

Metal driven self-assembly of pyridine appended ligands with *cis*-protected/naked Pd(II) ion: a comparative study

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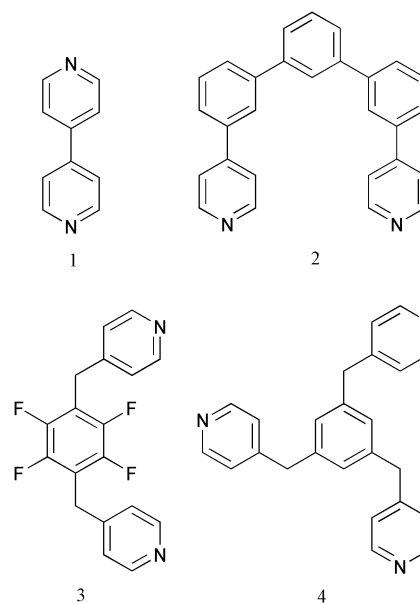
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Discrete self-assemblies prepared by designed pyridine appended ligands with *cis*-protected Pd(II) ion (**5**) are described. If ligands **2**, **3** and **4** are separately treated with (**5**), the formation of (i) dynamic equilibrium of macrocyclic M₂L₂ (**6**) and M₄L₄ assemblies (**7**); (ii) macrocyclic M₂L₂ product (**9**); and (iii) macrobicyclic M₃L₂ (**11**) occurred, respectively. The assembly so obtained from the combination of a ligand and (**5**) may be considered as a module or reminiscent of the assembly that is expected from the complexation of same ligand with naked Pd(II). In fact, complexation of the above mentioned ligands with *naked* Pd(II) resulted in discrete structures. This is in contrast to the possible polymeric structure usually obtained from such types of ligands in combination with *naked* Cd(II), Ni(II) etc. The result that the ligands **2**, **3**, and **4** with naked Pd(II) give macrotricyclic M₂L₄ (**8**); macropentacyclic M₄L₈ (**10**); and M₆L₈ spherical assembly (**12**), respectively, establishes interesting strategies. Thus we have shown rational comparison of a particular ligand for either *cis*-protected or *naked* Pd(II) ion for first time.

Introduction

Construction of discrete and well-defined molecular architectures using organic ligands and selected metal ions through the self-assembly route has received much attention during the last decade.¹ This method is a superior one to stepwise synthesis because desired assemblies having predetermined structural and functional properties are usually obtained by simply mixing the participating components under suitable conditions.² The structures formed *via* metal-driven self-assembly paths can be classified logically under M_xL_y types (where M and L denote metal ions and ligands involved) with varying composition of x and y. Previously reported structures are mostly formulated as M₂L₂,³ M₂L₄,⁴ M₃L₂,⁵ M₆L₄,⁶ or M₄L₆,⁷ types.

A particular series is represented by the assemblies of pyridine appended ligands with *cis*-protected Pd(II) which has been regarded as one of the efficient routes^{2a} to construct discrete structures. In this class of compounds it requires a control over two coordination sites of each participating metal centre for complexation. Molecular squares thus constructed from 4,4'-bipyridine (**1**), and Pd(en)(NO₃)₂, have been continuously enjoying frequent citation as an early and original design.⁸ Proceeding to use *naked* Pd(II) instead, one needs a control over all four coordination sites of the metal ion. The ligand 4,4'-bipyridine may not be a suitable choice as it possesses the binding sites which are as much as 180° divergent from each other (Scheme 1). In fact, also reported is a two-dimensional square network resulting from complexation of **1** with Cd(II).⁹ However, it should be possible to choose ligands which might form discrete structures with either type of Pd(II) ions. Our design here is based on the modulation of the relative positions of binding sites. The ligands of choice are such as to possess little flexibility or keep coordinating units in a less divergent manner. While the self-assembly chemistry of *cis*-protected Pd(II) and pyridine appended ligands has been explored^{2a} considerably, in contrast, little attention has been given to the use of *naked* Pd(II) as the metal centre. Formation of self-assembly utilizing a designed ligand separately with both kinds of the metal centres mentioned above could be an attractive subject for comparative study. As our initial effort we have recently communicated designed M₂L₄ and M₆L₈ type cage molecules



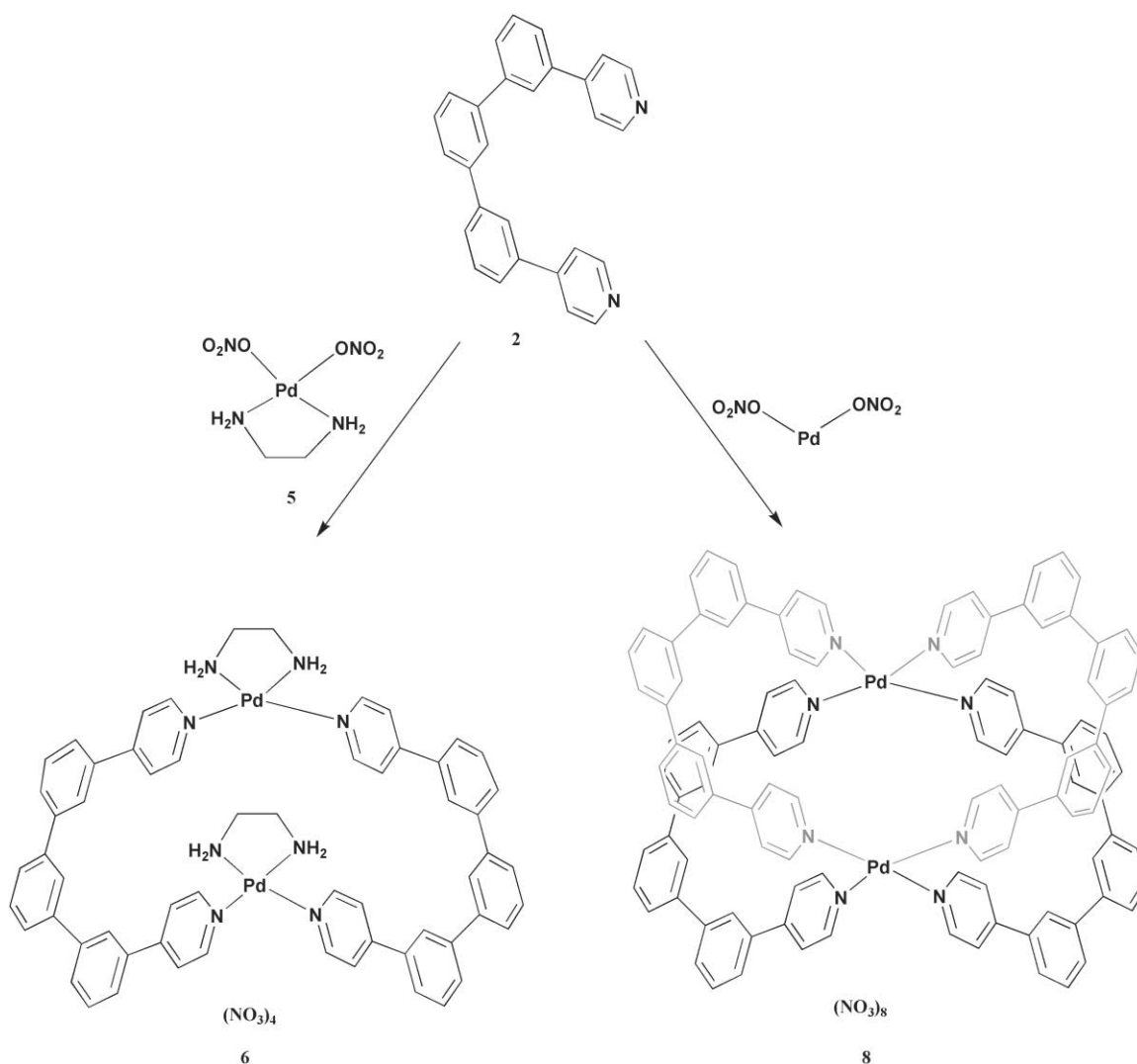
Scheme 1 Ligands.

employing *naked* Pd(II).¹⁰ Herein, we discuss a detailed comparative study on the complexation of selected non-chelating pyridine based ligands separately with Pd(en)(NO₃)₂ and Pd(NO₃)₂.

Results and discussion

Synthetic and characterization methods of ligands and complexes

Relevant ligands of this report are shown in Scheme 1. Ligand **2** was synthesized by Suzuki coupling of 1,3-bis(3-bromophenyl)benzene¹¹ with 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane.¹² The ligand **3** was obtained from the coupling of 4-picoline and hexafluorobenzene as reported earlier.^{3a} The tripodal tridentate ligand **4**,⁵ was obtained using a modified procedure by Negishi coupling of 1,3,5-tribromobenzene and 4-picoline. Complexation reactions with *cis*-protected or *naked*



Scheme 2 Macrocycle **6** and macrotricyclic **8**.

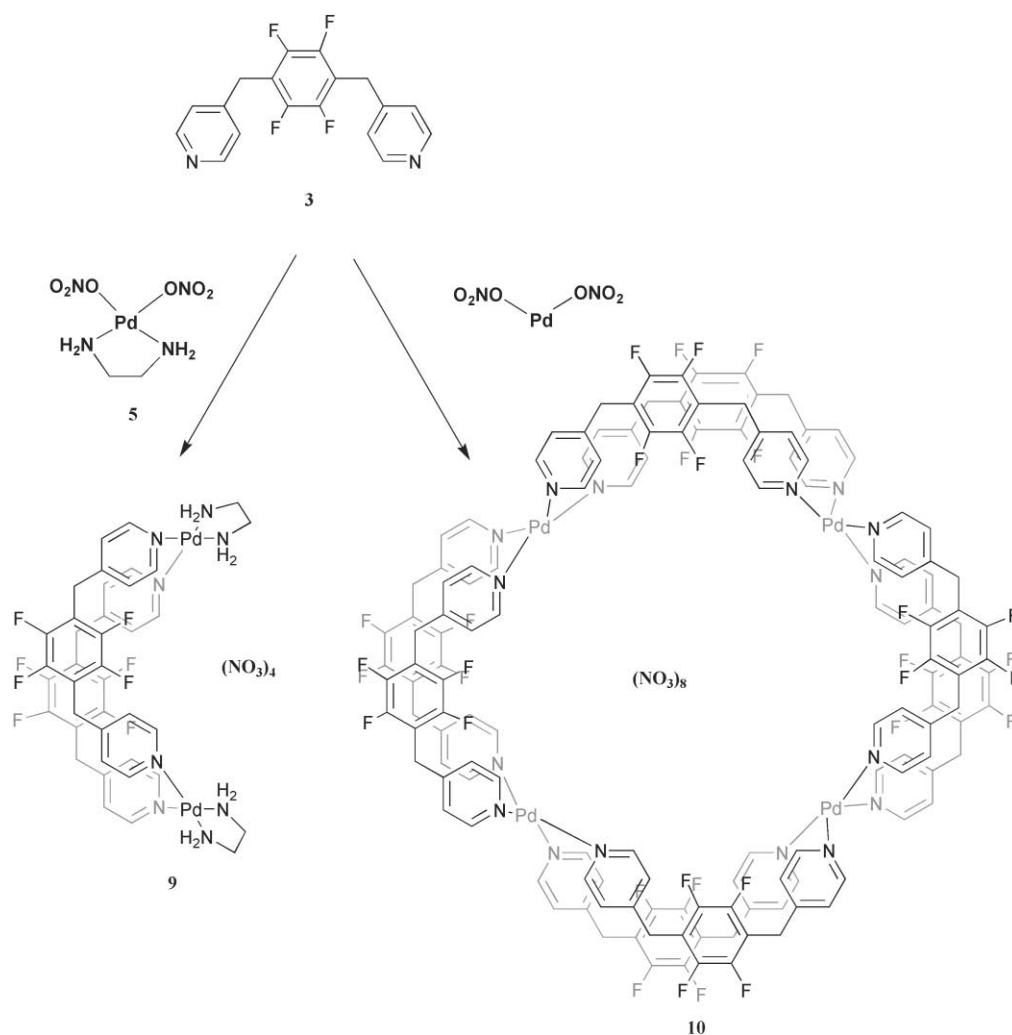
Pd(II) were carried out in DMSO or DMSO- d_6 . The solutions obtained from DMSO were subjected to CSI-MS study and those from DMSO- d_6 were used for NMR measurement. Compounds which assembled in pure forms in solution, as single discrete structures, were isolated in the solid state; no effort was made to isolate the assemblies which showed dynamic equilibrium and existing as a mixture of compounds. The NMR spectra obtained from solutions without isolating the complexes matched with the spectra of isolated complexes (only pure assemblies were isolated) when re-dissolved in suitable deuterated solvent.

Complexation study with *cis*-protected or *naked* Pd(II)

Ligand **2** was treated with *cis*-protected Pd(en)(NO₃)₂ in a ratio of 1 : 1 and stirred at 60 °C in DMSO for 10 min. A binuclear M₂L₂ macrocycle [(**2**)₂(Pd(en))₂](NO₃)₄, **6** was observed as a major product (Scheme 2) along with a minor amount of a possible tetranuclear macrocyclic compound [(**2**)₄(Pd(en))₄](NO₃)₈, **7**. In a separate reaction, ligand **2** was mixed with Pd(NO₃)₂ in a ratio of 2 : 1 in DMSO and stirred at 90 °C for 10 min whereupon the designed macrotricyclic M₂L₄ assembly [(Pd)₂(**2**)₄](NO₃)₈, **8** was obtained (Scheme 2). Ligand **3** gave a M₂L₂ compound [(**3**)₂(Pd(en))₂](NO₃)₄, **9** (Scheme 3) upon complexation with **5**.^{3a} We have shown here the complexation of **3** with Pd(NO₃)₂ giving rise to a macropentacyclic M₄L₈ double-walled square [(Pd)₄(**3**)₈](NO₃)₈, **10** (Scheme 3). In a similar way, when ligand **4** was complexed with Pd(en)(NO₃)₂, in a ratio of 2 : 3 it gave a mixture of compounds in aqueous⁵ or DMSO solution. However, the M₃L₂ compositional assembly

[(**4**)₂(Pd(en))₃](NO₃)₆, **11** could be obtained (Scheme 4) in aqueous solution⁵ upon using a suitable template *e.g.* 4-methoxyphenyl acetate. The assembly of ligand **4** with Pd(NO₃)₂ in a ratio of 8 : 6 gave the designed M₆L₈ molecular sphere [(Pd)₆(**4**)₈](NO₃)₁₂, **12** (Scheme 4). The characterization to identify the structures are described below.

Assemblies from ligand 2. First we describe the products obtained from ligand **2**. Proton NMR spectrum of **2**, **6** + **7**, and **8** are shown in Fig. 1 for comparison. The signals for the complexes as compared to ligand **2** in the proton NMR spectrum, particularly the py_α and py_β protons, were downfield shifted due to the complexation. All the peaks of proton and carbon NMR spectra were also assigned using suitable COSY techniques. Complexation of **2** with **5** gave a major and a minor product as seen from the py_α signal in the NMR spectrum; signals of other protons for both compounds are overlapped. CSI-MS measurement clearly showed intense peaks at *m/z* (%) = 414 (12), 440 (42), 466 (14) and 613 (100) corresponding to [(**6** - (NO₃)₃) + 1DMSO]³⁺, [(**6** - (NO₃)₃) + 2DMSO]³⁺, [(**6** - (NO₃)₃) + 3DMSO]³⁺ and [(**6** - (NO₃)₂) + DMSO]²⁺, respectively, due to the formation of **6**. Peaks at *m/z* (%) = 838 (14) and 1288 (8) correspond to [**7** - (NO₃)₃]³⁺ and [**7** - (NO₃)₂]²⁺ from structure **7**. We propose the major product a dinuclear complex, **6** and the minor product a tetranuclear complex, **7**. The proposition originates from entropic consideration, and the evidence that the intensity of the minor peak in the NMR spectrum decreases on lowering the concentration. Additionally, the peak intensity of **6** in CSI-MS is higher than that of **7**.



Scheme 3 Macrocycle 9 and macropentacycle 10.

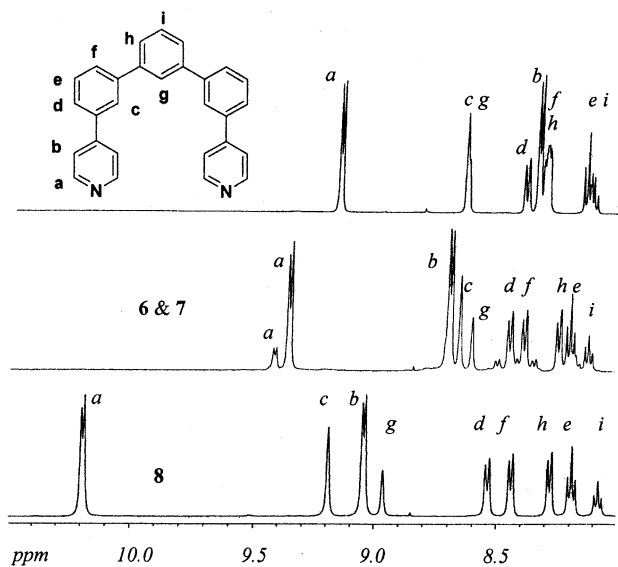


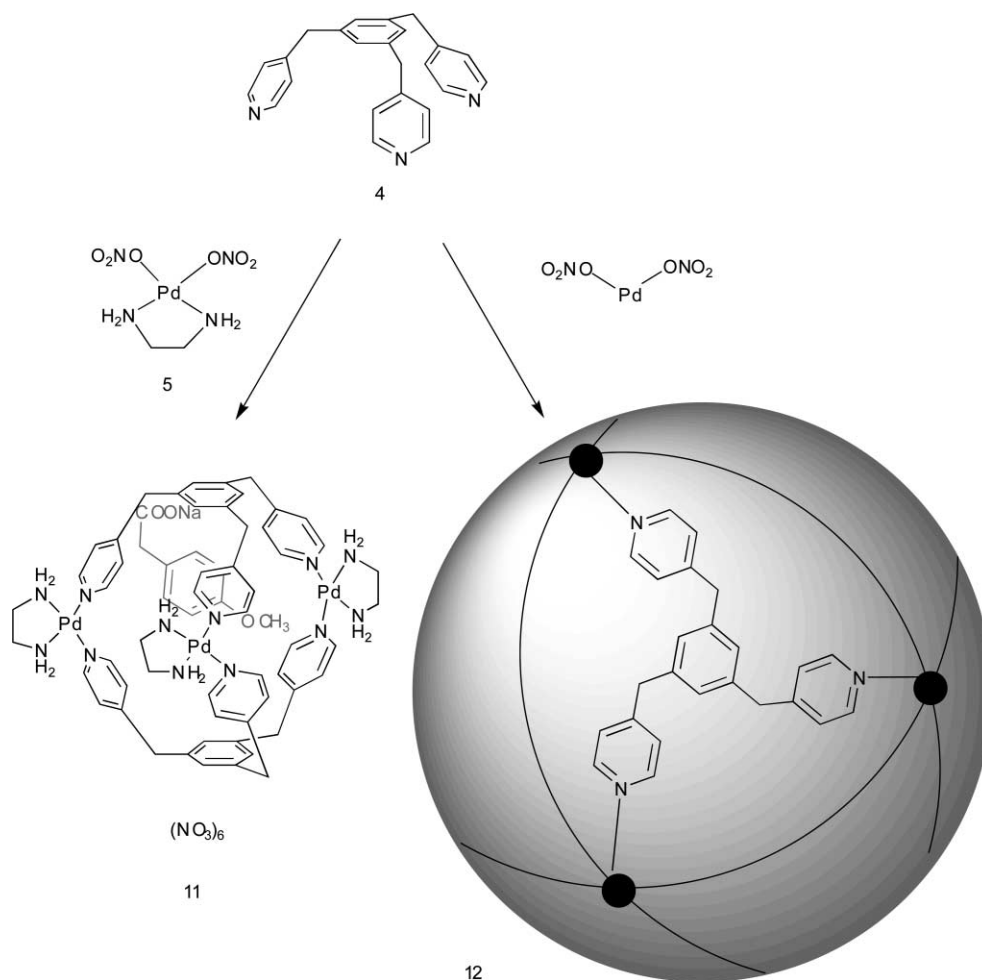
Fig. 1 ¹H NMR spectra, from top to bottom, of ligand 2, macrocycles 6 (major peaks) and 7, and the macrotricyclic 8 (500 MHz, DMSO-d₆, 25 °C, TMS as an external standard).

Quantitatively, the percentage distribution of ligand between assemblies 6/7 at ligand concentration of 10, 5 and 2.5 mmol are 79 : 19, 87 : 13, 93 : 7 respectively. Interestingly, and to our surprise, no trinuclear product was detected in our conditions.

The NMR spectrum obtained from the solution resulting from ligand 2 and Pd(NO₃)₂ indicated only one structure and

expected to contain the macrotricyclic compound 8. The simple pattern of the proton NMR spectrum (Fig. 1) suggests the formation of a discrete species. CSI-MS also showed a reliable result as concluded from the peaks at *m/z* (%) = 604 (40) and 937 (38) corresponding to [8 - (NO₃)₃]³⁺ and [8 - (NO₃)₂]²⁺. The findings are evident of the fact that the four arms in complex 8 are all equivalent and that it possesses a four-fold symmetry axis passing across the metal centers in solution. No peaks in NMR other than due to complex 8 were observed which thus indicates the quantitative self-assembly of 8. When the metal salt was added in a lesser amount than the required stoichiometry for the complexation, still all the signals of complex 8 were observed, without any indication of impurity, with additional signals corresponding only to the uncomplexed free ligand. Also, by adding excess of the metal salt, no other new structures were suggestive from the NMR pattern. All these findings support the quantitative formation and remarkable thermodynamic stability of 8.

Atwood *et al.* have reported an early example of an M₂L₄ cage^{4a} where two octahedral copper(II) ions are bridged by four units of a bidentate ligand. While all the four equatorial positions of each copper ions are coordinated with the terminal pyridyl groups of the ligand strands, the axial positions are occupied by water molecules. Dinuclear copper(II) complexes of the M₂L₄ family having twisted structures and including chloride^{4c} and perchlorate^{4d} anions in between the metal centers have also been reported. Another analogous structure to 8 is a dinuclear Pd(II) cage,^{4b} with inclusion of hexafluorophosphate ion inside the cavity. However, in none of the cases was the complexation reaction leading to the cage directly monitored using NMR spectroscopy, unlike our study in this work.



Scheme 4 Macrobicyclic cage **11** and sphere **12** (structure **12** is $M_6L_8(NO_3)_{12}$ in composition and shown in a cartoon form).

Assemblies from ligand 3. It is reported earlier that ligand **3** formed a M_2L_2 framework **9** upon complexation with **5**.^{3a} Here we have extended the complexation study of **3** with $Pd(NO_3)_2$. The complexation product gave a sharp single set of signals corresponding to a single structure. The py_a and py_b protons were downfield shifted due to the complexation. The methylene protons which are in restricted positions after complexation in this case appeared as a double doublet. CSI-MS results gave convincing evidence for the formation of an M_4L_8 double walled square structure $[(Pd)_4(3)_8](NO_3)_8$, **10**. The peaks at m/z (%) = 533 (9), 547 (10), 560 (23), 573 (23), 586 (14), 653 (43), 669 (23), 685 (13), 700 (7), 833 (31) and 1131 (22) correspond to $[(10 - (NO_3)_6) + nDMSO]^{6+}$ ($n = 0-4$), $[(10 - (NO_3)_5) + nDMSO]^{5+}$ ($n = 0-3$), $[10 - (NO_3)_4]^{4+}$ and $[10 - (NO_3)_3]^{3+}$, respectively. There is a possibility of macrocyclic units like **9** arranged in a one-dimensional poly-macrocyclic chain network in the absence of protection on Pd(II) in line with the report shown for the complexation of **3** and Cd(II).¹³ However a tetramer of macrocycles meets at both ends giving a discrete structure. The structure of **10** may be considered as complementary to the square molecule constructed from **1** and **5**. Also we are not aware of a compound similar to this new architectural structure. A four-fold symmetry axis passes through the center of the square **10** vertically.

Assemblies from ligand 4. Turning to the ligand **4**, it gave a macrobicyclic cage **11** only in the presence of a guest when complexed with *cis*-protected Pd(II).⁵ Anionic templates and related molecules are particularly suitable. With *naked* Pd(II) however a sphere **12** was obtained as described below. The surface of the sphere **12** is divided by three orthogonal planes into eight identical parts, each of which is capped by the tripodal tridentate ligand

4 (Scheme 4). At each of the six cross-sections is placed a Pd(II) ion 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 **4** in expectation of an aesthetically pleasing M_6L_8 type complex. Ligand **4** was mixed with $Pd(NO_3)_2$ in a ratio of 4 : 3 in DMSO, with a concentration of **4** of 10 mM, and stirred at 90 °C for 10 min to obtain **12**. Very recently, Liu *et al.* reported an M_6L_8 assembly which is topologically the same as our molecule but not spherical,¹⁴ while a related structure of a Ni(II) based cage was reported by Hong *et al.*¹⁵ Once again our study gave complete characterization in solution and the solid state (crystal structure) including determination of the molecular weight.

NMR and CSI-MS analyses indicated the formation of predetermined, discrete species **12** by the metal-driven route. In ¹H NMR, downfield shifting of the signals for complex **12** (Fig. 2), particularly for py_a ($\Delta\delta = 0.69$ 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 **12** was also characterized by ¹³C NMR spectroscopy. Peaks in the proton and carbon NMR spectra were completely assigned. 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 (12), 985 (36), 776 (28) and 701(18) correspond to $[12 - (NO_3)_3]^{3+}$, $[12 - (NO_3)_4]^{4+}$, $[12 - (NO_3)_5]^{5+}$ and $[(12 - (NO_3)_6) + 5DMSO]^{6+}$ and strongly support the formation of the assumed structure. Elemental analysis of the sample shows association of seventeen DMSO molecules with the complex some of which are probably trapped inside the spacious cavity. No peaks other than due to complex **12** were observed so establishing

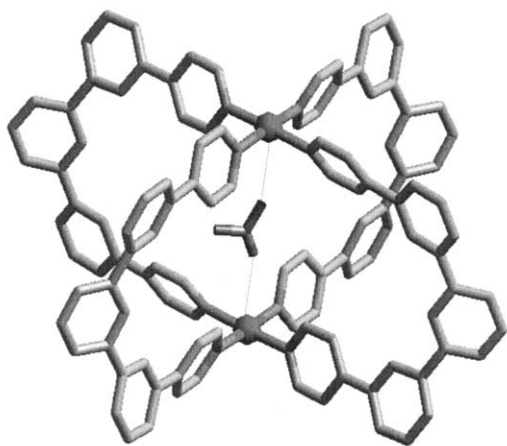


Fig. 2 Representation of $[(\text{Pd})_2(\mathbf{2})_4(\text{NO}_3)_3]^{3+}$ in the crystal structure of **8** (Pd: ball mode and others: cylinder mode). The disorder of the nitrate anion is not shown.

the quantitative self-assembly and remarkable thermodynamic stability of **12**.

Crystal structures

Structure of 8. The structure of complex **8** was determined unambiguously from an X-ray diffraction study, and has been published by us in a previous communication.^{10a} Needle-shaped crystals, suitable for X-ray diffraction analysis, were obtained in 2 d by layering diethyl ether over a solution of **8** in DMSO. A perspective view of the molecule is shown in Fig. 2. The crystal structure consists of the complexed cation $[(\text{Pd})_2(\mathbf{2})_4(\text{NO}_3)_3]^{3+}$, three nitrate anions, nine DMSO and two diethyl ether molecules. Each Pd(II) has a square planar geometry with Pd–N bond distances in the range of 2.024(7)–2.030(6) Å. The size of the 3-D cavity is *ca.* $11.1 \times 10.2 \times 8.4$ Å that is defined by the arms of the rectangular array formed from four hydrogen centers, H_g (see Fig. 1 for the labelling and Fig. 2 for comparison) and the Pd–Pd separation. The cavity size after correcting the van der Waals radius of the H centers is $8.7 \times 7.8 \times 6.0$ Å. While three out of four nitrate ions stay outside of the cavity, one nitrate ion is encapsulated inside by ionic interaction, a Pd–O distance being 3.135(7) Å.

Analysis of crystal packing displayed the extension of intermolecular interactions in a linear manner, where three DMSO molecules lie in the intermolecular cavity that is formed in between two consecutive molecules of **8** (Fig. 3). The Pd–Pd axes of the adjacent **6** adopt a perpendicular geometry to each other making a hydrophobic pocket.

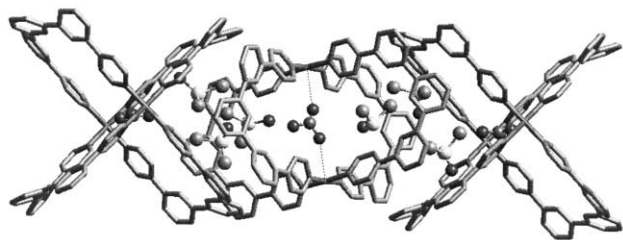


Fig. 3 Linear chain in the crystal structure of **8**. Three DMSO molecules are trapped in each of the intermolecular cavities. The disorder of the nitrate anions and DMSO molecules are not shown.

Structure of 12. The structure of complex **12** was also determined by X-ray diffraction study and also described recently in a communication.^{10b} Prismatic crystals suitable for analysis were obtained by slow diffusion of acetone into a DMSO solution of **12**. A perspective view of the molecule is shown in Fig. 4. The six Pd(II) ions involved in the structure occupy the apices of an imaginary octahedral array. Trigonal faces of the

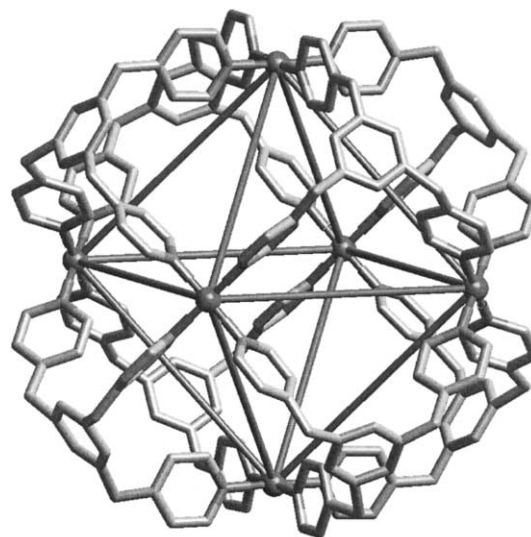


Fig. 4 Representation of $[(\text{Pd})_6(\mathbf{4})_8]^{12+}$ in the crystal structure of **12** (Pd: ball mode and others: cylinder mode). The anions and solvent molecules were not definitely located.

octahedron are capped by the tripodal non-planar ligands **4**, in a truncated fashion leading to a sphere. The plane of central aromatic ring lays 5.2 Å above the plane described by the Pd(II) triangle. It 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.

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.

Conclusion

In this work we have shown that use of *naked* Pd(II) for construction of self-assemblies is convenient to construct three-dimensional cage molecules. The complexation reaction goes to completion quickly providing a quantitative conversion of the reactants. When we look at the chemical drawing of the M_2L_2 structure of **6** there are two ethylenediamine units. In absence of such protection two more units of the ligands are required in positions equal to the mirror image of the existing ligands which should generate the structure **8**. The complex **9** is also M_2L_2 in nature, however due to the presence of sp^3 carbon center in the participating ligand it does not allow a macrocyclic structure with naked Pd(II). Rather a double-walled square was feasible. The macrobicyclic cage **11** possesses strain and therefore is not generated in the absence of a suitable template. The mixture of the structures thus obtained from **4** and **5** are possibly reminiscent of molecular sphere **12**. The formation of polymeric networks was not ruled out prior to the experimental result of the complexation of ligands with Pd(II). Networks are frequently observed with Ni(II) or Cd(II) and pyridine ligands. However, now we can state that the entropy term is dominant here due probably due to the fact that Pd–N bond is not as weak as that of Ni(II) and not as strong as that of Pt(II).

Experimental

General

All the chemicals were of reagent grade and used without any further purification. Ethylenediamine was used for the *cis*-protection of Pd(II), to obtain $\text{Pd}(\text{en})(\text{NO}_3)_2$. Deuterated solvents were acquired from Cambridge Isotopic Laboratories, Inc and used as supplied for the complexation reactions and

NMR measurements. NMR spectral data were recorded on a Bruker DRX 500 spectrometer, unless otherwise stated, at ambient temperature and the chemical shift values reported here are with respect to external TMS standard. CSI-MS (cold-spray ionization mass spectroscopy) data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source.

Synthesis of ligands

Ligand 2. A mixture of 1,3-bis(3-bromophenyl)benzene (0.388 g, 1.0 mmol), 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane (0.513 g, 2.5 mmol), K_3PO_4 (0.743 g, 3.5 mmol) and $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol), was refluxed in 1,4-dioxane (25 cm³) for 2 d at 100 °C under argon atmosphere. After quenching the reaction mixture with water it was extracted with $CHCl_3$. The organic layer was dried over anhydrous K_2CO_3 and evaporated to obtain a crude residue. The residue was chromatographed over silica gel ($CHCl_3$ -MeOH, 20 : 1 v/v) to obtain a white solid, which was recrystallized from methanol affording **2** as white needles 0.252 g, 65% yield. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 9.17 (d, 4H, a), 8.66(s, 2H, c), 8.65 (s, 1H, g), 8.41 (d, 2H, d), 8.36 (d, 4H, b), 8.32–8.34 (m, 4H, f & h), 8.16 (t, 2H, e), 8.13 (t, 1H, i); ¹³C NMR (125 MHz, DMSO-*d*₆, TMS): δ 151.04 (a), 147.92 (Cq), 142.04 (Cq), 141.51 (Cq), 138.84 (Cq), 130.70 (e), 130.47 (i), 128.86 (d), 127.41 (h), 126.97 (f), 126.64 (g), 126.45 (c), 122.47 (b); mp 192–193 °C. Anal. Calc. for $C_{28}H_{20}N_2(MeOH)_{0.3}$: C, 86.12; H, 5.44; N, 7.09. Found: C, 86.17; H, 5.16, N, 7.07%.

Ligand 3. Ligand **3** was reported earlier,^{3a} however, here we report the proton NMR spectral data recorded in DMSO-*d*₆. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 9.015 (d, 4H, py_a), 7.763 (d, 4H, py_β), 4.653 (s, 4H, -CH₂-).

Ligand 4. Freshly distilled 4-picoline (11.176 g, 11.68 cm³, 120 mmol) was added to a THF solution (50 cm³) of lithium diisopropylamide (LDA) prepared from diisopropylamine (12.143 g, 16.82 cm³, 120 mmol) and *n*-butyllithium (1.5 M hexane solution, 80 cm³, 120 mmol) at 0 °C and the solution was stirred for 30 min. A THF solution of $ZnCl_2$ (0.5 M, 240 cm³, 120 mmol) was then added to the solution at rt. After 1 h, 1,3,5-tribromobenzene (3.148 g, 10 mmol) and $PdCl_2(PPh_3)_2$ (0.351 g, 0.5 mmol) were added, and the mixture was heated at reflux for 3 d. The reaction was quenched by adding 50 cm³ of water and 15 cm³ of ethylenediamine. The mixture was extracted with $CHCl_3$, the organic layer was dried over anhydrous K_2CO_3 , and evaporated to obtain a crude residue. The residue was chromatographed over silica gel (EtOAc to EtOAc-MeOH (1 : 1 v/v)) to obtain **4** as a colorless solid⁵ 1.09 g, 31% yield. ¹H NMR (270 MHz, $CDCl_3$, TMS): δ 8.54 (d, 6H, py_a), 7.08 (s, 6H, py_β), 6.89 (s, 3H, -CH-), 3.95 (s, 2H, -CH₂-); ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 8.969 (d, 6H, py_a), 7.722 (d, 6H, py_β), 7.542 (s, 3H, Ar-H), 4.432 (s, 6H, -CH₂-); mp 98–100 °C. Anal. Calc. for $C_{24}H_{21}N_3(H_2O)_{0.7}$: C, 79.18; H, 6.20; N, 11.54%. Found: C, 79.15; H, 6.18, N, 11.49%.

Synthesis of the self assembly complexes

(a) Mixture of $\{[Pd(en)]_2(2)_2\}(NO_3)_4$, **6 and $\{[Pd(en)]_4(2)_4\}(NO_3)_8$, **7**.** To a solution of **2** (7.7 mg, 0.020 mmol) in 2 cm³ of DMSO (or DMSO-*d*₆) (concentration of **2** in solution: 10 mM) was added $Pd(en)_2(NO_3)_2$ (5.8 mg, 0.020 mmol). The mixture was stirred at 60 °C for 10 min where upon a clear solution was obtained. No attempt was made to purify the mixture of complexes. Compound **6**: ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 9.36 (d, 8H, a), 8.70 (d, 8H, b), 8.66 (s, 4H, c), 8.61 (s, 2H, g), 8.45 (d, 4H, d), 8.39 (d, 4H, f), 8.25 (d, 4H, h), 8.21 (t, 4H, e), 8.13 (t, 2H, i). Compound **7**: the signal of (Ha) from compound **7** is clearly separated and appears at δ 9.42, other signals are either merged or not well separated. CSI-MS: *m/z*

(%) = 414 (12), 440 (42), 466 (14) and 613 (100), corresponding to $[(6 - (NO_3)_3) + 1DMSO]^{3+}$, $[(6 - (NO_3)_3) + 2DMSO]^{3+}$, $[(6 - (NO_3)_3) + 3DMSO]^{3+}$ and $[(6 - (NO_3)_2) + DMSO]^{2+}$; *m/z* (%) = 838 (14) and 1288 (8), corresponding to $[7 - (NO_3)_3]^{3+}$ and $[7 - (NO_3)_2]^{2+}$.

(b) Tricycle $[(Pd)_2(2)_4](NO_3)_4$, **8.** A mixture of **2** (7.7 mg, 0.020 mmol) and $Pd(NO_3)_2$ (2.3 mg, 0.010 mmol) in 2 cm³ of DMSO (or DMSO-*d*₆) (concentration of **2** in solution: 10 mM) was stirred at 90 °C for 10 min and the solution was filtered to obtain a clear solution. Subsequent addition of chloroform-diethyl ether precipitated the complex **8** in 74% yield. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 10.18 (d, 16H, a), 9.20 (s, 8H, c), 9.04 (d, 16H, b), 8.96 (s, 4H, g), 8.53 (d, 8H, d), 8.44 (d, 8H, f), 8.27 (d, 8H, h), 8.19 (t, 8H, e), 8.06 (t, 4H, i). ¹³C NMR (125 MHz, DMSO-*d*₆, TMS): δ 152.39 (a), 151.17 (Cq), 141.77 (Cq), 140.58 (Cq), 135.71 (Cq), 131.12 (e), 130.74 (i), 130.25 (f), 127.28 (h), 127.19(c & d), 126.88 (g), 125.61 (b). CSI-MS: *m/z* (%) = 604 (40) and 937 (38), corresponding to $[8 - (NO_3)_3]^{3+}$ and $[8 - (NO_3)_2]^{2+}$. Anal. Calc. for $C_{112}H_{80}N_{12}O_{12}Pd_2(dmsO)_6$: C, 60.36; H, 4.74; N, 6.81. Found: C, 60.12; H, 4.59, N, 6.80%. In carbon-NMR of **8**, instead of 13 peaks only 12 peaks were observed. Here the signals of carbon c and d (see Fig. 1 for nomenclature) overlapped with each other as confirmed by its C-H COSY spectrum.

(c) Double-walled square $[(Pd)_4(3)_8](NO_3)_8$, **10.** A mixture of **3** (6.5 mg, 0.020 mmol) and $Pd(NO_3)_2$ (2.3 mg, 0.010 mmol) in 2 cm³ of DMSO (or DMSO-*d*₆) (concentration of **3** in solution: 10 mM) was stirred at 90 °C for 10 min and the solution was filtered to obtain a clear solution. Subsequent addition of chloroform-diethyl ether precipitated the complex **10** in 68% yield. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 9.77 (d, 32H, py_a), 8.12 (d, 32H, py_β), 4.73 (dd, 32H, -CH₂-), ¹³C NMR (125 MHz, DMSO-*d*₆, TMS): δ 152.62 (Cq), 151.75 (py_a), 145.59 (doublet, C-F), 127.76 (py_β), 27.87 (-CH₂-) CSI-MS: *m/z* (%) = 533 (9), 547 (10), 560 (23), 573 (23), 586 (14), 653 (43), 669 (23), 685 (13), 700 (7), 833 (31) and 1131 (22), corresponds to $[(10 - (NO_3)_6) + nDMSO]^{6+}$: (*n* = 0–4), $[(10 - (NO_3)_3) + nDMSO]^{5+}$: (*n* = 0–3), $[10 - (NO_3)_4]^{4+}$ and $[10 - (NO_3)_3]^{3+}$, respectively. Anal. Calc. for $C_{144}H_{96}F_{32}N_{24}O_{24}Pd_4(dmsO)_5$: C, 46.58; H, 3.20; N, 8.47. Found: C, 46.69; H, 3.35, N, 8.29%.

(d) Sphere $[(Pd)_6(4)_8](NO_3)_{12}$, **12.** A mixture of **4** (7.028 mg, 0.020 mmol) and $Pd(NO_3)_2$ (2.3 mg, 0.010 mmol) in 2 cm³ of DMSO (or DMSO-*d*₆) (concentration of **4** in solution: 10 mM) was stirred at 90 °C for 10 min and the solution was filtered to obtain a clear solution. Subsequent addition of acetone precipitated the complex **12** in 79% yield. ¹H 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). ¹³C 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). CSI-MS: *m/z* (%) = 1335 (12), 985 (36), 776 (28) and 701 (18) corresponding to $[12 - (NO_3)_3]^{3+}$, $[12 - (NO_3)_4]^{4+}$, $[12 - (NO_3)_5]^{5+}$ and $[(12 - (NO_3)_6) + 5DMSO]^{6+}$. Anal. Calc. for $C_{192}H_{168}N_{36}O_{36}Pd_6(dmsO)_{17}$: C, 49.15; H, 4.93; N, 9.13. Found: C, 48.79; H, 4.88, N, 9.45%.

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