 (br, 6H), 7.20 (s, 3H), 7.16 (m, 6H), 4.21 (s, 6H). Anal. Found: C, 50.51; H, 4.91; N, 12.43%. Calcd for $C_{69}H_{77}N_{15}Cl_6O_7Zn_3$: C, 50.62; H, 4.74; N, 12.83%.
10 Crystal data for $Zn_3(tbib)_2Cl_6 \cdot 3DMF \cdot 2H_2O$: M_r = 1597.20, monoclinic, space group $P2_1/n$, a = 16.678(3), b = 16.861(3), c = 28.196(7) Å, β = 99.660(10)°, V = 7817(3) Å^3, Z = 4, D_c = 1.357 g/cm^3, μ = 11.74 cm^{-1}, T = 296(2) K. A crystal with dimensions 0.52 × 0.40 × 0.36 mm was mounted and data collection were performed on a Siemens-P4 four-circle diffractometer by ω-scan techniques using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 12256 reflections were collected of which 10707 are independent (R_{int} = 0.0541). The structure was solved by direct method with SHELXS-97 and refined by full-matrix least-square calculations on F^2. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$; R_1 = 0.0563 and wR_2 = 0.1212 [I > 2σ(I)], max. min. residual density: +0.696, –0.296 e Å^{-3}.
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