Self-Assembly

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Self-Assembly of $M_{24}L_{48}$ Polyhedra Based on Empirical Prediction**

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Self-assembly of giant coordination polyhedra from metal ions and bridging ligands is one of the intriguing topics in current chemistry.[1–3] In theory, the structures of the polyhedra can be predicted based on the analysis of the coordination geometry at the metal and the bridging angles of the ligands.[4] In reality, however, unpredicted structures often appear because molecular components are much more flexible than expected and metal centers can permit considerable deviation in their coordination angles.[5,6] In particular, when the number of the components is considerably large (more than about 50), the prediction of self-assembled structures becomes increasingly difficult or impossible.

Recently, an $M_{12}L_{24}$ cuboctahedron[7] and an $M_{24}L_{48}$ rhombicuboctahedron[8] were constructed from very similar ligands **1** and **5**, respectively, upon complexation with Pd^{II} ions (Figure 1). The prediction of these two structures by theory was not possible, but when mixed ligands (**1** + **5**) were subjected to metal complexation, we observed the critical switch of the resultant structures from $M_{12}L_{24}$ to $M_{24}L_{48}$ at the mixing ratios of **1**:**5** = 8:2 ≈ 7:3, where the averaged ligand bend angle varies from 131 to 134°.[8] We assumed that the most important parameter that controls the resultant structures was the bend angle θ of the ligands and predicted that the critical structural switch would occur at around $\theta = 131$–134° if the bend angle was chemically modulated (Figure 1b). Herein, we show that this simple empirical prediction is applicable for self-assembly from ligands **2**–**4**. By referring the bend angles of these ligands to the empirical scale in Figure 1b, we predicted the self-assembly of $M_{24}L_{48}$, the largest hitherto known coordination polyhedron, from these ligands **2**–**4**.

DFT calculations (B3LYP/6-31G*) revealed that the angles between the pyridine rings of ligands **2**, **3**, and **4** have the values of 135°, 143°, and 147°, respectively.[9] These values fit nicely into the angle span that predicts the formation of $M_{24}L_{48}$ (Figure 1b). The larger bend angle in **4** than **2** is probably due to the steric demand of the N-methyl substituent in **4** that pushes the two pyridyl groups apart. These ligands could be easily prepared in relatively few steps by using Suzuki cross-coupling (for **2** and **4**) or [3+2] isocyanide–olefin cycloaddition (for **3**) as key reactions (for details, see the Supporting Information).

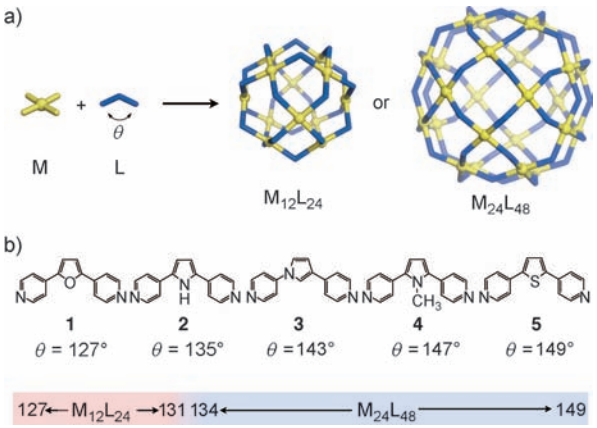

Figure 1. Self-assembly of $M_{12}L_{24}$ and $M_{24}L_{48}$ polyhedra in which the metal centers define a cuboctahedron and a rhombicuboctahedron, respectively. a) Representation. b) Structural formulae of ligands **1**–**5** with their bend angles. Angle spans used to predict the formation of $M_{12}L_{24}$ and $M_{24}L_{48}$ are indicated below the formulae.

The bend angle of ligand **4** is 147°, which is close to that of **5**. Therefore, formation of $M_{24}L_{48}$ is expected from this ligand. When ligand **4** was treated with $Pd(NO_3)_2$ in [D$_6$]DMSO (70 °C for 3 h), the selective formation of $M_{24}L_{48}$ complex **6** was indicated by NMR spectroscopy (Figure 2) and CSI-MS[10] (Figure 3). The roughly spherical $M_{24}L_{48}$ complex **6** has a rhombicuboctahedral symmetry and offers the ligands two different positions in the framework, which can be seen from two sets of signals in the ^{1}H NMR spectrum of the complex (Figure 2a). The signals show downfield shifts (particularly for pyridine α protons: $\Delta\delta_{Py\alpha} = 0.61$ ppm), which is indicative of the formation of Pd^{II} complexes. Furthermore, the signals are broadened, indicating the successful formation of a huge structure. In DOSY, the observation of a single band at $\log D = -10.60$ confirmed the single product formation (Figure 2d). Ultrahigh-resolution CSI-MS of **6** (BF_4^- salt) showed a series of prominent peaks for $[M-n(BF_4)]^{n+}$ ($n = 15$–22), with expected isotopic distributions, from which the molecular weight of **6** (18027.21 Da) was determined (Figure 3).

Ligand **3** has a slightly smaller bend angle (143°), from which $M_{24}L_{48}$ formation is still predicted. A disadvantage

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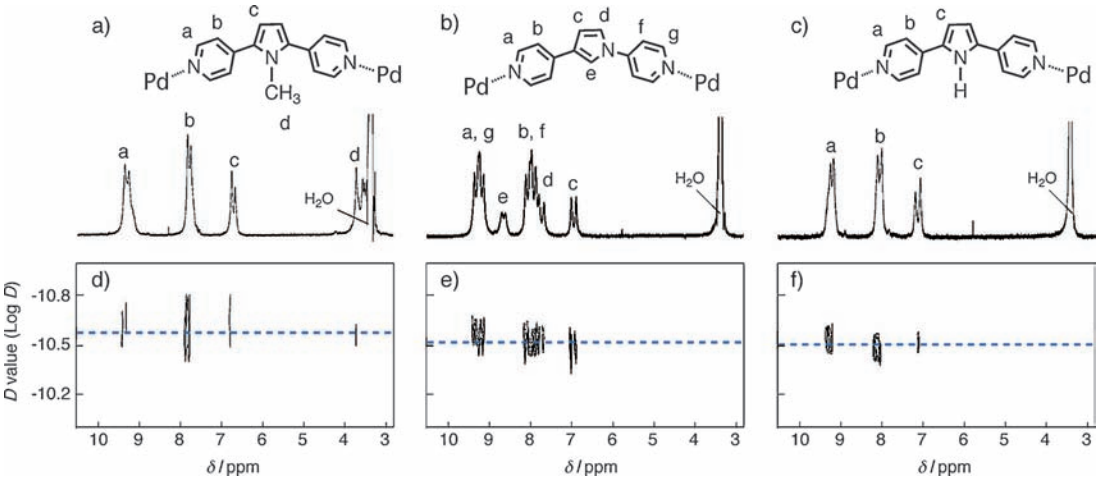

Figure 2. ^{1}H NMR spectra of a) **6**, b) **7**, and c) **8**, and ^{1}H DOSY NMR spectra of e) **6**, f) **7**, and g) **8** (NO_3^- salt, 500 MHz, [D_6]DMSO, 300 K).

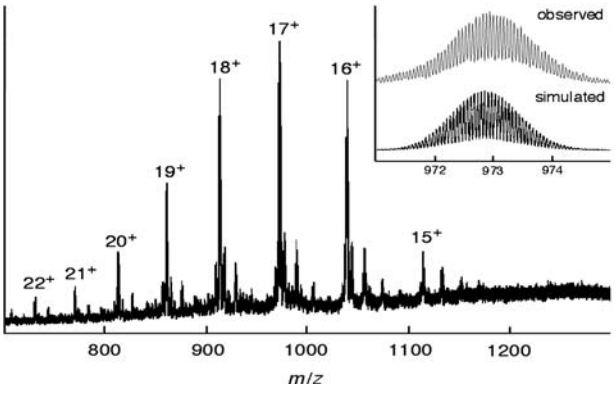

Figure 3. CSI-MS of complex **6** (BF_4^- salt). A series of [M-n(BF_4^-)]$^{n+}$ peaks are clearly observed. The inset shows the simulated (resolving power: 25 601) and observed isotopic patterns of the [M−17(BF_4^-)]$^{17+}$ ion.

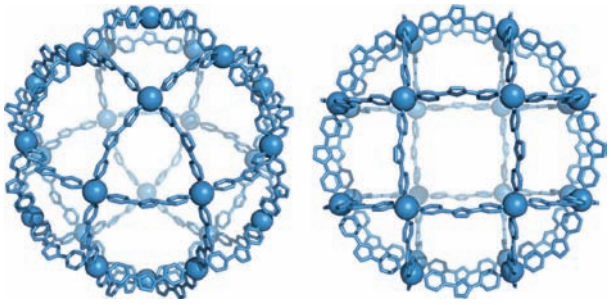

Figure 4. X-ray crystal structure of $M_{24}L_{48}$ complex **7**. Ligands and Pd^{II} ions are shown by stick and ball representations, respectively. Views are shown looking down along the C_3 (left) and C_4 (right) axes. Counterions and solvents are omitted for clarity. The unsymmetrical pyrrole core of ligand **3** is disordered in two positions.

accompanying the use of this lower-symmetry ligand is an increase in the demands upon analysis. Fortunately, after complexation with Pd^{II} ions, ^{1}H NMR spectrometry revealed that the lowered symmetry of ligand **3** was unimportant or actually averaged out in the analysis owing to its pseudosymmetry. As expected, two sets of broadened signals were observed in a ratio of 1:1, reflecting the two ligand positions (Figure 2b). A DOSY experiment again confirmed the generation of only one species in solution (Figure 2e). The log$D$ value (−10.52) was nearly identical to that of **6**. Furthermore, CSI-MS confirmed the molecular weight of $M_{24}L_{48}$ complex **7** (17 354.45 Da; see the Supporting Information).

Further to these satisfactory NMR and MS data, the structure of **7** was fully confirmed by X-ray crystallographic analysis (Figure 4). Single crystals of **7** were obtained by slow vapor diffusion of ethyl acetate into a DMSO solution of **7** (BF_4^- salt) over 6 weeks. Owing to the slight positional disorder of the sphere itself and the severe disorder of the anions and solvent molecules, the diffraction power of the crystals remained very low and no decent data were obtained with the in-house diffractometer. However satisfactory diffraction data (see the Supporting Information for further details) were collected after several trials with three different synchrotron X-ray sources, and the final dataset (to resolution of 1.32 Å) was obtained from the MX2 beamline at the Australian Synchrotron facility. The unsymmetric ligand **3** is disordered over two opposite orientations (50:50), showing its pseudosymmetry. The crystal structure clearly shows the roughly spherical rhombicuboctahedral framework of **7** with a huge ca. 110 000 Å^3 void space (ca. 82 %) in the unit cell. The cavity volume of the sphere itself is ca. 23 000 Å^3.

Finally, the Pd^{II} complexation was examined with ligand **2**. The empirical prediction of the self-assembled structure from this ligand is a borderline case because its bend angle (θ = 135°) is only slightly larger than the threshold (131–134°) for the $M_{12}L_{24}$/$M_{24}L_{48}$ critical switch (Figure 1b). When ligand **2** was complexed with Pd(NO_3)$_2$, we were surprised to observe the selective formation of expected $M_{24}L_{48}$ complex **8** by NMR and MS analyses. The ^{1}H NMR spectrum showed the two sets of broadened signals (1:1 ratio), which is typical for the $M_{24}L_{48}$ rhombicuboctahdron formation. The close coincidence of log$D$ value (−10.50) with those of **6** and **7** also supported the formation of **8**. CSI-MS revealed a typical pattern for the series of [M−n(OTf$^-$)]$^{n+}$ multiply charged ions from **8** (OTf$^-$ salt).

More importantly, neither DOSY nor CSI-MS measurement revealed the concomitant formation of an $M_{12}L_{24}$

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cuboctahedron[11] or any other by-products in the self-assembly of **8**. Considering the very similar structures of **1** and **2**, we thus confirmed the critical $M_{12}L_{24}/M_{24}L_{48}$ structural switch in a chemically well-defined system.

In summary, we succeeded in the self-assembly of three $M_{24}L_{48}$ rhombicuboctahedral complexes **6**–**8**, the largest hitherto known coordination polyhedra, from pyrrole-cored ligands **2**–**4**. Most importantly, the formation of the $M_{24}L_{48}$, at the exclusion of entropically more favored $M_{12}L_{24}$, is predictable from an empirical scale that is readily available from ligand-mixing experiments (**1** + **5**). It is particularly noteworthy that a mixture of $M_{12}L_{24}$ and $M_{24}L_{48}$ has never been obtained from any of ligands **1**–**5**, and, as a result, a small initial difference (particularly, θ values of 127 and 135° for **1** and **2**) was amplified into an incommensurable difference in the resultant structures ($M_{12}L_{24}$ or $M_{24}L_{48}$), referable as a molecular-level emergent behavior.[12,13]

Experimental Section

Preparation of $M_{24}L_{48}$ complexes **6**, **7**, and **8**: Ligand **4** (0.020 mmol) was treated with $Pd(NO_3)_2$ (0.010 mmol) in DMSO (1.00 mL) at 70 °C for 3 h. ^{1}H NMR confirmed the quantitative formation of an $M_{24}L_{48}$ spherical complex **6**. In a similar way, $M_{24}L_{48}$ spherical complexes **7** and **8** were obtained from ligands **3** and **2**, respectively. The BF_4^- or TfO^- salts were prepared using $Pd(BF_4)_2$ or $Pd(OTf)_2$ instead of $Pd(NO_3)_2$. Complex **6**: ^{1}H NMR (500 MHz, [D$_6$]DMSO, 300 K, NO_3^- salt): δ = 9.35 (br, 96 H), 9.25 (br, 96 H), 7.82 (br, 96 H), 7.74 (br, 96 H), 6.75 (br, 48 H), 6.66 (br, 48 H), 3.70 (br, 72 H), 3.54 ppm (br, 72 H); Complex **7**: ^{1}H NMR (500 MHz, [D$_6$]DMSO, 300 K, NO_3^- salt): δ = 9.58–8.95 (br, 192 H), 8.70 (br, 24 H), 8.60 (br, 24 H), 8.19–7.45 (br, 240 H), 7.74 (br, 96 H), 6.99 (br, 24 H), 6.90 ppm (br, 24 H); Complex **8**: ^{1}H NMR (500 MHz, [D$_6$]DMSO, 300 K, NO_3^- salt): δ = 12.20–11.60 (br, 48 H), 9.23 (br, 96 H), 9.15 (br, 96 H), 8.08 (br, 96 H), 7.98 (br, 96 H), 7.16 (br, 48 H), 7.03 (br, 48 H), 3.70 ppm. ^{13}C NMR, ^{1}H DOSY NMR and ultrahigh-resolution CSI-TOF-MS were also measured for **6**–**8** (see the Supporting Information).

X-ray crystallographic analysis of **7**: X-ray-quality single crystals were obtained by the slow diffusion of ethyl acetate vapor into a DMSO solution of **7** (BF_4^- salt). After several preliminary synchrotron X-ray diffraction studies at KEK and Spring-8 (both in Japan), the final diffraction data was collected at the MX2 beamline in AS (in Australia). Crystal data: M_r = 16742, colorless prism, 0.12 × 0.12 × 0.03 mm^3, tetragonal, space group $I4m$, $a = b$ = 43.756(1), c = 69.505(2) Å, V = 133073(2) Å^3, Z = 1, ρ_{calcd} = 0.418 g cm^{-3}, $F(000)$ = 16904, μ = 0.179 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 31.6°, 15157 unique reflections used, 8767 with $I_o > 2\sigma(I_o)$, R_{int} = 0.1565, 1394 parameters, 1241 restraints, GoF = 1.45, R = 0.1565 [$I_o > 2\sigma(I_o)$], wR = 0.419 (all reflections), $0.56 < \Delta\rho < -0.276$ e Å^3. CCDC 860617 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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