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A molecular sphere of octahedral symmetry†

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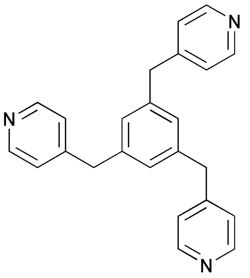
Complexation of tridentate ligand 1 with Pd(NO_3)$_2$ leads to the quantitative self-assembly of M_6L_8 molecular sphere 2.

Synthesis of molecular architectures from organic ligands and transition metal ions through the self-assembly route, in contrast to the troublesome stepwise synthesis, has received much attention during the last decade.[1] Designed structures having predetermined structural and functional properties can sometimes be obtained by simply mixing the participating components under suitable conditions. Recently, the focus of several groups has been on the construction of self-assembled species possessing internal cavities.[2,3] There are handful of structures with a 3-D cavity within a tetrahedron,[4] hexahedron,[5] dodecahedron,[6] and similar shapes,[7] obtained by a metal-directed self-assembly route. There are also reports of 3-D cavities constructed by utilizing the principle of hydrogen-bond interactions.[8] Secondary building units, the metal ion containing self-assembled structures possessing lateral sites capable of H-bonding interactions, are used successfully to construct cuboctahedron and faceted polyhedra.[9] However, not many reports are available on closed cavities which are more or less spherical in shape although the formation of discrete spherical structures through self-assembly process exists in some biological systems: *e.g.*, the capsids of bacteriophages P22[10] or HK97.[11]

Herein, we report the self-assembly of a novel and highly symmetrical molecular sphere and its X-ray crystal structure. The molecular sphere is constructed from ligand **1**[12] and Pd(NO_3)$_2$. The complexation reaction was also monitored by using NMR spectroscopy that establishes a quantitative self-assembly process. The findings show reliable evidence of both solution and solid-state structures. The spherical shape is important because the cavity volume is maximized when the components are oriented spherically. Very recently, Liu and Tong reported an M_6L_8 assembly which is topologically the same as our molecule but not spherical.[13]



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The surface of a sphere is divided by three orthogonal planes into eight identical parts, each of which is capped by the tripodal tridentate ligand **1** (Fig. 1). At each of the six cross sections, one Pd(II) ion is located and four ligand molecules are assembled around the square planar coordination environment of the metal center. Thus, we used Pd(NO_3)$_2$ in combination with **1** in expectation of an aesthetically pleasing M_6L_8 type complex. The ligand **1** was mixed with Pd(NO_3)$_2$ at a ratio of 4:3 in DMSO (concentration of **1** = 10 mM), and stirred at 90 °C for 1 h. Subsequent addition of acetone to the above solution precipitated a cream colored solid which was separated by filtration, washed with MeOH, and dried *in vacuo* to obtain hexanuclear complex [(Pd)$_6$(**1**)$_8$(NO_3)$_{12}$] (**2**) in 79% yield.‡

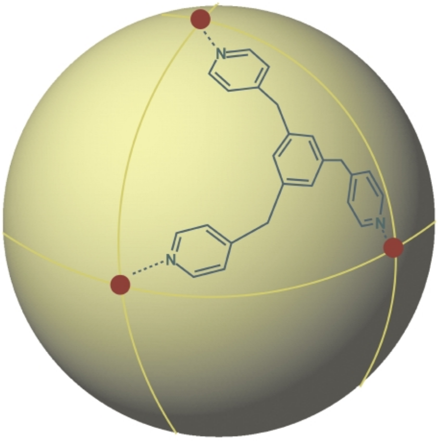

Fig. 1 Cartoon representation of a molecular sphere, conceptualized from eight tripodal tridentate ligands, and six metal ions that can provide a square planar coordination environment. All the 14 components are cooperatively embracing the surface of sphere.

NMR and CSI-MS analyses indicated the formation of predetermined, discrete species **2** by the metal-driven route. In ^{1}H NMR, down field shifting of the signals for complex **2** (Fig. 2), particularly for Py$_\alpha$ ($\Delta\delta$ = 0.69 ppm), can be ascribed to the metal–ligand complexation. A simple pattern of the spectrum suggested the formation of a highly symmetric discrete species. Complex **2** was also characterized by ^{13}C NMR spectroscopy.

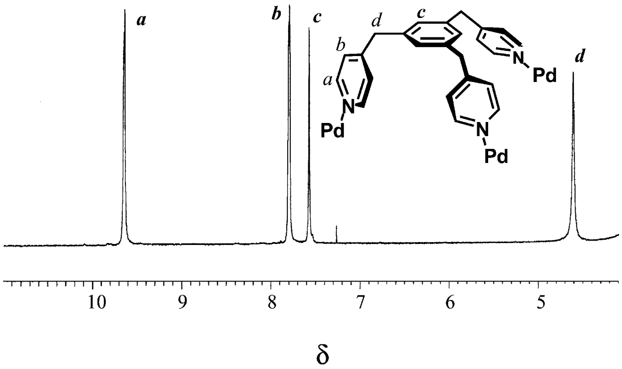

Fig. 2 ^{1}H NMR spectrum of sphere **2** (500 MHz, DMSO-d$_6$, 25 °C, TMS as an external standard). A partial structure of **2** is shown for convenience. Down field shifting of the signal as compared to free ligand **1**: $\Delta\delta$ = 0.69, 0.08, 0.05 and 0.19 ppm for H$_a$, H$_b$, H$_c$ and H$_d$, respectively.

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† Electronic supplementary information (ESI) available: crystallography section; Figs. S1–S8: ^{1}H NMR spectrum for **1**. ^{1}H, H–H COSY, NOESY, C–H COSY, ^{13}C, DEPT NMR and CSI–MS spectra for **2**. See http://www.rsc.org/suppdata/cc/b2/b206625b/

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Peaks in the proton and carbon NMR spectra were completely assigned using H–H COSY, C–H COSY and DEPT techniques. These spectroscopic evidences suggest that all the eight ligands involved in the structure are disposed in the same environment and four-fold symmetry axes pass through the axially located metal centers. The peaks observed in CSI–MS at *m*/*z* 1335, 985, 776, and 701 corresponding to $[\mathbf{2} - (NO_3)_3]^{3+}$, $[\mathbf{2} - (NO_3)_4]^{4+}$, $[\mathbf{2} - (NO_3)_5]^{5+}$, and $[(\mathbf{2} - (NO_3)_6) + 5DMSO]^{6+}$ strongly support the formation of the assumed structure. Elemental analysis of the sample shows association of seventeen DMSO molecules with the complex. Some of the solvent molecules are probably trapped inside the spacious cavity.

The same complexation reaction was also carried out in DMSO-d_6 and the solution was directly monitored by NMR spectroscopy. The spectrum obtained matched exactly with that of the isolated complex and reaction goes to completion within 5 min. No peaks other than due to complex **2** were observed that establishes the quantitative self-assembly and remarkable thermodynamic stability of **2**.

Finally, the structure of complex **2** was determined unambiguously by X-ray diffraction study.§ Prismatic crystals suitable for analysis were obtained by slow diffusion of acetone into a DMSO solution of **2**. A perspective view of the molecule is shown in Fig. 3. The six Pd(II) ions involved in the structure occupy the apices of an imaginary octahedral array. Trigonal faces of the octahedron are capped by the tripodal non-planar ligands **1**, in a truncated fashion leading to a sphere. The plane of central aromatic ring lies 5.2 Å above the plane described by the Pd(II) triangle. The strucure of **2** possesses twelve windows on its surface. All the metal centers have square planar geometry with Pd–N bond distances spanning the range of 1.9–2.0 Å.

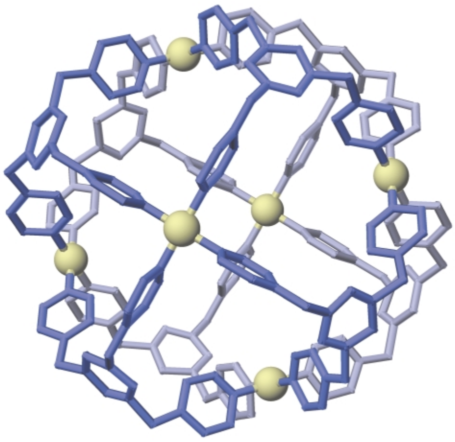

Fig. 3 Representation of $[(Pd)_6(\mathbf{1})_8]^{12+}$ in the crystal structure of **2**.

The giant, hollow structure of the sphere deserves particular attention. The average distance between axially located Pd centers is 15.2 Å and that of equatorial centers is 10.7 Å. The average distance between the central benzene rings of the ligands situated at the terminus of the three-fold axis is 19.2 Å.

In conclusion, the result shows quantitative self-assembly of a hollow, spherical molecule obtained from 14 small and simple components. The important features of the molecular sphere presented here are the extraordinarily large cavity, good solubility in polar solvents, and remarkable stability in solution. The nano-sized dimension of the molecule emphasizes that it is rather a molecular-based nanoparticle without size distribution. Ligand modification is currently under investigation in expectation of new and unique cage structures using the strategy employed here.

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Notes and references

‡ Ligand **1**: ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 8.969 (d, 6 H, a), 7.722 (d, 6H, b), 7.542 (s, 3H, c), 4.432 (s, 6H, d).

Complex **2**: ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 9.655 (d, 48 H, a), 7.807 (d, 48H, b), 7.588 (s, 24H, c), 4.621 (s, 48H, d). ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ 156.255 (Cq), 151.709 (a), 137.994 (Cq), 132.024 (c), 127.227 (b), 41.018–40.017 (d and DMSO). Anal. Calc. for $C_{192}H_{168}N_{36}O_{36}Pd_6 \cdot 17(DMSO)$: C, 49.15; H, 4.93; N, 9.13%. Found: C, 48.79; H, 4.88; N, 9.45%.

§ *Crystal data* for **2**: $C_{192}H_{168}N_{36}O_{36}Pd_6$ (formula without including solvent molecules), M = 4194.13, tetragonal, space group $P4_2/nnm$, $a = b$ = 34.312(4), c = 29.063(4) Å, U = 34217(7) Å^3, T = 193 K, Z = 4, λ = 0.71073 Å, 89663 reflections measured, 11580 unique ($R_{\rm int}$ = 0.1662) which were used in all calculations. $R1$ = 0.1203, and $wR2$ = 0.2800. See ESI†for further details. The crystal structure consists of a $[(Pd)_6(\mathbf{1})_8]^{12+}$ cation, nitrate anions and solvent molecules. However, the anions and solvent molecules were not located definitely due to the solvent dependent nature of the large cavity and high symmetry of the framework. CCDC reference number 189781. See http://www.rsc.org/suppdata/cc/b2/b206625b/ for crystallographic data in CIF or other electronic format.

1 *Comprehensive Supramolecular Chemistry*, chair. ed. J.-M. Lehn, exec. eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon Press, Oxford, 1996; vol. 9; J.-P. Sauvage and M. W. Hosseini, vol. eds.; see: J.-C. Chambron, C. Dietrich-Buchecker and J.-P. Sauvage, ch. 2; J. K. M. Sanders, ch. 4; P. N. W. Baxter, ch. 5; E. C. Constable, ch. 6; M. Fujita, ch. 7.

2 (*a*) R. W. Saalfrank, A. Stark, K. Peters and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 851; (*b*) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469.

3 (*a*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*b*) B. J. Holliday and C. A. Mirkin, *Angew. Chem.Int. Ed.*, 2001, **40**, 2022; (*c*) G. F. Swiegers and T. J. Malefeste, *Chem. Eur. J.*, 2001, **7**, 3636; (*d*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (*e*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

4 (*a*) T. Beissel, R. E. Powers, T. N. Parac and K. N. Raymond, *J. Am. Chem. Soc.*, 1999, **121**, 4200; (*b*) K. Umemoto, K. Yamaguchi and M. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 7150.

5 N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794.

6 B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield and P. J. Stang, *J. Am. Chem. Soc.*, 1999, **121**, 10434.

7 (*a*) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; (*b*) B. F. Abrahams, S. J. Egan and R. Robson, *J. Am. Chem. Soc.*, 1999, **121**, 3535; (*c*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *Chem. Commun.*, 1999, 841; (*d*) F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 6413; (*e*) F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759.

8 (*a*) L. R. MacGillivray and J. L. Atwood, *Nature*, 1997, **389**, 469; (*b*) J. Kang and J. Rebek Jr., *Nature*, 1997, **385**, 50; (*c*) R. Grotzfeld, N. Branda and J. Rebek Jr., *Science*, 1996, **271**, 487; (*d*) M. M. Conn and J. Rebek Jr., *Chem. Rev.*, 1997, **97**, 1647.

9 (*a*) M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368; (*b*) B. Moulton, J. Lu, A. Mondal and M. J. Zaworotko, *Chem. Commun.*, 2001, 863.

10 P. A. Thumman-Commike, B. Greene, J. Jakana, B. V. V. Prasad, J. King, P. E. Prevelige Jr. and W. Chiu, *J. Mol. Biol.*, 1996, **260**, 85.

11 W. R. Wikoff, L. Liljas, R. L. Duda, H. Tsuruta, R. W. Hendrix and J. E. Johnson, *Science*, 2000, **289**, 2129.

12 The tripodal tridentate ligand **1** was found to form a M_3L_2 type complex with *cis*-protected Pd(II) in presence of some specific guests by induced fit mechanism, see: M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649; our interest is also extending toward the use of *un*protected Pd(II) for obtaining self-assembled discrete structures, see: D. K. Chand, K. Biradha and M. Fujita, *Chem. Commun.*, 2001, 1652.

13 H.-K. Liu and X. Tong, *Chem. Commun.*, 2002, 1316.