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Finely Resolved Threshold for the Sharp $M_{12}L_{24}$/$M_{24}L_{48}$ Structural Switch in Multi-Component M_nL_{2n} Polyhedral Assemblies: X-ray, MS, NMR, and Ultracentrifugation Analyses

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Abstract: In the self-assembly of M_nL_{2n} polyhedra, the bend angle (θ) of the divalent ligand components determines the final structure. The threshold for the sharp structural switch between $M_{12}L_{24}$ and $M_{24}L_{48}$ was finely resolved to within just 4° by demonstrating the exclusive formation of $M_{12}L_{24}$ cuboctahedra or $M_{24}L_{48}$ rhombicuboctahedra from two similar ligands with θ values of 130° and 134°. This sharp structural switch was fully confirmed by X-ray crystallography, mass spectrometry, NMR spectroscopy, and ultracentrifugation analyses.

Introduction

The self-assembly of giant structures from a large number of small components is currently one of the most exciting challenges in chemistry, and allows the bottom-up control of chemical structures on the nanoscale.[1] Metal–ligand self-assembly provides a highly efficient and powerful approach to discrete giant structures, and several groups have been intensively studying the self-assembly of coordination polyhedra with framework topologies that are described by Platonic or Archimedean solids.[2–4] From four-coordinate metals (M) and divalent bridging ligands (L), a series of M_nL_{2n} regular/semi-regular polyhedra, in which four edges meet at every vertex, can be formed with geometrically restricted n values of 6, 12, 24, 30, and 60.[5] The most important structural parameter that determines the n value is the bend angle (θ) of the ligand component, and we have previously shown that θ values below 127° give $M_{12}L_{24}$ ($n=12$) structures, whereas those above 135° result in $M_{24}L_{48}$ ($n=24$) structures. We have not observed any mixtures of the two structures when using ligands with θ values over a range of roughly 120–150°.[6] To finely resolve the threshold of the sharp structural "switch",[7] we synthesized ligands **1** and **2**, which have θ values that are very close to each other (130° and 134° for **1** and **2**, respectively). To our surprise, despite such a small difference in the θ values, **1** and **2** exclusively assembled into $M_{12}L_{24}$ and $M_{24}L_{48}$, respectively (Figure 1). This indicates that there is a very distinct threshold for the θ value, and this is reminiscent of the phase transition of some bulk materials. The very sharp structural switch observed in this study was fully confirmed by combining reliable analysis methods: X-ray crystallography, NMR spectroscopy, mass spectrometry, and ultracentrifugation analyses.

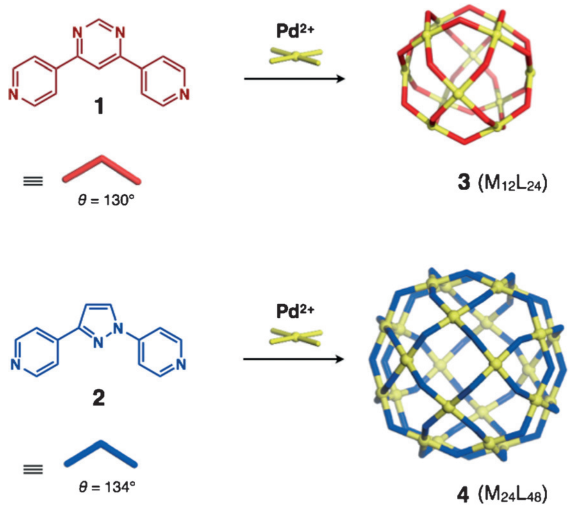

Figure 1. Self-assembly of bent ligands **1** and **2** into M_nL_{2n} polyhedra, **3** ($n=12$) and **4** ($n=24$), with cuboctahedral and rhombicuboctahedral symmetry, respectively.

Results and Discussion

Bent bridging ligands **1** and **2** were easily synthesized in a few steps using Suzuki–Miyaura cross-coupling (for **1**) or Ullmann condensation (for **2**) as key reactions (for details, see the Supporting Information). The bend angles of **1** and **2** were determined from DFT (B3LYP/6-31G*) calculations.[8] When **1** ($\theta=130°$) was treated with $[Pd(CH_3CN)_4](BF_4)_2$ in $[D_6]$DMSO at 70 °C for 3 days, the formation of a single product was indicated by ^1H NMR spectroscopic analysis (Figure 2a). The downfield shifts

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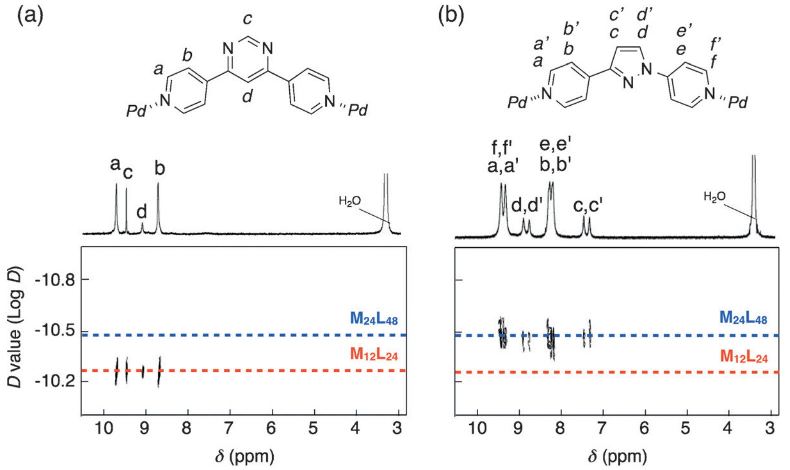

Figure 2. ^{1}H NMR spectra (1D and DOSY) of (a) **3** and (b) **4** (500 MHz, [D$_6$]DMSO, 300 K). All edges (ligands) are equivalent in cuboctahedral complex **3**, whereas there are two different edge (ligand) positions in rhombicuboctahedral complex **4**.

of the Py*Hα* and Py*Hβ* signals ($\Delta\delta$Py*Hα* = 0.76 ppm, $\Delta\delta$Py*Hβ* = 0.63 ppm) are characteristic of the coordination of the pyridine rings to the Pd^{II} ion. Observation of only one set of four signals indicates the equivalency of all the ligands in the complex; this is consistent with a complex of cuboctahedral symmetry in which all edges are equivalent. Diffusion-ordered NMR spectroscopy (DOSY) showed the formation of a single product with a diffusion coefficient (D) of 5.0×10^{-11} [m^{2}s^{-1}] (log$D$ = −10.30) at 300 K in [D$_6$]DMSO. This is comparable to the D values of previously reported cuboctahedral $M_{12}L_{24}$ complexes.[6,9] The product was therefore deduced to be cuboctahedron **3**.

Ligand **2** (θ = 134°) was treated with Pd(SbF$_6$)$_2$ in [D$_6$]DMSO at 70 °C for 3 h, and the product was analyzed by NMR spectroscopy. Despite having a very similar θ value to **1**, 1D NMR and DOSY experiments showed that the self-assembled product was not a cuboctahedron, but instead rhombicuboctahedral complex **4**. In the 1D NMR spectrum, two sets of signals were observed in a ratio of 1:1, which is consistent with rhombicuboctahedral symmetry (Figure 2b). All the signals were fully assigned to H_a-H_f and $H_{a'}$-$H_{f'}$ of the two ligands based on COSY, NOESY, and HSQC studies (see the Supporting Information). A DOSY experiment confirmed the generation of only one species with a log$D$ value of −10.45; this is nearly identical to those of other $M_{24}L_{48}$ complexes.[6,11]

The molecular weights and formulae of complexes **3** and **4**, as well as their exclusive formation, were clearly confirmed by cold-spray ionization mass spectrometry (CSI-MS)[11] (Figure 3). From the solution of **3**, a series of prominent peaks for $[Pd_{12}(\mathbf{1})_{24}(BF_4)_{24-n}]^{n+}$ (n = 10–13) were observed with very high resolution (>25 000), from which the molecular weight of **3** was determined to be 8982.46 Da. However, no peaks were observed that could be assigned to an $M_{24}L_{48}$ structure. In contrast, CSI-MS of **4** revealed a series of peaks corresponding to $[Pd_{24}(\mathbf{2})_{48}(SbF_6)_{48-n}]^{n+}$ (n = 16–19, resolving power: >22 000), from which the molecular weight was determined to be 24 537.78 Da. These mass spectrometric data support the NMR results, and show that the self-assembled polyhedral structure sharply switches from $M_{12}L_{24}$ to $M_{24}L_{48}$ at a threshold that lies between 130° and 134°.

The sharp structural switch between **3** and **4** was more carefully confirmed by analytical ultracentrifugation (AUC) measurements,[12] which have recently been applied to the estimation of the dispersity and average molecular weight of metal-ligand self-assembled complexes.[13] AUC sedimentation velocity measurements clearly showed the high monodispersity of **3** and **4** in solution with distinguishable sedimentation coefficients of 1.58 and 2.34 (Figure S22, Supporting Information). From these coefficients, the hydrodynamic diameters of **3** and **4** were calculated to be 3.1 and 5.7 nm, respectively. These values are consistent with those estimated from molecular modeling of **3** and **4** (3.3 and 4.3 nm, respectively).

Finally, X-ray crystallographic analysis was carried out on **3** and **4** to unambiguously confirm the $M_{12}L_{24}$ and $M_{24}L_{48}$ frameworks. Single crystals of **3** and **4** suitable for synchrotron X-ray crystallography were obtained by the very slow vapor diffusion of ethyl acetate into DMSO solutions of **3** (BF_4^- salt) and **4** (SbF_6^- salt). Structural refinements revealed the $M_{12}L_{24}$ cubocta-

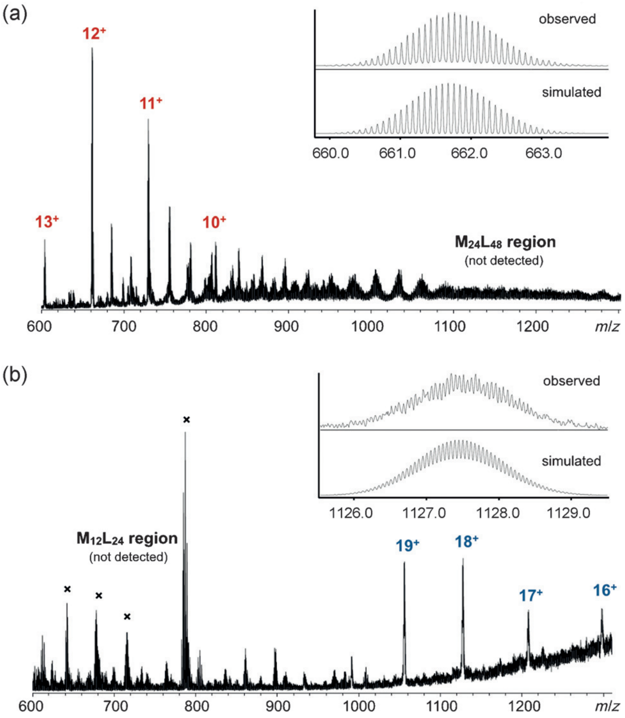

Figure 3. CSI-MS of (a) **3** (BF_4^- salt) and (b) **4** (SbF_6^- salt). A series of prominent peaks for $M_{12}L_{24}$ complex **3** and $M_{24}L_{48}$ complex **4** were observed. The insets show the observed and simulated isotopic patterns of the (a) $[M-12(BF_4^-)]^{12+}$ and (b) $[M-18(SbF_6^-)]^{18+}$ ions.

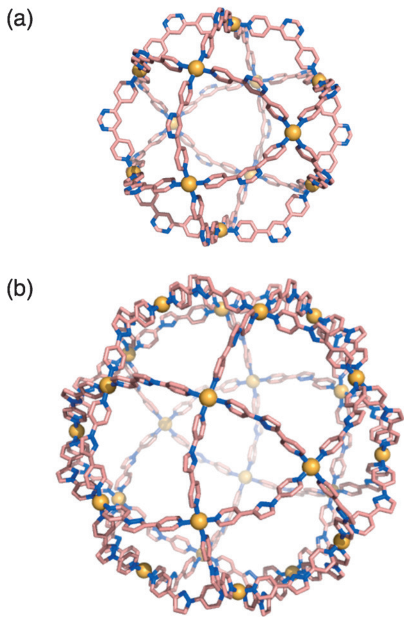

Figure 4. X-ray crystal structures of (a) $M_{12}L_{24}$ complex **3** and (b) $M_{24}L_{48}$ complex **4**. Ligands and Pd ions are shown as stick and ball representations, respectively. Counterions and solvents are omitted for clarity. The unsymmetrical pyrazole core of ligand **2** is disordered over two positions.

hedral and $M_{24}L_{48}$ rhombicuboctahedral structures of **3** and **4**, respectively (Figure 4). These structures are fully consistent with the NMR, mass spectrometric, and AUC experiments.

Conclusions

In conclusion, we finely resolved the sharp structural switch between $M_{12}L_{24}$ cuboctahedral and $M_{24}L_{48}$ rhombicuboctahedral complexes formed from bent ditopic ligands to within just 4°. We observed the exclusive formation of an $M_{12}L_{24}$ cuboctahedron from the self-assembly of **1** ($\theta = 130°$) and an $M_{24}L_{48}$ rhombicuboctahedron from the self-assembly of structurally very similar **2** ($\theta = 134°$). The small initial difference in the ligand structure ($\Delta\theta = 4°$) is amplified during the multicomponent self-assembly and results in a large energy difference in the final self-assembled structures. Therefore, a unique final structure is formed even though that structure is only slightly favored in the initial self-assembly steps. The observed distinct $M_{12}L_{24}/M_{24}L_{48}$ structural switch can be compared to the phase transition of some bulk materials.[14] Our observation may thus demonstrate that the phase transition behavior of bulk materials can be modeled with as few as about 50 components.

Experimental Section

General

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer equipped with a 5 mm BBO-Z-gradient probe, a Bruker AV-500 spectrometer equipped with a 5 mm TCI gradient cryo probe, and a JEOL ECA-600 spectrometer equipped with a gradient cold probe (53040HCNVC). All NMR spectral data were collected at 300 K and the chemical shift values reported here are with respect to an internal TMS standard for $CDCl_3$ and to a residual solvent signal for $[D_6]$DMSO. Melting points were determined on a Yanaco MP-500V melting-point apparatus. CSI-TOF mass spectra were measured on a Bruker maXis instrument. The data analysis of CSI-TOF mass spectra were processed using the Bruker Data Analysis (Version 4.0 SP 2) software and the simulations were performed using the Bruker IsotopePattern software. IR measurements were carried out as KBr pellets using a DIGILAB FTS-7000 instrument. Column chromatography was performed with silica gel 60N (spherical, neutral) purchased from Kanto Chemical Co. Inc. All the chemicals were of reagent grade and used without any further purification.

Synthesis of 4,6-bis(4-pyridyl)pyrimidine 1

A mixture of 4,6-diiodopyrimidine (995 mg, 3.00 mmol), [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II) (439 mg, 0.600 mmol), and 4-pyridyl boronic acid (1.84 g, 15.0 mmol) was dissolved in 1,4-dioxane (22.5 mL) and 2 M K_3PO_4 solution (9 mL) was added under argon atmosphere. After stirring at 80 °C for 2 days, 1,4-dioxane was evaporated in vacuo, and the residue was extracted with chloroform. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (ethyl actate/methanol = 10:1) and GPC (gel permeation chromatography) to give 4,6-bis(4-pyridyl)pyrimidine (149 mg, 0.634 mmol) as a brown solid in 21 % yield.

m.p. 175 °C; high-resolution ESI-TOF-MS *m/z* calcd for $[C_{14}H_{10}N_4\ ([M{+}H]^{+})]$: 235.0979, found 235.0978 (error = 0.4 ppm); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 9.46$ (s, 1 H), 8.86 (d, $J = 6.0$ Hz, 4 H), 8.21 (s, 1 H), 8.03 (d, $J = 6.0$ Hz, 4 H); ^{1}H NMR (500 MHz, $[D_6]$DMSO, 300 K): $\delta = 9.50$ (s, 1 H), 8.91 (s, 1 H), 8.85 (d, $J = 8.0$ Hz, 4 H), 8.32 ppm (d, $J = 8.0$ Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 163.2$ (C), 159.8 (CH), 151.0 (CH), 143.7 (C), 121.1 (CH), 113.5 ppm (CH); IR (KBr): $\tilde{\nu} = 3084$, 3037, 1956, 1576, 1507, 1458, 1411, 1370, 1309, 1256, 1213, 1174, 1061, 989, 839, 773, 704, 626, 548, 516, 421 cm^{-1}.

Synthesis of 1,3-bis(4-pyridyl)pyrazole 2

A mixture of 3-(4-pyridyl)pyrazole (436 mg, 3.0 mmol), 4-iodopyridine (616 mg, 3.0 mmol), Cs_2CO_3 (1.96 g, 6.0 mmol), salycylaldoxime (164 mg, 1.2 mmol), and Cu_2O (50.6 mg, 0.35 mmol) was dissolved in dry DMF (5 mL) under argon atmosphere. After stirring at 110 °C for 1 day, DMF was evaporated in vacuo, and the residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (ethyl actate/methanol = 20:1 to ethyl actate/methanol = 20:1 and 2 % dimethylamine) and GPC to give 1,3-bis(4-pyridyl)pyrazole (270 mg, 1.2 mmol) as a white solid in 41 % yield.

m.p. 182 °C, high-resolution ESI-TOF-MS *m/z* calcd for $[C_{13}H_{10}N_4\ ([M]^{+})]$: 223.0977, found 223.0978 (error = 0.5 ppm); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 8.72$ (d, $J = 6.0$ Hz, 2 H), 8.70 (d, $J = 6.0$ Hz, 2 H), 8.13 (d, $J = 2.5$ Hz, 1 H), 7.80 (d, $J = 6.0$ Hz, 2 H), 7.73 (d, $J = 6.0$ Hz, 2 H), 6.94 ppm (d, $J = 2.5$ Hz, 1 H); ^{1}H NMR (500 MHz, $[D_6]$DMSO, 300 K): $\delta = 8.87$ (d,, $J = 3.0$ Hz, 1 H), 8.70 (d, $J = 6.0$ Hz, 2 H), 8.68 (d, $J = 6.0$ Hz, 4 H), 7.98 (d, $J = 6.0$ Hz, 2 H), 7.93 (d, $J = 6.0$ Hz, 2 H), 7.42 ppm (d, $J = 3.0$ Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 151.8$ (C), 151.5 (CH), 150.5 (CH), 145.8 (C), 139.8 (C), 128.5 (CH), $\delta = 120.5$ (CH), 112.7 (CH), 107.2 ppm (CH); IR (KBr): $\tilde{\nu} = 3084$, 1589, 1508, 1420, 1371, 1308, 1209, 1051, 988, 957, 819, 762, 704, 515 cm^{-1}.

Self-assembly of sphere 3

To a solution of 4,6-bis(4-pyridyl) pyrimidine (0.80 mg, 3.42 μmol) in [D$_6$]DMSO (1.05 mL) was added a solution of Pd(NO$_3$)$_2$ or [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ in [D$_6$]DMSO (93.9 μL, 20.0 mM, 1.88 μmol), and the resulting mixture was stirred at 70 °C for 3 d. The quantitative formation of complex was confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, [D$_6$]DMSO, 300 K): $\delta = 9.61$ (br, 96 H), 9.48 (br, 48 H), 8.95 (br, 48 H), 8.66 ppm (br, 96 H); diffusion coefficient ([D$_6$]DMSO, 300 K, BF$_4^-$salt): $D = 5.0\times10^{-11}$ m^2 s^{-1}; ^{13}C NMR (125 MHz, [D$_6$]DMSO, 300 K): $\delta = 160.1$ (CH), 160.0 (CH), 151.9 (C), 146.2 (C), 125.7 (C), 124.5 (CH), 115.4 ppm (CH); CSI-TOF-MS (BF$_4^-$ salt, CH$_3$CN): The following picked signals are those of monoisotropic ion signals (Figure S16 in the Supporting Information). *m/z* calcd for $[M-10(\mathrm{BF_4}^-)]^{10+}$ 811.9085, found 811.9078; calcd for $[M-11(\mathrm{BF_4}^-)]^{11+}$ 730.1893, found 730.1889; calcd for $[M-12(\mathrm{BF_4}^-)]^{12+}$ 662.0899, found 662.0898; calcd for $[M-13(\mathrm{BF_4}^-)]^{13+}$ 604.4674, found 604.4669; calcd for $[M-14(\mathrm{BF_4}^-)]^{14+}$ 555.0767, found 555.0740.

Self-assembly of sphere 4

To a solution of 1,3-bis(4-pyridyl)pyrazole (4.42 mg, 20.2 μmol) in [D$_6$]DMSO (146 μL) was added a solution of Pd(SbF$_6$)$_2$ in [D$_6$]DMSO (517 μL, 20.0 mM, 10.5 μmol) and the resulting mixture was stirred at 70C° for 3 h. The quantitative formation of complex was confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, [D$_6$]DMSO, 300 K): $\delta = 9.32$(br, 192 H), 8.77(br, 48 H), 8.18 (br, 192 H), 7.33 ppm (br, 48 H). Diffusion coefficient ([D$_6$]DMSO, 300 K, SbF$_6^-$salt): $D = 3.5\times10^{-11}$ m^2 s^{-1}.^{13}C NMR (125 MHz, [D$_6$]DMSO, 300 K): $\delta = 151.9$ (CH), 151.4 (CH), 150.0 (C), 146.9 (C), 141.9 (C), 131.8 (CH), 123.0 (CH), 115.2 (CH), 109.2 ppm (CH). CSI-TOF-MS (SbF$_6^-$ salt, DMSO): The following picked signals are those of monoisotopic ion signals (Figure S18 in the Supporting Information). *m/z* calcd for $[M-16(\mathrm{SbF_6}^-)]^{16+}$ 1296.4185, found 1296.4191; calcd for $[M-17(\mathrm{SbF_6}^-)]^{17+}$ 1206.3412, found 1206.3472; calcd for $[M-18(\mathrm{SbF_6}^-)]^{18+}$ 1126.2725, found 1126.2628; calcd for $[M-19(\mathrm{SbF_6}^-)]^{19+}$ 1054.6322, found 1054.6305; calcd for $[M-20(\mathrm{SbF_6}^-)]^{20+}$ 990.1588, found 990.1498; $[M-21(\mathrm{SbF_6}^-)]^{21+}$ 931.8201, found 931.8078.

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