Molecular Capsules

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Isostructural Coordination Capsules for a Series of 10 Different d^5–d^{10} Transition-Metal Ions[**]

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Supramolecular assembly of predesigned organic and inorganic building blocks has been recognized as an excellent tool in constructing well-defined nanosized molecules for potential application in molecular devices.[1] In particular, discrete hollow structures such as capsules[2] formed by metal-mediated assembly of organic ligands are of great interest because of the chemical phenomena that may occur in their inner space.[3] However, the number of metals used to maintain the shapes of metal-assembled architectures is still limited. Metal-exchangeable coordination architectures with a series of transition-metal ions would give rise to a large number of metal-dependent functions. Here we present a novel disk-shaped tris-monodentate ligand **1** that forms 10 structurally equivalent coordination capsules, $[M_6(\mathbf{1})_8]^{12+}$, with a series of divalent d^5–d^{10} transition-metal ions, M^{2+} (M = Mn, Fe, Co, Ni, Pd, Pt, Cu, Zn, Cd, and Hg) through self-assembly protocols. The resulting complexes have an octahedron-shaped structure in which the six metal ions lie on the apexes and the eight sides are occupied with eight ligands **1**. X-ray structural analysis of a single crystal of $[Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ revealed a 3-nm-sized octahedron-shaped capsule structure, with sides of 1.8 nm in length. Some of these complexes have two axial ligands at each hexacoordinate metal center, one each from inside and outside the cavity. Note that the inner space of the capsule was successfully decorated with other anionic ligands as a result of the site-selective replacement of the six $CF_3SO_3^-$ ligands coordinated from inside the capsule.

The disk-shaped C_3-symmetric tris-monodentate ligand **1** comprises a central hexaphenylbenzene core whose six peripheral rings are alternately 4-substituted with 3-pyridyl and methyl groups (Figure 1). The distance between the two neighboring pyridyl nitrogen atoms is approximately 1.8 nm.

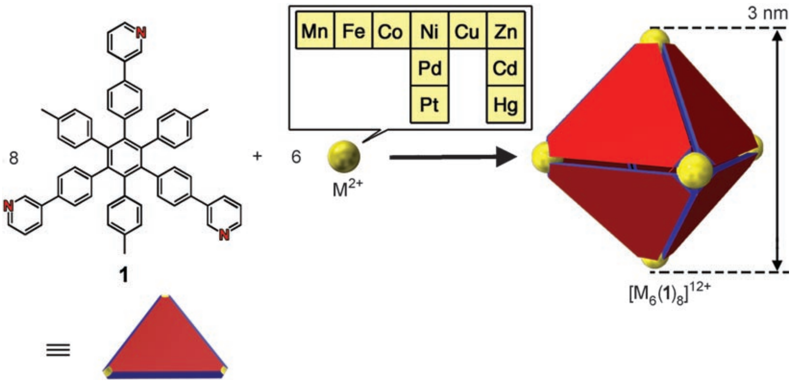

Figure 1. Schematic representation of the formation of $[M_6(\mathbf{1})_8]^{12+}$ coordination capsules formed from eight disk-shaped tris-monodentate ligands **1** and six divalent d^5–d^{10} transition-metal ions, M^{2+}.

Titrimetric complexation studies with a series of transition-metal ions revealed that 10 different $[M_6(\mathbf{1})_8]^{12+}$ complexes are formed from **1** and 10 divalent d^5–d^{10} transition-metal ions which prefer a square-planar or an octahedral coordination geometry (M = Mn, Fe, Co, Ni, Pd, Pt, Cu, Zn, Cd, and Hg).

The most studied example was that with M = Hg. The ^1H NMR spectrum of the $[Hg_6(\mathbf{1})_8]^{12+}$ complex is given in Figure 2b. A ^1H NMR titration study of ligand **1** with $Hg(CF_3SO_3)_2$ in CD_3CN at 293 K revealed that a highly symmetrical complex is quantitatively constructed when **1** and Hg^{2+} are mixed in a ratio of 4:3. All the proton signals for phenylene and *p*-tolyl groups (H_e–H_h) were divided into two sets (H_{e1}, H_{e2}, H_{f1}, H_{f2}, H_{g1}, H_{g2}, H_{h1}, and H_{h2}) at the same integral ratio, indicating that all the pyridyl nitrogen atoms are directed towards Hg^{2+}. Note that the signals for the methyl protons (H_i) were shifted upfield as a result of shielding effects from the neighboring ligands assembled by Hg^{2+}. The ESI-TOF mass spectrum of this solution showed five signals at m/z 1202.1, 1426.9, 1742.3, 2215.1, and 3003.2. These signals are all assignable to positively charged $\{Hg_6(\mathbf{1})_8\}$ complexes with the loss of $CF_3SO_3^-$ anions (Figure 3), and this result is in good agreement with the convergence ratio 4:3 for $\mathbf{1}/Hg^{2+}$ observed in the ^1H NMR titration study. Thus, a discrete, highly symmetrical $[Hg_6(\mathbf{1})_8]^{12+}$ complex was quanti-

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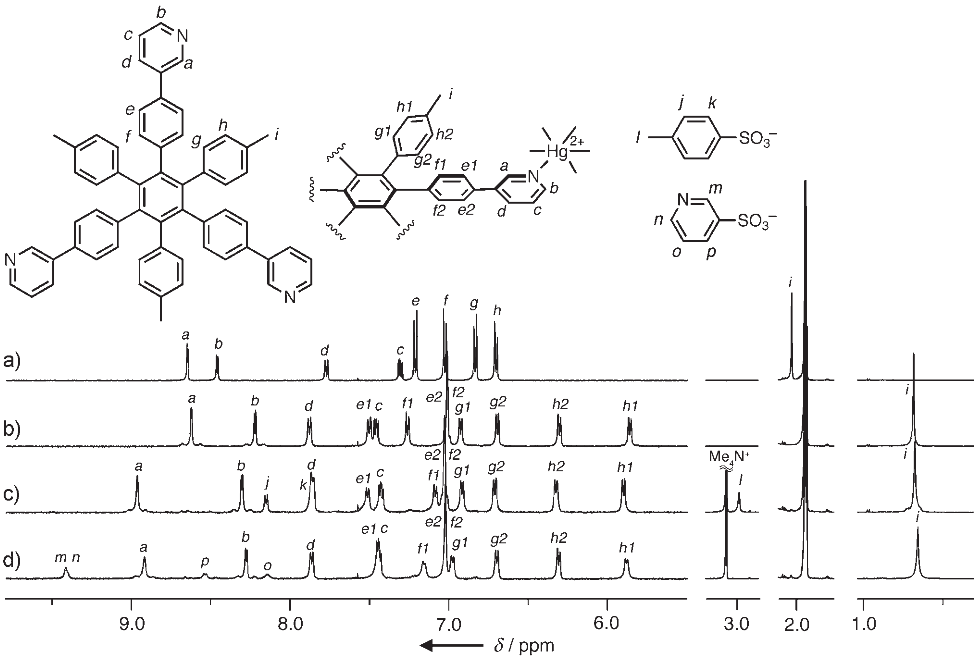

Figure 2. ^{1}H NMR spectra for complexation of Hg^{2+} with **1** in CD_3CN at 293 K ([**1**] = 3.0 mM). a) Metal-free ligand **1**; b) Hg^{2+} complex (**1**/$Hg(CF_3SO_3)_2$ = 4:3); c) Hg^{2+} complex with added *p*-$MeC_6H_4SO_3NMe_4$ (**1**/$Hg(CF_3SO_3)_2$/*p*-$MeC_6H_4SO_3NMe_4$ = 4:3:3); and d) Hg^{2+} complex with added tetramethylammonium 3-pyridinesulfonate (**1**/$Hg(CF_3SO_3)_2$/tetramethylammonium 3-pyridinesulfonate = 4:3:3).

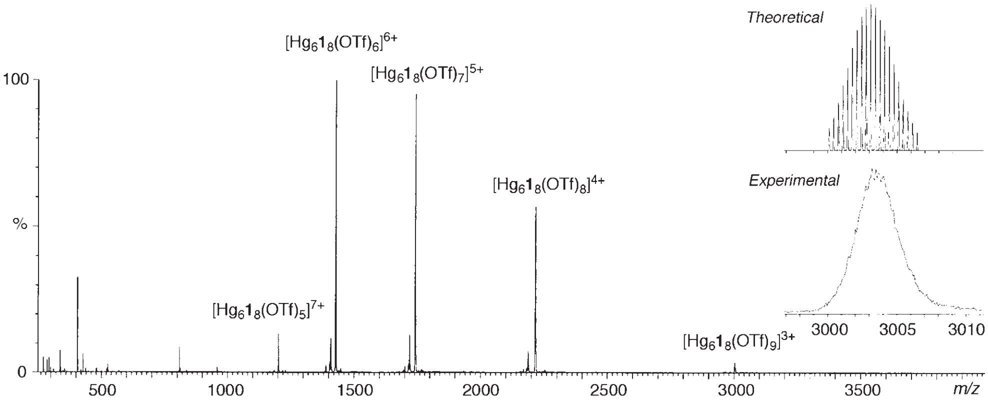

Figure 3. ESI-TOF mass spectrum of the Hg^{2+} complex in CD_3CN ([**1**] = 3.0 mM, [Hg^{2+}] = 2.3 mM). Inset: expansion and simulation of the signal at *m*/*z* 3003.2. OTf = $CF_3SO_3^-$.

tatively formed in solution. The formation of the $[M_6(\mathbf{1})_8]^{12+}$ complexes with other diamagnetic divalent transition-metal ions (Pd^{2+}, Pt^{2+}, Zn^{2+}, and Cd^{2+}) in solution was demonstrated in the same way.

Single-crystal X-ray structural analysis demonstrated an octahedron-shaped capsule structure of the $[Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ complex (Figure 4). The complex cocrystallized with a non-metallated ligand cluster (see Supporting Information), and a crystal cell contains four such units. As for the $[Hg_6(\mathbf{1})_8]^{12+}$ part, eight ligands are arranged into an octahedron-shaped framework in which six Hg^{2+} ions occupy the six apexes. Each Hg^{2+} is hexacoordinate and bound by four pyridyl nitrogen atoms of four separate ligands and two oxygen atoms of the axial $CF_3SO_3^-$ ligands, one each from inside and outside the capsule (Figure 4b). The distances between two neighboring Hg^{2+} ions and two diagonal Hg^{2+} ions are on average 17.9 Å and 25.4 Å, respectively. The eight tris-monodentate ligands **1** in $[Hg_6(\mathbf{1})_8]^{12+}$ are densely arranged through π–π stacking of the *p*-tolyl rings and a close contact between the methyl groups of the *p*-tolyl and the phenylene rings. As a result, the inner space of the capsule is almost completely isolated from outside. The inner volume was estimated to be approximately 2700 Å^3.

As for paramagnetic $[M_6(\mathbf{1})_8]^{12+}$ complexes (M = Mn, Fe, Co, Ni, and Cu), the signals in the ^{1}H NMR spectra for metal-free ligand **1** completely disappeared when 0.75 equiv of metal ions (**1**/M^{2+} = 4:3) were added to the solutions and broadened signals for metal complexes appeared with a significant shift to lower magnetic field. Their complexation in solution was then examined by UV titration experiments and ESI-TOF mass measurements.[4] ^{1}H DOSY measurement is a powerful tool to estimate the size of macromolecules in solution and can be utilized even for paramagnetic metal species. The diffusion coefficients (*D*) of $[M_6(\mathbf{1})_8]^{12+}$ complexes in solutions were estimated as $D = 3.8 \pm 0.4 \times 10^{-10}\,m^2 s^{-1}$ (except for M = Mn^{2+}),[5] which corresponds to a 3-nm-sized spherical structure, as confirmed by the X-ray crystal structure analysis of the $[Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ capsule.

The metals used in this study can be divided according to their coordination geometries, namely octahedral and square-planar. The coordination exchange of two axial ligands at each octahedral metal center is of great interest because these two ligands are more labile than equatorial ligands and hence are placed in inequivalent circumstances. For example, as seen in the X-ray crystal structure analysis, two inequivalent $CF_3SO_3^-$ ions coordinate to each Hg^{2+} ion of the $[Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ capsule complex, that is, one from inside and the other from outside. To investigate the dynamic behaviors of these axial ligands in solution, we measured the ^{19}F NMR

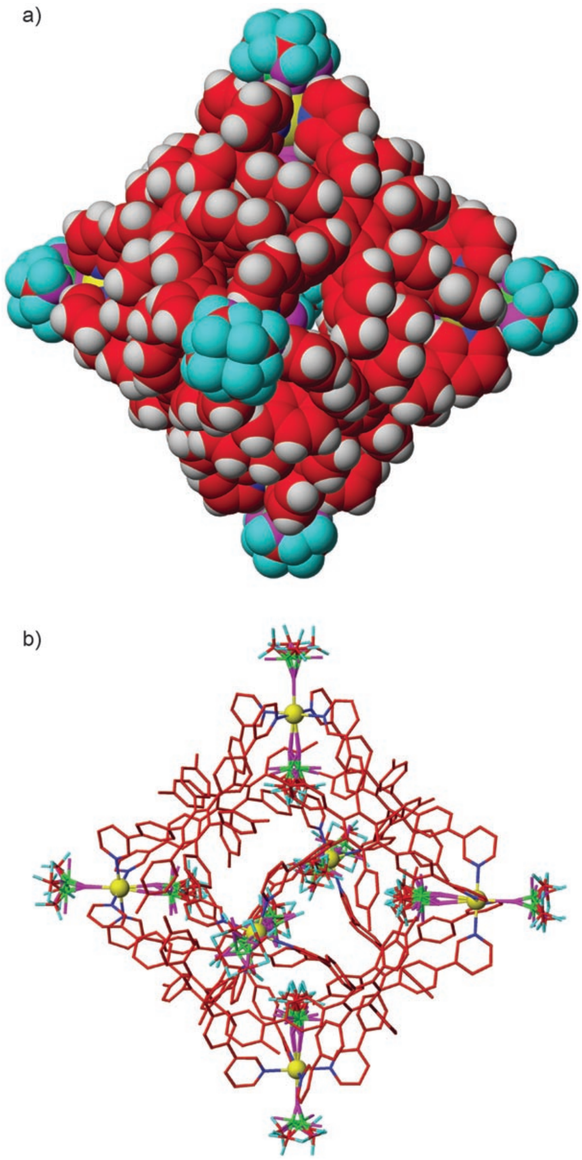

Figure 4. Crystal structure of [$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$]. Axially coordinated $CF_3SO_3^-$ ions are disordered. a) Space-filling model; b) cylinder model (hydrogen atoms are omitted for clarity). C red, Hg yellow, N blue, O purple, S green, F cyan, H white.

spectrum of the [$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$] complex. Two broadened signals were observed at 293 K in a 1:1 integral ratio at $\delta =$ 85.2 and 86.1 ppm, which are assignable to the outer and the inner $CF_3SO_3^-$ ligands, respectively.[6] The axial ligand exchange between both sides was slightly slower than the NMR timescale. This result clearly indicates that each Hg^{2+} center of the complex is in an octahedral coordination geometry with two axial $CF_3SO_3^-$ ligands in solution.[7] Furthermore, all six $CF_3SO_3^-$ axial ligands coordinating from inside the capsule were site-selectively replaced by six p-$MeC_6H_4SO_3^-$ ligands upon addition of 6 equiv of p-$MeC_6H_4SO_3NMe_4$ to a solution of the [$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$] complex. Aromatic ^{1}H NMR signals for the [$Hg_6(\mathbf{1})_8$]$^{12+}$ capsule (H_a, H_b, and H_f) as well as both aromatic and methyl signals for p-$MeC_6H_4SO_3^-$ were shifted to lower magnetic field as compared to the original signals (Figure 2c) upon addition of 6 equiv of p-$MeC_6H_4SO_3NMe_4$. The ^{19}F NMR spectrum showed only one sharp signal at $\delta =$ 85.1 ppm, which coincides with the chemical shift of $Hg(CF_3SO_3)_2$ at $\delta = 85.1$ ppm, indicating that all the $CF_3SO_3^-$ ligands exist outside the capsule. ESI-TOF mass measurement of the mixed solution showed distinct signals which are assignable to [$Hg_6(\mathbf{1})_8(p\text{-}MeC_6H_4SO_3)_6(CF_3SO_3)_n$]$^{6-n}$ ($n = 0$–2). This finding would allow us to utilize the six metal centers at the apexes of the capsule for chemical modification of the inner space with functional anionic molecules or for the hub of signal transfer between the inner and outer spaces. For example, the inner space of the [$Hg_6(\mathbf{1})_8$]$^{12+}$ capsule was decorated with six 3-pyridinesulfonate groups coordinated to the Hg^{2+} centers (Figure 2d).

In summary, we have demonstrated that a series of 10 isostructural octahedron-shaped coordination nanocapsules [$M_6(\mathbf{1})_8$]$^{12+}$ can be constructed from disk-shaped tris-monodentate ligands **1** and 10 divalent d^5–d^{10} transition-metal ions. One can anticipate their ability to fine-tune metal-dependent functions such as magnetic, redox, optical, and dynamic properties because the metal ions at the six apexes can be exchanged with preservation of the structure. Moreover, site-specific replacement of the internal axial ligands of the six metal centers would allow functionalization of the interior of the coordination capsule. Such metal-exchangeable capsules that have a large hollow structure surrounded by organic and inorganic components would, therefore, be endowed with an isolated space for size- or shape-selective dynamic molecular recognition and metal-triggered chemical reactions.

Experimental Section

A single crystal of [$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$] suitable for X-ray crystal structure analysis was obtained by slow diffusion of diethyl ether into a solution of **1** (5.7 mg, 7.1 μmol) and $Hg(CF_3SO_3)_2$ (2.6 mg, 5.4 μmol) in CH_3CN. After 2 days, colorless cubic crystals appeared. The crystals were collected and then dried in vacuo to obtain [$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$]·8(**1**) (5.7 mg, 0.36 μmol, 81 %). Crystallographic data: $C_{972}H_{744}F_{36}Hg_6N_{48}O_{48}S_{12}$ ([$Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}$]·8 $C_{60}H_{45}N_3$·12 H_2O), $M_r = 16137.06$, colorless block ($0.25 \times 0.20 \times 0.10$ mm^3), density 0.964, cubic, space group $F432$, $a = b = c = 48.0818(13)$ Å, $V = 111158(5)$ Å^3, $Z = 4$, $R_1(I > 2\sigma(I)) = 0.0901$, $wR(F_o^2) = 0.2868$, GOF = 0.968. As the reflections in the range of high 2θ angle are very weak, the positional and thermal parameters are not accurate. Large R and wR values might be due to a poor quality of the crystal used and the disordered structure. CCDC-295986 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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[4] ^{1}H NMR spectra, ESI-TOF mass spectra, and changes in UV absorption for the complexation of **1** with metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) are summarized in the Supporting Information.

[5] DOSY spectra of the complexes are shown in the Supporting Information. For the Mn^{2+} complex, no cross peaks were observed at the signals for **1** because of the significantly broadened ^{1}H NMR signals.

[6] The assignment of the two ^{19}F NMR signals was conducted by ^{19}F DOSY measurement. ^{19}F DOSY measurement of $[Zn_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ was used to determine the diffusion coefficient from the signal at the lower field as $D = 2.8 \times 10^{-10}\,m^2 s^{-1}$, which is comparable to that of the $\{Zn_6(\mathbf{1})_8\}$ capsule determined by ^{1}H DOSY measurement ($D = 4.2 \times 10^{-10}\,m^2 s^{-1}$) and significantly smaller than that determined from the signal at higher field ($D = 1.2 \times 10^{-9}\,m^2 s^{-1}$). The ^{19}F DOSY spectrum is shown in the Supporting Information.

[7] The ^{19}F NMR spectrum of the $[Zn_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ complex showed two relatively sharp signals at $\delta = 85.9$ and 85.1 ppm, indicating its much slower coordination exchange at the axial ligands of each metal center as compared with the $[Hg_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ complex. The ^{19}F NMR spectrum of $[Cu_6(\mathbf{1})_8(CF_3SO_3)_{12}]$ showed two signals in a 1:1 integral ratio, indicating an octahedral coordination geometry of Cu^{2+} centers in the complex.