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Coordination Compounds

Solvato-Controlled Assembly of Pd_3L_6 and Pd_4L_8 Coordination "Boxes"**

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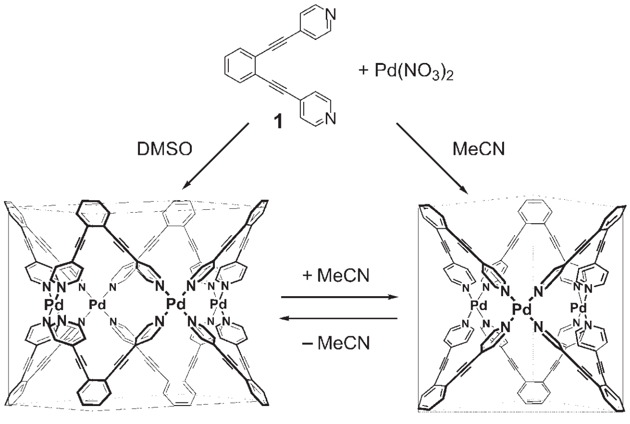
Owing to the reversibility of metal–ligand coordination bonds, molecular assemblies from metals and ligands are often in equilibrium when their thermodynamic stabilities are comparable.[1] The equilibrium ratio can be controlled usually by changing conditions (concentration, temperature, etc.)[2,3] or by adding a template molecule that selectively binds to and stabilizes one particular assembly.[4,5] Ring numbers of cyclic assemblies have been often controlled in these ways.[2,4] A solvent is often an important factor that controls the stability of the assemblies, but the solvato-control of the equilibrium has been seldom achieved because a solvent does not make a significant difference to the relative stabilities of the equilibrated assemblies.[6] Herein we report a drastic solvent effect in controlling the self-assembly of two coordination compounds. Pd^{II} ions and 1,2-bis[2-(pyridin-4-yl)ethynyl]benzene (**1**) are assembled into a mixture of M_4L_8 (**2**) and M_3L_6 (**3**) box-shaped structures (Scheme 1). We show that the ratio of these two assemblies is almost completely controlled by changing solvents. To control the cavity size in such a simple way is important, as the cavities of Pd^{II}-linked boxes have shown many interesting properties through host–guest complexation.[7]



2 (M_4L_8)

3 (M_3L_6)

Scheme 1. The solvato-controlled assembly of M_4L_8 (**2**) and M_3L_6 (**3**) structures and their interconversion. DMSO: dimethyl sulfoxide.

Ligand **1** was prepared by the Sonogashira coupling reaction of 4-ethynylpyridine with 1,2-dibromobenzene. When a mixture of ligand **1** (20 mM) and $Pd(NO_3)_2$ (10 mM) in $[D_6]$DMSO (1 mL) was heated for 4 h at 60 °C, the quantitative formation of a single and highly symmetric product was indicated by ^1H NMR spectroscopy (Figure 1 a).

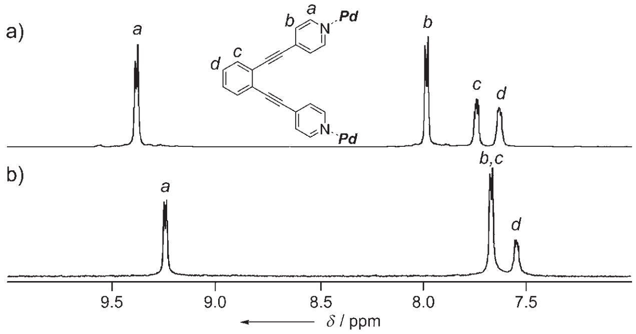


Figure 1. ^1H NMR spectra (500 MHz, 300 K) of a) complex **2** ($[D_6]$DMSO, [**1**] = 20 mM) and b) complex **3** (CD_3CN, [**1**] = 2 mM).

The downfield shift of the signals for the product as compared to those for ligand **1**, particularly for the pyridyl α- and β-hydrogen atoms ($\Delta\delta = 0.72$ and 0.45 ppm, respectively), was attributed to metal–ligand complexation. Cold-spray ionization mass spectrometry (CSI-MS)[9] clearly confirmed an M_4L_8 stoichiometry from a series of prominent peaks of $[\mathbf{2}-(NO_3^-)_n]^{n+}$ ($n = 2$–5). Four intense peaks at m/z 1520.8, 993.0, 729.2, and 571.2 were assigned to $[\mathbf{2}-(NO_3^-)_2]^{2+}$, $[\mathbf{2}-(NO_3^-)_3]^{3+}$, $[\mathbf{2}-(NO_3^-)_4]^{4+}$, and $[\mathbf{2}-(NO_3^-)_5]^{5+}$, respectively (Figure 2 a). The structure of complex **2** was unambiguously determined by an X-ray diffraction study (Figure 3 a). Block-shaped single crystals, suitable for X-ray diffraction analysis, were obtained by slow diffusion of ethyl acetate into a solution of complex **2** in DMSO. In this complex, four Pd^{II} ions are arranged at the corners of a square, in which the averaged adjacent and diagonal Pd–Pd distances are 9.7 and 13.7 Å, respectively. Each Pd^{II} center adopts a square-planar geometry with Pd–N bond lengths of 2.0 Å.

Surprisingly, the same components (Pd^{II} ions and **1**) assembled into another structure when CD_3CN was used, instead of $[D_6]$DMSO, as solvent. On complexation of **1** (2 mM) and $Pd(NO_3)_2$ (1 mM) in CD_3CN, the ^1H NMR spectrum of the complex indicated the quantitative self-

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

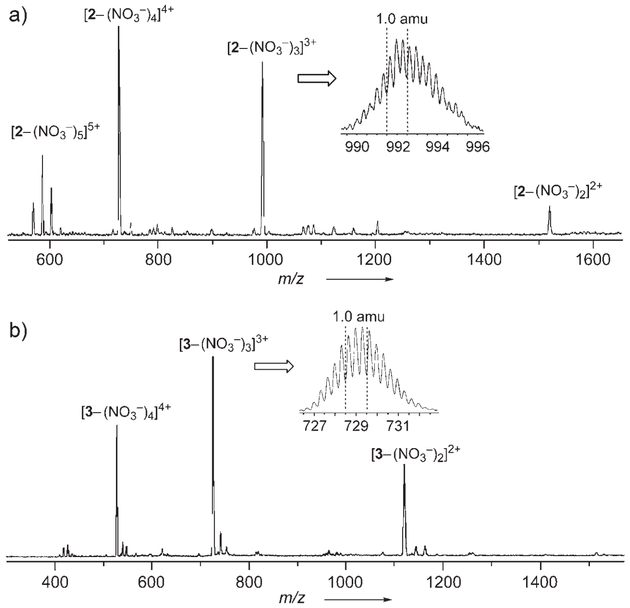

Figure 2. CSI mass spectra of complexes a) **2** and b) **3**.

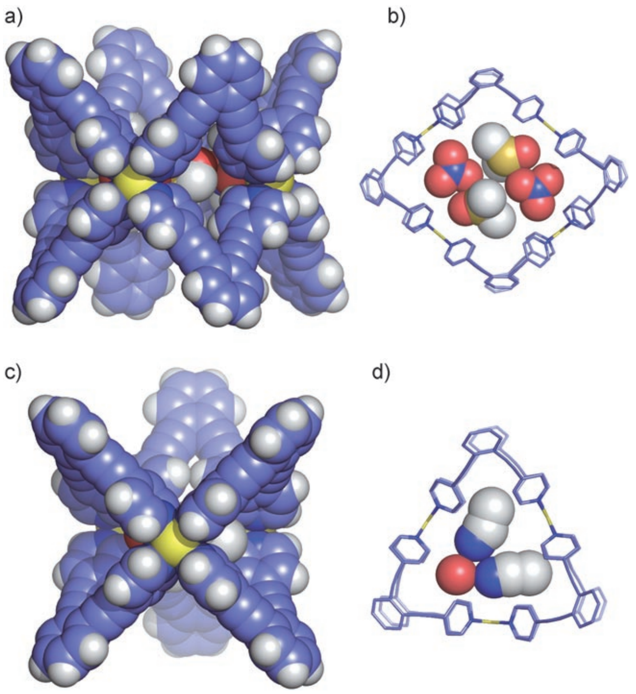

Figure 3. Crystal structures of **2** (a, b) and **3** (c, d). Parts (a) and (c) show side views (space-fill representation: Pd yellow, C, N blue, H gray), and parts (b) and (d) show top views (stick framework: Pd yellow, C, N blue; space-fill representation of guests: C gray, N blue, O red, S yellow). For clarity, some of the solvent molecules and anions are omitted.

assembly of another highly symmetrical complex (Figure 1 b).[8] From CSI-MS measurement, this complex was revealed to be a M_3L_6 structure **3** (Figure 2 b). By the slow diffusion of THF into the acetonitrile solution of **3**, we successfully obtained single crystals that were suitable for crystallographic analysis. Reliable evidence for the M_3L_6 structure of **3** was obtained by X-ray analysis (Figure 3 c). Three Pd^{II} ions are arranged in a regular triangle, in which the distance between the metal centers is 8.7 Å.

Owing to the reversibility of Pd^{II}–N bonds, the M_4L_8 and M_3L_6 assemblies **2** and **3** are in equilibrium. Thus, we observed facile interconversion between **2** and **3** by addition or removal of solvent. Addition of CD_3CN to the solution of complex **2** in [D$_6$]DMSO (20 mM) followed by stirring of the solution at 60 °C for 3 h promoted the smooth conversion of complex **2** into **3** as revealed by ^{1}H NMR spectroscopy (Figure 4 a–f).

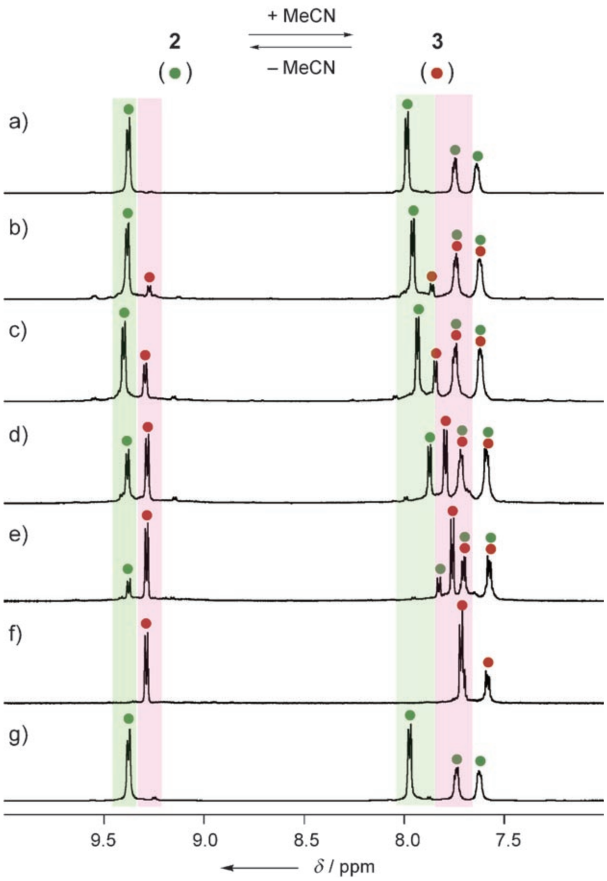

Figure 4. ^{1}H NMR spectra demonstrating the structural conversion from M_4L_8 to M_3L_6. a) M_4L_8 (**2**) in [D$_6$]DMSO ([**1**] = 20 mM). b–f) After addition of CD_3CN to the sample in part (a) and stirring at 60 °C for 3 h; [D$_6$]DMSO/CD_3CN = 75:25 (b), 67:33 (c), 50:50 (d), 33:67 (e), 25:75 (f). g) After removal of CD_3CN from the sample in part (f), which corresponds to a M_3L_6 structure (**3**), and stirring at room temperature for 3 h, the structure reverts back to that of **2** (M_4L_8).

Upon increasing the ratio of CD_3CN, the ^{1}H NMR signals of complex **2** decreased while those of complex **3** increased. Finally, at a ratio of DMSO to acetonitrile of 25:75, complex **2** was almost completely converted into **3**. This solution was taken and CD_3CN was removed by evaporation. In the resulting [D$_6$]DMSO solution, complex **3** was completely converted back into complex **2** after 3 h at room temperature (Figure 4 g). The switching between the two structures by addition/removal of solvent was repeated at least three times without forming any by-products or precipitates (see the Supporting Information).

Although there are no significant distortions in the structures of both **2** and **3**, an entropy effect should push the equilibrium toward the M_3L_6 structure **3** because it assembles from fewer components.[10] Thus, the selective formation of **3** in CD_3CN is explained in terms of the entropy effect. Meanwhile, an advantage in enthalpy, which predominates over the entropy effect, should be considered in DMSO as solvent to account for the selective formation of **2** therein. An implication is provided by the crystal structure of **2**, in which two DMSO molecules and two nitrate ions form a 2:2 aggregate inside the cavity (Figure 3b). We assume that this aggregated structure exists even in solution to some extent and templates the formation of the M_4L_8 structure. Indeed, the following experiments showed the importance of the cooperation of DMSO and nitrate anions. When $Pd(OTf)_2$[11] was used instead of $Pd(NO_3)_2$ in $[D_6]$DMSO, a mixture of **2** and **3** (62:38) was formed. Dilution of the $[D_6]$DMSO solution of complex **2** with any other solvents (methanol, ethanol, 1,4-dioxane, chloroform, and so on) also induced the conversion of **2** into **3** (see the Supporting Information). Thus, both DMSO and nitrate ions are essential to the selective formation of **2**. In the crystal structure of **3**, two acetonitrile molecules form hydrogen bonds with one water molecule at the center of the cavity (Figure 3d). This aggregation may enhance the selectivity for the formation of **3**.

In summary, we have developed the solvato-controlled assembly of M_3L_6 and M_4L_8 hollow complexes such that the two complexes can be interconverted by simply adding or removing a solvent. The cavities of both the box-shaped compounds are efficient for molecular recognition as they are surrounded by large hydrophobic ligands and Pd^{II} centers. Therefore, further extension of the present work to solvent-dependent guest recognition is a particularly interesting subject.

Experimental Section

Crystal data for **2**: $C_{188}H_{96}N_{23}O_{56}S_{14}Pd_4$, $M_r = 4447.32$, pale yellow block ($0.28 \times 0.26 \times 0.22$ mm^3), monoclinic, space group $P2_1/c$, $a = 21.232(3)$, $b = 15.524(2)$, $c = 35.481(5)$ Å, $\beta = 97.139(2)°$, $V = 11604(3)$ Å^3, $T = 80$ K, $Z = 2$, $\rho_{calcd} = 1.273$, 19815 unique reflections out of 28706 with $I > 2\sigma(I)$, The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1569 parameters, $1.63 < \theta < 28.89°$, $R_1(I > 2\sigma(I)) = 0.0877$, $wR_2 = 0.2790$, GOF = 1.050, max/min residual density 1.652/−1.479 e Å^{-3}. Inside of the cavity, DMSO molecules and water molecules are disordered with occupancies of 0.58 and 0.42, respectively.

Crystal data for **3**: $C_{138}H_{108}N_{22}O_{31.5}Pd_3$, $M_r = 2891.67$, pale yellow needle ($0.40 \times 0.30 \times 0.05$ mm^3), trigonal, space group $P\bar{1}$, $a = b = 19.841(5)$, $c = 27.850(12)$ Å, $V = 9494(6)$ Å^3, $T = 90$ K, $Z = 2$, $\rho_{calcd} = 1.014$, 4735 unique reflections out of 17705 with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 594 parameters, $2.18 < \theta < 30.06°$, $R_1(I > 2\sigma(I)) = 0.1227$, $wR_2 = 0.3963$, GOF = 0.899, max/min residual density 0.856/−0.916 e Å^{-3}. Several solvent molecules and nitrate anions are disordered. The bond lengths of severely disordered molecules were chemically restrained.

CCDC 630654 (**2**) and 630653 (**3**) contain 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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[1] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 2455–2463.

[2] a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535–1536; b) O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. von Zelewsky, *Chem. Eur. J.* **2001**, *7*, 533–539; c) T. Bark, M. Düggeli, H. Stoeckli-Evans, A. von Zelewsky, *Angew. Chem.* **2001**, *113*, 2924–2927; *Angew. Chem. Int. Ed.* **2001**, *40*, 2848–2851; d) A. Sautter, D. G. Schmid, G. Jung, F. Würthner, *J. Am. Chem. Soc.* **2001**, *123*, 5424–5430; e) T. Yamamoto, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309–12317; f) T. Kraus, M. Budšěínský, J. Cvačka, J.-P. Sauvage, *Angew. Chem.* **2006**, *118*, 264–267; *Angew. Chem. Int. Ed.* **2006**, *45*, 258–261.

[3] a) J.-M. Senegas, S. Koeller, G. Bernardinelli, C. Piguet, *Chem. Commun.* **2005**, 2235–2237; b) C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J.* **1999**, *5*, 3487–3494.

[4] a) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956–10962; b) G. Ma, Y. S. Jung, D. S. Chung, J.-I. Hong, *Tetrahedron Lett.* **1999**, *40*, 531–534; c) M. Schweiger, S. R. Seidel, A. M. Arif, P. J. Stang, *Inorg. Chem.* **2002**, *41*, 2556–2559; d) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell, K. R. Dunbar, *J. Am. Chem. Soc.* **2005**, *127*, 12909–12923; e) P. A. Brady, R. P. Bonar-Law, S. J. Rowan, C. J. Suckling, J. K. M. Sanders, *Chem. Commun.* **1996**, 319–320; f) P. A. Brady, J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3237–3253.

[5] a) S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 10239–10240; b) M. Scherer, D. L. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1689–1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 1587–1592; c) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 980–981; d) M. Albrecht, I. Janser, J. Runsink, G. Raabe, P. Weis, R. Fröhlich, *Angew. Chem.* **2004**, *116*, 6832–6836; *Angew. Chem. Int. Ed.* **2004**, *43*, 6662–6666; e) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1*, 82–90; f) R. T. S. Lam, A. Belenguer, S. L. Roberts, C. Naumann, T. Jarrosson, S. Otto, J. K. M. Sanders, *Science* **2005**, *308*, 667–669.

[6] a) M. Fujita, F. Ibukuro, H. Hagihara, K. Ogura, *Nature* **1994**, *367*, 720–723; b) S. J. Park, D. M. Shin, S. Sakamoto, K. Yamaguchi, Y. K. Chung, M. S. Lah, J.-I. Hong, *Chem. Eur. J.* **2005**, *11*, 235–241; c) L. Pirondini, A. G. Stendardo, S. Geremia, M. Campagnolo, P. Samorì, J. P. Rabe, R. Fokkens, E. Dalcanale, *Angew. Chem.* **2003**, *115*, 1422–1425; *Angew. Chem. Int. Ed.* **2003**, *42*, 1384–1387; d) S. A. Schuetz, V. W. Day, A. L. Rheingold, J. A. Belot, *Dalton Trans.* **2003**, 4303–4306; e) O. Mamula, M. Lama, H. Stoeckli-Evans, S. Shova, *Angew. Chem.* **2006**, *118*, 5062–5066; *Angew. Chem. Int. Ed.* **2006**, *45*, 4940–4944; f) P. N. W. Baxter, R. G. Khoury, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4140–4148; g) C. A. Schalley, T.

Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, *8*, 3538–3551.

[7] For reviews, see: a) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusuwaka, K. Biradha, *Chem. Commun.* **2001**, 509–518; b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369–378.

[8] While complex **2** was prepared at 20 mM in [D$_6$]DMSO, the assembly of complex **3** was carried out at 2 mM in CD_3CN because of its low solubility in acetonitrile. The concentration effect was not a dominant factor for controlling the equilibration, as we confirmed that the ratio of **2**/**3** was approximately 5:1 when the complexation of **1** and $Pd(NO_3)_2$ was examined at 2 mM in [D$_6$]DMSO.

[9] CSI-MS is quite effective for analyzing the solution structures of metal complexes: a) S. Sakamoto, M. Fujita, K. Kim, K. Yamaguchi, *Tetrahedron* **2000**, *56*, 955–964; b) K. Yamaguchi, *J. Mass Spectrom.* **2003**, *38*, 473–490.

[10] The entropic advantage of an assembly from fewer components has been discussed for equilibrations between M_3L_3 and M_4L_4 assemblies. See Refs. [2a] and [2f].

[11] $Pd(OTf)_2$ was prepared by treating $PdCl_2$ with AgOTf in DMSO at 50 °C for 12 h and removing precipitated AgCl.