Assembly of Polyhedra by Molecular Paneling *via* Coordination

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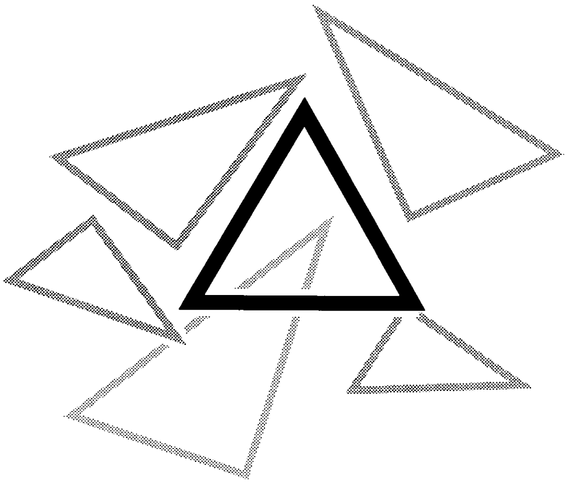
Chapter 1



Introduction and General Summary

1.1 Introduction

Self-organization is an important mechanism in nature for constructing most of biological structures.[1-5] A well-known example of self-organization is the tobacco mosaic virus (TMV). TMV is formed spontaneously from 2130 identical protein units that form the viral protein coat around a single stretch of RNA.[6] Another remarkable example is the self-organization of a hollow, spherical virus HK97 whose structure has been recently solved by a crystallographic analysis.[7] In this structure, five or six identical protein subunits are assembled into a pentagonal or a hexagonal "protein panel", respectively. These panels are further linked together into a giant capsule, with a diameter of ca. 600 Å, that involves 12 pentagonal and 60 hexagonal protein panels. By making the stable hollow framework, the DNA of the capsid itself is encapsulated and transferred into the living cell of other organisms. Such nature's mechanisms have inspired the author to design molecular panels which are polygon-shaped and are spontaneously assembled into hollow frameworks.

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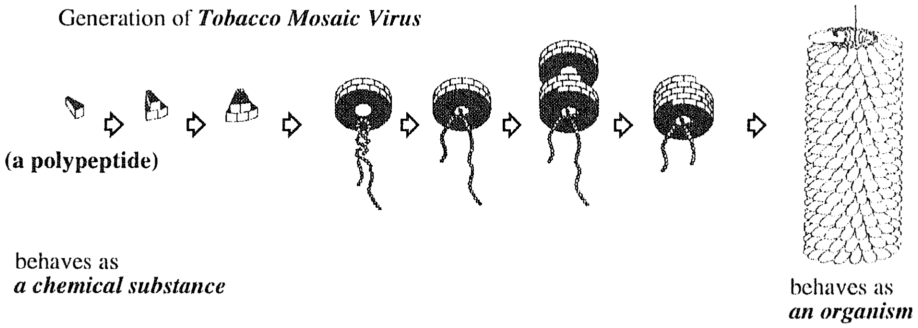

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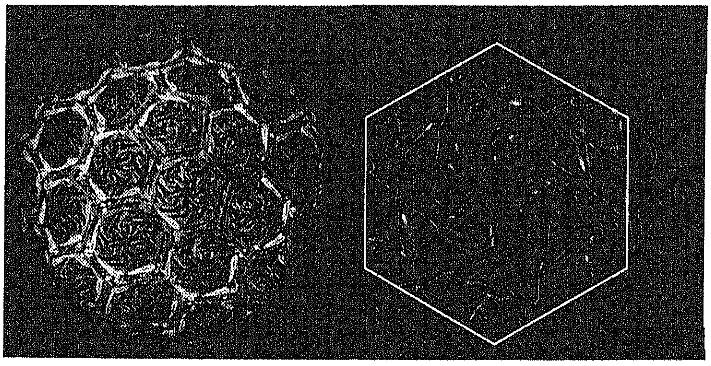


Figure 1. Self-organization of biological structures. a) Self-assembly of tobacco mosaic virus. b) Structure of the HK97 and hexagonal "protein panel".

Here, the author proposes the concept of "***molecular paneling***" as an efficient method for constructing 3D polyhedral structures. Of many polygons, the author designs triangular molecular panels because a triangle is the simplest basic unit for the construction of polyhedra (Figure 2). To induce the self-organization of the panels into polyhedra, the author exploits metal-ligand interaction in such a way that the molecular panels are linked together by metal coordination.[8–10] Thus, a family of triangular molecular panels with coordination donor sites (nitrogen atoms) are designed as basic building units for polyhedra: some of them have been already known[11,12] while some are designed by the author.[13,14] In the present thesis, the author presents how they are effectively assembled into polyhedra and related 3D architectures through coordination.

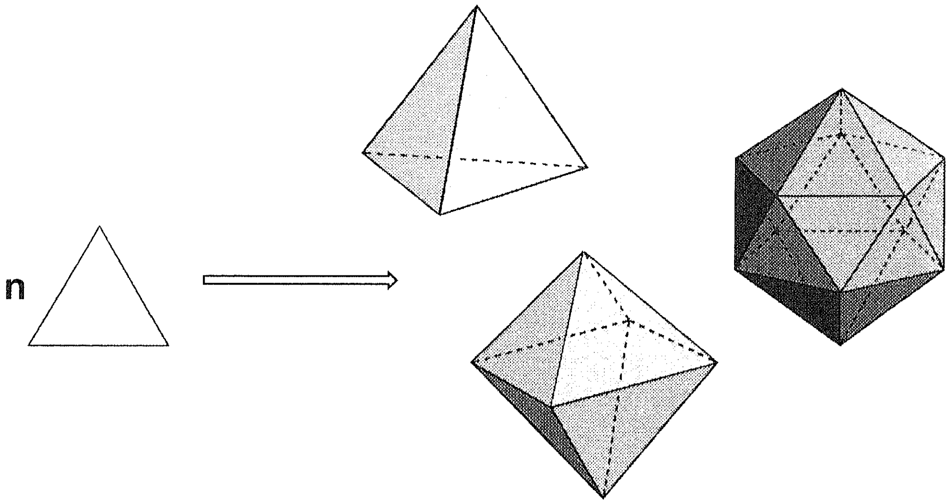
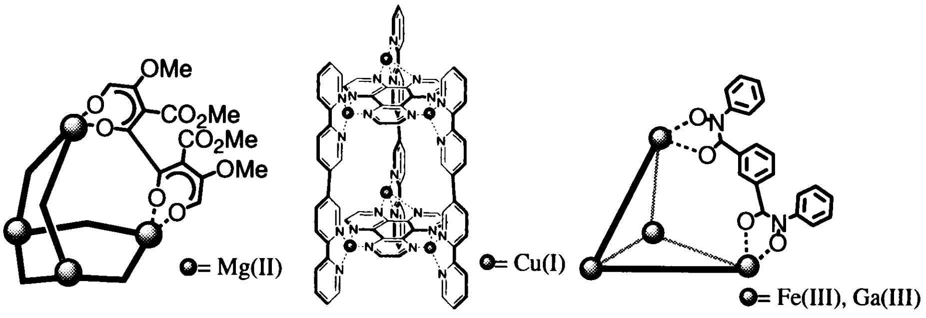


Figure 2. Schematic representation of assembling of polyhedra from a triangular unit.

There are several reports on the construction of polyhedral structures by self-assembly.[15–21] Typical examples are shown in Figure 3. In most polyhedral structures reported so far, however, organic ligands occupy the ridges of the polyhedra. In contrast, the author's "molecular paneling" strategy provides substantial polyhedral-shaped entities in which the molecular panels occupy not the ridges but the faces of polyhedra.



Saalfrank et al. [15] Lehn et al. [16] Raymond et al. [17]

Figure 3. Examples of metal coordination three-dimensional structures.

1.2 Metal-Directed Self-Assembly

As mentioned above, the author exploits metal-coordination to induce the self-assembly of polyhedra. Metal-directed self-assembly is characterized by the spontaneous generation of well-defined molecular architectures from organic ligands and metal ions. The metal ions provide (1) a set of coordination geometries, (2) a range of binding strengths, from weak to very strong, (3) a variety of photochemical and electrochemical properties, and (4) reaction centers. Most significantly, they allow the reversible assembly-disassembly of molecular architectures and represent switchable interaction sites. In this manner the choice of the metal ions is of growing importance in order to produce defined architectures in a controlled fashion from multiple subunits. In general, metal-directed self-assembly has been designed using naked metal ions such as tetrahedral Cu(I), octahedral Fe(II), Co(II), Ni(II), and square-planar Pd(II). However, with such naked metals ions, it is often difficult to control the number and direction of the coordination of the ligands (Figure 4).

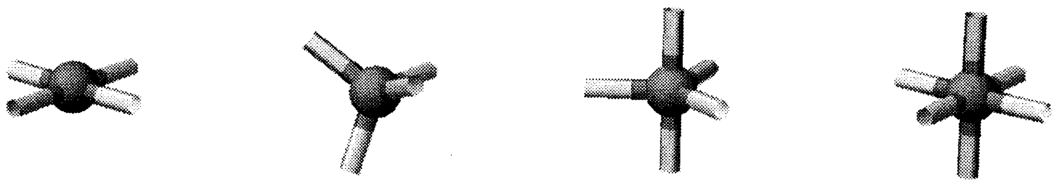


Figure 4. Schematic representation of the metal coordination geometry.

To reduce the number of coordination sites for easy control, *cis*-protected Pd(II) complex **1** to exploit 90° bond angle (Figure 5) has been designed by Fujita.[22] According to this concept, ethylendiamine-protected Pd(II) complex is employed in this work. The Pd(II) building block **1** has shown a remarkable ability to induce the self-assembly of variety of coordination architectures.

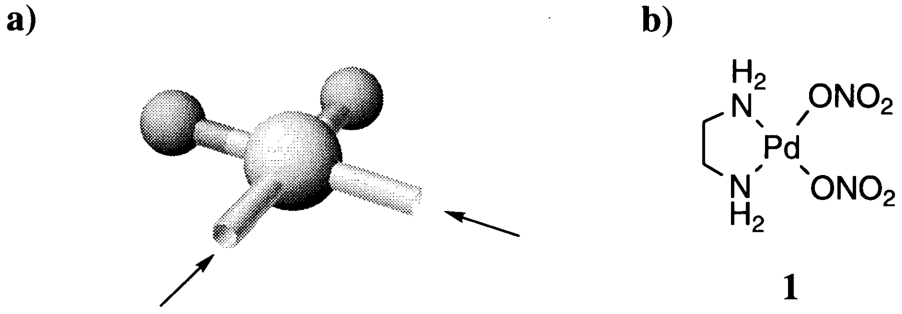


Figure 5. a) Cartoon representation of *cis*-protected Pd(II) building block **1**. b) structural drawing of **1**.

1.3 The Design of Ligands: *Molecular panels*

The idea of the molecular paneling comes from the assembly of a 2D square complex from a 1D rod-like ligand. For example, 4,4'-bipyridine, a simple rod-like ligand, was assembled into square macrocycle **2** upon treatment with transition metals **1** (Figure 6a).[22] The efficient formation of the 2D assembly was extended into a 3D system. Namely, 2D components with more than two linking sites are expected to assemble into 3D coordination architectures if the ligand and metal components are appropriately designed. Among many possible 2D components, triangular-shaped, panel-like ligands were selected as units for the construction of 3D architectures. This idea has been realized by the synthesis of an octahedral 3D structure **3** (Figure 6b).[11]

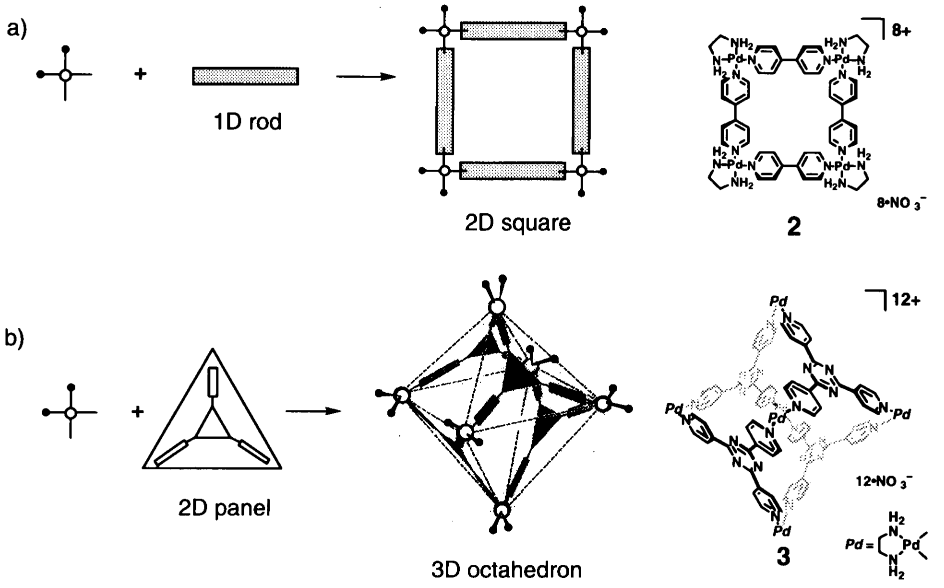


Figure 6. Schematic representation of molecular paneling. a) from 1D-rods to 2D-molecules and b) from 2D-panels to 3D-molecules.

The polyhedral architectures are of special interest in mathematics, architecture of arts and also not least in chemistry. The Platonic solids comprise a family of polyhedra and are made of the same regular polygons (e.g. equilateral triangle) arranged in space such that the vertices, edges, and three coordinate directions of each solid are equivalent.[23] Thus, Platonic and Archimedean solids (this family is made up of at least two different regular polygons) may be used as models for host design. The author shows that two-dimensional planar organic ligands (molecular panels) are assembled into various large three-dimensional Platonic solids through metal coordination. This new concept that the author terms as "molecular paneling" offers an efficient method for the construction of 3D architectures. The author designs a family of molecular panels with the basic shapes of triangle which lead to different types of unusual 3D giant structures (Figure 7).

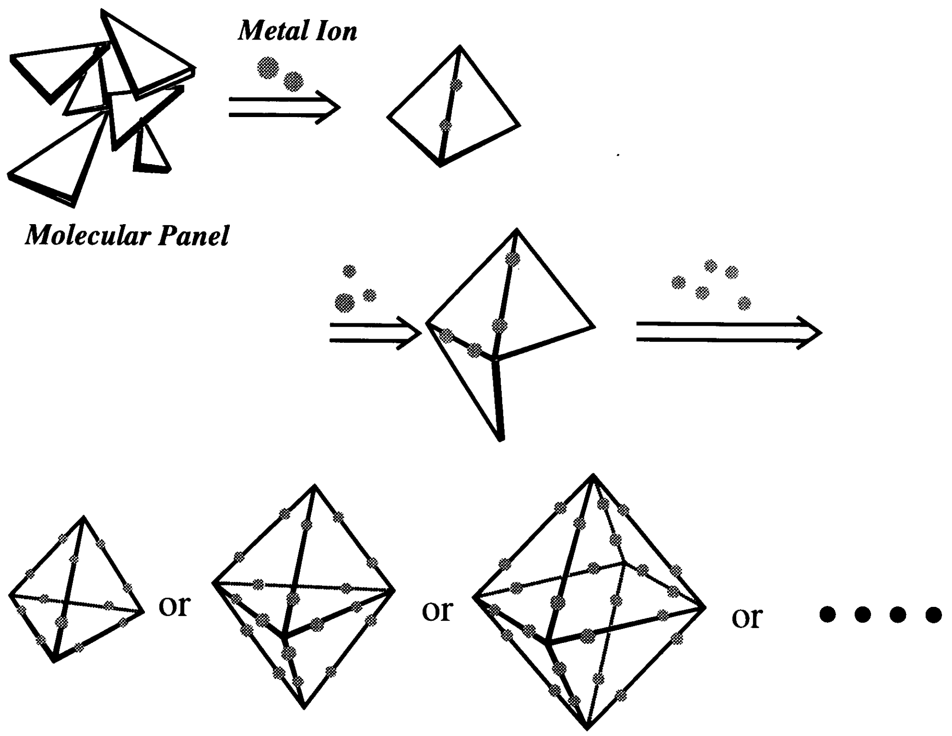


Figure 7. Self-assembly process of molecular panels and metal ions.

Accordingly, the triangular molecular panels such as **4**–**8** are designed. In these ligands, only the difference is number, varies from three to six, and position of the binding sites. The molecular panels **4** and **5** contain three binding sites each but the position of the sites differs, whereas the molecular panels **6**, **7** and **8** contain four, five and six binding sites respectively.

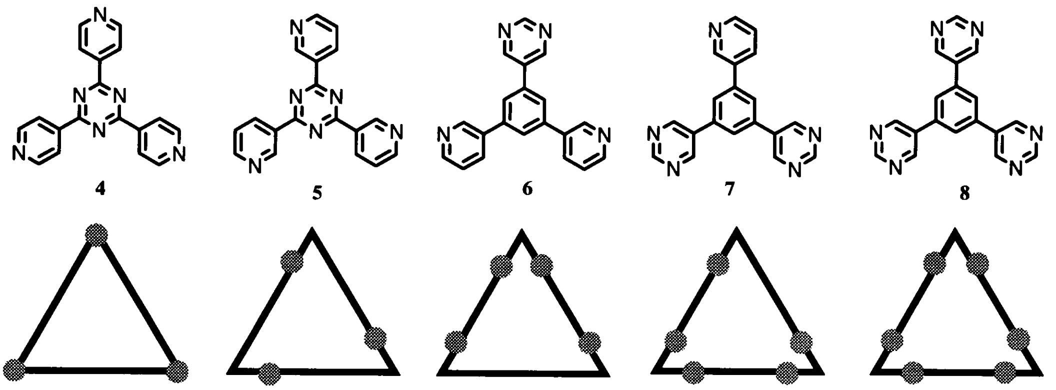


Figure 8. Structural presentations of molecular panels.

1.4 Previous Studies

1.4.1 Self-Assembly of an Octahedral M_6L_4-type Cage

The concept of "molecular paneling" has been in fact realized by the self-assembly of an M_6L_4-type complex **3**.[11] By treating Pd(II) complex **1** with ligand **4** in 3:2 ratio, the complex **3** is quantitatively assembled (Figure 9). In this complex, the four triangular panels are linked together at the corners of the triangles such that every alternate face of the octahedron contains either molecular panel or portal. This particularly interesting case of self-assembly of a 3D coordination compound represented a first step in his studies on the design of molecular panels. Molecular recognition ability of this complex has been extensively studied.

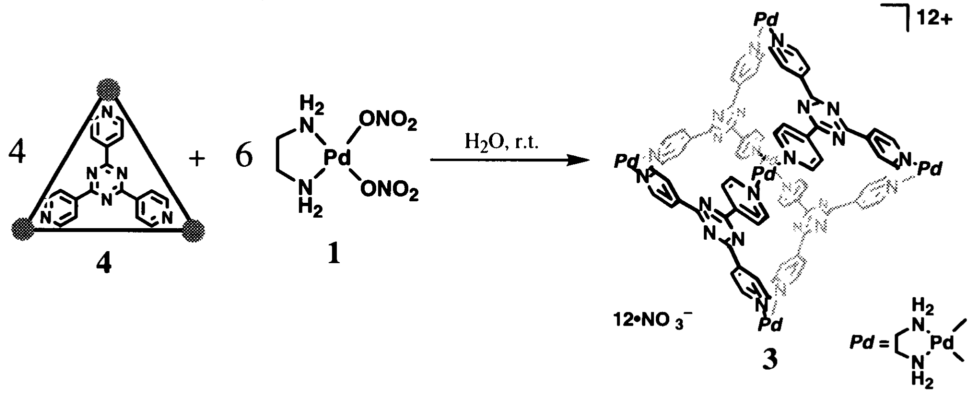


Figure 9. Schematic representation of molecular paneling of **4** to form **3**.

1.4.2 An M_6L_4 bowl-type cage

Another example of molecular paneling previously reported exploits molecular panel **5** which contains three binding sites. Panels **4** and **5** are very similar to each other: only the position of N-atoms differs. Nevertheless, panel **5** is assembled into bowl-like M_6L_4 square pyramidal cone **9**.[12] The structure of **9** has nano-meter dimensions (ca. 3 × 3 × 2 nm). Square pyramidal cone **9** has been found to assemble into dimeric capsule **10** that contains a large hydrophobic pocket inside the framework.[24] The X-ray analysis has shown the dimeric capsule structure accommodating as many as six neutral organic molecules (Figure 10).

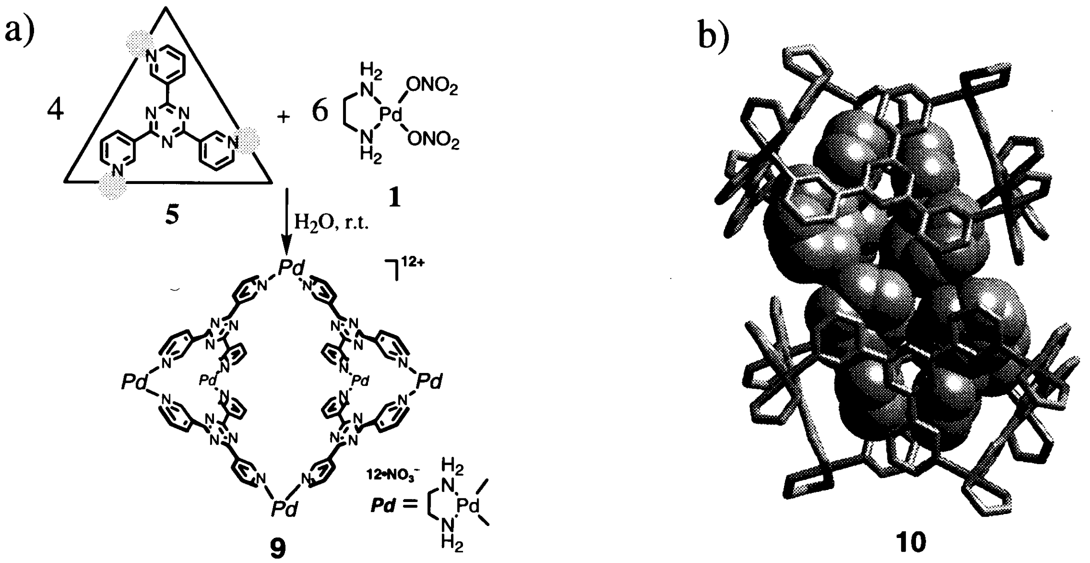


Figure 10. a) Schematic representation of molecular paneling of **5** to form **9**. b) Dimeric capsules of **10** accommodating *o*-terphenyl exhibited in their crystal structure.

1.5 General Summaries of the Present Study

1.5.1 A Coordination Capsule Assembled from 24 components

Encouraged by the successful examples of molecular paneling discussed above, the author expects that, by taking advantage of suitably designed ligand, it is possible to generate a perfect polyhedron with a closed-shell framework. 3D capsules consist of closed, hollow frameworks within which encapsulated molecules are isolated from interaction with external molecules. In this environment, otherwise reactive molecules can be stabilized. In **Chapter 2**, an exo-hexadentate ligand, 1,3,5-tris(3,5-pyrimidyl)benzene **8**, is designed as a triangular molecular panel. The author shows that panel **8** is assembled into hexahedron **11** whose structure has been evidenced by ^1H NMR and X-ray crystallographic analysis.[13] The structure **11** is a trigonal bipyramidal capsule with a chemical formula of $C_{144}H_{216}N_{108}Pd_{18}$, a molecular mass of 7103 Da, and a dimension of 3 × 2.5 × 2.5 nm. The apical corners are very closed, while a small pinhole (2 × 2 Å) in each equatorial corners. These holes do not allow entry or escape of ordinary organic molecules. The free volume inside the capsule is ~900 Å^3 (Figure 11).

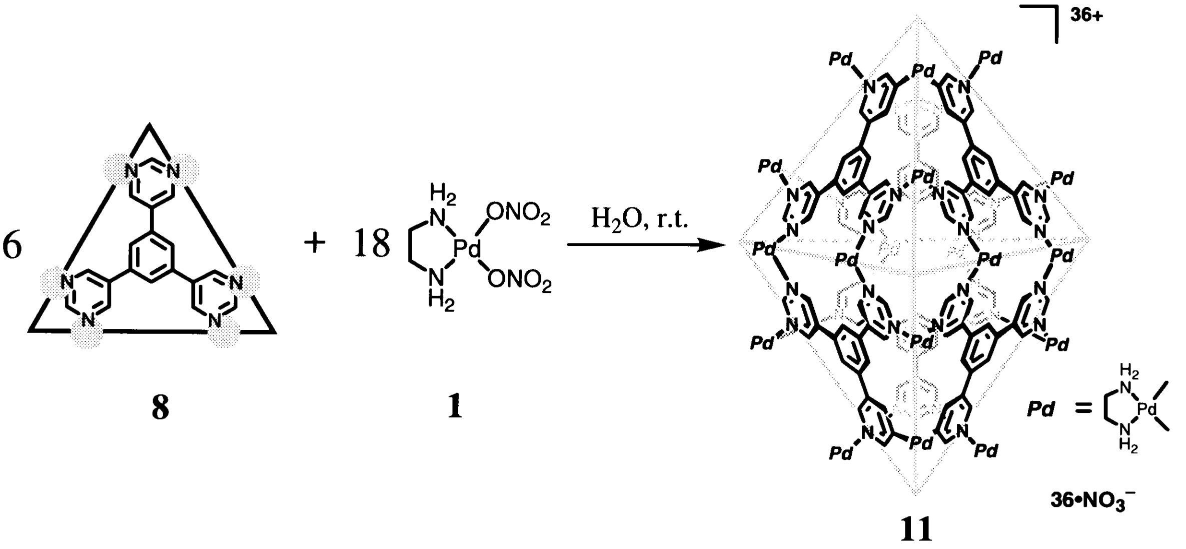


Figure 11. Schematic representation of molecular paneling of **8** to form **11**.

1.5.2 $M_{15}L_6$ Coordination Capsule; Reversible Guest Inclusion

While capsule **11** possesses a large hollow space within its closed shell framework, the structure seems to be too stable to open the framework by metal-ligand dissociation. Thus the author designs a molecular panel based on the concept that an assembled capsule has not only large 3D cavity but sufficient ability for guest inclusion. He has devised the strategies for construction of a molecular capsule which possesses the entrance for guest molecules. In **Chapter 3**, pentadentate molecular panel **7** is designed by eliminating one nitrogen from hexadentate ligand **8**. This ligand is found to assemble into hexahedron **12** that has more flexibility to encapsulate/exchange guest molecules. The structure of **12** has been evidenced by 1D, 2D NMR and X-ray diffraction. Interestingly, **12** encapsulates two CBr_4 molecules and exchange the encapsulated CBr_4 with EtOH (Figure 12).

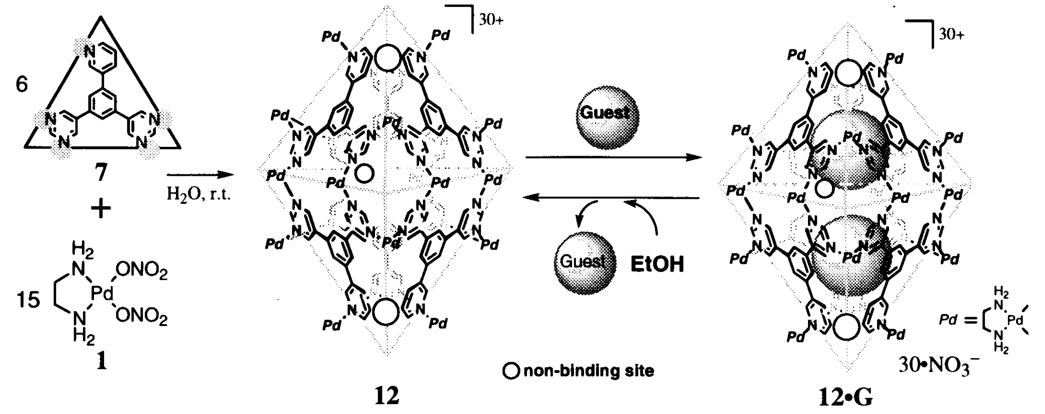


Figure 12. Schematic representation of molecular paneling of **7** to form **12**.

1.5.3 Dynamic Molecular Paneling

In **Chapter 4**, the author considers that by taking advantage of suitable molecular panels it will be possible to control the guest selected formation of its optimal rigid receptor structure from an equilibrium mixture of receptors.[25–32] He designs a triangular panel-like ligand, 3,5-bis(3-pyridyl)-1-(3,5-pyrimidyl)benzene **6**, which possesses four donor sites on the two edges of the triangle, linked with a 90-degree coordination unit, (en)Pd$(NO_3)_2$ **1**. It is worth noting that, while previous triangular ligands all possess C_3 symmetry,[33–35] panel **6** is C_2-symmetric and hence can be linked in two different ways: parallel and anti-parallel links. Interestingly, these two options are perfectly controlled by the guests as shown in Figure 13.[14] Thus, some large guests induce the parallel link of the triangles leading to open cone (tetragonal pyramidal) structure **13** whereas antiparallel link is selected by some small tetrahedral guests giving closed tetrahedron structure **14**. Both assemblies have the same M_8L_4 composition and, therefore, constitute a dynamic receptor library[49,50] from which each receptor is selected by its optimal guests.

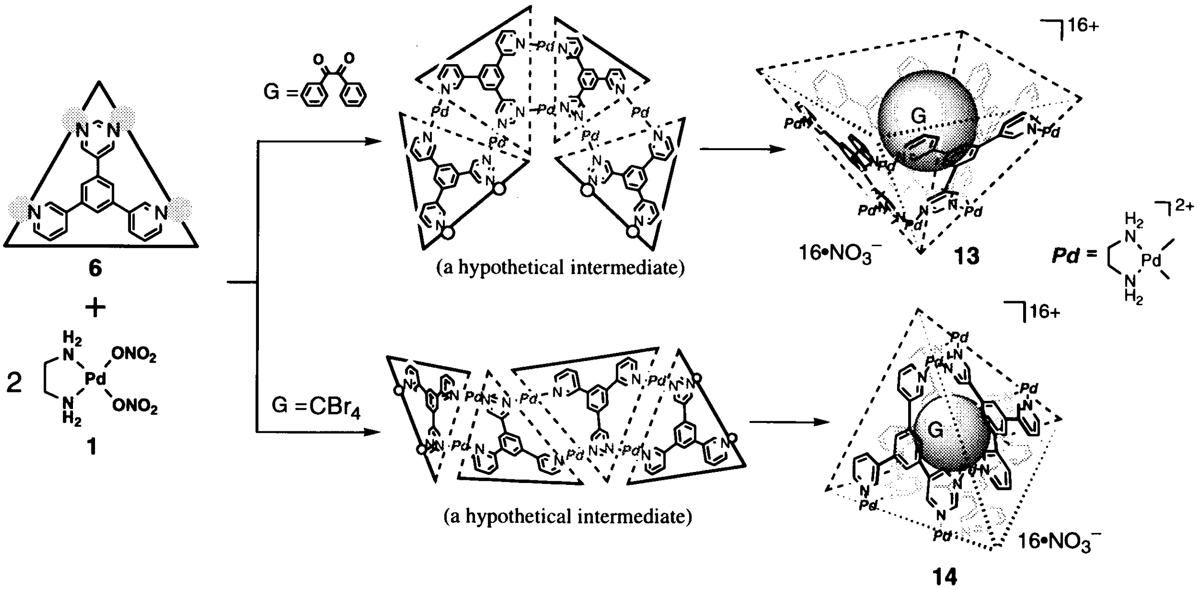
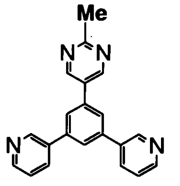


Figure 13. Schematic representation of molecular paneling of **6** to form **13** and **14**.

1.5.4 Side Chain-Directed Molecular Paneling

In the previous chapter, the guest controlled orientation of a molecular panel is discussed, where two options for the panel orientation (parallel or antiparallel) can be directed by the guests. In **Chapter 5**, the author examines the control of the two options by the structure of the panel itself. Namely, directing group(s) are attached on the panel so that only one orientation will be allowed. Thus the author has designed molecular panels with directing group(s): ligands **15–17** (Figure 14).



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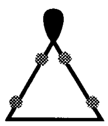

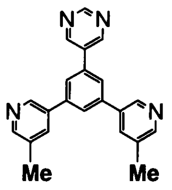

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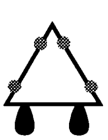

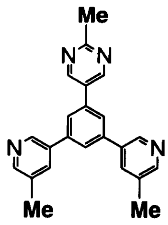

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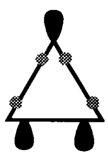

Figure 14. Structural presentations of molecular panels concomitant with the functional group(s).

Usually C_2-symmetric panels such as **6** can be linked in two different ways: parallel and antiparallel links as discussed in the previous chapter. In contrast, molecular panel **15** containing a directing group (a methyl substituent) on the pyrimidine is allowed to orient only in the antiparallel fashion because of steric repulsion between the methyl groups attached on the pyrimidine ring. Accordingly, only cage complex **18** is selectively formed upon the addition of suitable guest molecules, but a square pyramidal open cone structure like **13** is never assembled in the presence of any guests. Obviously, the orientation is strictly controlled by the directing group (a methyl on the pyrimidine).

Another important role of substituents on the molecular panels is to fill cracks and holes which otherwise exist in a self-assembled polyhedron. Contrary to **15**, molecular panel **16** with two methyl substituents can be linked in two different ways as panel **6** is. However, due to the presence of methyl substituents on the panel, tetrahedron **19** has distortion in its shape, unlike **14**, and cracks and holes among the panels are efficiently filled by the substituents as revealed by 1D, 2D NMR.

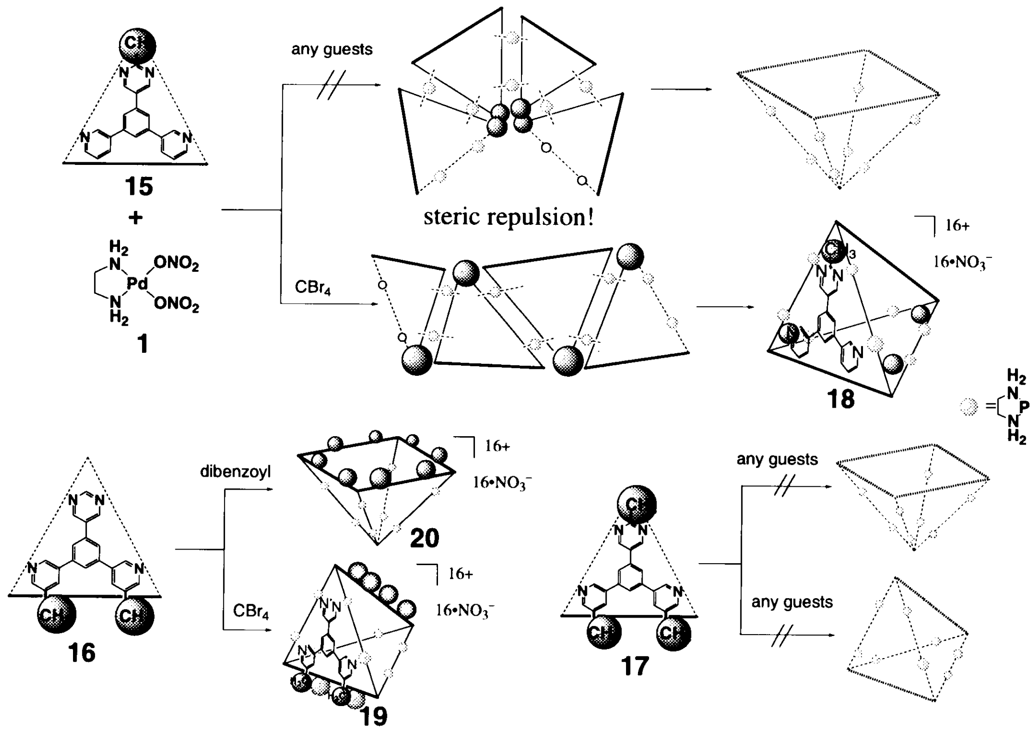

Figure 15. Schematic representation of molecular paneling of **15**, **16** and **17**.

1.5.5 Conclusion

The author's achievement in this thesis study is expected to contribute the development of *"Molecular Self-Assembly"*, displaying desired specific structural features by introducing the new concept "**Molecular Paneling *via* Coordination**" with efficiency and selectivity. In particular, this concept provides very efficient ways for constructing large and hollow polyhedral architectures within which any species are isolated from external events and are expected to show new properties and functions. Exploring such new chemical events within isolated microspace of the coordination polyhedra will be a new paradigm in host-guest chemistry, molecular recognition chemistry, and molecular nanotechnology, in the due course of the present study.

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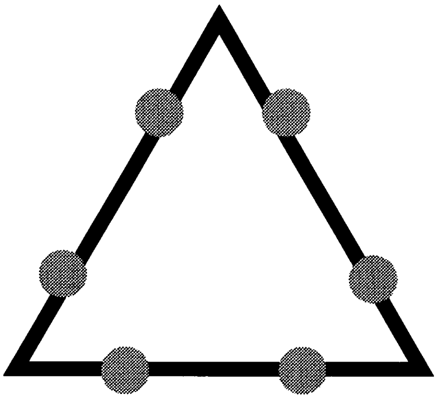
Chapter 2



A Nanometre-sized Hexahedral Coordination Capsule Assembled from 24 Components

Nature **1999**, *398*, 794.

Abstract: Transition metal-coordination chemistry is used to assemble a stable, nanometer-scale capsule from 24 small components: 18 metal ions and six triangular ligands. Thus, reaction of $Pd(en)(NO_3)_2$ with 1,3,5-tris(3,5-pyrimidyl)benzene in water afforded a self-assembled hydrated trigonal-bipyramidal coordination capsule of formula $C_{144}H_{216}N_{108}Pd_{18}\bullet 27H_2O$, of molecular mass 7,103 Da and of dimensions 3 × 2.5 × 2.5 nm. The capsule is roughly hexahedral and comprises of six edge-sharing triangles with two metal ions on each edge. The internal space has a volume of 900 $Å^3$ and is fully closed to all but only very small molecules can enter.

2.1 Introduction

Molecular capsules consist of closed, hollow frameworks within which encapsulated molecules are isolated from interaction with external molecules.[1] In this environment, otherwise reactive molecules can be stabilized.[2–5] Although some molecular capsules have been prepared by conventional synthetic chemistry, recent progress in non-covalent synthesis has allowed the creation of capsules held together by hydrogen bonds.[6–9] Here, we report the use of transition-metal-based coordination chemistry[10–19] to assemble a stable, nanometer-scale capsule from small molecular components: eighteen metal ions and six triangular ligands. Capsule structure was confirmed by NMR and an X-ray crystallographic analysis.

2.2 Result and Discussion

2.2.1 The Assembly Process of Triangular Ligands and Metal Ions

The triangle is the simplest unit for the assembly of polyhedra. To construct molecular polyhedra we designed an exo-hexadentate ligand, 1,3,5-tris(3,5-pyrimidyl)benzene (**1** in Fig. 1), as a triangular assembly unit. This ligand is an almost coplanar triangle and is expected to give edge-sharing polyhedra when its aromatic nitrogens are ligated at the *cis*-coordination site of a metal ion as shown schematically in Fig. 1. A *cis*-protected palladium(II), Pd(NO_3)$_2$(en) (**2**, en = ethylenediamine), provides a 90° coordination angle, and has been shown to be useful for constructing well-defined discrete structures on complexation with a variety of exo-polydentate ligands.[12,20,21] The angles between the planes of tetra-, hexa-, and octahedra do not significantly deviate from 90°, hence we expected the assembly of such a polyhedra on complexation of ligand **1** with Pd(II) unit **2** (Fig. 1).

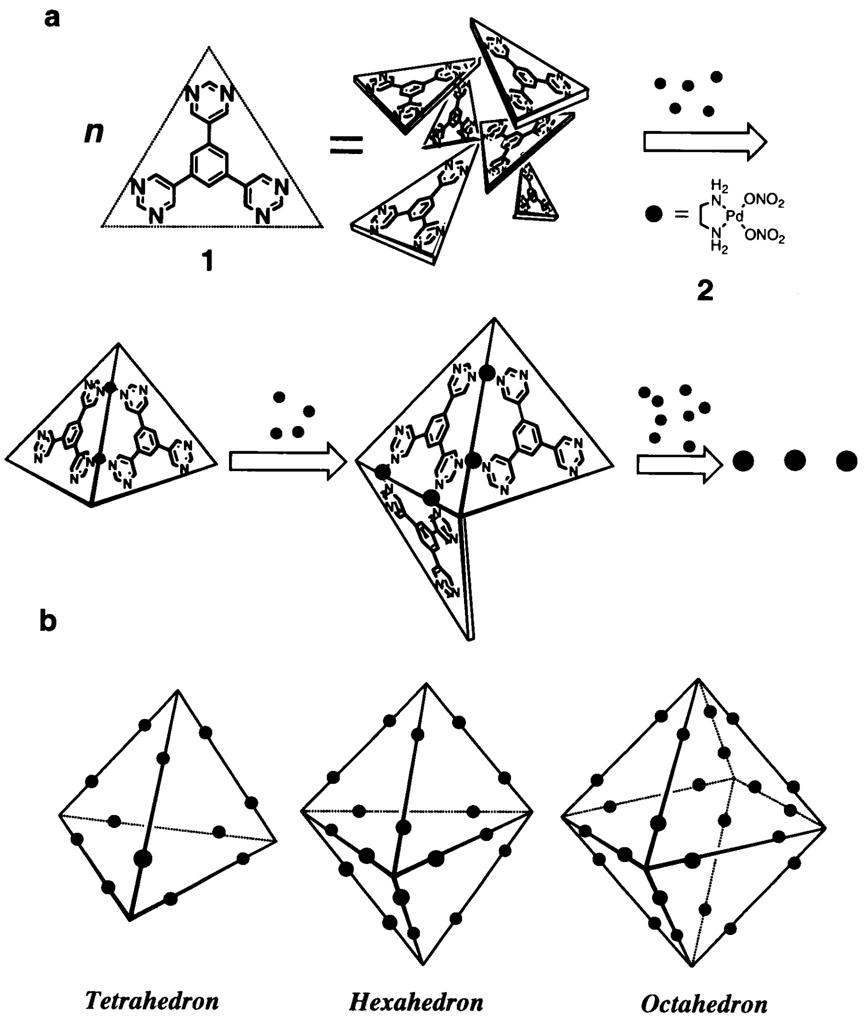


Figure 1. The assembly process of ligand **1** and metal ion **2** (**a**) and the polyhedral frameworks which are possible to assemble (**b**).

2.2.2 Self-Assembly of Hexahedron Capsule

Of the several possibilities, the assembly of a molecular hexahedron from **1** and **2** was strongly suggested by proton nuclear magnetic resonance (^{1}H NMR) observations. When ligand **1** was treated with Pd(II) complex **2** (3 equiv.) in D_2O, we observed the predominant formation of a single component whose ^{1}H NMR spectrum showed seven singlet-like signals in an integral ratio of 2:2:2:2:2:1:1. This observation confirms that, after complexation the ligand **1** (of C_3 symmetry) is placed in a less-symmetrical (σ_2) environment with only one symmetry axis passing through a 3,5-pyrimidyl (pym) ring and a core benzene ring (Fig. 2). The assignments were fully conformed by the two-dimensional NMR techniques (H–H correlation spectroscopy (COSY), C–H COSY,

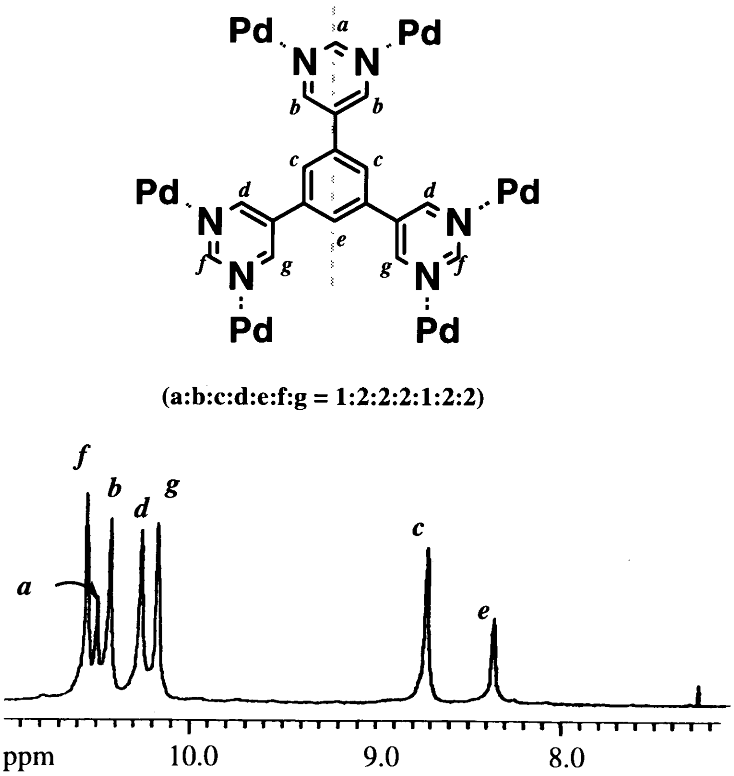
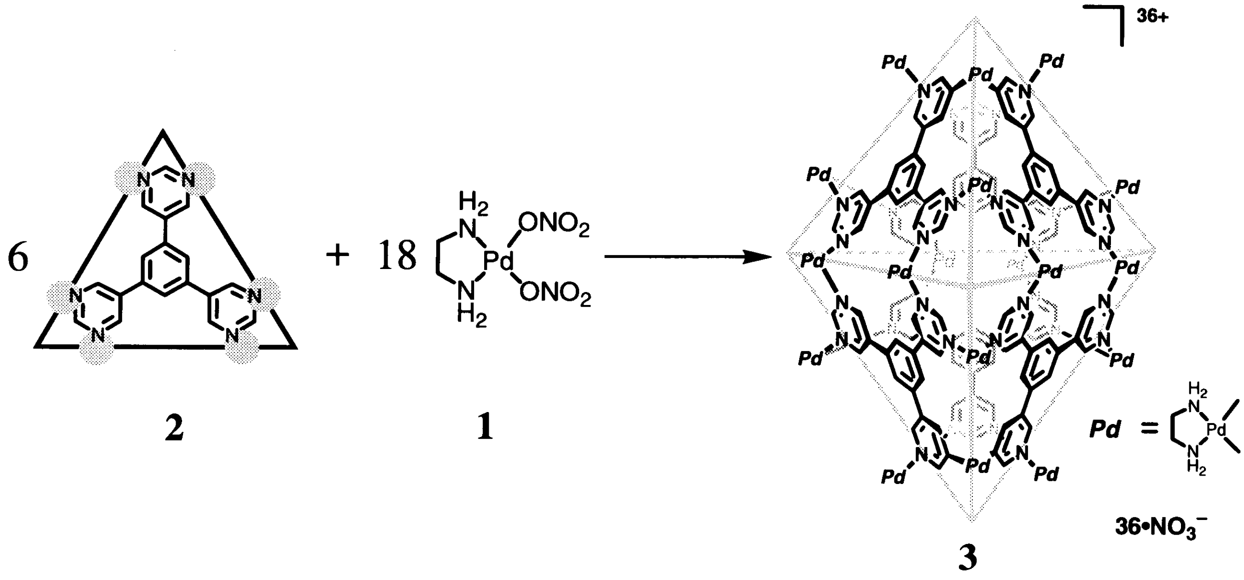


Figure 2. The ^{1}H NMR spectrum of the product assembling from **1** and **2** (3.3 equiv.). The spectrum was obtained with 500 MHz NMR and show the aromatic region; D_2O was used as the solvent.

nuclear Overhauser and exchange spectroscopy (NOESY); and homonuclear Hahn spectroscopy (HOHAHA), see experimental section.

The σ_2 symmetry is in good agreement with the trigonal bipyramidal structure of molecular hexahedron **3** (see Scheme 1) in which pyrimidine (pym) groups at the apical corners are non-equivalent to those are at the equatorial corners. A small amount of by-products, showing very complex NMR spectra, were also detected. However, the by-product formation was completely suppressed by employing a small excess of **2** (3.3 equiv.), suggesting that the by-products and free **2** are in equilibrium with **3**. From the crude reaction solution, complex **3** was isolated in 95% yield as a precipitate by adding a large amount of ethanol. Elemental analysis of **3** suggested the chemical formula of $3 \bullet (H_2O)_n$ (n = 26–28).

Scheme 1



2.2.3 X-ray Crystallographic Analysis of Hexahedron

Reliable evidence for the trigonal bipyramidal structure of hexahedron **3** was provided by X-ray crystallographic analysis. A single crystal of **3** was obtained by slow diffusion of methanol into an aqueous solution of **3** at 4 °C for 4 d, and the X-ray diffraction study was done with a CCD diffractometer. The crystal structure of **3** clearly demonstrates that the assembly is a trigonal bipyramidal coordination capsule with a chemical formula of $C_{144}H_{216}N_{108}Pd_{18}$, a molecular mass of 7,103 Da and of dimension 3 × 2.5 × 2.5 nm (Fig. 3). The pym rings are slightly tilted from the plane of the core benzene ring of ligand **1**. In addition, Pd(II)–pym bonds and pym rings are not completely coplanar. Such small distortions make the pym–Pd–pym coordination angle close to 90°.

Each equatorial corner of the hexahedron is made up by the assembly of four triangle units, where a $(Pd(II)–pym)_4$ cyclic framework gives a small 'pinhole' (2 × 2 Å). Through these holes, only small molecules such as water and molecular oxygen may pass, but ordinary organic molecules cannot enter or escape. We note that not even such a 'pinhole' exists at the apical corners of **3** (Fig. 3b).

The free volume inside the capsule into which guests can be accommodated is ~900 $Å^3$, implying that complex **3** can host large molecules such as buckminsterfullerene, C_{60}. Out of 36 nitrate anions of **3**, 14 have been found in the crystal structure: five are found inside and nine are found outside of the capsule (Fig. 4). The five nitrate anions inside the capsule are situated at apical and equatorial positions of hexahedron. The remaining anions are highly disordered.

2.2.4 Intermediates in the Assembly of Hexahedron

The thermodynamic stability of **3** can be explained by a strong cooperative effect of 36 Pd(II)–pym coordination bonds involved in the framework of **3**. Each coordination bond is weak, because coordination by two Pd(II) ions at the 1,3-position of a pym ring is

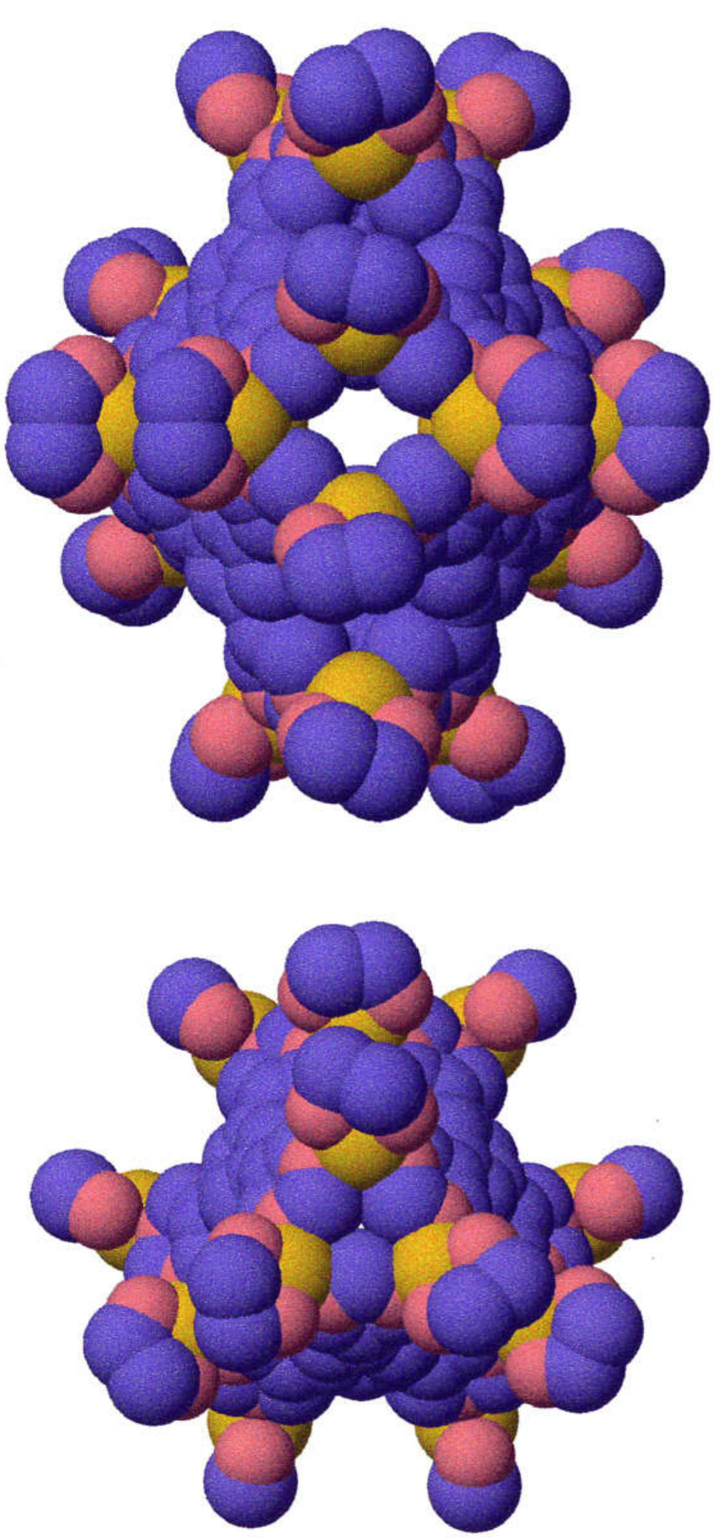


Figure 3. A space-filling presentation of the X-ray crystal structure of **3**. Top: a view from an equatorial direction; bottom: a view from an apical direction.

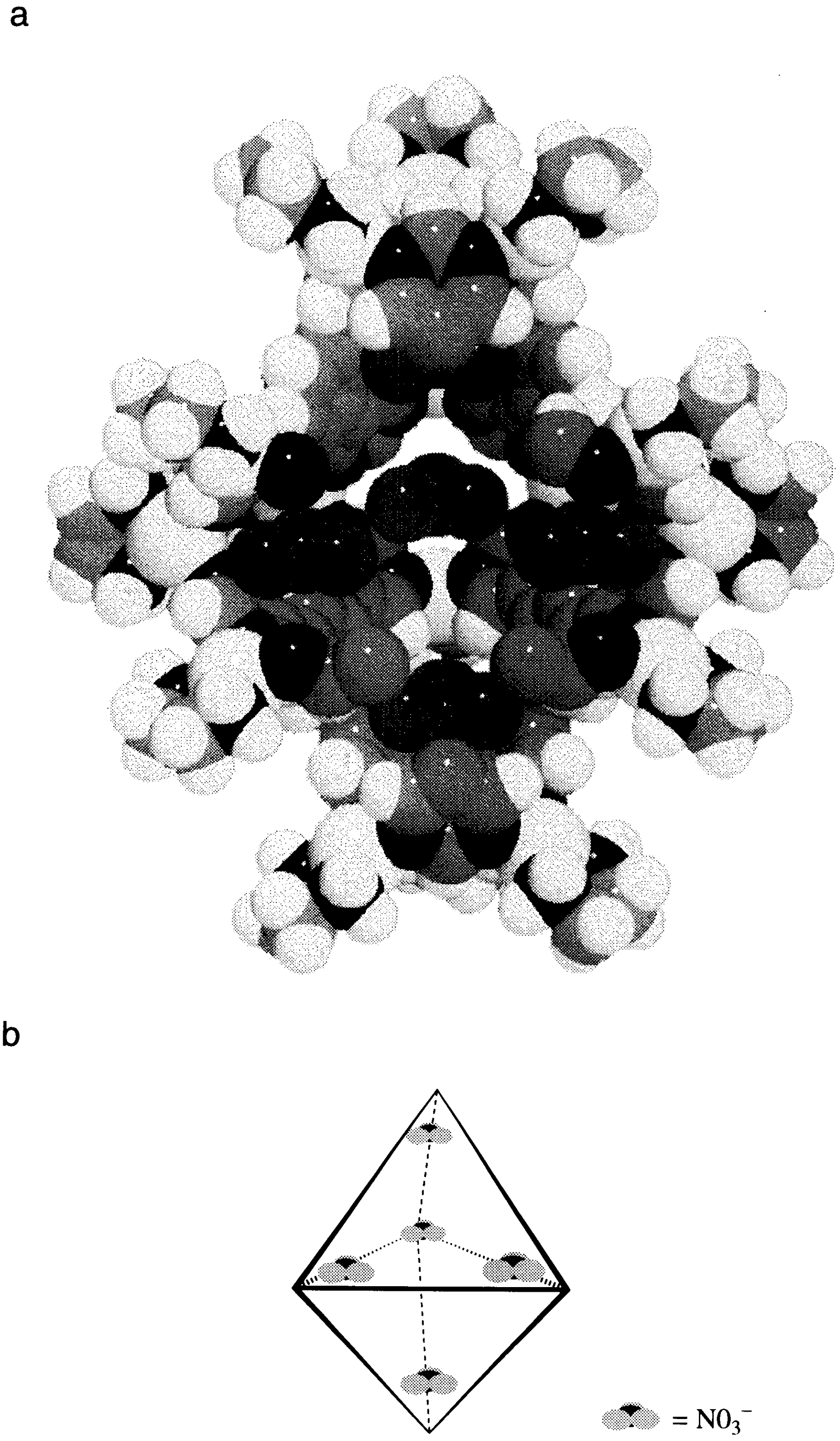


Figure 4. Crystal structure showing the inside of the capsule of **3**. (a) Space-filling representation. (b) Schematic depicting.

unfavorable due to the charge repulsions between two adjacent Pd(II) ions and the electron-withdrawing effects of adjacent Pd(II)–pym bonds on each other. In fact, macrocycles with (Pd(II)–pym)$_n$ frameworks (n = 3,4) did not assemble from **2** and 1,3-pyrimidine; instead, oligomers showing broad peaks in NMR were observed. A strong cooperative effect of Pd(II)–pym bonds should be a probable reason for the formation of a nanosized capsule structure in quantitative yield.

The metal-linked dimer **4** and trimer **5** (Fig. 5a, b) may be involved as intermediates in the assembly process of **3**, because these species were observed when ligand **1** was titrated with Pd(II) complex **2** in D_2O. At **1**:**2** = 1:1 stoichiometry, NMR displayed the high-yield formation of a single product which was assigned as dimer **4** (Fig. 5c). Dimer **4** was isolated as a salt with PF_6^- (96% yield) and characterized by NMR, electrospray mass spectrometry (ESI–MS), and elemental analysis. Further addition of **2** into the D_2O solution made the spectrum very complex. However, the spectrum again became simpler at **1**:**2** = 3:4 stoichiometry showing 16 singlet signals with a total integral ratio of 36H

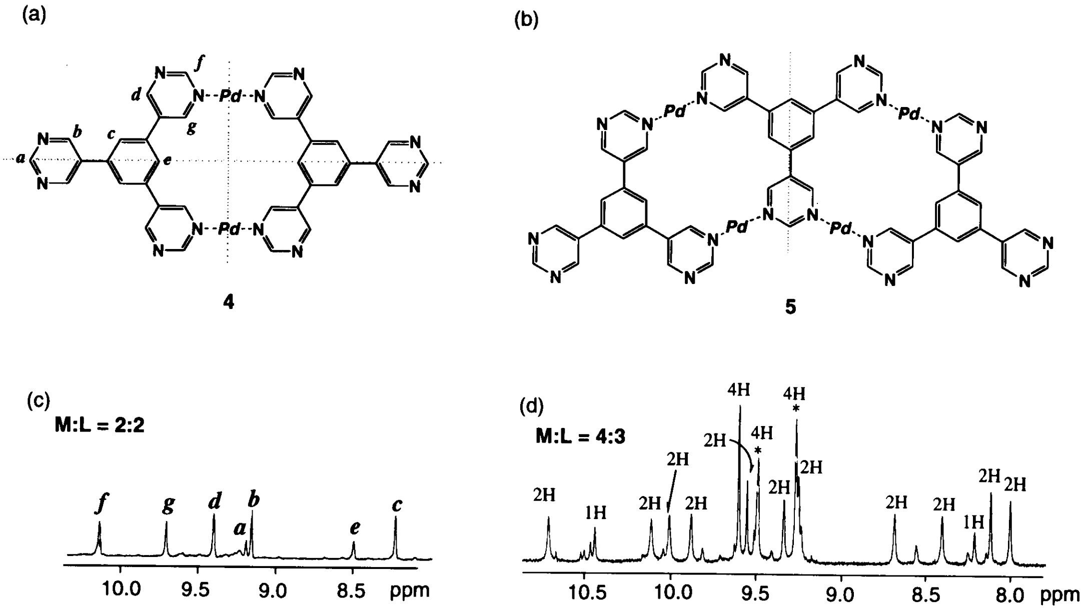


Figure 5. Proposed intermediates in the assembly of **3**. (a) The structure of dimer **4**. (b) The structure of trimer **5**. (c) ^1H NMR (aromatic region) of dimer **4**. The assignments are supported by H–H COSY. (d) ^1H NMR (aromatic region) of trimer **5**.

(4H × 3, 2H × 11, 1H × 2) in the aromatic region, consistent with the trimer structure of **5** (Fig. 5d). Two singlet signals with 2H integration may be overlapped, at signals marked by an asterisk. As trimer **5** was observed only at low concentrations, satisfactory ^{13}C NMR and two-dimensional NMR spectra were not obtained.

2.3 Conclusion

The present results complement the synthesis of a corner-sharing octahedron assembling from an exo-tridentate ligand, 1,3,5-tris(4-pyridyl)triazine, and Pd(II) complex **2**.[12,15,16] The framework of this octahedron complex has large windows and encloses large guest molecules (for example, as many as four carborane molecules) which can enter or exit through the openings. In contrast, the ligand described in this chapter upon reaction with Pd(II) building block **2** formed coordination trigonal bipyramid. This coordination capsule has a closed shell structure and should be able to encage large molecules.

2.4 Experimental Section

Synthesis and physical properties of 5-Trimethylstannylpyrimidine. To a THF solution (115 mL) of 5-bromopyrimidine (3.18 g, 20.0 mmol), 1.54 M *n*-butyllithium (a hexane solution, 13.0 mL, 20.0 mmol) was added at –98 °C. After stirring for 1 h at –80 to –90 °C, a THF solution of chlorotrimethyltin (1 M, 20.0 mL, 20.0 mmol) was added dropwise at –98 °C. The mixture was gradually warmed to 0 °C over 2 h and stirred at the same temperature for 20 h. The reaction mixture was poured into 10% aqueous solution of NH_4Cl (90 mL) and stirred for 10 min. The mixture was extracted three times with chloroform and the organic layer was washed with brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified with column chromatography ($CHCl_3$:ethyl acetate = 2:1) to give 5-trimethylstannylpyrimidine (3.97 g, 16.4 mmol, 82%). A pale yellow oil; bp 75–77 °C (tube oven temp)/27 mmHg; ^1H NMR (270 MHz, $CDCl_3$) δ 0.40 (s, 9H), 8.72 (s, 2H), 9.13 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ –9.7, 134.3, 158.4, 162.7; IR (neat) 1545, 1409, 1345, 1070, 777, 720, 637, 534 cm^{-1}; MS(EI) *m/z* 244 (MH^+ based on ^{120}Sn).

Synthesis and physical properties of 2,4,6-Tri(5-pyrimidyl)benzene. A mixture of 5-Trimethylstannylpyrimidine (2.91 g, 12.0 mmol), 2,4,6-tribromobenzene (945 mg, 3.0 mmol), and $PdCl_2(PPh_3)_2$ (167 mg, 0.24 mmol) in acetonitrile (75 mL) was refluxed for 21 h. The grey suspension was filtered and the precipitate was washed with hexane and ethyl acetate. The grey solid was dissolved with 5 M HCl (40 mL) and the small amount of insoluble product was removed by filtration. Acetone (180 mL) was added to the solution, and the resulting white precipitate was filtered and suspended in aqueous NH_3. After stirring over night, the precipitate was filtered and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave 2,4,6-tri (5-pyrimidyl)benzene (682 mg, 2.18 mmol, 73%): light grey powder; mp 340–343 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.85 (s, 3H), 9.07 (s, 6H), 9.33 (s, 3H); IR (Kbr) 1560, 1418, 1399, 1352, 1194, 1045, 881, 841, 722, 636 cm^{-1}; MS (EI) *m/z* 312 (M^+). HRMS Calcd for $C_{18}H_{12}N_6$: 312.1123; found: 312.1134. The ^{13}C NMR spectrum of 2,4,6-tri(5-pyrimidyl)benzene could not be measured because of its low solubility in almost all common deuterated solvents.

Synthesis and physical properties of 3. Ligand **1** (31 mg, 0.10 mmol) was suspended in an aqueous solution (3 mL) of **2** (96 mg, 0.33 mmol) and the mixture was stirred at ambient temperature for 24 h. Addition of ethanol (10 mL) to the solution gave a precipitate of **3** as pale yellow crystals (120 mg, 95%): mp ~220 °C (decomposed); ^1H

NMR (500MHz, D_2O tetramethylsilane as external standard) δ 2.9–3.3 (m, 72 H), 8.36 (s, 6H), 8.73 (s, 12 H), 10.18 (s, 12 H), 10.26 (s, 12 H), 10.43 (s, 12 H), 10.50 (s, 6 H), 10.55 (s, 12 H); ^{13}C NMR (125MHz, D_2O) δ 47.5 (CH_2), 47.6 (CH_2) 47.8 (CH_2), 125.6 (CH), 127.0 (CH), 130.3 (quaternary carbon, Cq), 131.7 (Cq), 133.4 (Cq), 134.7 (Cq), 157.7 (CH), 158.8 (CH), 159.3 (CH), 159.5 (CH), 160.3 (CH); IR (KBr) 3,209, 1,384, 1,057, 879, 709 cm^{-1}. Elemental analysis: calculated for ($C_{144}H_{216}N_{108}O_{108}Pd_{18}$•27$H_2O$, C, 22.77; H, 3.56; N, 19.92; found: C, 23.06; H, 3.51; N, 19.60.

Synthesis and physical properties of 4. Ligand **1** (12.5 mg, 0.04 mmol) was suspended in dimethyl sulphoxide solution (1.0 mL) of **2** (11.6 mg, 0.04 mmol) and the mixture was stirred for 8.5 h at ambient temperature. The pale yellow solution was added dropwise to a saturated aqueous solution (10 mL) of KPF_6 and the resulting white precipitate was filtered to obtain **4** (PF_6^- salts) (31.4 mg, 0.019 mmol, 96%): mp ~250 °C (decomposed): ^{1}H NMR (500 MHz, D_2O) δ 2.76 (s, 8H), 8.25 (s, 4H), 8.49 (s, 2H), 9.17 (s, 4H), 9.21 (s, 2H), 9.41 (d, *J* = 2.5 Hz, 4H), 9.71 (s, 4H), 10.10 (d, *J* = 2.5 Hz, 4H); IR (KBr) 1,559, 1,421, 1,399, 1,058, 839, 709, 559 cm^{-1}. ESI–MS *m/z* 1,392.2 (M–PF_6), 1,430.9 (M–PF_6 + CH_3CN), 1,474.0 (M-PF_6 + 2CH_3CN), 1,557.1 (M–PF_6 + 4CH_3CN). Elemental analysis: calcd. for ($C_{18}H_{12}N_6$)[$C_2H_8N_2Pd(PF_6)_2$]•5H_20, C, 29.52; H, 3.10; N, 13.77; found: C, 29.19; H, 2.76; N, 13.50.

X-ray structural analysis of 3. Ligand **1** (12.5 mg, 0.040 mmol) was suspended in a D_2O solution (1 mL) of **2** (34.9 mg. 0.120 mmol), and methanol (14 μl) was added to the mixture. After stirring at ambient temperature for 17 h, diffusion of methanol into the resulting pale yellow solution at 4 °C for 4 d gave yellow single crystals of **3**. A single crystal of **3** (0.25 × 0.30 × 0.35 mm) was mounted on a glass fibre. All measurements were made on a charge coupled device (CCD) plate area detector with graphite monochromated Mo–Kα radiation. The data were collected at 296K. Crystal data for **3**: formula $C_{148}H_{216}N_{108}O_{106}Pd_{15}$•27$H_2O$. *M* = 7,589.56, hexagonal, space group $P6_3/m$ (#

176), $a = 23.168(8)$, $c = 34.10(2)$Å, $V = 15851(16)$Å^3, $\rho_{\text{calcd.}} = 1.60$ g cm^{-3}, $Z = 2$, $F(000) = 7{,}596$, $\mu(\text{MoK}\alpha) = 11.03$ cm^{-1}, $\lambda(\text{MoK}\alpha) = 0.71069$ Å; 99,000 reflections measured, 3.034 observed ($I > 3.50\ \sigma(I)$); number of variables 425; $R_1 = 0.129$; $wR_2 = 0.166$.

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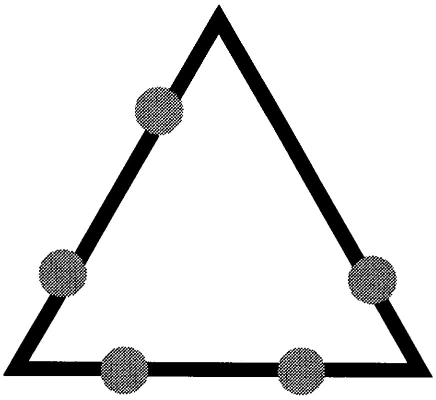
Chapter 3



$M_{15}L_6$ *Coordination Capsule: Reversible Guest Inclusion*

manuscript in preparation

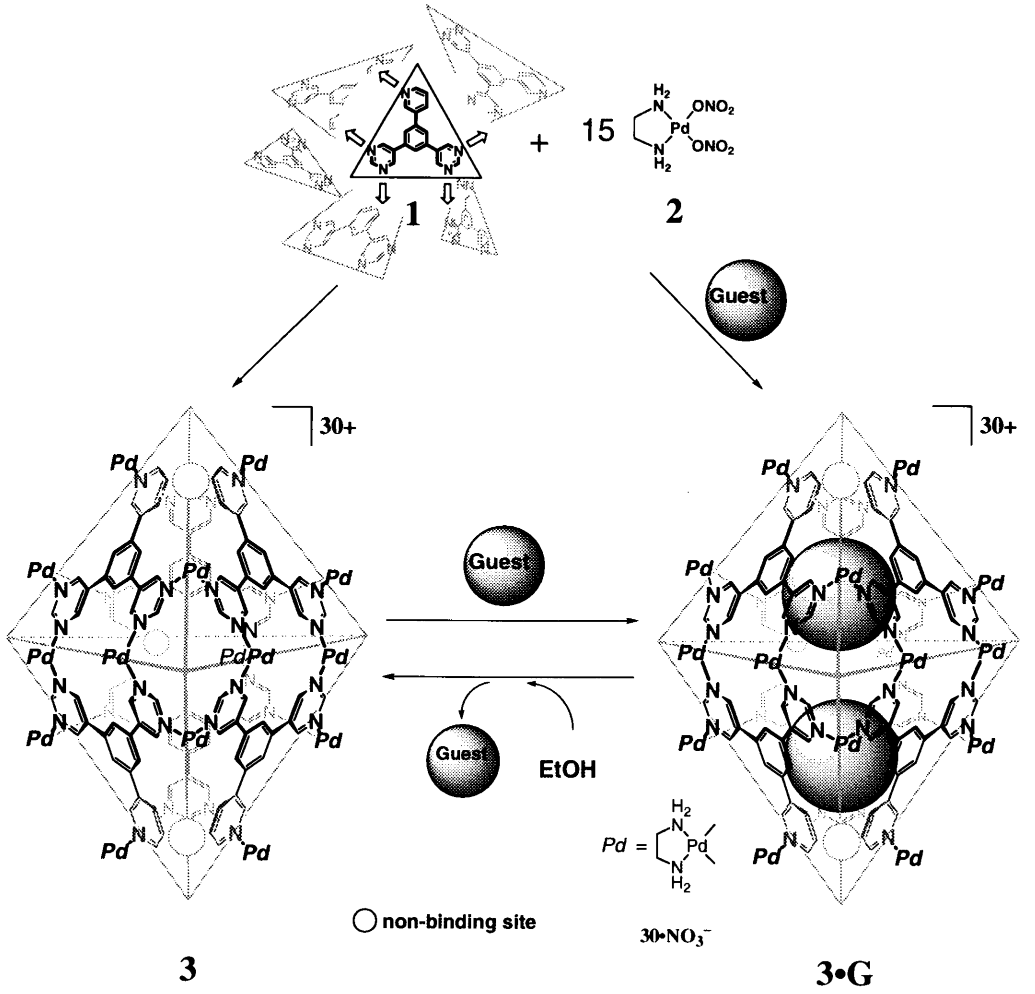
Abstract: Although the previous capsule (Chapter 2) possesses a large hollow space within its closed shell framework, the structure seems to be too stable to open the framework by metal-ligand dissociation. Thus the author designed a molecular panel so that an assembled capsule has not only large 3D cavity but sufficient ability for guest inclusion. A pentadentate triangular ligand with a Pd(II) building block is assembled into a hexahedron coordination capsule which possesses the entrance for guest molecules such as CBr_4. Moreover, the capsule can be applied to the encapsulation/exchange of guest molecules with EtOH.

3.1 Introduction

For constructing molecular-based nanostrucutres, self-assembly through weak non-covalent interaction has been recognized as a powerful method.[1-3] In Chapter 1, it has been discussed that, among many possible two-dimensional components, triangular panel-like ligands have attracted considerable current interest because of their potential abilities for constructing a family of polyhedral structures.[4-7] Three-dimensional cage compounds have become the most extensively studied molecular capsules.[1a,8] In Chapter 2, it has been shown that exo-hexadentate triangular ligand, having two-binding sites on each of its edges, upon reaction with Pd(II) building block **2** forms coordination trigonal bipyramid.[5b] However, this coordination capsule has a closed shell structure and hence has no ability to encapsulate/exchange guest molecules.

He has devised the strategies for construction of a molecular capsule which possesses the entrance for guest molecules. In this chapter, the triangular panel-like ligand with five donor sites was designed: namely, compound **1**. It has two donor sites each on its two edges while only one donor site on the remaing edge. Due to the one binding site less on one edge of **1**, upon reaction with **2** it is expected to form the coordination capsule **3** which possess the entrance/exist for guest molecules (Scheme 1). Indeed it is observed that the formed **3** has an entrance for the encapsulation of CBr_4 and an exit for the release of CBr_4 by the addition of EtOH.

Scheme 1



3.2 Result and Discussion

3.2.1 The Assembly of $M_{15}L_6$ Coordination Capsule

Self-assembly provides coordination compounds where the ligand geometry makes the possibility to synthesize complex structures, namely tetrahedron, hexahedron and polyhedron. From the reaction of **1** and **2**, of the several possibilities, a molecular hexahedron was obtained as the sole structure, which was assembled from six ligands (**1**) and fifteen metal ions. When ligand **1** (0.025 mmol) was treated with Pd(II) complex **2** (0.07 mmol) in D_2O (0.7 mL), he observed the formation of a single component, whose ^1H NMR spectrum revealed 39 proton signals in an aromatic region (Figure 1). A glance at the NMR spectrum showed the 39 signals which could not be assigned to any single component. However, H–H relay COSY and NOESY experiments elucidated a hexahedron coordination capsule as the sole structure **3**. To bigin with, it is noteworthy that the significant peak of double doublet at 6.2 ppm was observed for the *H*c" of ligand **1**. Based on the *H*c" assignment, *H*a", *H*b" and *H*d" in the 3-pyridine ring (Py) were

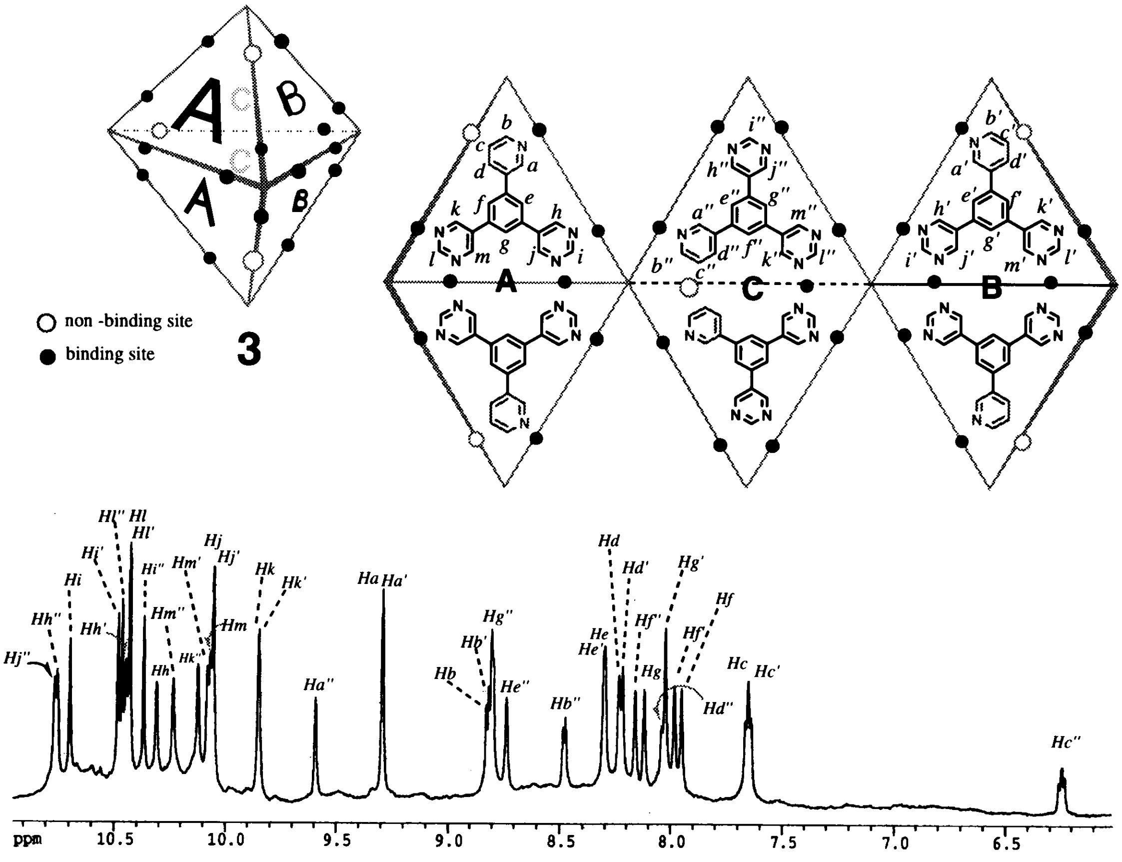
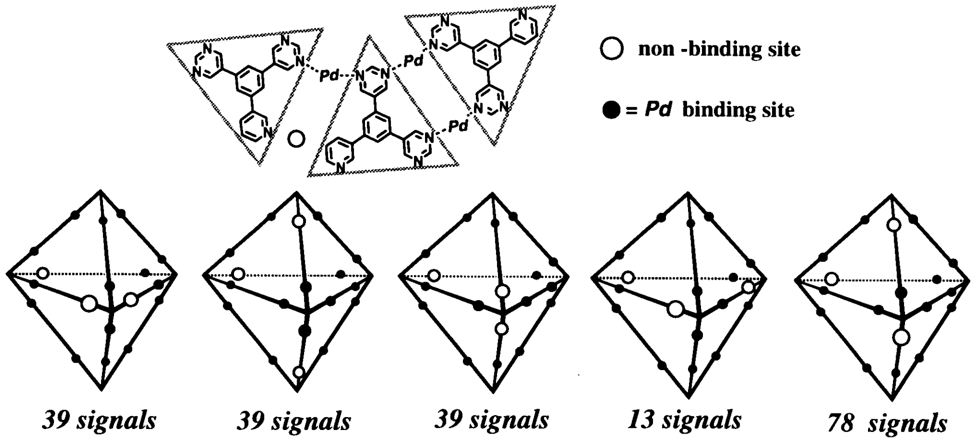


Figure 1. Schematic representation of the hexahedron and ^{1}H NMR spectrum of **3**.

assigned with the help of the H–H relay COSY. A NOESY experiment was used to distinguish core C_6H_3 ring protons from Py ring which enabled him to determine the *H*e" and *H*f". *H*g" of C_6H_3 ring was determined by COSY experiments. The pyrimidine rings were assigned in a similar method as stated above. From the NMR, it is clear that the ligand **1** (C_2 symmetry) is placed in an asymmetric environment. Consequently, 13 of 39 signals in an aromatic region were found to belong to a one unit of the ligand **1** out of three. The presence of 39 signals in aromatic region indicates that the capsule **3** is composed of three (Figure 1. panel A, B, and C) inequivalent ligands of **1**. Namely this polyhedron is constructed from $(3 \times L)_n$ ligands. Entropic and enthalpic considerations indicate that the discrete supramolecular architectures are favored over polymeric products, which is just a hexahedron.

The hexahedron assembled from C_2-symmetric ligand **1**, in principle, can have five types of stereoisomers (Figure 2). The isomers differ in the position of the non-binding site, which reflects the number of aromatic proton signals. A NOESY experiment revealed the link of adjacent ligands, 39 proton signals which stems from the sole structure **3**, two of three non-binding sites located on the apical corners and the third one is situated in the equatorial corner. The coordination complex **3** can be unequivocally assigned as a hexahedron assembled from 21 small components: 15 metal ions and 6 panel like ligands. The complex **3** was isolated as a colorless precipitate in 83% yield by adding a large amount of EtOH. Elemental analysis of **3** was consistent with a formula of $3{\bullet}(H_2O)_{25}$.



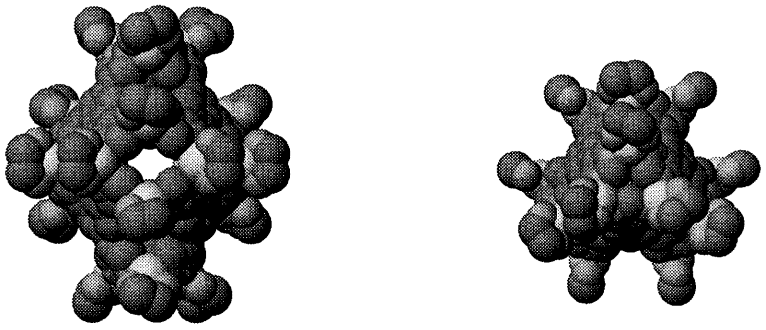
39 signals *39 signals* *39 signals* *13 signals* *78 signals*

Figure 2. Schematic representation of the stereoisomers of hexahedron and expected number of signals in an aromatic region.

3.2.2 X-ray Crystallographic Analysis of Capsule

A Reliable evidence for the trigonal bipyramidal structure of hexahedron **3** is provided by an X-ray crystallographic analysis (Figure 3). The single crystal was obtained by slow diffusion of methanol into an aqueous solution of **3** at 20 °C for ten days. As expected, the crystal structure of **3** displayed the hexahedron. Two non-binding sites located on the apical corners and another one is situated on the equatorial corner (Figure 3a). As a result, the ligand **1** is placed on three different environments. Thirty-nine protons of **3** were observed independently in ^{1}H NMR. The 21-components assembly makes a trigonal bipyramidal coordination capsule which possesses the entrance for small molecules. Out of 30 nitrate anions of **3**, 15 have been found in the crystal structure: three are found inside the capsule and twelve outside.

The complex **3** has a 'pinhole' (2 × 2 Å) of equatorial corner constructed by four triangular units (Figure 3b). Through these holes, only water and molecular oxygen may pass, but ordinary organic molecules cannot enter or escape. As compared with previous trigonal bipyramidal structure **4** (Chapter 2), which is assembled from an exo-hexadentate ligand, structure **3** has a similar shape and a dimension (3 × 2.5 × 2.5 nm). Structure **4** is a very closed and rigid structure.


a view of equatorial direction a view of apical direction

Crystal structure **4**

It is worth noting that in **3**, the non-binding site, 3-py rings which face each other behaves more flexible entrance for encapsulation/exchange small guest molecules (Figure 3b). The dimensions of entrance are approximately 3.5 × 5.0 Å. On the other hand, he notes that it is impossible, for the entrance located at the equatorial corners,

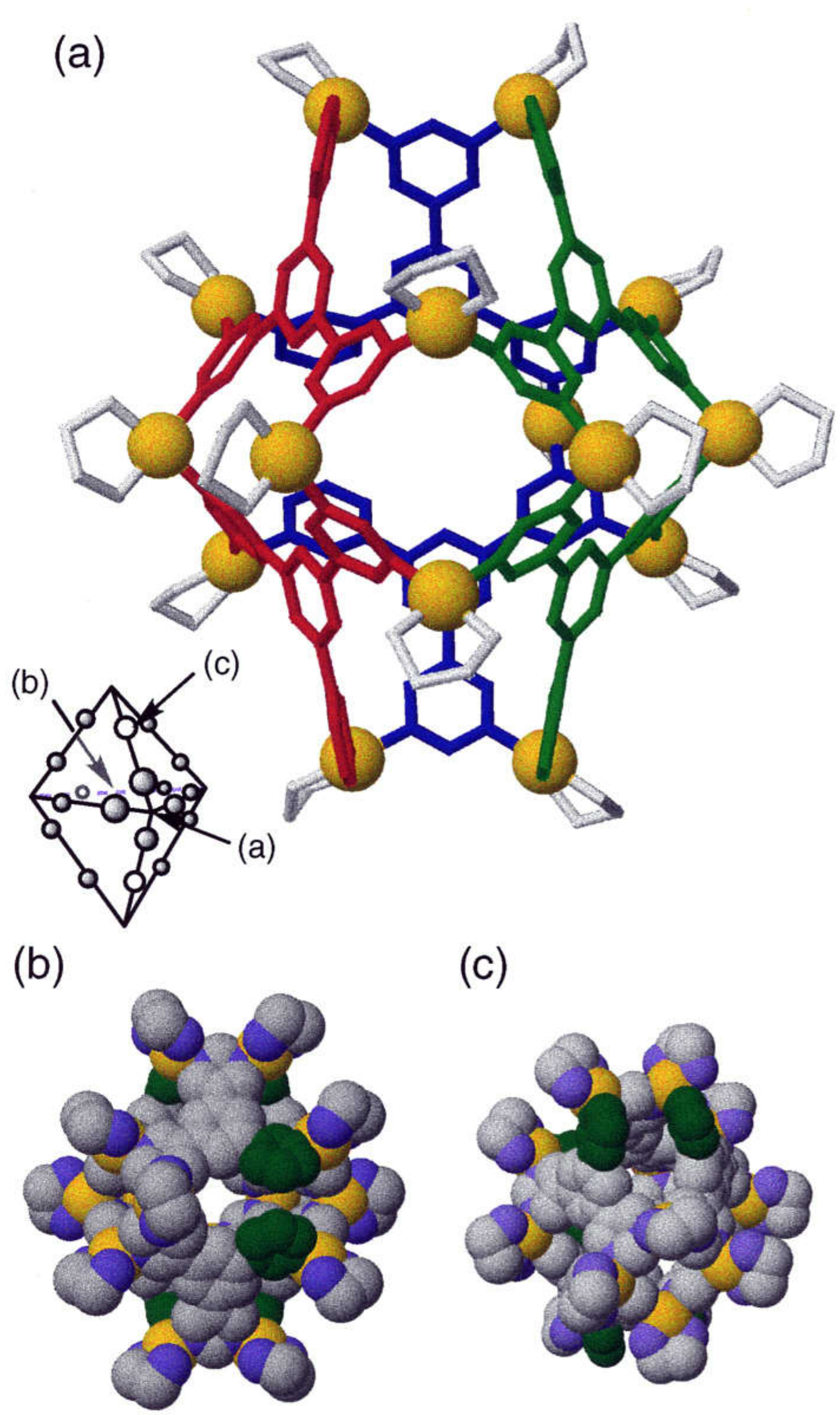


Figure 3. Crystal structure of **3**. (a) ball and cylindrical representation. (b) a view from the back direction. (c) a view from an apical direction.

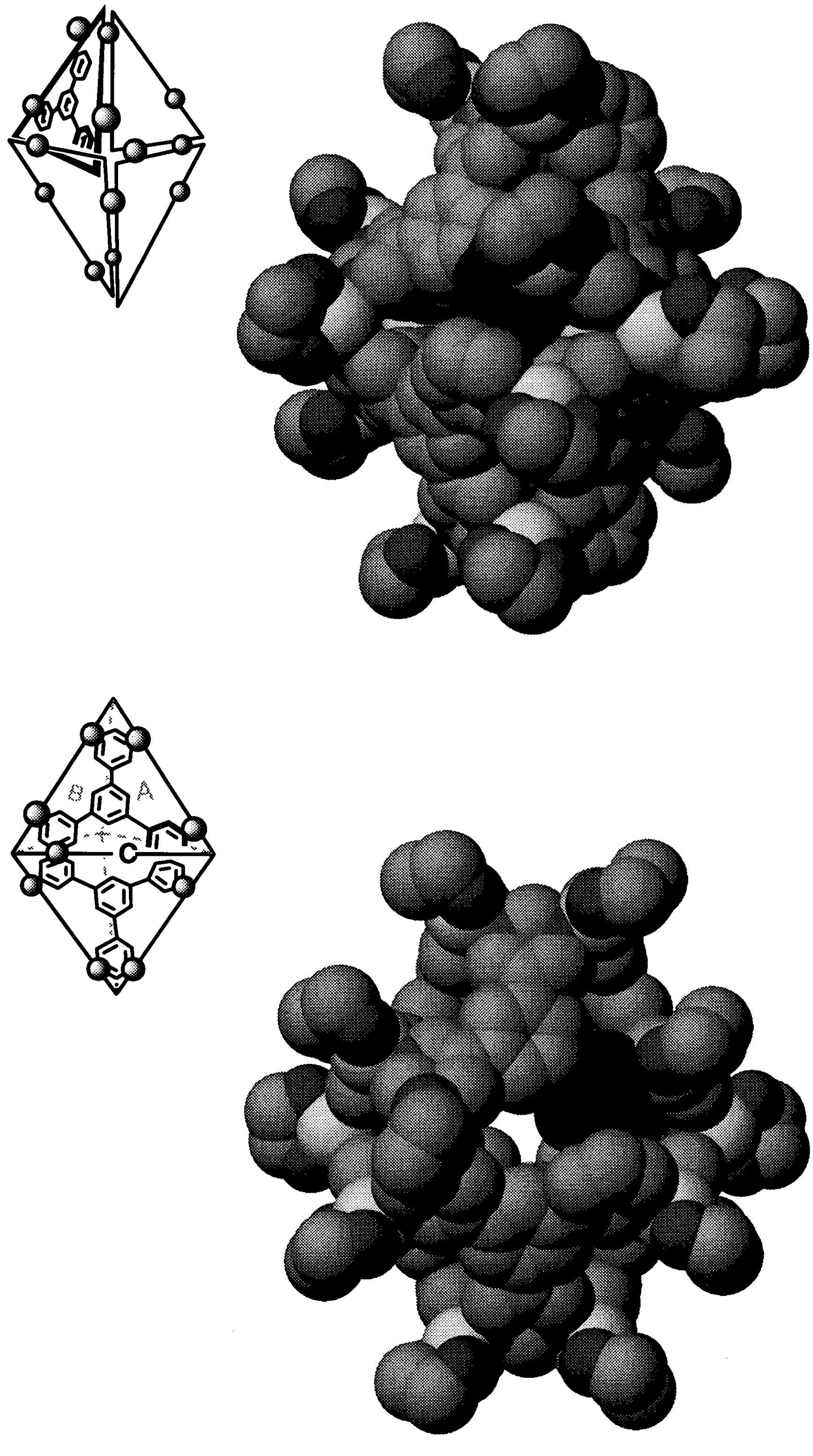


Figure 4. Crystal structure of **3'**. (a) a view from an equatorial direction. (b) a view from the back direction.

to exchange the guest molecules (Figure 3c). Furthermore, the crystal structure of **3** is particularly interesting, for they exist in two structurally isomeric forms (Figure 4). That is, one is usual hexahedron **3**, and another is a distorted hexahedron **3'**. The two structures are different in the non-binding site at the equatorial corner. Thus, 3-py rings located in equatorial corner of **3'** get in hexahedron frameworks (Figure 4 dark indication). In solution, the accommodation of 3-py ring in the hexahedron frameworks was strongly suggested by the outstanding up-field shift of signal (6.2 ppm of *H*c" of ligand **1–C** as shown in Figure 1) in D_2O. Since its NMR shows equilibration **3** $\rightleftarrows$ **3'**.

3.2.3 Guest Inclusion by the $M_{15}L_6$ Hexahedron capsule

He observed the remarkable ability of **3** to encapsulate small guest molecules such as CBr_4. The encapsulation of guest molecules was observed by the addition of solid CBr_4 to D_2O solution of **3**, **3•G** was supported by the significant change of signals in aromatic region (Figure 5). The **3•G** hexahedron showed 39 proton signals in an aromatic region which were analyzed by various 2D NMR, and consequently, the framework was identified as hexahedron. Moreover, the entrapped CBr_4 was observed at –26.9 ppm in ^{13}C NMR. The host-guest ratio was estimated to be 1 : 2 by ^{13}C NMR spectroscopy with " Inverse Gated ^1H–Decoupling Method ".[9] The encapsulation of guest molecules was also observed with similar small guests such as CH_2Br_2 and $CHCl_3$.

The template effect of guest molecules in the formation of capsule **3** was studied by taking **1**, **2** and guest molecule (small or large) in D_2O. It is observed that only small guest molecules can be accommodated in **3**. In short, the guest molecules did not show any template effect for the assembly of **3**.

Particularly interesting is that the application of controlling the encapsulation/release of guest molecules. The encapsulated guest escaped from the cavity of **3** offer adding EtOH to the **3•G** solution. This result clearly showed that the interior of **3** has a hydrophobic cavity with properties that are quite different from those of the bulk phase.

Reversible conversion between **3** and **3•G** is achieved by the change of environments, adding of an excess amount of CBr_4 or EtOH.

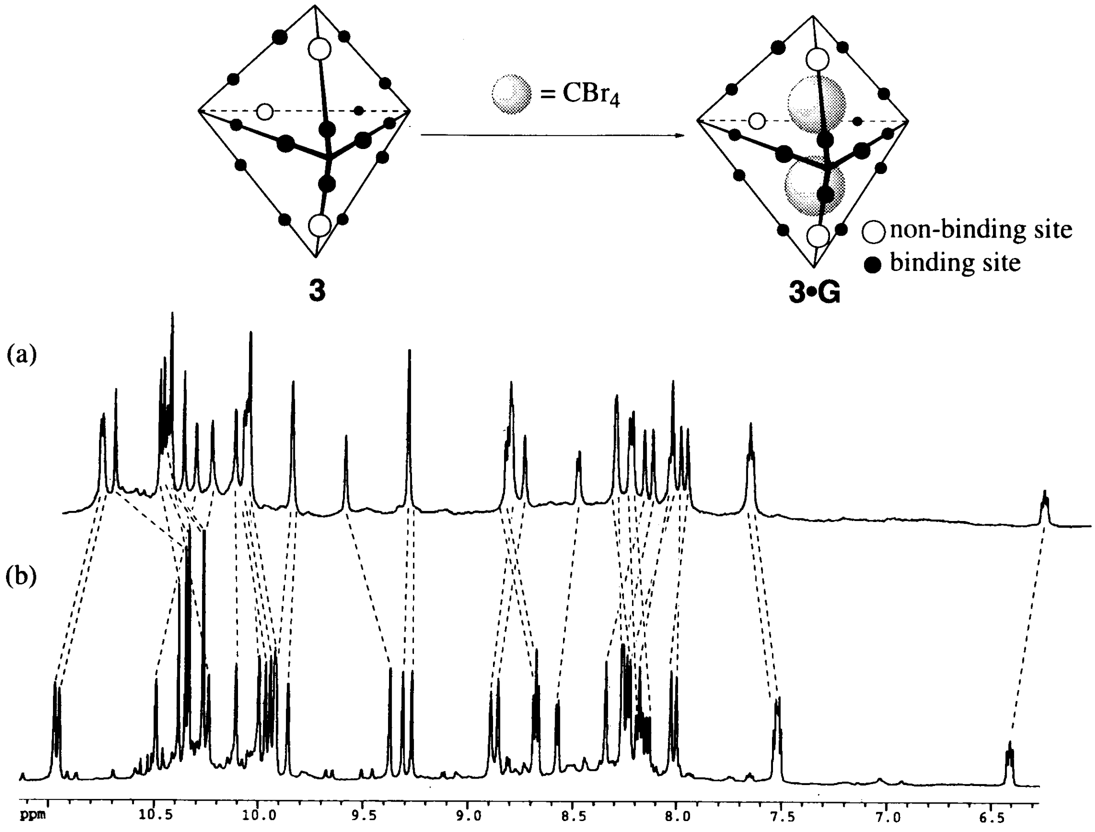


Figure 5. The ^{1}H NMR observation of the capsule (500 MHz, D_2O, TMS as a external standard). (a) The complex **3** assembled from **1** and **2**. (b) The complex **3•G** assembled upon the addition of an excess amount of CBr_4 (suspended).

3.3 Conclusion

The triangular panel-like ligand with five donor sites upon the reaction with **2** lead to the formation of a coordination capsule which possesses the entrance/exit for guest molecules. The present results fulfil the drawback in the previous hexahedron capsule, described in Chapter 2, which has closed shell structure and could not be encapsulate/exchange guest moleules. In addition to encapsulation, the hexahedron capsule proved to release the accommodated guests with the addition of EtOH. Moreover, the present report demonstrated that the coordination chemistry can be used for the formation of nanometer-sized molecular containers.

3.4 Experimental Section

3,5-Dibromo-1-(3-pyridyl)benzene. The cross coupling reaction of 1,3,5-tribromobenzene (40.0 mmol, 12.6 g) with 3-pyridylboronic acid pinacol ester (15.0 mmol, 3.08 g) using catalytic amount of $Pd(PPh_3)_4$ (0.75 mmol, 0.867 g) in the presence of K_3PO_4 (45.0 mmol, 9.55 g) was carried out in refluxing dioxane (120 mL) for 48 h. The reaction solution was quenched by H_2O (100 mL) and extracted with $CHCl_3$. After the organic layer was dried over Na_2SO_4, filtered, and condensed in vacuo, followed by the purification of the crude mixture by silica gel column chromatography (AcOEt : Hexane = 1 : 4) gave desired 3,5-dibromo-1-(3-pyridyl)benzene as a colorless solid (4.07 g; 13.0 mmol) in 87% yield. Mp 77.8–78.9 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.38 (dd, J = 4.8, 7.8 Hz, 1H), 7.65 (s, 2H), 7.71 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 8.65 (d, J = 4.8 Hz, 1H), 8.79 (s, 1H). ^{13}C NMR (74.8 MHz, $CDCl_3$, 25 °C) δ 123.6, 123.7, 129.0, 133.5, 134.0, 134.4, 141.4, 148.1, 149.6. IR (KBr) 3047, 1573, 1420, 1388, 1024, 852, 805 cm^{-1}. MS (EI) *m/z* 311 (M^+). Anal. Calcd for $C_{11}H_7NBr_2$: C, 42.24; H, 2.25; N, 4.48. Found: C, 42.21; H, 2.24; N, 4.32.

1-(3-pyridyl)-3,5-bis(3,5-pyrimidyl)benzene (1). A mixture of 3,5-pyrimidylboronic acid pinacol ester (2.64 g; 12.8 mmol), 3,5-dibromo-1-(3-

pyridyl)benzene (1.0 g; 3.20 mmol), and $Pd(PPh_3)_4$ (0.37 g; 0.32 mmol in the presence of K_3PO_4 (2.72 g; 12.8 mmol) was carried out in refluxing dioxane (80 mL) for 48 h. The gray suspension was filtered and the precipitates was washed with hexane and ethyl acetate. The gray solids was dissolved with 5 M HCl (5.0 mL) and the small amount of insoluble product was removed by filtration. Acetone (50 mL) was added to the solution, and the resulting white precipitate was filtred and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave **1** (0.836 g; 2.68 mmol) as a white solid in 84% yield. Mp 319–320 °C. ^{1}H NMR (300 MHz, DMSO, 25 °C) δ 7.55 (dd, *J* = 4.8, 8.1 Hz, 1H), 8.28 (s, 2H), 8.32 (s, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.64 (d, *J* = 4.8 Hz, 1H), 9.18 (s, 1H), 9.25 (s, 2H), 9.42 (s, 4H). ^{13}C NMR (125 MHz, DMSO, 25 °C) δ 125.3, 127.4, 134.3, 136.3, 136.3, 137.4, 140.9, 149.9, 150.6, 156.79, 156.83, 159.2. IR (KBr) 3435, 1560, 1416, 1395, 885, 723, 634 cm^{-1}. MS (DI) *m/z* 311 (M$^+$). Anal. Calcd for $C_{19}H_{13}N_5 \bullet 0.4DMSO$: C, 69.42; H, 4.53; N, 20.44. Found: C, 69.51; H, 4.49; N, 20.74.

Synthesis and physical properties of 3 complex. Ligand **1** (7.9 mg; 0.025 mmol) was suspended in an aqueous solution (0.7 mL) of **2** (20.3 mg; 0.07 mmol) and it was stirred for 24 h at room temperature. The complex **3**was isolated as a colorless precipitate (22.1 mg; 0.0035 mmol) in 83% yield by adding large amount of EtOH. Mp ~240 °C (decomposed). ^{1}H NMR (500 MHz, D_2O, 25 °C) δ 2.90–3.15 (m, 30H), 6.24 (dd, *J*=5.3, 6.1 Hz, 1H), 7.65 (dd, *J*=5.3, 6.1 Hz, 2H), 7.95 (s, 1H), 7.98 (s, 1H), 8.02 (s, 1H), 8.03 (d, *J* = 6.1 Hz, 1H), 8.12 (s, 1H), 8.16 (s, 1H), 8.22 (d, *J* = 6.1 Hz, 2H), 8.30 (s, 2H), 8.48 (d, *J* = 5.3 Hz, 1H), 8.73 (s, 1H), 8.80 (s, 1H), 8.81 (d, *J* = 5.3 Hz, 2H), 9.29 (s, 2H), 9.59 (s, 1H), 9.85 (s, 2H), 10.05 (s, 2H), 10.06 (s, 1H), 10.07 (s, 1H), 10.12 (s, 1H), 10.23 (s, 1H), 10.31 (s, 1H), 10.37 (s, 1H), 10.43 (s, 2H), 10.45 (s, 1H), 10.46 (s, 1H), 10.48 (s, 1H), 10.69 (s, 1H), 10.75 (s, 1H), 10.76 (s, 1H); ^{13}C NMR (125 MHz, D_2O, 25 °C) δ 47.4 (CH), 47.6 (CH), 47.7 (CH), 124.6 (CH), 125.0 (CH), 125.5 (CH), 126.3 (CH), 126.6 (CH), 127.0 (CH), 127.1 (CH),127.9 (CH), 128.0 (CH), 128.4 (CH), 128.8 (CH), 129.2 (CH), 130.5 (Cq), 131.1 (Cq), 131.6 (Cq), 131.7 (Cq), 131.9 (Cq), 132.3 (Cq), 134.8 (Cq), 135.0 (Cq), 135.2 (Cq), 135.3 (Cq), 136.0 (Cq), 136.8 (Cq), 136.9 (Cq), 137.3 (Cq), 137.4 (Cq), 137.6 (Cq), 137.7 (Cq), 137.9 (Cq), 138.5 (CH), 138.6 (CH), 139.0 (CH), 149.4 (CH × 2), 149.6 (CH), 150.7 (CH), 150.8 (CH × 2), 158.5 (CH), 158.7 (CH), 158.8 (CH), 158.9-159.0 (CH × 4), 159.8-160.3 (CH × 9), 160.6 (CH), 160.9 (CH); IR (KBr) 3480, 3210, 3100, 1610, 1431, 1380, 1080, 840, 725 cm^{-1}. Anal. Calcd for $C_{144}H_{198}N_{90}O_{90}Pd_{15}{\bullet}25H_2O$: C, 25.91; H, 3.74; N, 18.88. Found: C, 25.93; H, 3.81; N, 18.94.

X-ray structural analysis of 3. The single crystal was obtained by the slow diffusion of methanol into an aqueous solution of **3** at 20 °C for 7 d. A single crystal of **3** (0.20 × 0.15 × 0.15 mm^3) was mounted on a glass fibre. All measurements were made on a charge coupled device (CCD) plate area detector with graphite monochromated Mo-Kα radiation. The data were collected at 173(2) K. Crystal data for **3**: formula $C_{144}H_{198}N_{90}O_{90}Pd_{15}{\bullet}57.5H_2O{\bullet}1.5MeOH$, M=7309.91, triclinic, space group $P\bar{1}$, a = 26.503(3), b = 30.887(3), c = 35.743(4) Å, V = 29086(6) $Å^3$, $\rho_{calcd.}$ = 1.669 mg/m^3, Z = 4, F(000) = 14816, μ(Mo-Kα) = 1.016 mm^{-1}, λ(Mo-Kα) = 0.71073 Å; 189592 reflections measured, 131409 observed ($I>2\sigma(I)$); number of variables 6859; R_1 = 0.0867; wR_2 = 0.2189. Crystallographic data (excluding structure factors) for **3** has been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC –159454. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email:deposit@ccdc.cam. ac. uk).

Synthesis and physical properties of 3•G complex. Ligand **1** (7.9 mg; 0.025 mmol) was suspended in an aqueous solution (0.7 mL) of **2** (20.3 mg; 0.07 mmol). Then, CBr_4(10 equiv., suspended) was added and the solution was stirred for 24 h at room temperature. The complex **3•G** was measured with NMR. ^{1}H NMR (500 MHz, D_2O, 25

°C) δ 2.90–3.15 (m, 30H), 6.41 (dd, *J* = 5.6, 8.1 Hz, 1H), 7.52 (dd, *J* = 5.6, 8.1 Hz, 2H), 8.00 (s, 1H), 8.03 (s, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 8.23 (s, 1H), 8.24 (s, 1H), 8.26 (s, 1H), 8.27 (s, 1H), 8.34 (s, 1H), 8.58 (d, *J* = 5.6 Hz, 1H), 8.67 (d, *J* = 5.6 Hz, 1H), 8.68 (d, *J* = 5.6 Hz, 1H), 8.86 (s, 1H), 8.89 (s, 1H), 9.23 (s, 1H), 9.31 (s, 1H), 9.37 (s, 1H), 9.86 (s, 1H), 9.92 (s, 1H), 9.93 (s, 1H), 9.94 (s, 1H), 9.97 (s, 1H), 10.00 (s, 1H), 10.11 (s, 1H), 10.24 (s, 1H), 10.27 (s, 3H), 10.33 (s, 1H), 10.34 (s, 1H), 10.35 (s, 1H), 10.39 (s, 1H), 10.49 (s, 1H), 10.95 (s, 1H), 10.97 (s, 1H); ^{13}C NMR (125 MHz, D_2O, 25 °C) δ –27.2 (CBr_4), 47.3 (CH), 47.5 (CH), 47.8 (CH), 123.8 (CH), 125.5 (CH), 126.3 (CH), 126.8 (CH), 127.1 (CH), 127.2 (CH), 127.3 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH × 2), 128.9 (CH), 130.6 (Cq), 131.4 (Cq), 132.2 (Cq), 132.3 (Cq), 132.4 (Cq), 132.9 (Cq), 134.4 (Cq), 134.5 (Cq), 134.6 (Cq), 135.0 (Cq), 136.0 (Cq), 136.2 (Cq), 137.3 (Cq), 137.5 (Cq), 137.7 (Cq), 137.8 (Cq), 138.0 (Cq), 138.3 (Cq), 138.8 (CH), 138.9 (CH), 139.1 (CH), 147.7 (CH), 148.9 (CH × 2), 151.1 (CH), 151.3 (CH × 2), 152.0 (CH), 157.3 (CH), 157.4 (CH), 158.1 (CH), 158.5 (CH), 158.7 (CH), 158.8 (CH), 159.1 (CH), 159.3 (CH), 159.9 (CH), 160.1 (CH × 2), 160.3 (CH × 3), 160.7 (CH), 160.9 (CH), 162.0 (CH).

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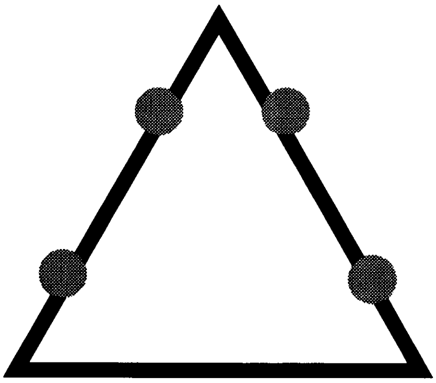
Chapter 4



Guest-Controlled Assembly of Open Cone and Tetrahedron Structures from Eight Metals and Four Ligands

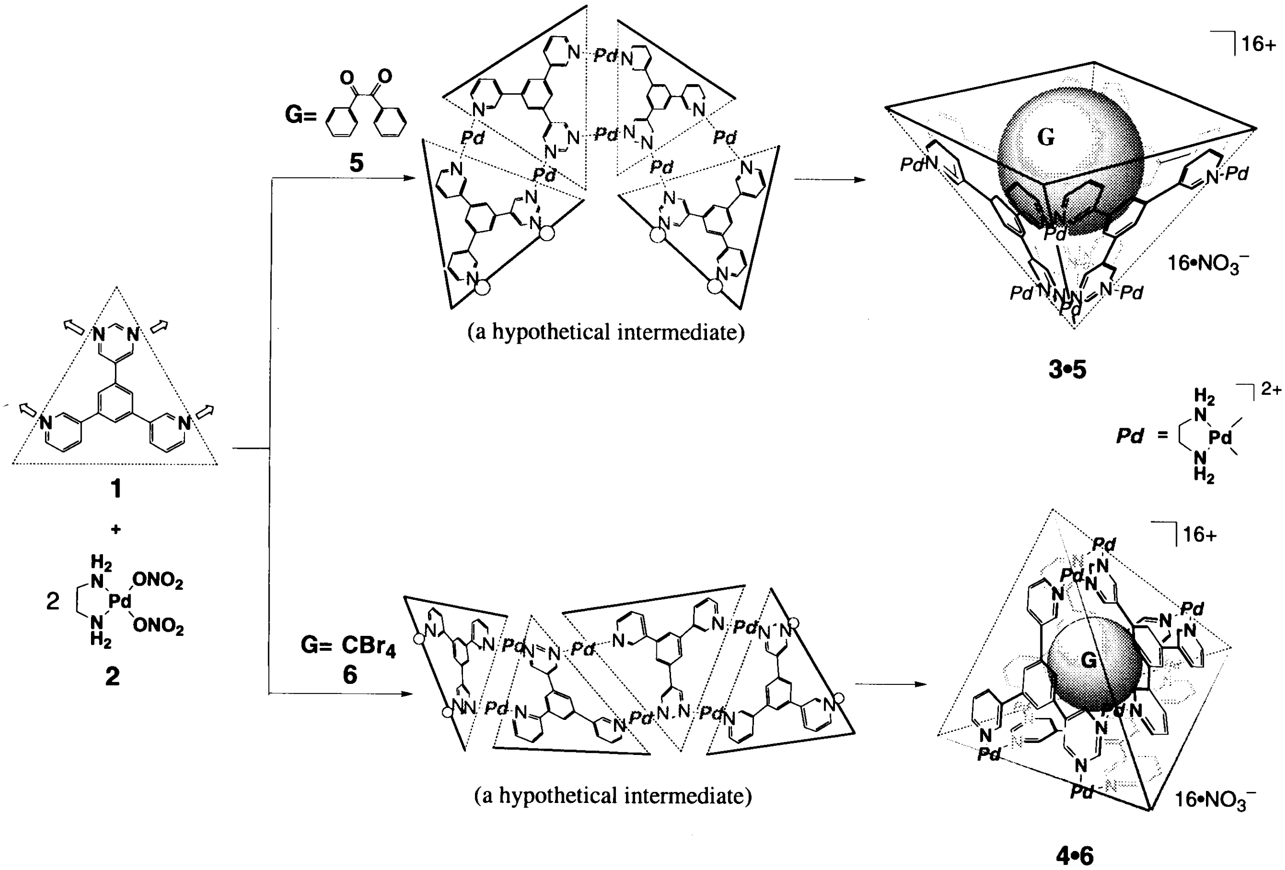
J. Am. Chem. Soc. **2000**, *122*, 7150.

Abstract: A planar and triangular ligand, 1-(3,5-pyrimidyl)-3,5-bis(3-pyridyl)benzene, which possesses four donor sites on the two edges of the triangle, is linked by a 90-degree coordination unit, (en)Pd(NO_3)$_2$, in two ways: parallel and antiparallel fashions. The parallel link is induced by some large guest molecules to give an open cone (tetragonal pyramidal) structure. On the other hand, antiparallel link is selected by some small tetrahedral guests giving closed tetrahedron structure. Both structures have M_8L_4 composition and are confirmed by ESI-MS or X-ray analysis.

4.1 Introduction

It was shown in the previous chapters that by linking triangles at their corners or edges, a family of polyhedral structures can in principle be engaged at will.[1-4] For instance, hexadentate ligand or pentadentate ligand assembled into two types of hexahedron as shown in Chapters 2 and 3. Here, he designs a triangular panel-like ligand with four donor sites on the two edges of the triangle (two donor sites on each edge): namely, compound **1** in Scheme 1. Having two-point binding sites on its two edges, this triangular unit is expected to assemble into edge-sharing polyhedral entity upon complexation with (en)Pd(NO_3)$_2$ (**2**), which is a versatile 90-degree coordination unit for metal-directed assembly. The triangular ligands which are designed in the previous chapters can be linked in only one way, whereas **1** due to its C_2-symmetry can be linked in two different ways: parallel and antiparallel. Interestingly, these two options are perfectly controlled by the guests, like dibenzoyl or CBr_4.[5] That is some large guests induces the parallel link of the triangles leading to open cone (tetragonal pyramidal) structure **3** whereas antiparallel link is selected by some small tetrahedral guests giving closed tetrahedron structure **4** (Scheme 1). Both assemblies have the same M_8L_4 composition and therefore, constitute a dynamic receptor library[5–7] from which each receptor is selected by its optimal guests.

Scheme 1.



4.2 Result and Discussion

4.2.1 Guest-Selected Formation of an Open Cone Structure

The quantitative assembly of M_8L_4 open cone **3** was induced by large guest molecules such as dibenzoyl (**5**). Thus, ligand **1** (0.025 mmol) and guest **5** (0.25 mmol) were suspended in the aqueous solution (2.5 mL) of **2** (0.05 mmol). After the mixture was stirred for 24 h at ambient temperature, excess **5** was filtered off and the resulting solution was analyzed by NMR and ESI-MS, which clearly evidenced the formation of open cone **3** accommodating one molecule of **5**. In ESI-MS, major peaks were assigned as $[\mathbf{3}\bullet(\mathbf{5})_m\bullet(NO_3)_{16-n}]^{n+}$ $m = 0$–2, $n = 3,4$],[8] excluding the possibility of other cone structures (e.g., M_6L_3 and $M_{10}L_5$ types, etc.). NMR displayed eight proton signals, which stems from ligand **1** located on a C_2-symmetric environment, in good agreement with the structure of **3**. The accommodation of **5** in the cone-shaped cavity of **3** was strongly suggested by the outstanding up-field shifts of signals of **5** in D_2O. The host-guest ratio was estimated to be 1:1 by NMR integration ratio. After the aqueous solution was allowed to stand at room temperature for one week, a colorless precipitate was obtained, which was washed with small portions of water and dried in vacuo to give **3•5** complex in 78% yield. The same 1:1 complexes were also obtained with other bulky guests such as 1,2-diphenyl-1,2-ethanediol and 1,1′-ferrocenedicarboxylic acid.

4.2.2 Guest-Selected Formation of a Tetrahedron Structure

The combination of components **1** and **2** enjoys another way of molecular paneling: the antiparallel link of adjacent ligands leading to tetrahedral coordination assembly **4** (Scheme 1). This was achieved in an efficient fashion by using small template molecule such as CBr_4 (**6**). Thus, the reaction of **1** (0.048 mmol) and **2** (0.106 mmol) in the presence of **6** (10 equiv., suspended) in D_2O (5.0 mL) resulted in the selective formation of **4•6** complex (Figure 1). Obviously, **6** templated the assembly of **4** and was efficiently entrapped within the framework of **4**. In fact, the entrapped **6** was observed at –26.9 ppm in ^{13}C NMR when ^{13}C-enriched **6** was employed. The antiparallel link of the ligands in **4** was strongly supported by the observation of NOE between the adjacent ligands, which was not observed in **3**. The complex was isolated as a colorless precipitate in 93% yield by adding large amount of EtOH and the **4•6** stoichiometry was confirmed by elemental analysis. The selective formation of tetrahedron **4** was also observed with similar small guests such as $CHCl_3$ and $CBrCl_3$.

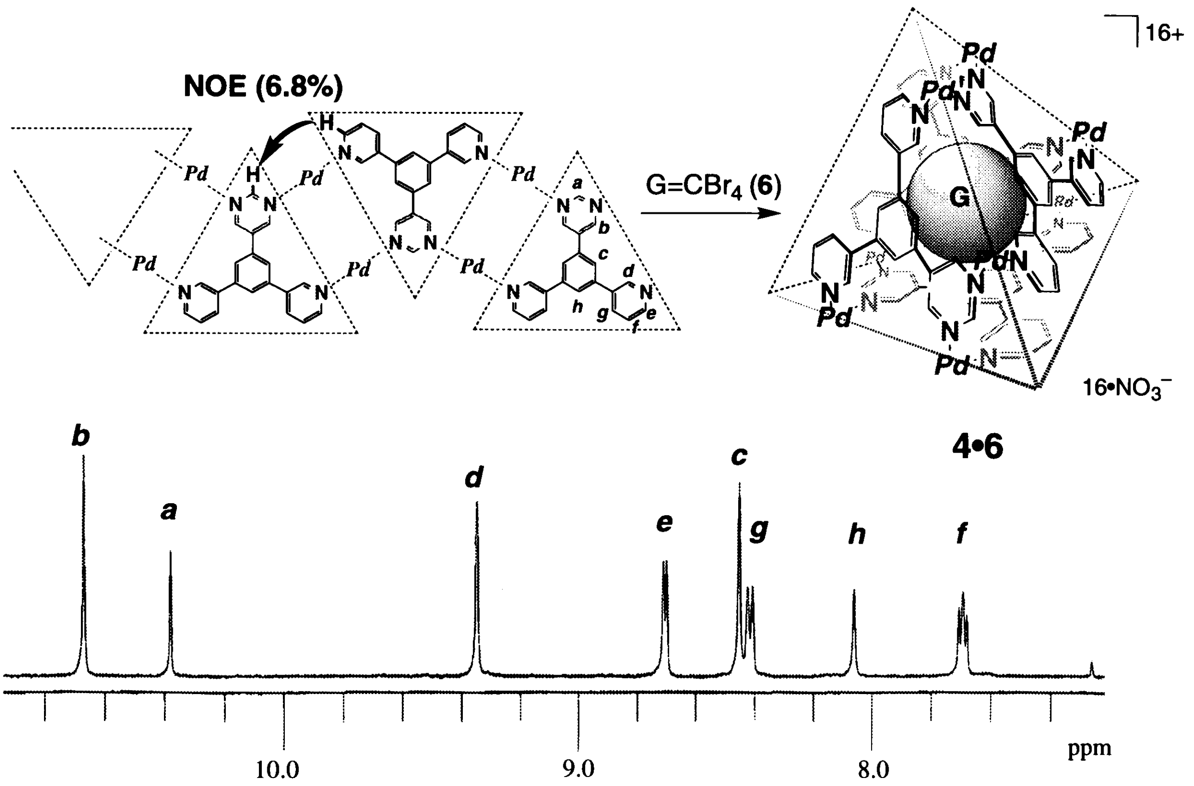


Figure 1. Schematic representation of the antiparallel link of the triangles leading to tetrahedron and ^{1}H NMR spectrum of **4•6** (500 MHz, D_2O, 25 °C, TMS as an external standard).

4.2.3 X-ray Crystallographic Analysis of a Tetrahedron Structure

The structure of **4•6** complex was also determined by an X-ray crystallographic analysis (Figure 2). The single crystals were obtained by standing the aqueous solution of **4•6** at ambient temperature for 3 days. As expected, the crystal structure of **4•6** displayed the antiparallel junction of ligands. The whole tetrahedral structure is somewhat distorted in such a way that efficient host-guest interaction and aromatic contact between the ligands are gained. As a result, the 12-component assembly makes a closed shell framework in which the guest molecule is completely insulated (Figure 2, bottom). The structure is roughly spherical with a diameter of 11 Å and the internal volume of tetrahedral capsule **4** is approximately 300 Å^3. The longest Pd–Pd distance is 15.4 Å.

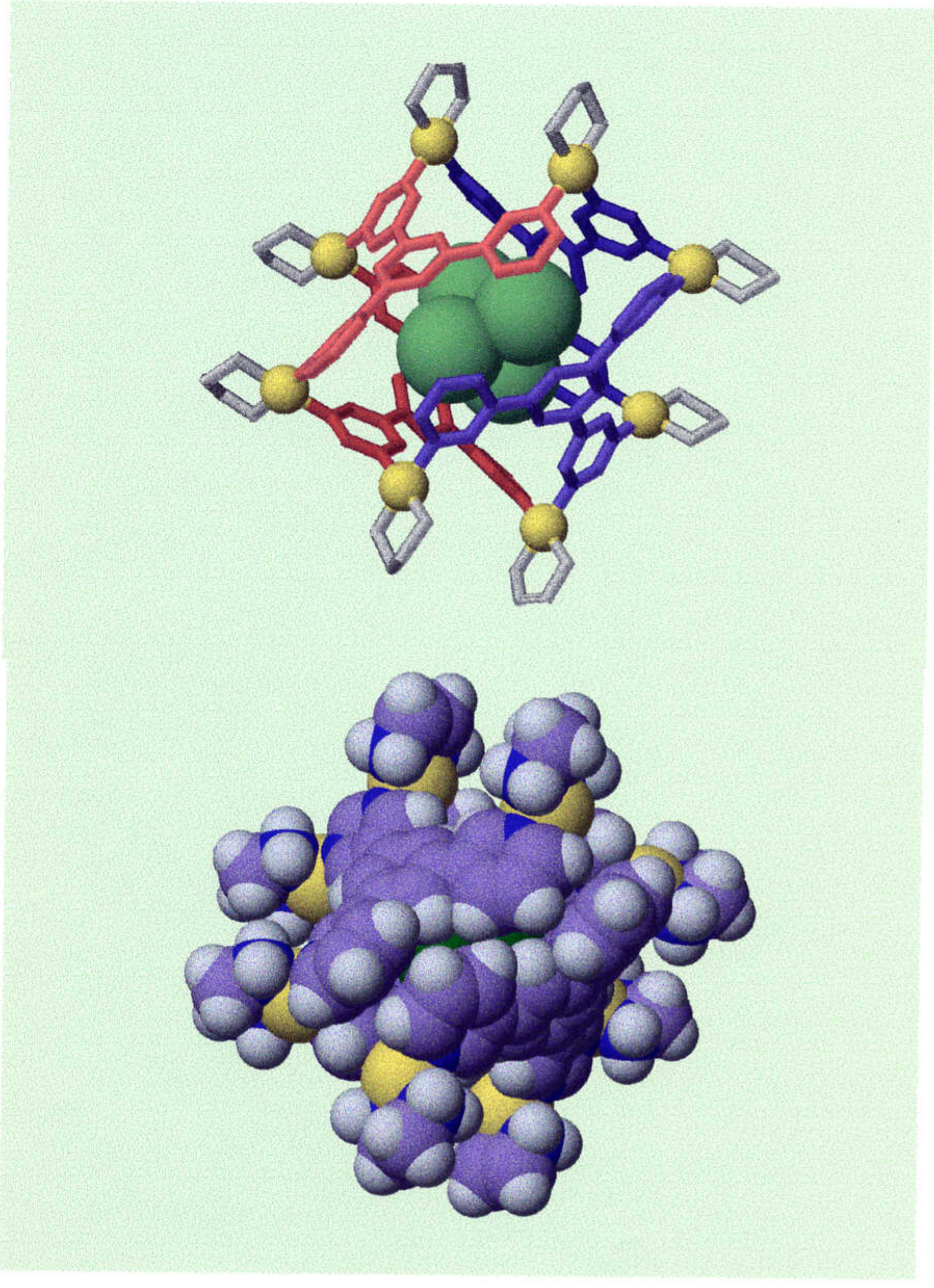


Figure 2. Crystal structure of **4•6**. Top: ball and cylindrical representation; bottom: Space-filling representation.

4.2.4 Dynamic Receptor Library

In the absence of guests at 25 mM concentration, **1** and **2** were assembled into a 3:2 mixture of two components, and the minor component was identified as **3** (Figure 3). The proportion of the major component increased at lower concentrations, indicating that this component is composed of fewer components than **3**. Since its NMR is qualitatively the same to that of **3**, the major component was assigned as trimeric cone **7**. Thus, the equilibrium **3**•**3** ⇄ **4**•**7** shifts towards the right side at low concentrations. ^{1}H NMR from the mixture of **3** and **7** is in good agreement with this phenomenon.

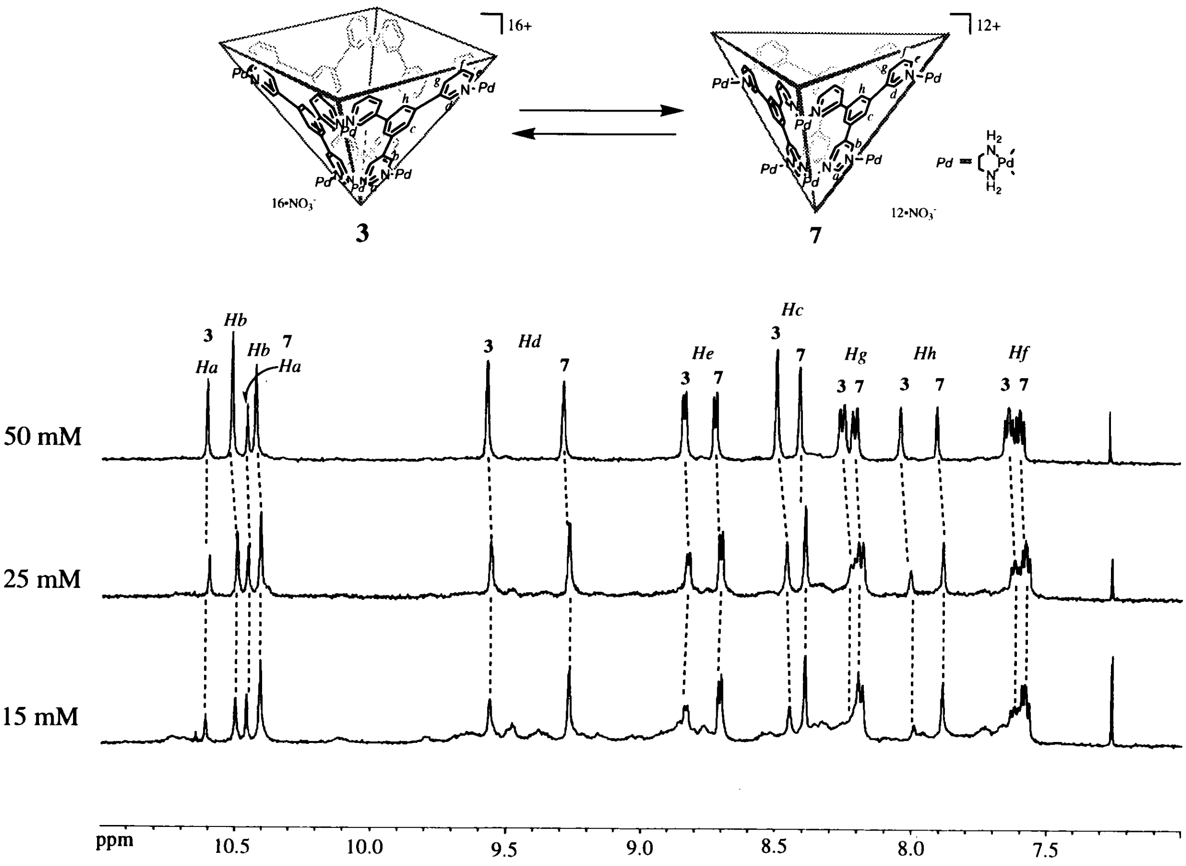


Figure 3. Monitoring the effect of concentration on **3** and **7**.

Being generated under thermodynamic control, three components **3**, **4**, and **7** are interconvertable by guest addition or exchange *via* remarkably effective reorganization processes. For example, trimeric cone **7** (in the mixture of **3** and **7**) was converted upon the addition guest such as **5** to tetrameric cone **3** within 24 h (Experimental Section). Molecular modeling predicted that the cavity of **7** was too small to host **5**. Thus, only **3** is stabilized by host-guest interaction. In a similar way, the addition of **6** to the mixture of **3** and **7** resulted in the disappearance of both components and reorganization into **4•6** complex within a day (Experimental Section). More interestingly, once assembled open cone **3•5** was transformed into **4•6** complex upon the addition of excess amount of **6** *via* guest exchange. During the reorganization process, initially accommodated guest **5** was kicked out from the cavity of **3** as monitored by disappearance of the guest signals in ^{1}H NMR (Figure 4).

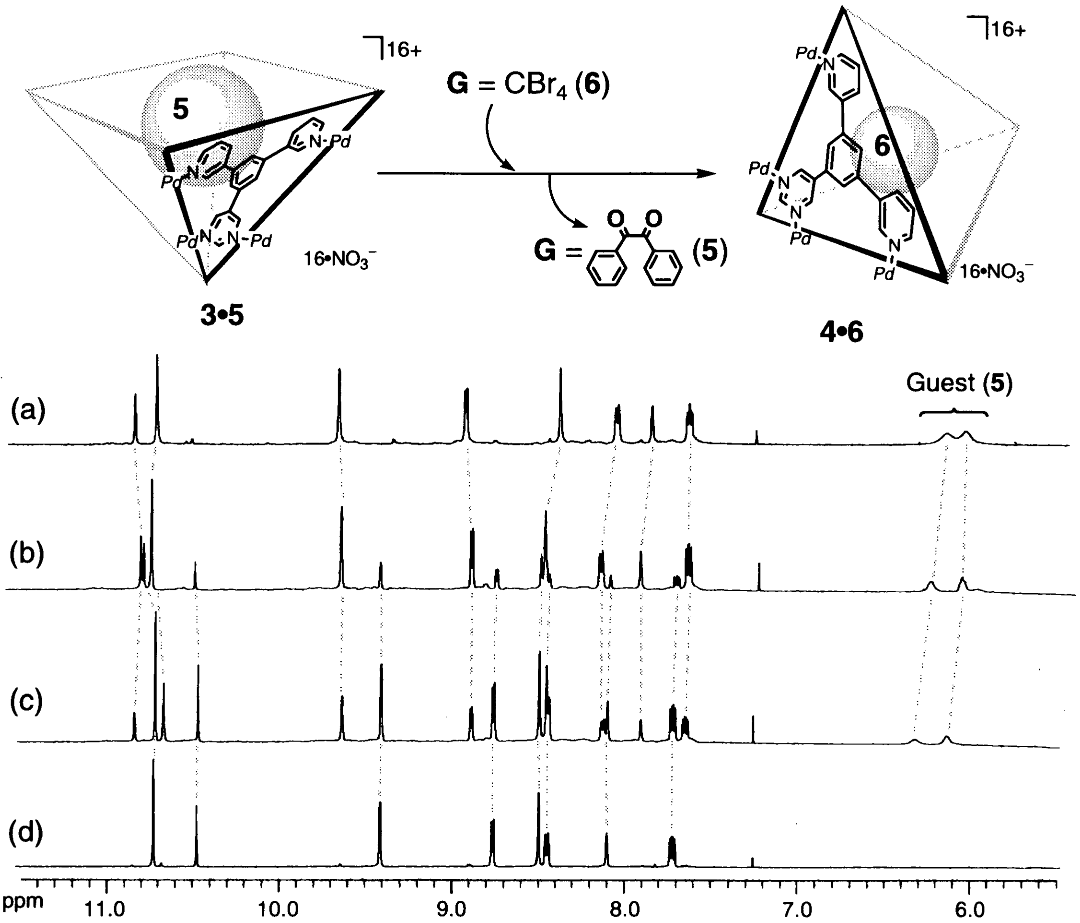
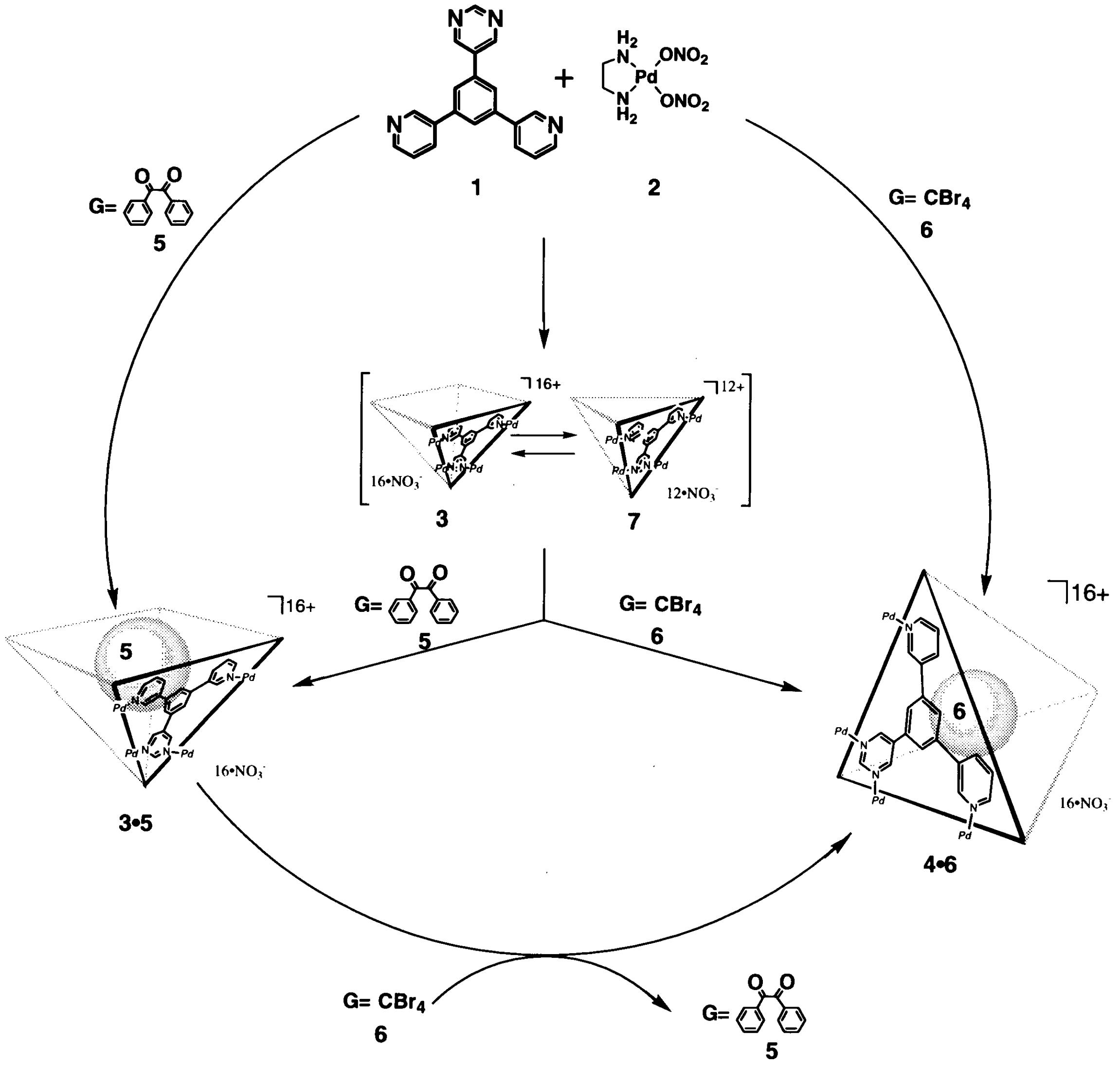


Figure 4. The ^{1}H NMR monitoring of recognition process from **3•5** to **4•6** *via* guest exchange. (a) **3•5** complex in D_2O; (b)–(d) After the addition of excess amount of **6** at 25 °C ((b) 3 h, (c) 8 h, (d) 24 h).

4.3 Conclusion

It was shown that molecular paneling can be applied to "*dynamic receptor library*". By taking advantage of suitably designing molecular panels it can be controlled the guest induced formation of the optimal rigid receptor structure from an equilibrium mixture of receptors. The host frameworks were organized so that maximum hydrophobic interaction can be gained. Therefore, large guest selected host **3**, whereas small guests preferred host **4**. The guest selective assembly and guest exchange formation process of the "*molecular paneling*" suggests that it possesses potential abilities for application to not only separation of materials but also phase transfer catalysis for specific chemical transformations.



4.4 Experimental Section

General:

Preparation of 3,5-Dibromo-1-(3,5-pyrimidyl)benzene. To a toluene solution (140 mL) of 1,3,5-tribromobenzene (19.4 g; 61.8 mmol), 5-trimethylstannyl-1,3-pyrimidine (5.0 g; 20.6 mmol), $PdCl_2(PPh_3)_2$ (0.72 g; 1.0 mmol) and LiCl (4.4 g; 103 mmol) were added at room temperature and then the reaction mixture was refluxed for 12 h. The reaction solution was quenched by H_2O (100 mL) and extracted with $CHCl_3$. After the organic layer was dried over Na_2SO_4, filtered, and condensed in vacuo, followed by the purification of the crude mixture by silica gel column chromatography (AcOEt:Hexane=7:1) gave desired 3,5-dibromo-1-(3,5-pyrimidyl)benzene as a colorless solid (2.6 g; 8.4 mmol) in 41% yield. Mp 165–166 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.66 (d, J = 1.75 Hz, 2H), 7.78 (t, J = 3.4 Hz, 1H), 8.91 (s, 2H), 9.26 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 124.0 (CH), 128.8 (CH), 131.9 (Cq), 134.5 (CH), 137.8 (Cq), 154.9 (CH), 158.4 (CH). IR (KBr) 3053, 3026, 1564, 1406, 1186, 858, 744 cm^{-1}. MS (EI) *m/z* 314 (M^+). Anal. Calcd for $C_{10}H_6N_2Br_2$: C, 38.25; H, 1.93; N, 8.92. Found: C, 38.20; H, 1.75; N, 8.91.

Preparation of 1-(3,5-pyrimidyl)-3,5-bis(3-pyridyl)benzene (1). A mixture of trimethyl(3-pyridyl)tin (2.5 g; 6.7 mmol), 3,5-dibromo-1-(3,5-pyrimidyl)benzene (0.7 g; 2.23 mmol), and $PdCl_2(PPh_3)_2$ (0.16 g; 0.223 mmol) in toluene was refluxed for 24 h. The gray suspension was filtered and the precipitates were washed with hexane and ethyl acetate. The grey solid as dissolved with 5 M HCl (5.0 mL) and the small amount of insoluble solid was removed by filtration. Acetone (50 mL) was added to the solution, and the resulting white precipitate were filtered and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave **1** (0.37 g; 1.2 mmol) as a gray solid in 53% yield. Mp 269–270 °C. ^1H NMR (500 MHz, DMSO, 25 °C) δ 8.17 (dd, J = 5.4, 8.1 Hz, 2H), 8.55 (s, 2H), 8.56 (s, 1H), 8.99 (d, J = 5.4 Hz, 2H), 9.13 (d, J = 8.1 Hz, 2H), 9.34 (s, 1H), 9.54 (s, 2H), 9.62 (s, 2H). ^{13}C NMR (125 MHz, DMSO, 25 °C) δ 126.5, 126.7, 126.8, 132.2, 136.0, 136.4, 137.1, 141.9, 142.1, 142.7, 155.4, 157.9. IR (KBr) 3418, 3034, 1560, 1418, 1194, 1026 cm^{-1}. MS (DI) *m/z* 310 (M^+). Anal. Calcd for $C_{20}H_{14}N_4 \bullet H_2O$: C, 73.15; H, 4.91; N, 17.06. Found: C, 73.31; H, 4.54; N, 16.74.

Synthesis and physical properties of 3•5 complex. Ligand **1** (7.7 mg; 0.025 mmol) and guest **5** (53 mg; 0.25 mmol) were suspended in the aqueous solution (2.5 mL) of **2** (15.9 mg; 0.05mmol). After the mixture was stirred for 24 h at ambient temperature, excess **5** was filtered off and the resulting solution was allowed to stand at room temperature. After 7 days, white powder was obtained and washed with a small amount of H_2O and drying in vacuo gave **3•5** (18 mg) in 78% yield. Mp ~238 °C (decomposed). ^1H NMR (500 MHz, D_2O, 25 °C) δ 2.7–3.1 (m, 32H), 5.99–6.20 (m, 3H), 7.59 (dd, *J* = 5.7, 7.9 Hz, 2H), 7.80 (s, 2H), 8.00 (d, *J* = 7.9 Hz, 2H), 8.33 (s, 2H), 8.86 (d, *J* = 5.7 Hz, 2H), 9.58 (s, 2H), 10.61 (s, 2H), 10.73 (s, 1H). ^{13}C NMR (125 MHz, D_2O, 25 °C) δ 46.8 (CH), 47.3 (CH), 47.8 (CH), 49.0 (CH), 125.5 (CH), 126.8 (CH), 127.2 (CH), 127.6 (CH), 128.2 (CH), 128.5 (CH), 131.0 (Cq), 133.8 (CH), 135.6 (Cq), 137.2 (Cq), 137.2 (Cq), 138.3 (CH), 149.8 (CH), 150.6 (CH), 159.2 (CH), 160.6 (CH). IR (KBr) 3063, 2956, 1763, 1594, 1373, 1059 cm^{-1}. Anal. Calcd for $C_{110}H_{130}N_{48}O_{50}Pd_8 \bullet 15H_2O$: C, 32.65; H, 3.99; N, 16.62. Found: C, 32.26; H, 3.70; N, 16.27.

Synthesis and physical properties of 4•6 complex. Ligand **1** (15.0 mg; 0.048 mmol) was suspended in an aqueous solution (5.0mL) of **2** (30.9 mg; 0.106 mmol). Then, **6** (10 equiv., suspended) was added and the solution was stirred for 24 h at room temperature. The **4•6** complex was isolated as a colorless precipitate (43 mg; 0.011 mmol) in 93% yield by adding large amount of EtOH. Mp ~213 °C (decomposed). ^1H NMR (500 MHz, D_2O, 25 °C) δ 2.98–3.01 (m, 16H), 3.03–3.07 (m, 16H), 7.71 (dd, *J* = 5.7, 7.9 Hz, 2H), 8.09 (s, 1H), 8.43 (d, *J* = 7.9 Hz, 2H), 8.48 (s, 2H), 8.73 (d, *J* = 5.7 Hz, 2H), 9.37 (s, 2H), 10.40 (s, 1H), 10.70 (s, 2H). ^{13}C NMR (125 MHz, D_2O, 25 °C) δ –26.9 (CBr_4), 47.6 (CH), 47.8 (CH), 47.9 (CH), 127.0 (CH), 127.6 (CH), 128.3 (CH), 132.1 (Cq), 136.8 (Cq), 137.6 (Cq), 138.0 (Cq), 138.8 (CH), 149.6 (CH), 150.1 (CH), 156.0 (CH), 160.3 (CH). IR (KBr) 3366, 3062, 1607, 1580, 1370, 1057 cm^{-1}. Anal. Calcd for $C_{97}H_{120}N_{48}O_{48}Pd_8Br_4{\bullet}22H_2O$: C, 27.13; H, 3.85; N, 15.66. Found: C, 27.06; H, 3.70; N, 15.64.

Self-assembly of tetrameric cone 3 and trimeric cone 7. Ligand **1** (15.0 mg; 0.048 mmol) was suspended in an aqueous solution (5.0mL) of **2** (30.9 mg; 0.106 mmol) and the solution was stirred for 24 h at room temperature. The open cone **3** and **7** were assembled into 2:3 mixture of two components and the mixed solution of **3** and **7** were measured with NMR. ^{1}H NMR (500 MHz, D_2O, 25 °C) **trimeric cone 7:** δ 2.94–3.07 (m, 32H), 7.59 (dd, *J* = 5.6, 7.8 Hz, 2H), 7.90 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 2H), 8.41 (s, 2H), 8.71 (d, *J* = 5.6 Hz, 2H), 9.28 (s, 2H), 10.42 (s, 2H), 10.48 (s, 1H). **tetrameric cone 3:** δ 2.94–3.07 (m, 32H), 7.63 (dd, *J* = 5.6, 7.8 Hz, 2H), 8.03 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 2H), 8.49 (s, 2H), 8.84 (d, *J* = 5.6 Hz, 2H), 9.57 (s, 2H), 10.51 (s, 2H), 10.61 (s, 1H).

X-ray structural analysis of 4•6. Ligand **1** (15.0 mg; 0.048 mmol) was suspended in an aqueous solution (1.0mL) of **2** (30.9 mg; 0.106 mmol). Followed by the addition of **6** (10 equiv, suspended) the solution was stirred for 24 h. After filtration, the pale yellow solution of **4•6** complex was allowed to stand at ambient temperature for 3 days to give single crystal of **4•6**. A single crystal of **4•6** (0.20 ×0.15 × 0.15 mm^3) was mounted on a glass fibre. All measurements were made on a charge coupled device (CCD) plate area detector with graphite monochromated Mo–Kα radiation. The data were collected at 193(2) K. Crystal data for **4•6**: formula $C_{97}H_{120}N_{48}O_{48}Pd_8Br_4{\bullet}22H_2O$, M = 4281.25, monoclinic, space group *C2/c*, a = 40.32(3), b = 15.767(9), c = 30.83(2) Å, β = 127.36(2)°, V = 15583(18) Å^3, $\rho_{\mathrm{calcd.}}$ = 1.82 mg/m^3, Z = 4, $F(000)$ = 8488, μ(Mo–Kα) = 11.0 cm^{-1}, λ(Mo–Kα) = 0.71069 Å; 17874 reflections measured, 11680 observed ($I > 2\sigma(I)$); number of variables 1050; R_1 = 0.0720; wR_2 = 0.185. The data for 4•6 was collected on a Siemens SMART/CCD diffractometer. Diffracted data were corrected for absorption using the SADABS[9] program. SHELXTL[10] was used for the structure solution and refinement was based on F^2. All non-hydrogen atoms were refined isotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C-atoms [U(H) = 1.2 Ueq(C)]. Pertinent crystallographic data will be presented in the Appendix.

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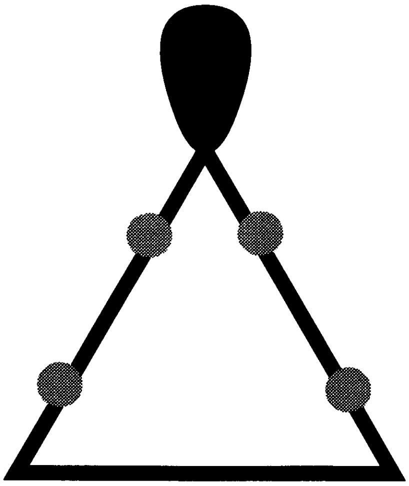
Chapter 5



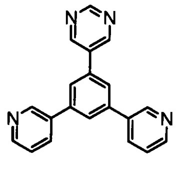
Side Chain-Directed Molecular Paneling

manuscript in preparation

***Abstract*:** The previously described C_2-symmetric triangular ligand **2** is linked with (en)Pd(NO_3)$_2$ in two ways: parallel and antiparallel.[1] The orientation of a molecular panel can be directed by the guests.[1–4] Here the author considered the control of the panel orientation by attaching the side chain to the panel itself. Namely, the author has designed molecular panels with directing group(s). The directing group(s) are attached on the panel so that only one orientation will be allowed. Another important role of substituents on the molecular panels is to fill cracks and holes which otherwise exist in a self-assembled polyhedron. All the coordination nanostructures are confirmed by 1D, 2D NMR or X-ray analysis.

5.1 Introduction

It was shown in the previous chapters that by linking triangles at their corners or edges, a family of polyhedral structures can be constructed at will.[1,5] Furthermore, in Chapter 4, the guest controlled orientation of a molecular panel is discussed, where two options for the panel orientation (parallel or antiparallel) can be directed by the guests. Here the author examines the control of the two options by changing the structure of the panel itself. Namely, directing group(s) are attached on the panel so that only one orientation will be allowed. Thus the author has designed molecular panels with directing group(s): ligands **3–5**.



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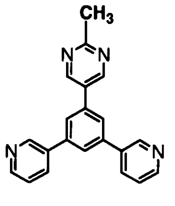

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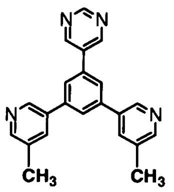

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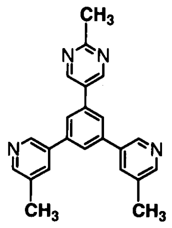

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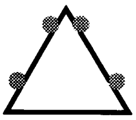
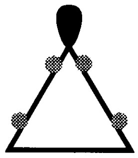
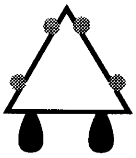
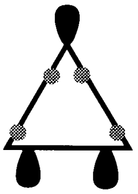


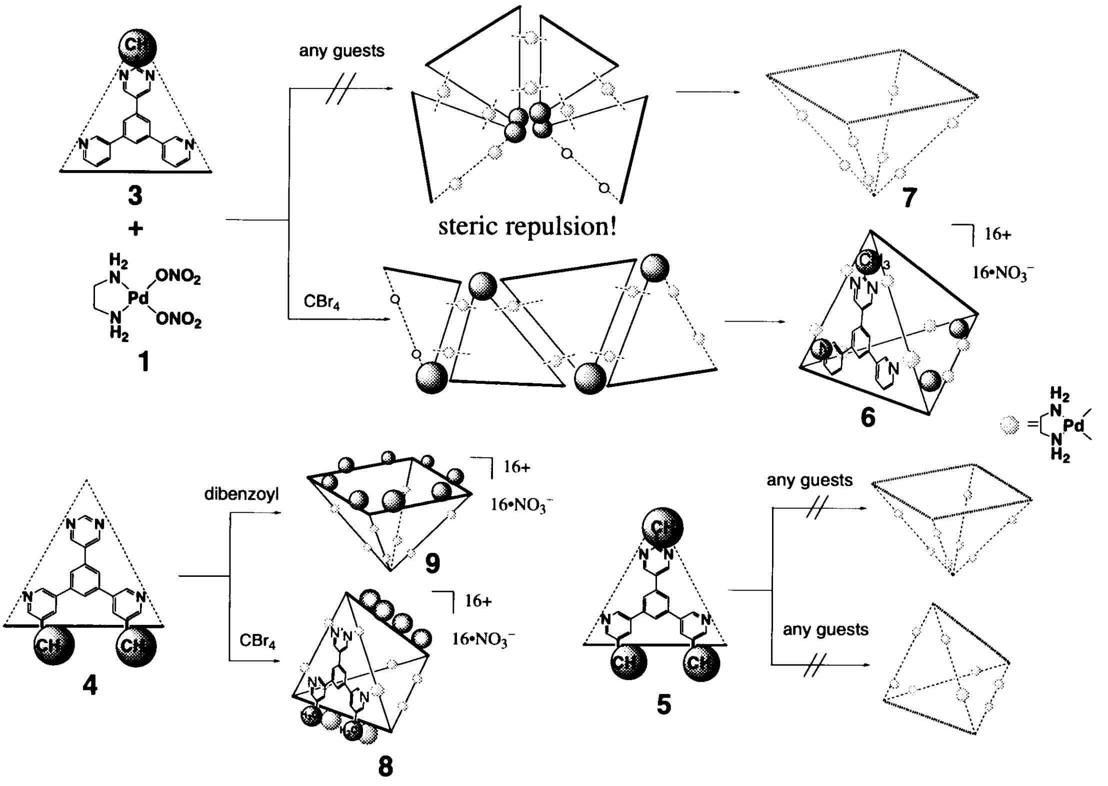






The molecular panel **3** containing a directing group (a methyl substituent) on the pyrimidine is allowed to orient only in the antiparallel fashion because of steric repulsion between the methyl groups attached on the pyrimidine ring. Accordingly, only cage complex **6** is selectively formed from the reaction of **1** and **3** upon the addition of suitable guest molecules, but a square pyramidal open cone structure like **7** did not assembled in the presence of any guests. Obviously, the orientation is strictly controlled by the directing group (a methyl on the pyrimidine) in Scheme 1.

Another important role of substituents on the molecular panels is to fill the cracks and holes which otherwise exist in a self-assembled polyhedron. Contrary to **3**, molecular panel **4** with two methyl substituents can be linked in two different ways similar to previous C_2-symmetric panel.

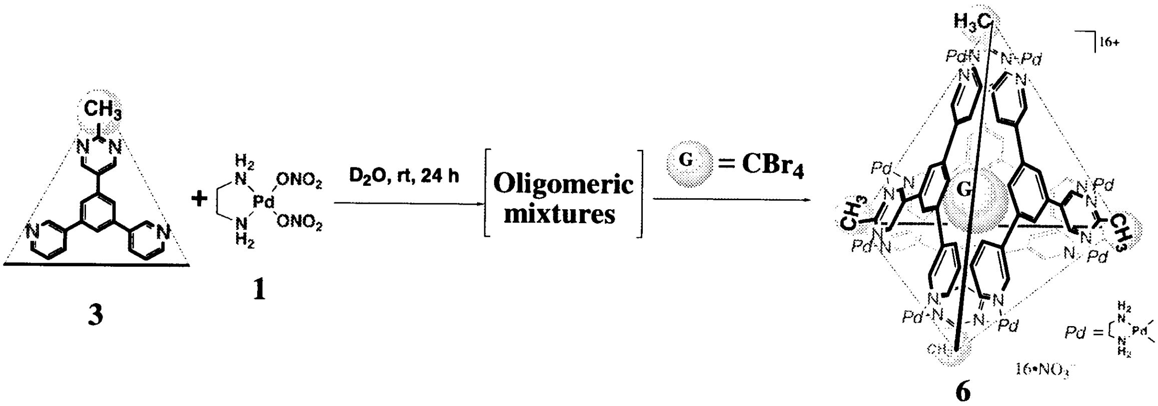


Scheme 1. Schematic representation of molecular paneling of **3**, **4** and **5**.

5.2 Result and Discussion

5.2.1 Guest-Selected Formation of a Tetrahedron Structure

In fact, the formation of pyramidal open cone structure was restricted by the steric repulsion of directing group(s). The C_2-symmetric panel **2** can be linked in parallel way in the absence of guests, whereas the reaction of **1** with **3** in D_2O first resulted in the formation of a mixture of oligomeric compounds (Figure 1a). However, the oligomers disappeared upon addition of CBr_4 (Scheme 1). Thus, the quantitative assembly of coordination capsule formed only in the presence of specific guest molecules. Interestingly, this guest-induced assembly process was monitored by a time-dependent ^{1}H NMR measurement (Figure 1). After adding CBr_4 to a reaction mixture of **1** and **3**, the oligomers gradually disappeared and the signals of **6** became stronger. The assembly process of **6** was completed within 24 h.



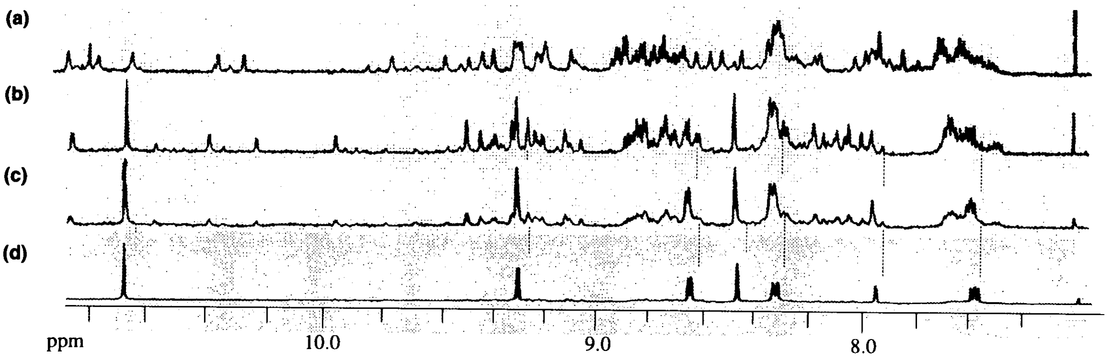


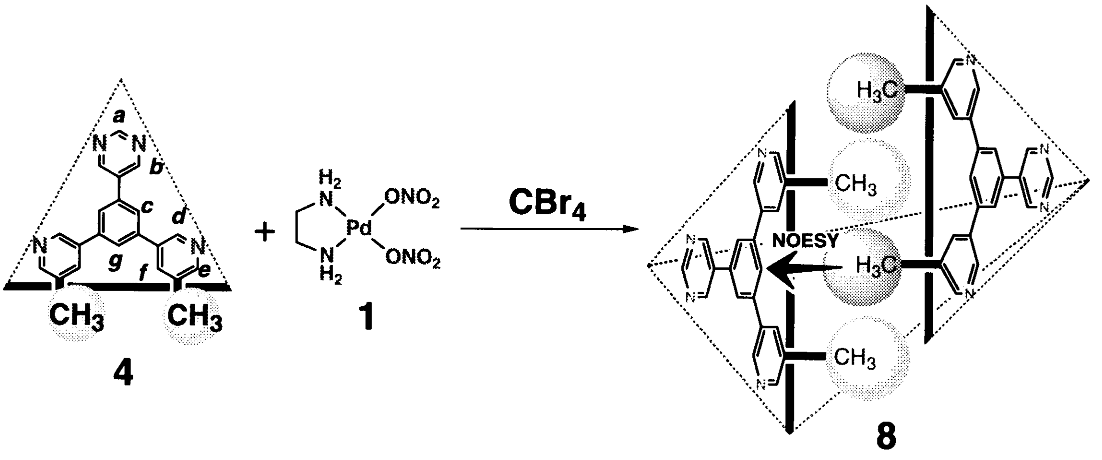
Figure 1. Monitoring of the guest-induced self-organization of by ^{1}H NMR (500 MHz, D_2O, 25 °C). (a) Spectra were collected at 0 h, (b) 1 h, (c) 7 h, and (d) 24 h after the addition of CBr_4 to a oligomeric mixture arising from **1** and **3** in D_2O.

5.2.2 Guest-Selected Formation from di-substituted molecular panels

The combination of components **1** and **4** expected to show two ways of molecular paneling: parallel and antiparallel links. This was achieved in an efficient fashion by using specific template molecules such as dibenzoyl or CBr_4. The quantitative assembly of M_8L_4 open cone **9** was induced by large guest molecules such as dibenzoyl. Thus, ligand **4** (0.025 mmol) and dibenzoyl (0.25 mmol) were suspended in the aqueous solution (2.5 mL) of **1** (0.05 mmol). NMR displayed seven proton signals in an aromatic region, which stems from ligand **3** located on a C_2-symmetric environment, in good agreement with the structure of **9**. The accommodation of guest in the cone-shaped cavity of **9** was strongly suggested by the outstanding up-field shifts of signals of dibenzoyl in D_2O. The host-guest ratio was estimated to be 1:1 by NMR integration ratio.

The quantitative assembly of coordination nanocapsule **8** was achieved, with the aid of the remarkable template effect of a small guest molecule. The antiparallel link of the ligands in **8** was strongly supported by the observation of NOESY between the directing methyl groups and H_g of the host C_6H_3 ring, which was not observed in **9**. Contrary to **3**, molecular panel **4** with two methyl substituents is to fill cracks and holes which otherwise exist in a self-assembled polyhedron. However, due to the presence of methyl substituents on the panel, tetrahedron **8** has distortion in its shape, and cracks and holes among the panels are efficiently filled by the substituents as revealed by 1D, 2D NMR (Scheme 2). The selective formation of tetrahedron **8** was also observed with similar small guests such as $CHCl_3$ and $CBrCl_3$. Molecular panel **5** with three methyl substituents is too severe steric repulsion between the methyl groups to assembly neither tetrahedron nor open cone structures.

Scheme 2.



5.2.3 X-ray Crystallographic Analysis of a Tetrahedron Structure

The tetrahedron structure of **6•G** complex was also determined by an X-ray crystallographic analysis (Figure 2). The single crystals were obtained by standing the aqueous solution of **6•G** at 4 °C for two days. As expected, the crystal structure of **6•G** displayed the antiparallel junction of ligands. Moreover, the X-ray analysis clearly evidenced the formation of tetrahedron **6** accommodating one molecule of CBr_4. The methyl groups are arranged on each top of tetrahedron. The whole tetrahedral structure is somewhat distorted in such a way that efficient host-guest interaction and aromatic contact between the ligands are gained. As a result, the 12-component assembly makes a closed shell framework in which the guest molecule is completely insulated (Figure 2, bottom). The cage is more symmetrical in case of unsubstituted structure (Chapter 4) than in symmetrical structure. As a consequence there are only half the cage and half CBr_4 present in the former structure. Whereas in the present structure the asymmetric unit contains full cage and full CBr_4. The unit cell parameters and the bond angles and lengths are shown in Table 1.

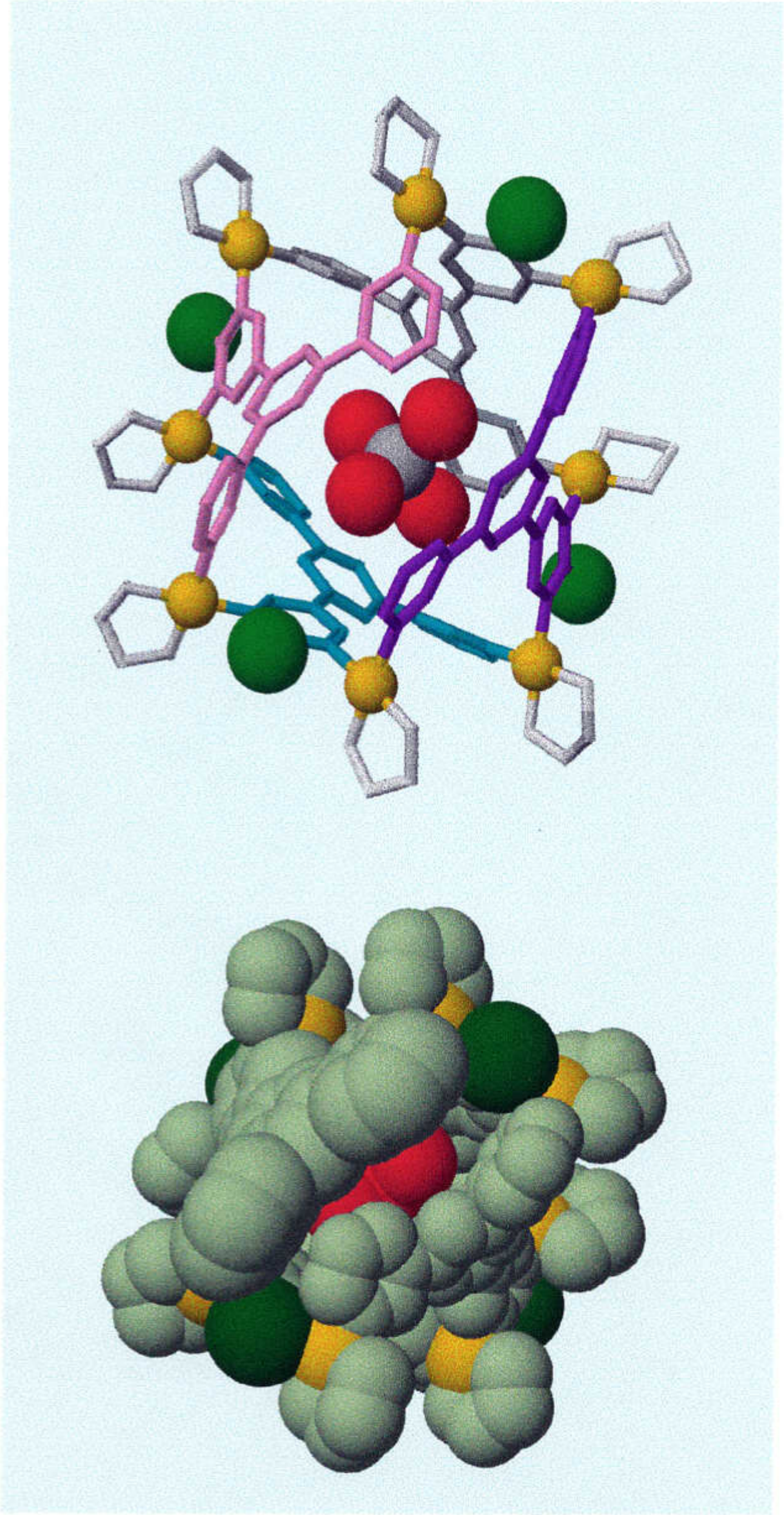
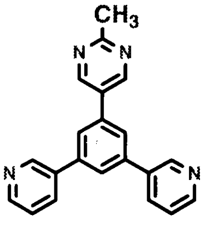
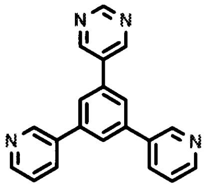


Figure 2. Crystal structure of 5•CBr_4. Top: cylindrical representation; bottom: Space-filling representation.

Table 1. C–Br distances and C–Br angles.

 3	 2
$C_{101}H_{128}N_{48}O_{48}Pd_8Br_4$	$C_{97}H_{120}N_{48}O_{48}Pd_8Br_4$
$M = 4337.35$,	$M = 4281.25$,
$C2/c$	$C2/c$
$a = 31.683(5)$ Å $b = 44.654(7)$ Å $c = 27.985(4)$ Å $\alpha = \gamma = 90$ °; $\beta = 106.907(3)$ $V = 37881$ Å^3 $R = 0.138$	$a = 40.32(3)$ Å $b = 15.767(9)$ Å $c = 30.83(2)$ Å $\alpha = \gamma = 90$ °; $\beta = 127.35(2)$ $V = 15583(18)$ Å^3 $R = 0.072$
C-Br distances: **1.900, 1.948, 2.018, 1.843 Å** **Angles:** **109.5, 113.1, 119.9, 105.7, 111.0, 105.1**	**C-Br distances:** **1.927, 1.907 Å** **Angles:** **109.1, 107.9, 110.4, 109.5**

5.3 Conclusion

The linking direction of molecular panels can be directed by changing the panel itself. Namely, the author has designed molecular panels with directing group(s) so that only one orientation will be allowed. For example, molecular panel **3** containing a directing group (a methyl substituent) on the pyrimidine is allowed to orient only in the antiparallel fashion because of steric repulsion between the methyl groups attached on the pyrimidine ring. The molecular panel **4** with two methyl substituents suffice to fill the cracks and holes which otherwise exist in a self-assembled polyhedron. However, molecular panel **5** with three methyl substituents due to the greater steric repulsion between the methyl groups neither tetrahedron nor open cone structures were assembled. Side chain-directed molecular paneling is an effective way for the construction nanostructures without the aid of the templates.

5.4 Experimental Section

Preparation of 3,5-Dibromo-1-(4-methyl-3,5-pyrimidyl)benzene. To a toluene solution (50 mL) of 1,3,5-tribromobenzene (5.51 g; 5.84 mmol), 2-methyl-5-trimethylstannyl-1,3-pyrimidine (1.5 g; 1.75 mmol), $PdCl_2(PPh_3)_2$ (0.21 g; 0.29 mmol) and LiCl (1.24 g; 29.2 mmol) were added at room temperature and then the reaction mixture was refluxed for 48 h. The reaction solution was quenched by H_2O (10 mL) and extracted with $CHCl_3$. After the organic layer was dried over Na_2SO_4, filtered, and condensed in vacuo, followed by the purification of the crude mixture by silica gel column chromatography (AcOEt:Hexane=7:1) gave desired 3,5-dibromo-1-(4-methyl-3,5-pyrimidyl)benzene as a colorless solid (0.70 g; 2.12 mmol) in 36% yield. Mp 217–218 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 8.80 (s, 2H), 7.75 (s, 1H), 7.63 (s, 2H), 2.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 25.78 (CH), 123.9 (CH), 128.6 (CH), 128.7 (Cq), 134.1 (CH), 138.1 (Cq), 154.9 (CH)), 168.2 (Cq). IR (KBr) 3045, 3026, 2360, 1558, 1463, 854, 752 cm^{-1}. MS (EI) *m/z* 328 (M^+). Anal. Calcd for $C_{11}H_8N_2Br_2$: C, 40.28; H, 2.46; N, 8.54. Found: C, 40.47; H, 2.27; N, 8.55.

Preparation of 1-(4-methyl-3,5-pyrimidyl)-3,5-bis(3-pyridyl)benzene (3). A mixture of trimethyl(3-pyridyl)tin (2.3 g; 6.1 mmol), 3,5-dibromo-1-(4-methyl-3,5-pyrimidyl)benzene (0.67 g; 2.64 mmol), and $PdCl_2(PPh_3)_2$ (0.14 g; 0.20 mmol) and LiCl (0.87 g; 20.4 mmol) in toluene (60 mL) was refluxed for 48 h. The gray suspension was filtered and the precipitates were washed with hexane and ethyl acetate. The gray solid as dissolved with 5 M HCl (5.0 mL) and the small amount of insoluble solid was removed by filtration. Acetone (50 mL) was added to the solution, and the resulting white precipitate were filtered and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave **3** (0.26 g; 0.79 mmol) as a gray solid in 39% yield. Mp 241–243 °C. ^{1}H NMR (500 MHz, DMSO, 25 °C) δ 3.22 (s, 3H), 8.07 (dd, J = 4.9, 8.5 Hz, 2H), 8.65 (s, 1H), 8.68 (s, 2H), 8.87 (d, J = 4.9 Hz, 2H), 9.16 (d, J = 8.5 Hz, 2H), 9.67 (s, 2H), 9.79 (s, 2H). ^{13}C NMR (125 MHz, DMSO, 25 °C) δ 25.5, 124.0, 125.0, 125.6, 129.8, 134.9, 135.1, 135.9, 139.1, 148.3, 149.0, 155.4, 166.6. IR (KBr) 3040, 1654, 1590, 1440, 1025, 708 cm^{-1}. MS (DI) *m/z* 324 (M$^+$).

Preparation of 1-(3,5-pyrimidyl)-3,5-bis(3-methyl-5-pyridyl)benzene (4). A mixture of 3-methyl-5-trimethyl(pyridyl)tin (0.53 g; 2.1 mmol), 3,5-dibromo-1-(3,5-pyrimidyl)benzene (0.26 g; 0.84 mmol), and $PdCl_2(PPh_3)_2$ (0.059 g; 0.084 mmol) and LiCl (0.35 g; 8.4 mmol) in toluene (25 mL) was refluxed for 24 h. The gray suspension was filtered and the precipitates were washed with hexane and ethyl acetate. The gray solid as dissolved with 5 M HCl (5.0 mL) and the small amount of insoluble solid was removed by filtration. Acetone (50 mL) was added to the solution, and the resulting white precipitate were filtered and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave **4** (0.143 g; 0.43 mmol) as a gray solid in 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 2.46 (s, 6H), 7.77 (s, 2H), 7.79 (s, 2H), 7.84 (s, 1H), 8.52 (s, 2H), 8.75 (s, 2H), 9.07 (s, 2H), 9.29 (s, 1H). MS (DI) *m/z* 338 (M$^+$).

Preparation of 1-(4-methyl-3,5-pyrimidyl)-3,5-bis(3-methyl-5-pyridyl)benzene (5). A mixture of 3-methyl-5-trimethyl(pyridyl)tin (0.64 g; 2.5 mmol), 3,5-dibromo-1-(4-methyl-3,5-pyrimidyl)benzene (0.33 g; 1.0 mmol), and $PdCl_2(PPh_3)_2$ (0.070 g; 0.10 mmol) and LiCl (0.424 g; 10.0 mmol) in toluene (25 mL) was refluxed for 36 h. The gray suspension was filtered and the precipitates were washed with hexane and ethyl acetate. The gray solid as dissolved with 5 M HCl (2.5 mL) and the small amount of insoluble solid was removed by filtration. Acetone (25 mL) was added to the solution, and the resulting white precipitate were filtered and washed with water and a small amount of acetone. Drying under vacuum for 12 h gave **5** (0.289 g; 0.82 mmol) as a gray solid in 82% yield. ^{1}H NMR (500 MHz, DMSO, 25 °C) δ 2.46 (s, 6H), 2.83 (s, 3H), 7.74 (s, 2H), 7.78 (s, 2H), 7.81 (s, 1H), 8.51 (s, 2H), 8.75 (s, 2H), 8.95 (s, 2H). MS (DI) *m/z* 352 (M^+).

Self-assembly of tetrahedron 6. Ligand **3** (1.6 mg; 0.005 mmol) was suspended in an aqueous solution (0.5 mL) of **1** (2.9 mg; 0.011 mmol). Followed by the addition of CBr_4 (10 equiv, suspended) the solution was stirred for 24 h. The tetrahedron **6** was assembled and the solution of **6•CBr$_4$** was measured with NMR. ^{1}H NMR (500 MHz, D_2O, 25 °C) δ 2.95–2.99 (m, 8H), 3.03–3.09 (m, 8H), 4.44 (s, 3H), 7.63 (dd, *J* = 5.4, 8.3 Hz, 2H), 8.00 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 2H), 8.51 (s, 2H), 8.69 (d, *J* = 5.4 Hz, 2H), 9.33 (s, 2H), 10.76 (s, 2H). ^{13}C NMR (125 MHz, D_2O, 25 °C) δ –25.5 (CBr_4), 30.75 (CH_3), 47.7 (CH), 47.8 (CH), 126.7 (CH), 127.6 (CH), 128.7 (CH), 131.8 (Cq), 133.6 (Cq), 137.8 (Cq), 138.6 (Cq), 139.4 (CH), 149.5 (CH), 151.1 (CH), 160.5 (CH), 169.6 (Cq).

Self-assembly of tetrahedron 8. Ligand **4** (1.6 mg; 0.0048 mmol) was suspended in an aqueous solution (0.5 mL) of **1** (3.5 mg; 0.012 mmol). Followed by the addition of CBr_4 (10 equiv., suspended) the solution was stirred for 24 h. The tetrahedron **8** was assembled and the solution of **8•CBr$_4$** was measured with NMR. ^{1}H NMR (500 MHz, D_2O, 25 °C) δ 2.51 (s, 6H), 2.97–3.04 (m, 16H), 7.89 (s, 1H), 8.21 (s, 2H), 8.45 (s, 2H), 8.67 (s, 2H), 9.17 (s, 2H), 10.32 (s, 1H), 10.70 (s, 2H).

Self-assembly of open cone 9. Ligand **4** (1.6 mg; 0.0048 mmol) was suspended in an aqueous solution (0.5 mL) of **1** (3.5 mg; 0.012 mmol). Followed by the addition of *meso*-hydrobenzoin (10 equiv., suspended) the solution was stirred for 24 h. The open cone **9** was assembled and the solution of **9•G** was measured with NMR. ^{1}H NMR (500

MHz, D_2O, 25 °C) δ 2.30 (s, 6H), 2.97–3.04 (m, 16H), 6.94–7.06 (m, 10H), 7.71 (s, 3H), 8.20 (s, 2H), 8.76 (s, 2H), 9.47 (s, 2H), 10.47 (s, 2H), 10.66 (s, 1H).

X-ray structural analysis of 6•CBr$_4$. Ligand **3** (16.0 mg; 0.050 mmol) was suspended in an aqueous solution (1.0mL) of **1** (30.9 mg; 0.106 mmol). Followed by the addition of CBr_4 (10 equiv., suspended) the solution was stirred for 24 h. After filtration, the pale yellow solution of **6•CBr$_4$** complex was allowed to stand at 4 °C for 2 days to give single crystal of **6•CBr$_4$**. A single crystal of **6•CBr$_4$** ($0.20 \times 0.15 \times 0.15$ mm^3) was mounted on a glass fibre. All measurements were made on a charge coupled device (CCD) plate area detector with graphite monochromated Mo–Kα radiation. The data were collected at 193(2) K. Crystal data for **6•CBr$_4$**: formula $C_{101}H_{128}N_{48}O_{48}Pd_8Br_4$, M=4337.35, monoclinic, space group $C2/c$, a = 31.683(5), b = 44.654(7), c = 27.985(4) Å, β = 106.907(3)°, V = 37881 Å^3, R_1 = 0.138. The data for **6•CBr$_4$** was collected on a Siemens SMART/CCD diffractometer. Diffracted data were corrected for absorption using the SADABS[6] program. SHELXTL[7] was used for the structure solution and refinement was based on F^2. All non-hydrogen atoms were refined isotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C-atoms [U(H) = 1.2 Ueq(C)]. Pertinent crystallographic data will be presented in the Appendix.

5.5 References and Notes

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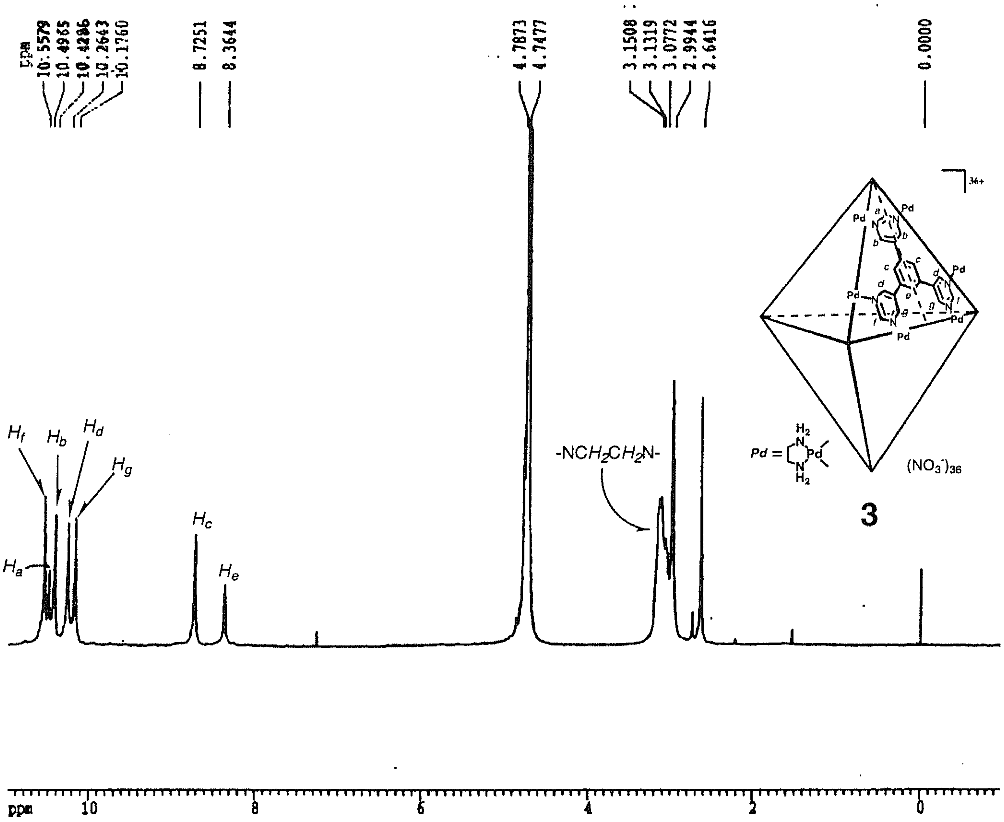
Appendix

NMR data and X-ray data

^{1}H NMR of **3**



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AQ             1.5860212 sec
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DE                   6.00 usec
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PL1                 -4.00 dB

F2 - Processing parameters
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1D NMR plot parameters
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F1                5502.53 Hz
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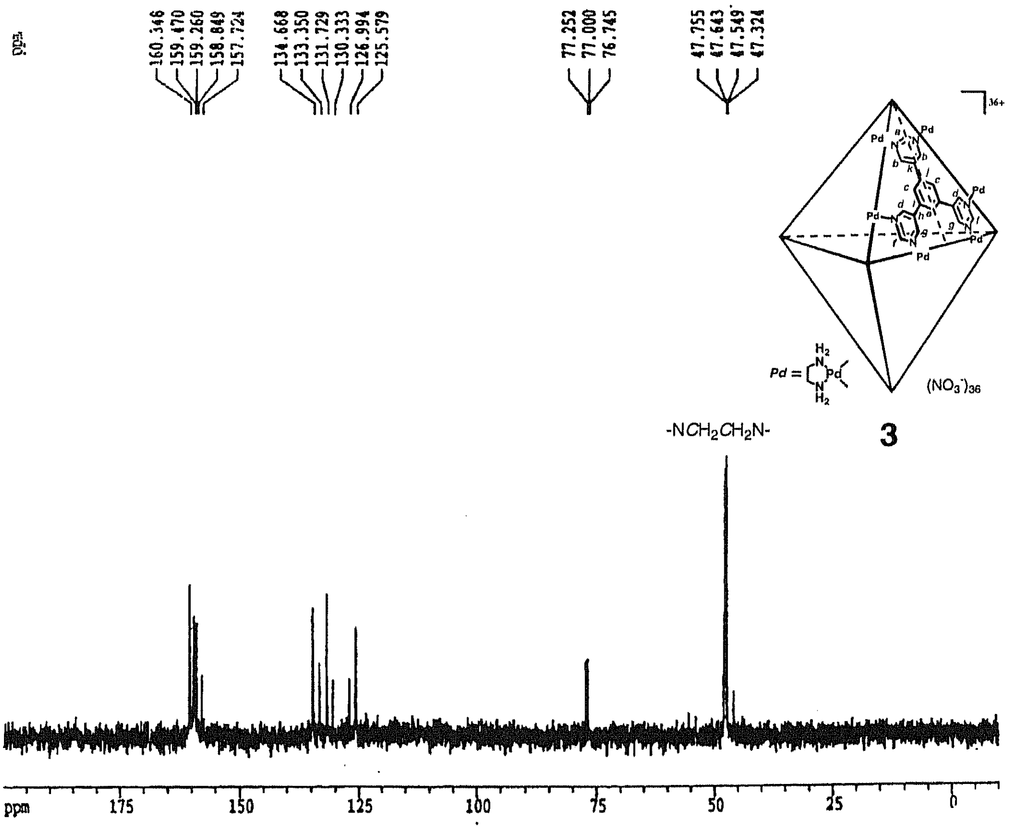
^{13}C NMR of **3**



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PL1                  2.00 dB

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1D NMR plot parameters
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F1               25156.59 Hz
F2P               -10.000 ppm
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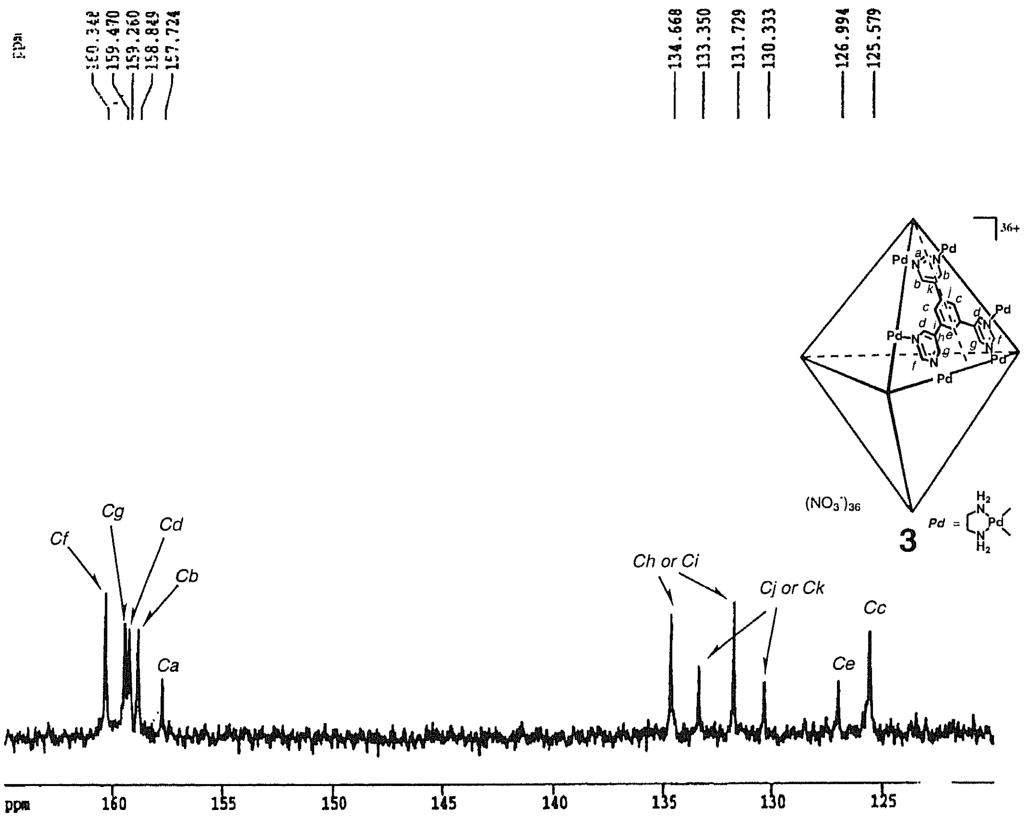
^{13}C NMR of 3



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F1            20754.18 Hz
F2P            120.000 ppm
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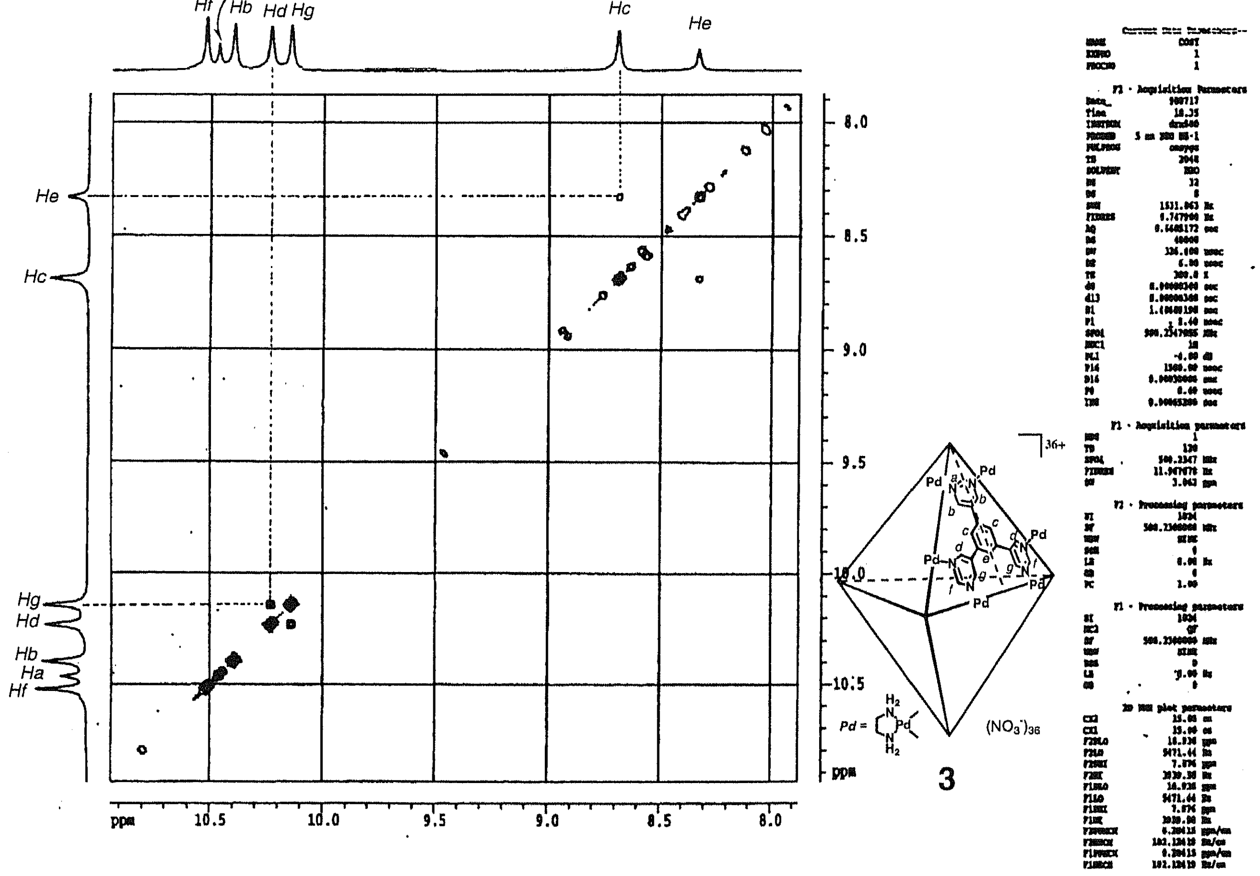
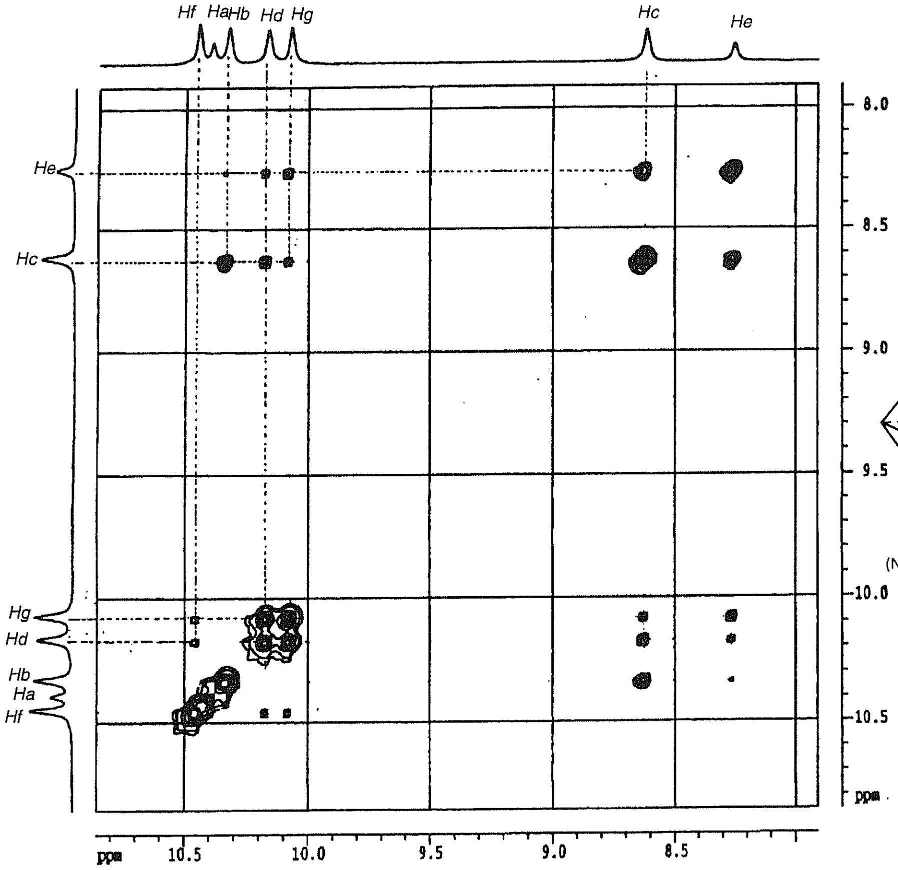
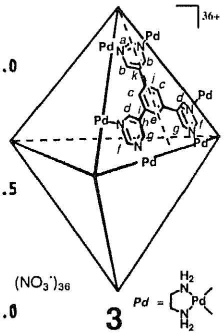
^{1}H-^{1}H COSY of 3



HOHAHA of **3**





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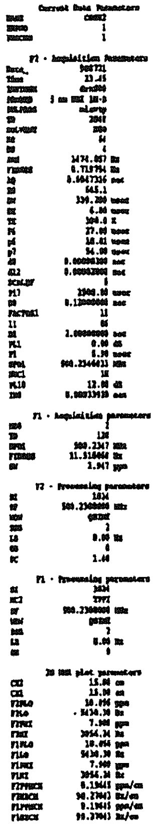
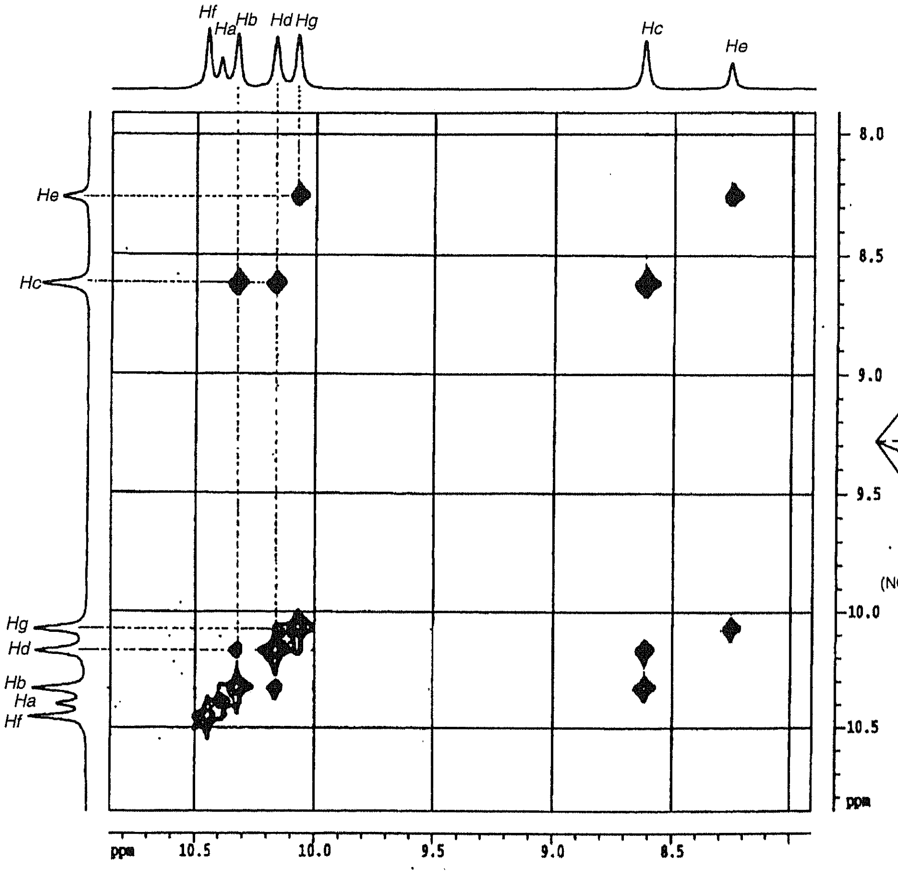
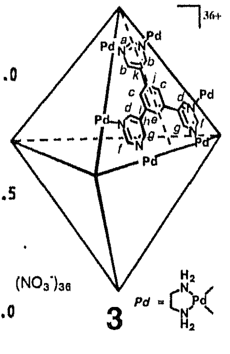


NOESY of **3**





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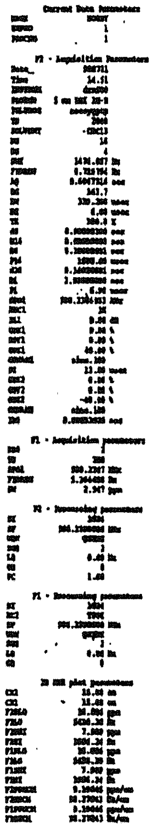
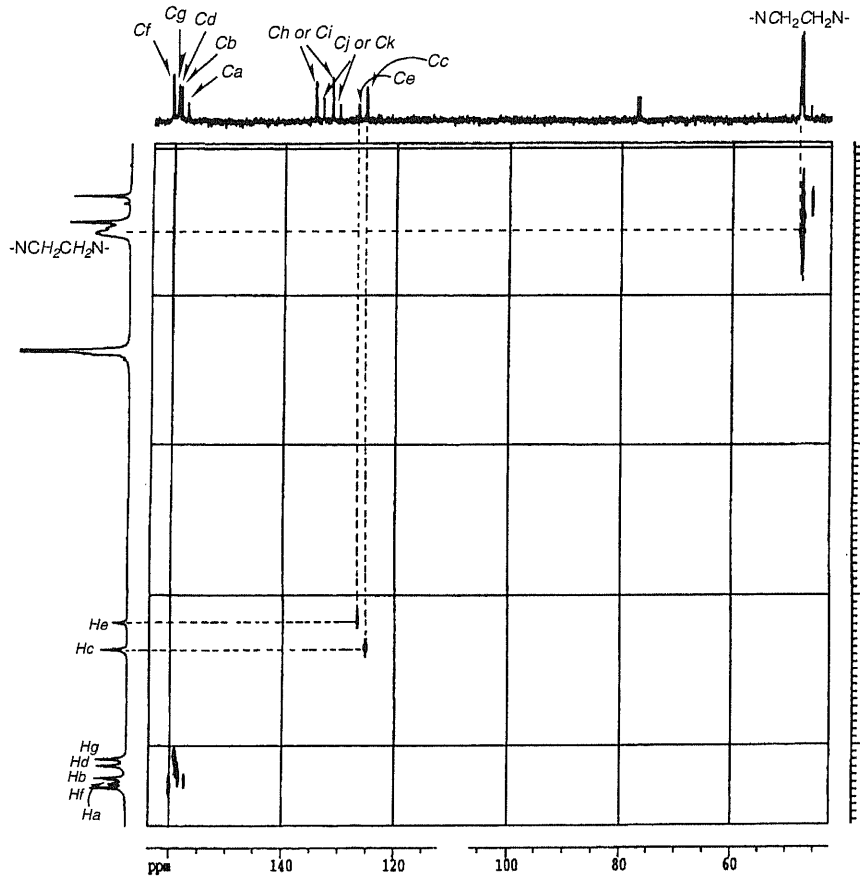
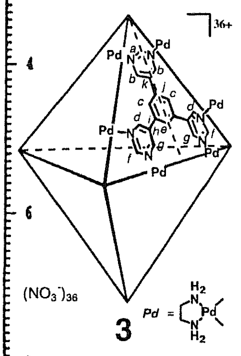


C-H COSY of **3**





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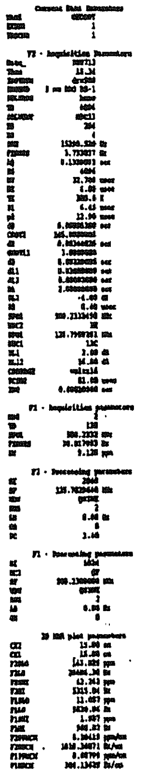
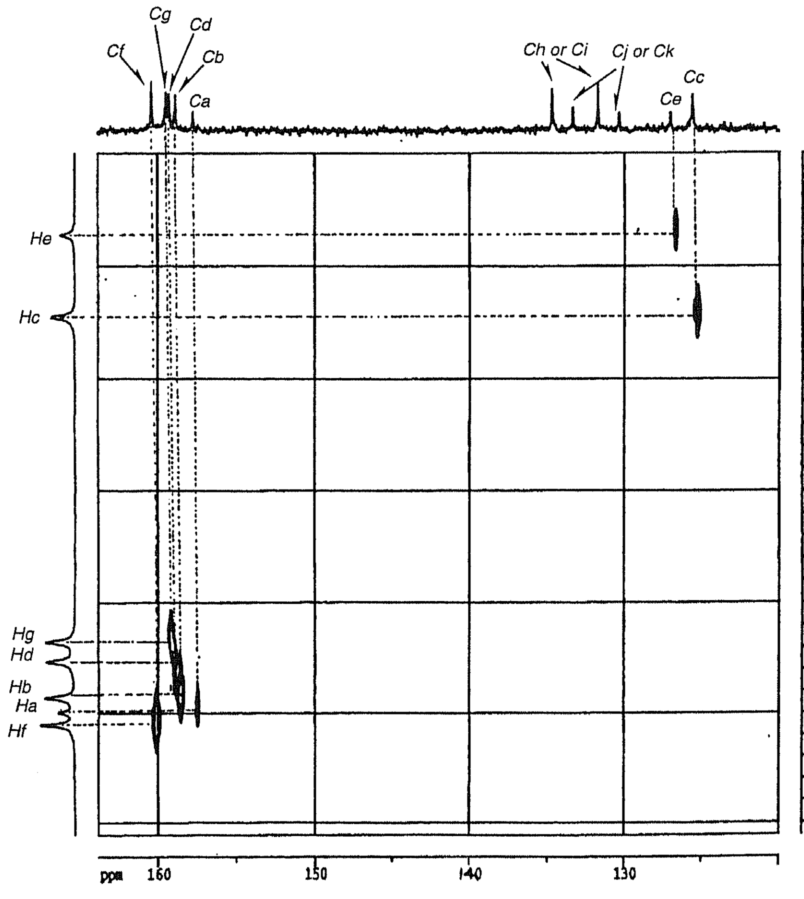
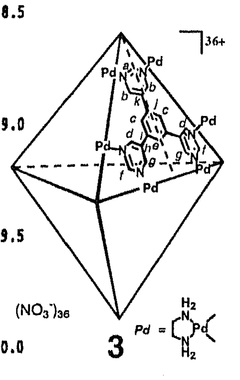


C-H COSY of **3**





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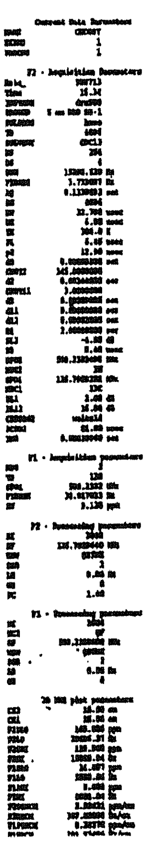

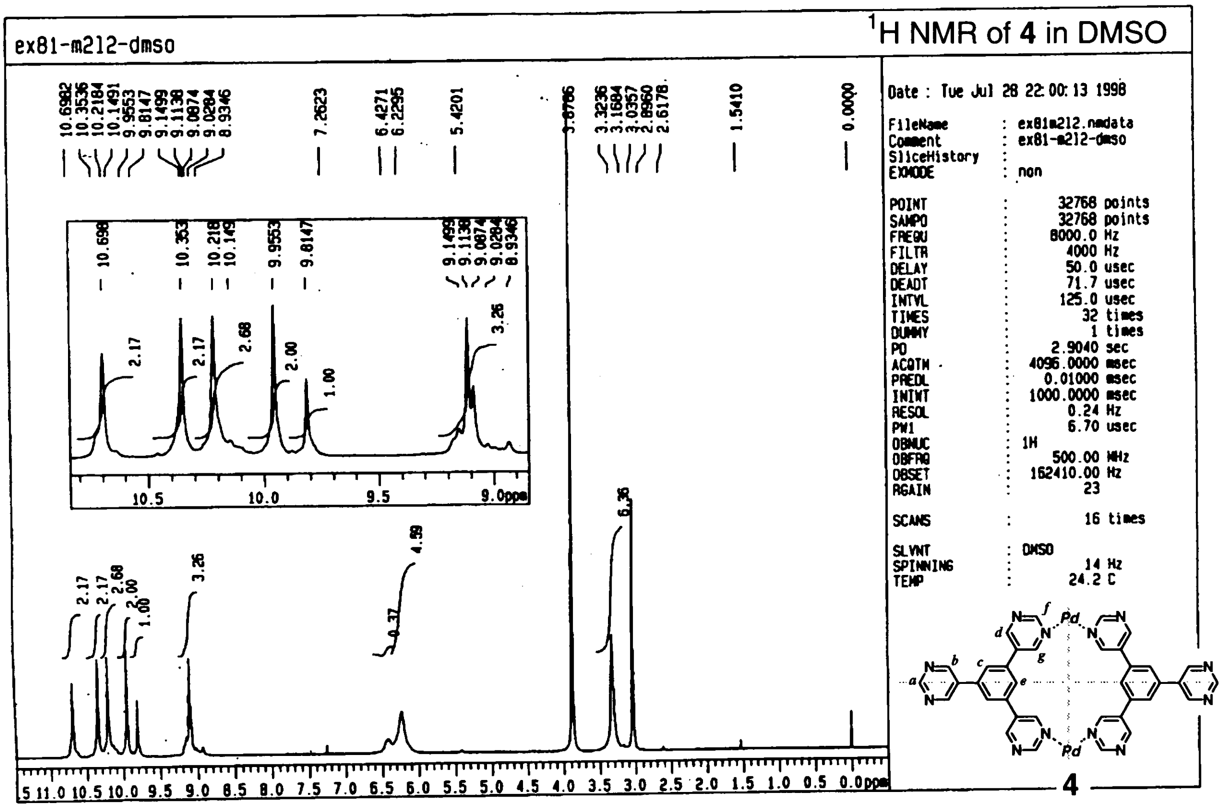

^{1}H NMR of **4** in DMSO

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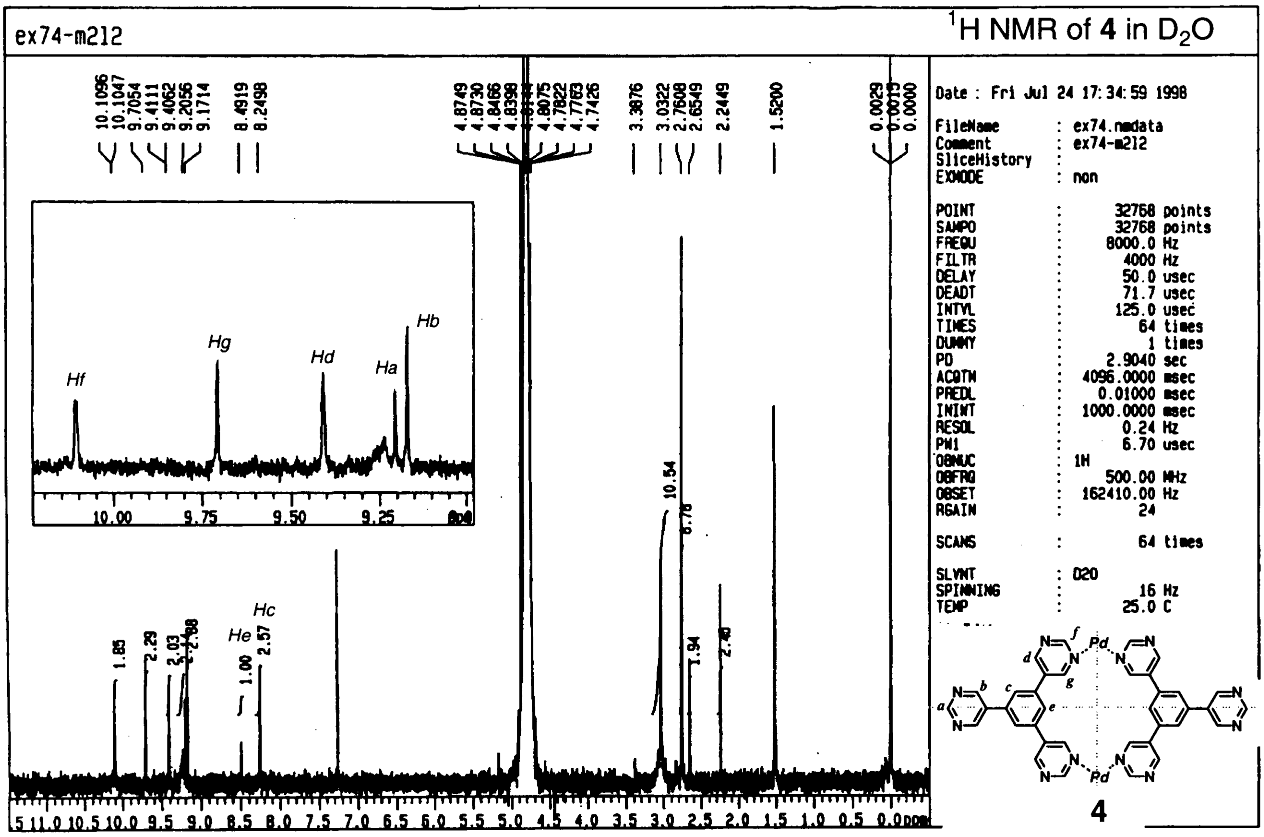
FILTR           :         4000 Hz
DELAY           :         50.0 usec
DEADT           :         71.7 usec
INTVL           :        125.0 usec
TIMES           :           32 times
DUMMY           :            1 times
PD              :       2.9040 sec
ACQTM           :    4096.0000 msec
PREDL           :      0.01000 msec
ININT           :    1000.0000 msec
RESOL           :         0.24 Hz
PW1             :         6.70 usec
OBNUC           : 1H
OBFRQ           :       500.00 MHz
OBSET           :    162410.00 Hz
RGAIN           :           23

SCANS           :           16 times

SLVNT           : DMSO
SPINNING        :           14 Hz
TEMP            :         24.2 C
```

4



^{1}H NMR of **4** in D_2O

```
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SliceHistory    :
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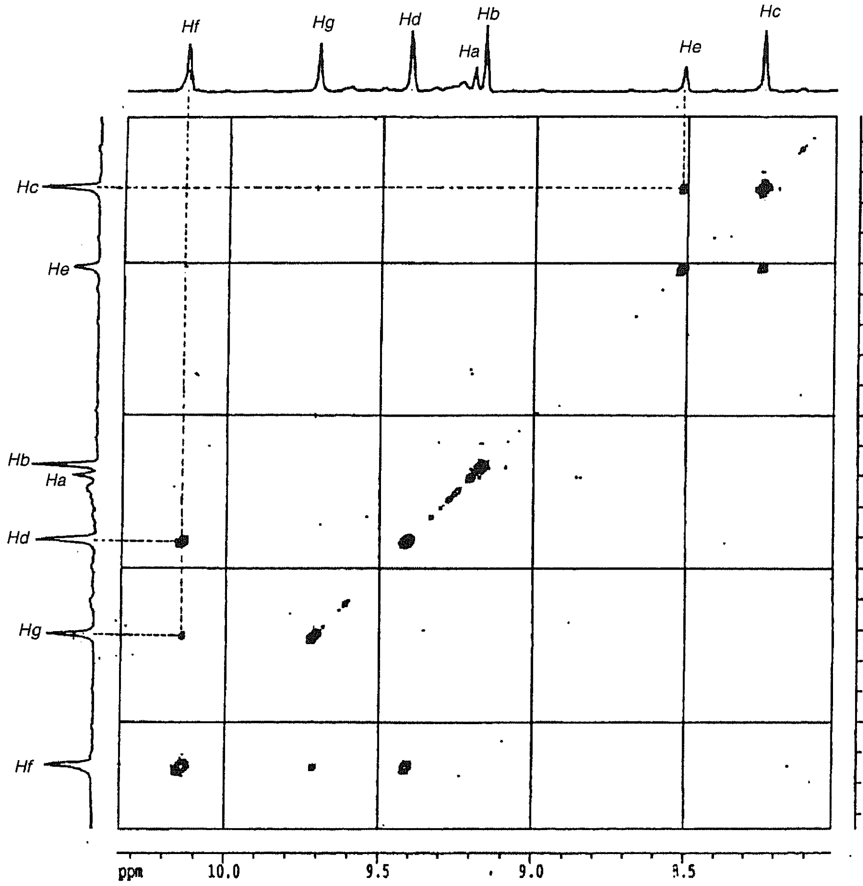
DELAY           :         50.0 usec
DEADT           :         71.7 usec
INTVL           :        125.0 usec
TIMES           :           64 times
DUMMY           :            1 times
PD              :       2.9040 sec
ACQTM           :    4096.0000 msec
PREDL           :      0.01000 msec
ININT           :    1000.0000 msec
RESOL           :         0.24 Hz
PW1             :         6.70 usec
OBNUC           : 1H
OBFRQ           :       500.00 MHz
OBSET           :    162410.00 Hz
RGAIN           :           24

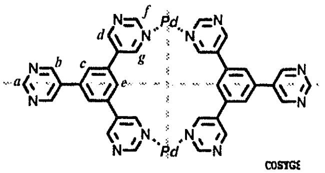
SCANS           :           64 times

SLVNT           : D2O
SPINNING        :           16 Hz
TEMP            :         25.0 C
```

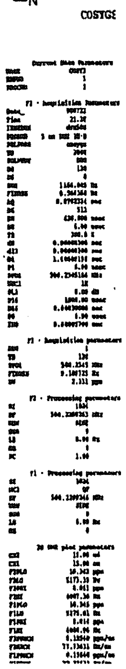
4



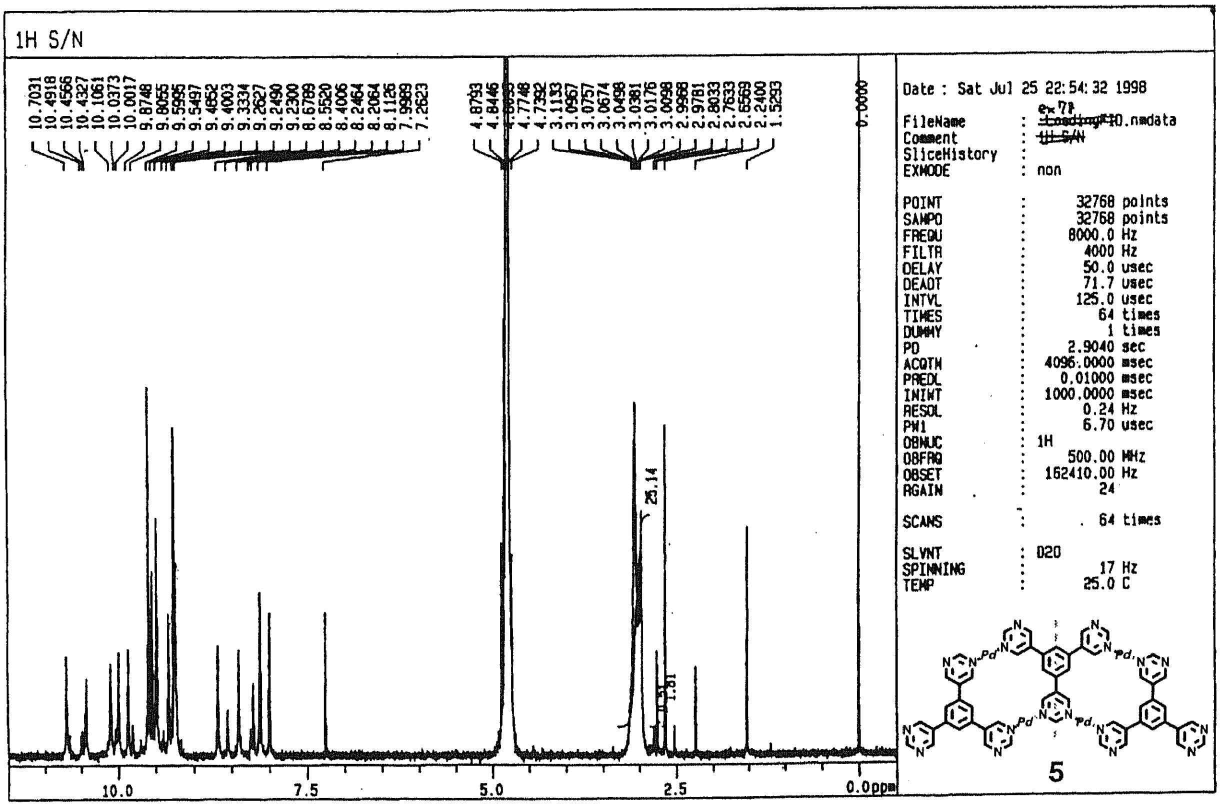
^1H-^1H COSY of **4** in D_2O



4



^1H NMR of **5** in D_2O



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Date : Sat Jul 25 22:54:32 1998
                   ex 7f
FileName     : ~~LoadingFI~~D.nmdata
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DEADT        :      71.7 usec
INTVL        :     125.0 usec
TIMES        :        64 times
DUMMY        :         1 times
PD           :    2.9040 sec
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INIWT        : 1000.0000 msec
RESOL        :      0.24 Hz
PW1          :      6.70 usec
OBNUC        : 1H
OBFRQ        :    500.00 MHz
OBSET        : 162410.00 Hz
RGAIN        :        24

SCANS        :        64 times

SLVNT        : D2O
SPINNING     :        17 Hz
TEMP         :      25.0 C
```
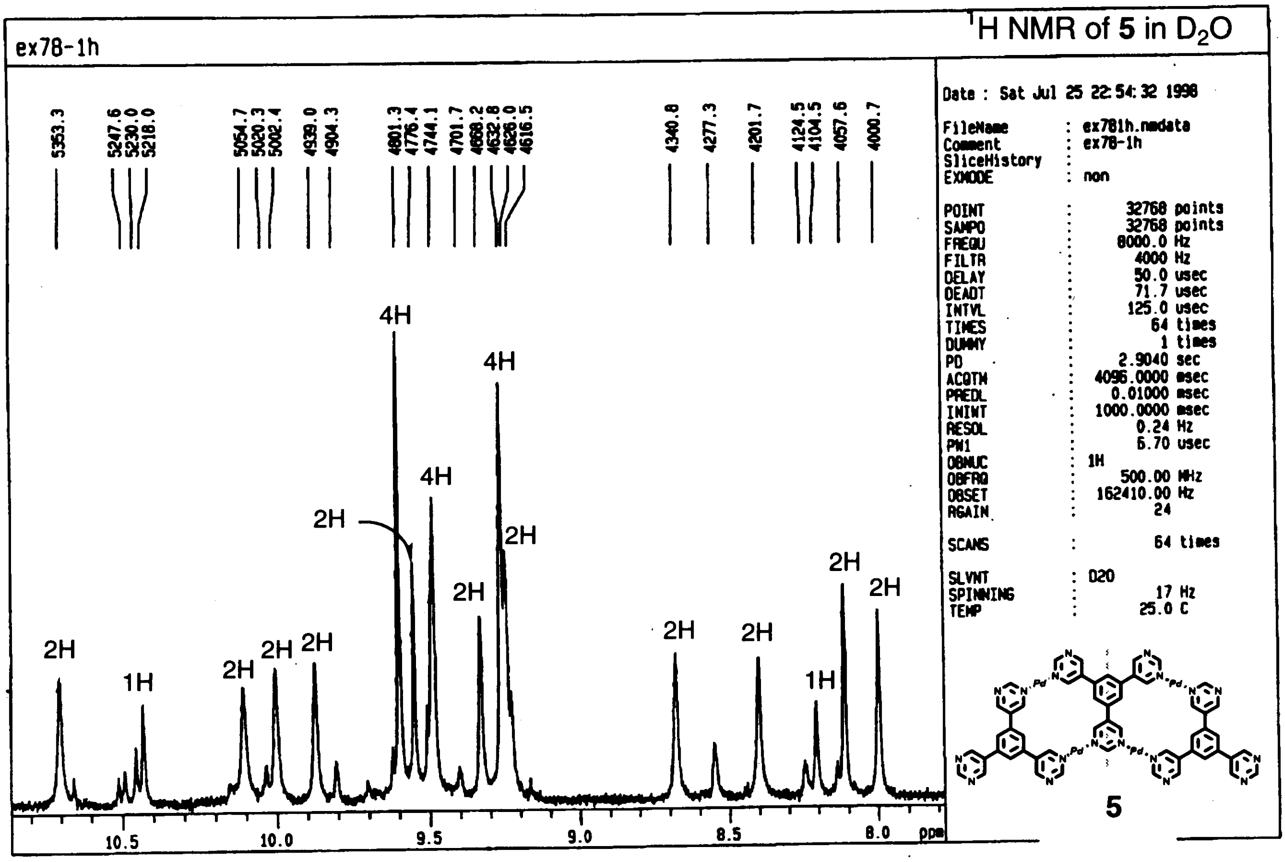

^{1}H NMR of **5** in D_2O



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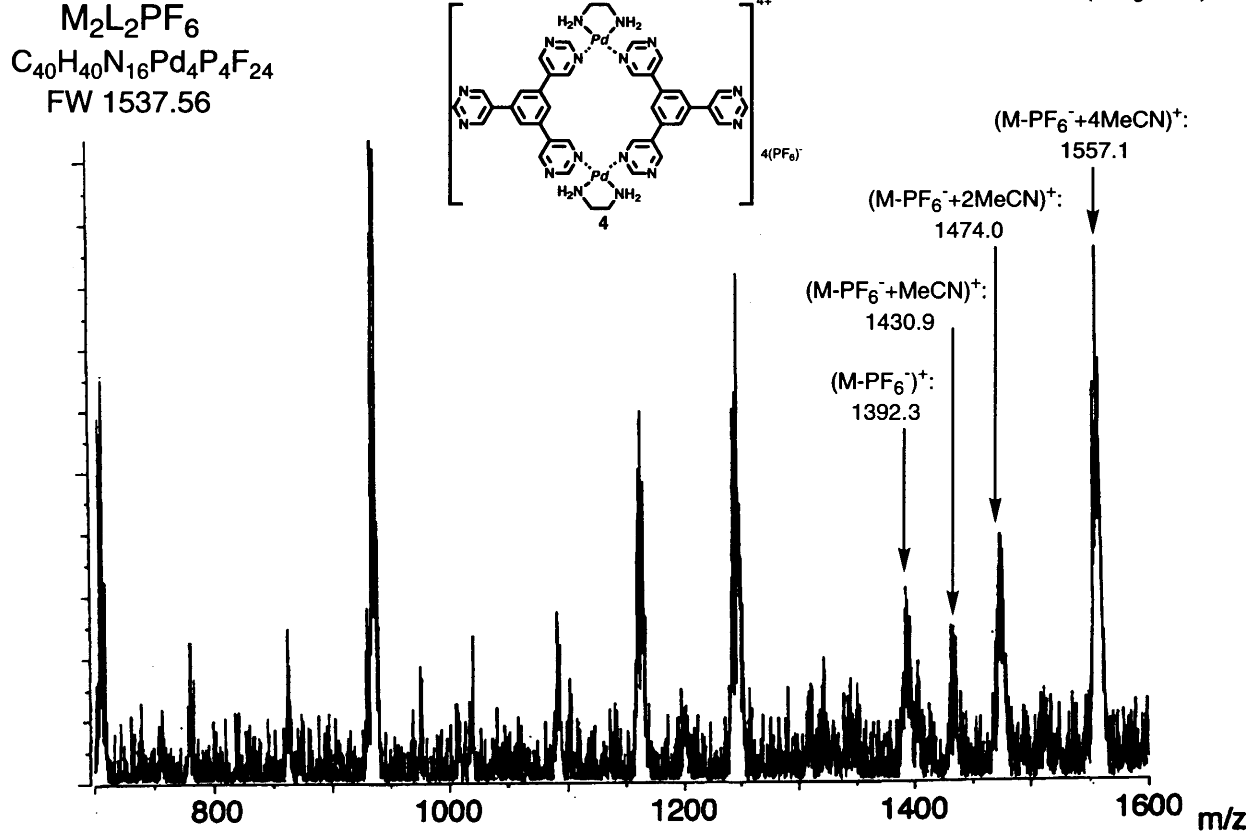
DEADT           :        71.7 usec
INTVL           :       125.0 usec
TIMES           :          64 times
DUMMY           :           1 times
PD              :      2.9040 sec
ACQTM           :   4096.0000 msec
PREDL           :     0.01000 msec
ININT           :   1000.0000 msec
RESOL           :        0.24 Hz
PW1             :        6.70 usec
OBNUC           : 1H
OBFRQ           :      500.00 MHz
OBSET           :   162410.00 Hz
RGAIN           :          24

SCANS           :          64 times

SLVNT           : D2O
SPINNING        :          17 Hz
TEMP            :        25.0 C
```

ESI-MS of **4** (PF_6 salt)



X-ray crystallographic data of **3**

Experimental Details

Table 1. A. Crystal data.

Empirical Formula	C144H270N108O135Pd18
Formula Weight	7589.56
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.20 x 0.20 x 0.40 mm
Crystal System	hexagonal
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	18(19.0-24.7 °)
Omega Scan Peak Width at Half-height	0.26 °
Lattice Parameters	a = 23.168(8) Å α = 90.0000° c = 34.10(2) Å V = 15852(6) Å
Space Group	$P6_3/m$ (#176)
Z value	2
Density (calculated)	1.590 g/cm^3
F(000)	7596.00
μ(CuKα)	89.06 cm^{-1}

B. Intensity Mesurements

Diffractometer	Rigaku AFC7S
Radiation	CuKα (λ = 1.54178 Å) graphite monochromated
Attenuator	Ni foll (factor = 8.99)
Take-off Angle	6.0 °
Detector Aperture	9.0 mm horizontal
Crystal to Detector Distance	235 mm
Temperature	230.0 °C
Scan Type	ω-2θ
Scan Rate	16.0 °/min (in ω) (up to 3 scans)
Scan Width	(1.26 + 0.30 tan θ)°
$2\theta_{max}$	120.2 °
No. of Reflections Measured	Total: 8700 Unique: 8026 (R_{int} = 0.200)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.1782-1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 3.50 σ(I))	1244
No. Variables	406
Reflection/Parameter Ratio	3.06
Residuals: R; Rw	0.129; 0.171
Goodness of Fit Indicator	3.81
Max Shift/Error in Final Cycle	1.66
Maximum peak in Final Diff. Map	1.53 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.69 $e^-/Å^3$

Table 2. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Pd(1)	0.7001(3)	0.2080(3)	0.4588(2)	6.6(2)	1/2
Pd(2)	0.9525(4)	0.2149(4)	0.7500	4.8(3)	
Pd(3)	0.7422(3)	0.0474(3)	0.6418(2)	5.3(2)	
Pd(4)	0.5187(4)	-0.0806(4)	0.7500	5.5(3)	1/2
N(1)	0.640(3)	0.124(3)	0.427(3)	10(3)	
N(2)	0.781(3)	0.212(3)	0.432(2)	8(2)	
N(3)	0.615(4)	0.204(3)	0.477(2)	9(3)	
N(4)	0.767(3)	0.300(3)	0.477(2)	7(2)	
N(5)	0.808(2)	0.142(2)	0.664(1)	1(1)	
N(6)	0.888(4)	0.207(3)	0.709(2)	9(2)	
N(7)	1.014(3)	0.216(4)	0.796(3)	12(3)	
N(8)	0.826(3)	0.049(2)	0.623(2)	4(2)	
N(9)	0.686(3)	-0.037(3)	0.614(3)	9(2)	
N(10)	0.655(2)	0.038(2)	0.666(2)	1(1)	
N(11)	0.564(3)	-0.010(2)	0.700(2)	3(2)	
N(12)	0.473(4)	-0.153(3)	0.799(2)	8(2)	
C(1)	0.763(7)	0.144(6)	0.413(2)	17(4)	
C(2)	0.680(5)	0.113(5)	0.395(3)	13(4)	
C(3)	0.758(3)	0.349(3)	0.468(2)	5(2)	
C(4)	0.789(3)	0.305(3)	0.513(3)	5(2)	
C(5)	0.828(3)	0.358(3)	0.537(2)	3(2)	
C(6)	0.820(4)	0.422(5)	0.516(3)	8(3)	
C(7)	0.853(3)	0.383(4)	0.583(2)	7(2)	
C(8)	0.897(4)	0.441(3)	0.607(4)	9(3)	
C(9)	0.907(4)	0.435(4)	0.642(2)	4(2)	
C(10)	0.897(3)	0.378(3)	0.660(2)	2(2)	
C(11)	0.870(3)	0.324(3)	0.641(2)	1(2)	
C(12)	0.846(2)	0.316(3)	0.600(3)	4(2)	
C(13)	0.861(3)	0.257(3)	0.660(3)	5(2)	
C(14)	0.897(3)	0.255(4)	0.693(2)	4(2)	
C(15)	0.845(3)	0.149(3)	0.698(2)	3(2)	
C(16)	0.803(3)	0.193(3)	0.646(2)	5(2)	
C(17)	1.051(4)	0.217(4)	0.776(2)	8(3)	
C(18)	0.808(3)	-0.001(4)	0.593(2)	7(3)	
C(19)	0.733(4)	-0.055(4)	0.605(3)	10(3)	
C(20)	0.627(4)	-0.006(3)	0.687(3)	4(2)	
C(21)	0.528(4)	0.014(3)	0.687(2)	5(2)	
C(22)	0.565(3)	0.053(2)	0.653(2)	1(1)	
C(23)	0.637(2)	0.072(3)	0.643(2)	3(2)	
C(24)	0.432(5)	-0.202(6)	0.773(2)	13(4)	

$_{eq}=8/3\pi^2(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}(aa^*bb^*)\cos\gamma+2U_{13}(aa^*cc^*)\cos\beta+ 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 3. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	0.073(4)	0.081(5)	0.105(7)	0.044(3)	0.001(6)	-0.002(5)
Pd(2)	0.033(5)	0.059(6)	0.09(1)	0.023(4)	0.0000	0.0000
Pd(3)	0.052(4)	0.041(3)	0.105(6)	0.021(3)	0.002(5)	-0.003(5)
Pd(4)	0.054(6)	0.043(5)	0.11(1)	0.023(4)	0.0000	0.0000
N(1)	0.04(4)	0.09(5)	0.2(1)	0.03(3)	0.02(6)	-0.07(6)
N(2)	0.04(5)	0.09(6)	0.09(7)	-0.02(4)	0.04(5)	0.05(5)
N(3)	0.21(7)	0.01(3)	0.15(9)	0.06(4)	0.02(7)	0.02(5)
N(4)	0.11(4)	0.05(3)	0.15(9)	0.07(3)	-0.06(5)	-0.03(5)
N(5)	0.04(3)	0.01(3)	-0.02(4)	0.02(2)	0.04(3)	0.04(3)
N(6)	0.10(6)	0.03(4)	0.16(8)	0.00(4)	-0.05(6)	-0.02(5)
N(7)	0.02(3)	0.25(7)	0.22(9)	0.07(3)	0.11(4)	-0.01(6)
N(8)	0.05(4)	0.04(4)	0.05(6)	0.01(3)	0.07(4)	0.04(4)
N(9)	0.05(4)	0.02(3)	0.3(1)	0.03(3)	0.02(6)	-0.03(5)
N(10)	-0.01(3)	-0.04(2)	0.04(5)	-0.05(2)	-0.02(3)	0.03(3)
N(11)	0.10(5)	-0.03(2)	0.03(6)	-0.01(3)	0.01(5)	-0.01(3)
N(12)	0.14(7)	-0.00(4)	0.12(8)	-0.01(4)	-0.03(6)	-0.04(5)
C(1)	0.4(2)	0.1(1)	-0.04(5)	-0.0(1)	0.0(1)	-0.01(8)
C(2)	0.08(8)	0.12(9)	0.2(1)	-0.06(7)	0.07(8)	-0.0(1)
C(3)	0.07(5)	0.05(4)	0.05(5)	0.02(4)	-0.02(4)	-0.11(4)
C(4)	0.05(5)	0.03(5)	0.08(9)	0.01(4)	0.03(6)	-0.03(6)
C(5)	0.00(4)	0.03(4)	0.04(5)	-0.02(3)	-0.08(4)	-0.04(5)
C(6)	0.05(6)	0.13(8)	0.09(9)	0.01(5)	0.09(6)	0.02(8)
C(7)	0.07(5)	0.17(7)	0.05(6)	0.08(4)	0.03(5)	0.11(5)
C(8)	0.04(5)	-0.01(4)	0.3(1)	-0.01(3)	0.04(8)	-0.04(7)
C(9)	0.07(5)	0.09(6)	-0.04(5)	0.00(5)	-0.06(4)	0.00(5)
C(10)	0.10(5)	-0.00(3)	-0.01(4)	0.02(3)	-0.00(5)	0.01(4)
C(11)	0.04(4)	0.05(4)	-0.03(4)	0.04(3)	-0.03(4)	-0.05(3)
C(12)	-0.01(3)	-0.02(3)	0.2(1)	-0.01(2)	-0.04(5)	0.01(5)
C(13)	-0.00(3)	0.08(5)	0.11(9)	0.03(3)	0.00(5)	0.02(6)
C(14)	0.02(4)	0.11(6)	0.04(7)	0.05(3)	-0.02(5)	-0.04(6)
C(15)	0.03(4)	0.05(4)	0.02(4)	0.02(3)	-0.03(4)	0.04(3)
C(16)	0.05(4)	0.01(3)	0.14(9)	0.03(3)	0.10(5)	0.04(5)
C(17)	0.14(7)	0.06(5)	0.07(8)	0.04(4)	-0.09(5)	0.05(4)
C(18)	0.02(5)	0.12(7)	0.07(8)	0.00(4)	0.05(5)	-0.04(6)
C(19)	0.14(8)	0.07(6)	0.2(1)	0.04(5)	-0.14(8)	-0.13(6)
C(20)	0.06(5)	-0.00(4)	0.08(8)	-0.01(4)	-0.02(6)	0.04(5)
C(21)	0.06(6)	-0.01(4)	0.07(8)	-0.02(4)	-0.04(6)	-0.05(5)
C(22)	0.07(4)	0.02(2)	0.00(4)	0.05(2)	0.04(3)	0.07(2)
C(23)	-0.03(3)	0.12(5)	0.01(6)	0.01(3)	0.02(4)	0.06(4)
C(24)	0.2(1)	0.2(1)	0.1(1)	0.02(8)	0.07(7)	0.07(8)

$$\exp(2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}+2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$$

Table 4. Bond Lengths (≈)

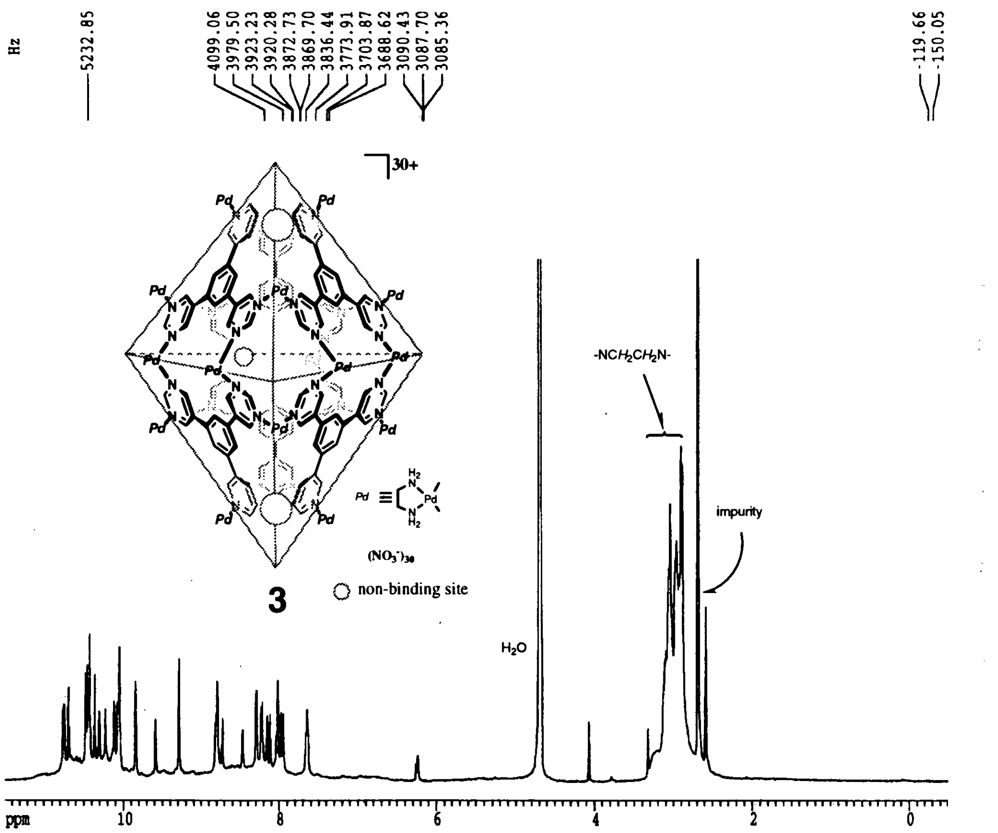
atom	atom	distance	atom	atom	distance
Pd(1)	N(1)	2.05(7)	Pd(1)	N(2)	2.05(7)
Pd(1)	N(3)	2.03(9)	Pd(1)	N(4)	2.00(6)
Pd(2)	N(6)	1.99(8)	Pd(2)	N(6)	1.99(8)
Pd(2)	N(7)	2.11(9)	Pd(2)	N(7)	2.11(9)
Pd(3)	N(5)	2.09(4)	Pd(3)	N(8)	2.01(6)
Pd(3)	N(9)	1.96(6)	Pd(3)	N(10)	2.10(5)
Pd(4)	N(11)	2.21(5)	Pd(4)	N(11)	2.21(5)
Pd(4)	N(12)	2.22(7)	Pd(4)	N(12)	2.22(7)
O(4)	N(14)	1.29(9)	O(5)	N(15)	1.3(1)
O(7)	N(16)	1.7(1)	O(9)	O(9)	1.72(9)
O(9)	N(17)	1.57(9)	O(11)	N(18)	1.6(1)
N(1)	C(2)	1.5(1)	N(2)	C(1)	1.6(1)
N(3)	C(3)	1.28(9)	N(3)	C(6)	1.4(1)
N(4)	C(3)	1.30(9)	N(4)	C(4)	1.3(1)
N(5)	C(15)	1.40(7)	N(5)	C(16)	1.39(7)
N(6)	C(14)	1.2(1)	N(6)	C(15)	1.26(8)
N(7)	C(17)	1.1(1)	N(8)	C(18)	1.47(8)
N(9)	C(19)	1.4(1)	N(10)	C(20)	1.14(7)
N(10)	C(23)	1.31(7)	N(11)	C(20)	1.50(9)
N(11)	C(21)	1.29(9)	N(12)	C(24)	1.4(1)
C(1)	C(2)	1.8(2)	C(4)	C(5)	1.36(8)
C(5)	C(6)	1.7(1)	C(5)	C(7)	1.68(9)
C(7)	C(8)	1.5(1)	C(7)	C(12)	1.59(9)
C(8)	C(9)	1.2(1)	C(9)	C(10)	1.36(9)
C(9)	C(22)	1.59(9)	C(10)	C(11)	1.27(7)
C(11)	C(12)	1.48(9)	C(11)	C(13)	1.59(9)
C(13)	C(14)	1.4(1)	C(13)	C(16)	1.51(8)
C(17)	C(17)	1.8(2)	C(18)	C(19)	1.6(1)
C(21)	C(22)	1.47(9)	C(22)	C(23)	1.53(7)
C(24)	C(24)	1.6(2)			

Table 5. Bond Angle (°)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Pd(1)	N(2)	89(3)	N(1)	Pd(1)	N(3)	86(3)
N(1)	Pd(1)	N(4)	166(3)	N(2)	Pd(1)	N(3)	172(3)
N(2)	Pd(1)	N(4)	83(3)	N(3)	Pd(1)	N(4)	100(3)
N(6)	Pd(2)	N(6)	90(5)	N(6)	Pd(2)	N(7)	175(3)
N(6)	Pd(2)	N(7)	86(3)	N(6)	Pd(2)	N(7)	86(3)
N(6)	Pd(2)	N(7)	175(3)	N(7)	Pd(2)	N(7)	97(3)
N(5)	Pd(3)	N(8)	84(2)	N(5)	Pd(3)	N(9)	172(3)
N(5)	Pd(3)	N(10)	97(2)	N(8)	Pd(3)	N(9)	91(2)
N(8)	Pd(3)	N(10)	173(2)	N(9)	Pd(3)	N(10)	88(2)
N(11)	Pd(4)	N(10)	100(3)	N(11)	Pd(4)	N(12)	179(2)
N(11)	Pd(4)	N(11)	82(2)	N(11)	Pd(4)	N(12)	82(2)
N(11)	Pd(4)	N(12)	179(2)	N(12)	Pd(4)	N(12)	97(3)
O(9)	O(9)	N(17)	57(3)	Pd(1)	N(1)	C(2)	110(5)
Pd(1)	N(2)	C(1)	112(6)	Pd(1)	N(3)	C(3)	129(6)
Pd(1)	N(3)	C(6)	108(7)	C(3)	N(3)	C(6)	116(9)
Pd(1)	N(4)	C(3)	119(5)	C(1)	N(4)	C(4)	116(5)
C(3)	N(4)	C(4)	111(8)	Pd(3)	N(5)	C(15)	121(4)
Pd(3)	N(5)	C(16)	113(4)	C(15)	N(5)	C(16)	125(6)
Pd(2)	N(6)	C(14)	119(6)	C(2)	N(6)	C(15)	118(6)
C(14)	N(6)	C(15)	123(9)	C(2)	N(7)	C(17)	93(7)
Pd(3)	N(8)	C(18)	109(4)	Pd(3)	N(9)	C(19)	100(5)
Pd(3)	N(10)	C(20)	114(6)	Pd(3)	N(10)	C(23)	106(4)
C(20)	N(10)	C(23)	135(6)	Pd(4)	N(11)	C(20)	112(5)
Pd(4)	N(11)	C(21)	114(6)	C(20)	N(11)	C(21)	133(7)
Pd(4)	N(12)	C(24)	92(6)	O(9)	N(17)	O(9)	66(5)
N(2)	C(1)	C(2)	103(11)	N(1)	C(2)	C(1)	108(8)
N(3)	C(3)	N(4)	127(8)	N(4)	C(4)	C(5)	133(8)
C(4)	C(5)	C(6)	103(6)	C(4)	C(5)	C(7)	145(7)
C(6)	C(5)	C(7)	105(6)	N(3)	C(6)	C(5)	115(8)
C(5)	C(7)	C(8)	143(8)	C(5)	C(7)	C(12)	100(7)
C(8)	C(7)	C(12)	112(7)	C(7)	C(8)	C(9)	121(8)
C(8)	C(9)	C(10)	126(8)	C(8)	C(9)	C(22)	98(7)
C(10)	C(9)	C(22)	134(6)	C(9)	C(10)	C(11)	120(7)
C(10)	C(11)	C(12)	125(6)	C(10)	C(11)	C(13)	122(6)
C(12)	C(11)	C(13)	114(6)	C(7)	C(12)	C(11)	112(6)
C(11)	C(13)	C(14)	124(6)	C(11)	C(13)	C(16)	118(6)
C(14)	C(13)	C(16)	118(7)	N(6)	C(14)	C(13)	125(8)
N(5)	C(15)	N(6)	119(7)	N(5)	C(16)	C(13)	107(6)
N(7)	C(17)	C(17)	129(6)	N(8)	C(18)	C(19)	100(6)
N(9)	C(19)	C(18)	123(7)	N(10)	C(20)	N(11)	110(7)
N(11)	C(21)	C(22)	104(7)	C(9)	C(22)	C(21)	103(6)
C(9)	C(22)	C(23)	127(5)	C(21)	C(22)	C(23)	125(6)
N(10)	C(23)	C(22)	109(5)	N(12)	C(24)	C(24)	129(5)

Table 6. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
Pd(1)	O(4)	3.56(8)	1	Pd(3)	O(9)	3.27(5)	65504
O(2)	O(2)	2.0(1)	65502	O(2)	O(2)	2.0(1)	66503
O(2)	O(3)	2.49(9)	1	O(2)	O(6)	3.3(1)	66503
O(2)	C(5)	3.34(9)	1	O(2)	C(4)	3.4(1)	1
O(2)	C(7)	3.41(9)	1	O(2)	C(7)	3.5(1)	66503
O(2)	C(12)	3.58(8)	1	O(3)	C(16)	3.3(1)	1
O(3)	C(12)	3.5(1)	1	O(3)	C(23)	3.5(1)	1
O(3)	C(11)	3.56(9)	1	O(5)	N(12)	2.8(1)	55610
O(5)	N(1)	3.0(1)	65607	O(5)	C(21)	3.2(1)	1
O(5)	N(11)	3.3(1)	1	O(5)	C(22)	3.3(1)	1
O(5)	C(2)	3.5(1)	65607	O(6)	C(3)	3.44(9)	65607
O(6)	C(3)	3.44(9)	55608	O(6)	C(3)	3.44(9)	54609
O(7)	O(8)	1.9(1)	1	O(7)	N(6)	3.2(1)	65404
O(7)	N(6)	3.2(1)	65607	O(7)	C(15)	3.2(1)	65404
O(7)	C(15)	3.2(1)	65607	O(7)	C(14)	3.4(1)	65404
O(7)	C(14)	3.4(1)	65607	O(7)	N(5)	3.60(7)	65404
O(7)	N(5)	3.60(7)	65607	O(8)	N(16)	2.1(1)	1
O(8)	C(15)	2.8(1)	65404	O(8)	C(15)	2.8(1)	65607
O(8)	O(9)	3.1(1)	1	O(8)	O(9)	3.1(1)	10
O(8)	N(5)	3.26(6)	65404	O(8)	N(5)	3.26(6)	65607
O(8)	N(17)	3.3(2)	1	O(8)	C(20)	3.4(1)	65404
O(8)	C(20)	3.4(1)	65607	O(8)	N(10)	3.36(7)	65404
O(8)	N(10)	3.36(7)	65607	O(8)	N(6)	3.4(1)	65404
O(8)	N(6)	3.4(1)	65607	O(9)	C(15)	3.25(8)	65404
O(9)	C(20)	3.53(9)	65404	O(11)	N(7)	2.7(1)	64611
O(11)	N(8)	3.0(1)	64502	O(11)	C(15)	3.3(1)	64502
O(11)	N(6)	3.3(1)	64502	O(11)	N(5)	3.3(1)	64502
O(11)	C(14)	3.5(1)	64502	N(1)	N(15)	3.5(1)	65607
N(2)	N(15)	3.5(1)	66608	N(3)	N(13)	3.42(9)	1
N(4)	N(15)	3.5(1)	66608	N(4)	N(13)	3.59(9)	1
N(9)	N(15)	3.6(1)	1	N(12)	N(15)	3.5(1)	55610
N(13)	C(3)	3.21(9)	1	N(13)	C(3)	3.21(9)	65502
N(13)	C(3)	3.21(9)	66503	N(13)	C(6)	3.23(7)	1
N(13)	C(6)	3.23(7)	65502	N(13)	C(6)	3.23(7)	66503
N(13)	C(4)	3.36(8)	1	N(13)	C(4)	3.36(8)	65502
N(13)	C(4)	3.36(8)	66503	N(13)	C(5)	3.49(6)	1
N(13)	C(5)	3.49(6)	65502	N(13)	C(5)	3.49(6)	66503
N(14)	C(23)	3.31(9)	1	N(14)	C(16)	3.4(1)	1
N(14)	C(6)	3.4(1)	66503	N(14)	C(4)	3.6(1)	1
N(15)	C(3)	3.5(1)	54609	N(17)	C(20)	3.3(1)	65404
N(17)	C(20)	3.3(1)	65607	N(18)	C(13)	3.3(1)	64502
N(18)	C(16)	3.5(1)	64502				



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PROCNO                  1

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PULPROG              zg30
TD                  32768
SOLVENT               D2O
NS                     16
DS                      2
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860212 sec
RG                    256
DW                 48.400 usec
DE                   6.00 usec
TE                  300.0 K
D1            1.00000000 sec
P1                   8.40 usec
SFO1          500.1330885 MHz
NUC1                   1H
PL1                 -4.00 dB

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SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                11.500 ppm
F1                5751.50 Hz
F2P                -0.500 ppm
F2                -250.07 Hz
PPMCM             0.60000 ppm/cm
HZCM            300.07800 Hz/cm
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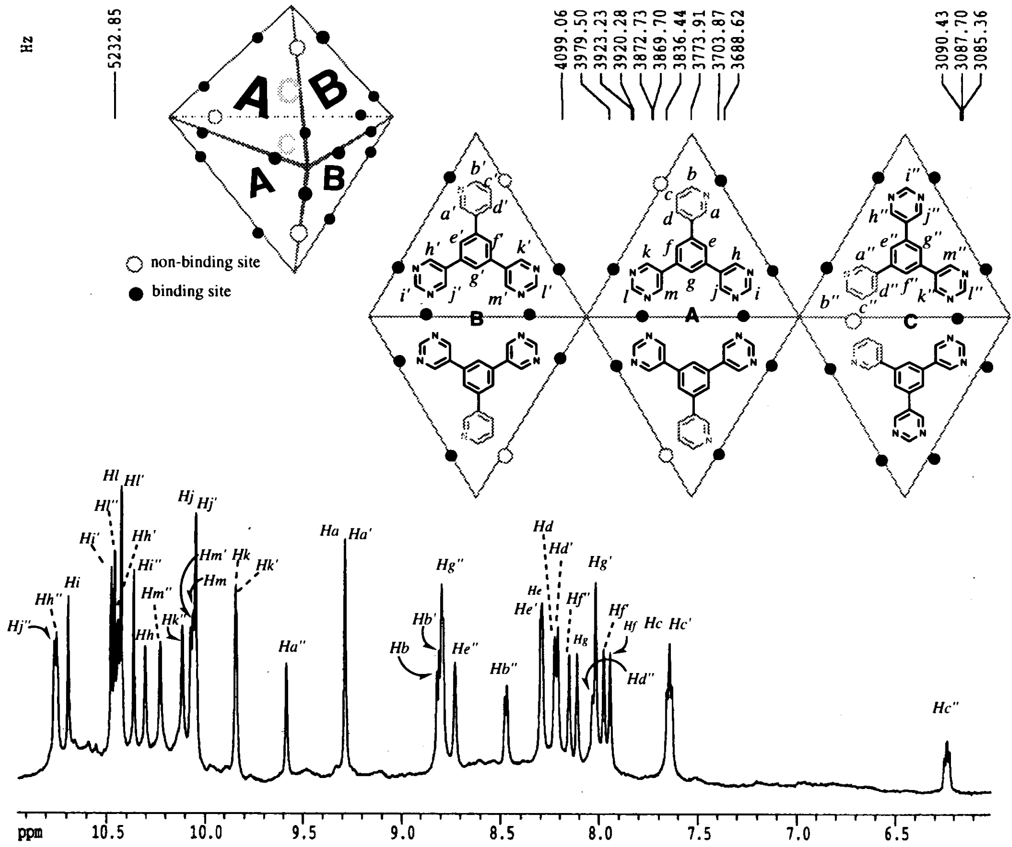
^{1}H NMR of **3**



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EXPNO                   1
PROCNO                  1

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PULPROG              zg30
TD                  32768
SOLVENT               D2O
NS                     16
DS                      2
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860212 sec
RG                    256
DW                 48.400 usec
DE                   6.00 usec
TE                  300.0 K
D1            1.00000000 sec
P1                   8.40 usec
SFO1          500.1330885 MHz
NUC1                   1H
PL1                 -4.00 dB

F2 - Processing parameters
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SF            500.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                10.950 ppm
F1                5476.33 Hz
F2P                 6.013 ppm
F2                3007.29 Hz
PPMCM             0.24684 ppm/cm
HZCM            123.45217 Hz/cm
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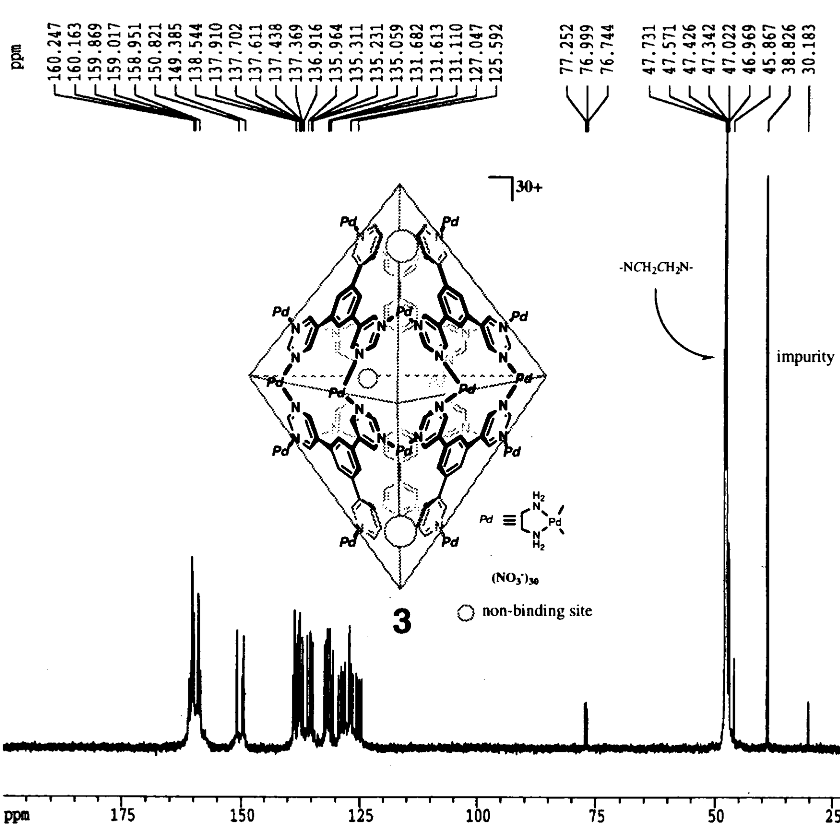
^{1}H NMR of **3**



^{13}C NMR of 3

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EXPNO                 1
PROCNO                1

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PULPROG         zgpg30
TD                65536
SOLVENT             D2O
NS                70000
DS                    2
SWH           39682.539 Hz
FIDRES         0.605507 Hz
AQ            0.8258036 sec
RG               3649.1
DW               12.600 usec
DE                 6.00 usec
TE                300.0 K
d11          0.03000000 sec
d12          0.00002000 sec
PL13              18.00 dB
D1           2.00000000 sec
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PCPD2             85.00 usec
SFO2        500.1320005 MHz
NUC2                 1H
PL2               -6.00 dB
PL12              10.00 dB
P1                10.30 usec
SFO1        125.7736214 MHz
NUC1                13C
PL1                0.00 dB

F2 - Processing parameters
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SF          125.7577849 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             200.000 ppm
F1             25151.56 Hz
F2P             -10.000 ppm
F2             -1257.58 Hz
PPMCM          10.50000 ppm/cm
HZCM         1320.45667 Hz/cm
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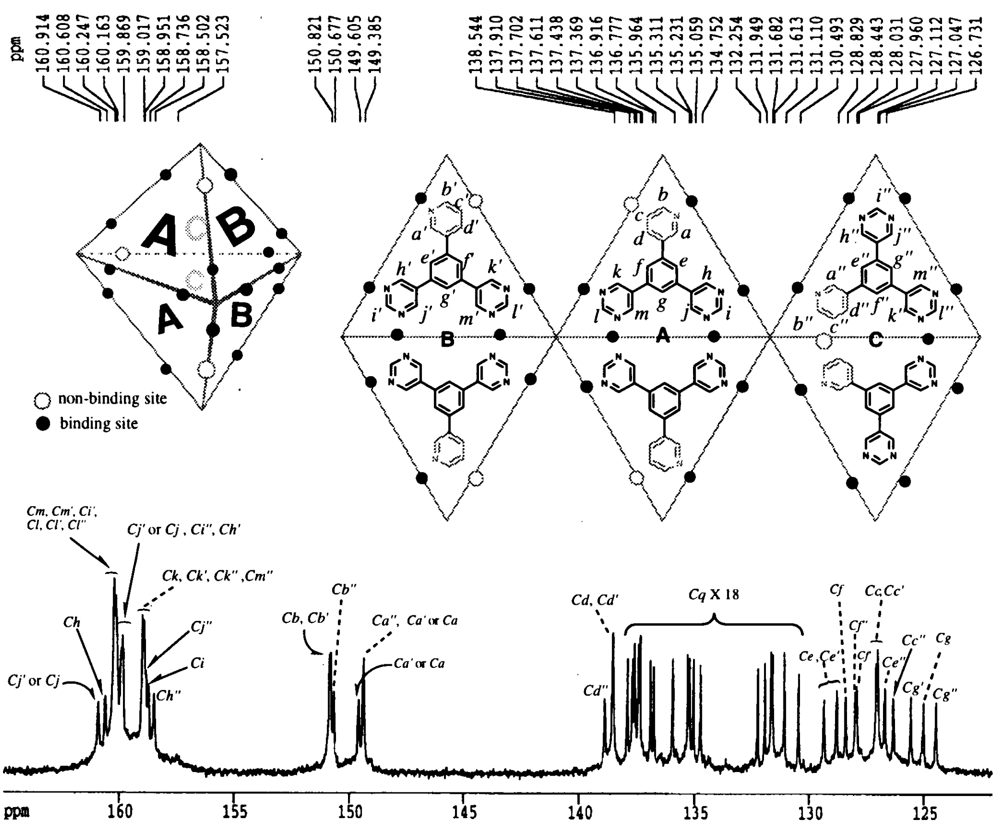

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Current Data Parameters
NAME                ume
EXPNO                 1
PROCNO                1
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^{13}C NMR of 3

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PROBHD   10 mm BBO BB-1
PULPROG         zgpg30
TD                65536
SOLVENT             D2O
NS                70000
DS                    2
SWH           39682.539 Hz
FIDRES         0.605507 Hz
AQ            0.8258036 sec
RG               3649.1
DW               12.600 usec
DE                 6.00 usec
TE                300.0 K
d11          0.03000000 sec
d12          0.00002000 sec
PL13              18.00 dB
D1           2.00000000 sec
CPDPRG2         waltz16
PCPD2             85.00 usec
SFO2        500.1320005 MHz
NUC2                 1H
PL2               -6.00 dB
PL12              10.00 dB
P1                10.30 usec
SFO1        125.7736214 MHz
NUC1                13C
PL1                0.00 dB

F2 - Processing parameters
SI                32768
SF          125.7577849 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             165.000 ppm
F1             20750.03 Hz
F2P             122.000 ppm
F2             15342.45 Hz
PPMCM           2.15000 ppm/cm
HZCM          270.37924 Hz/cm
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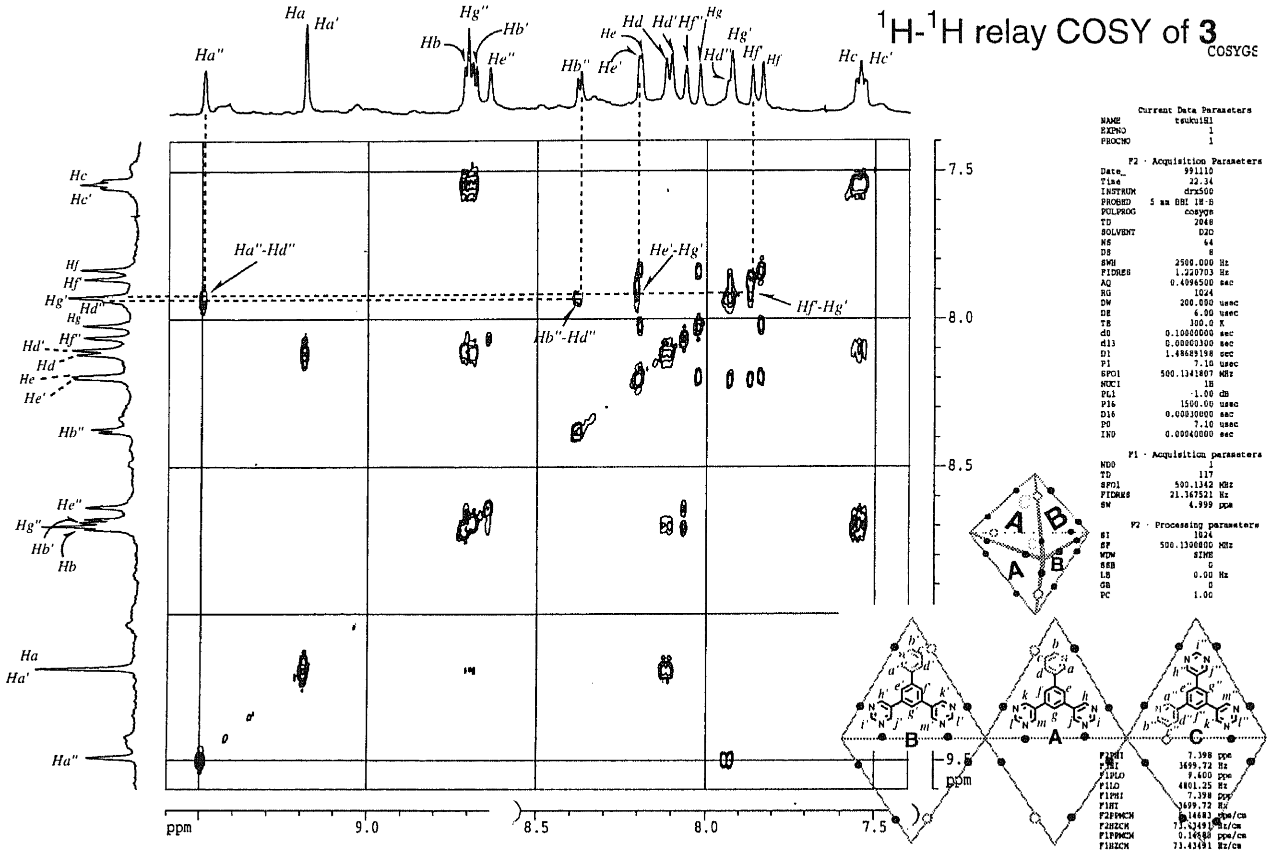

^{1}H-^{1}H relay COSY of **3**

COSYGS

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PROCNO                   1

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INSTRUM             drx500
PROBHD     5 mm BBI 1H-B
PULPROG             cosygs
TD                    2048
SOLVENT                D2O
NS                      64
DS                       8
SWH               2500.000 Hz
FIDRES            1.220703 Hz
AQ               0.4096500 sec
RG                    1024
DW                 200.000 usec
DE                    6.00 usec
TE                   300.0 K
d0              0.10000000 sec
d13             0.00000300 sec
D1              1.48689198 sec
P1                    7.10 usec
SFO1           500.1341807 MHz
NUC1                    1H
PL1                  -1.00 dB
P16                1500.00 usec
D16             0.00030000 sec
P0                    7.10 usec
IN0             0.00040000 sec

      F1 - Acquisition parameters
ND0                      1
TD                     117
SFO1              500.1342 MHz
FIDRES           21.367521 Hz
SW                   4.999 ppm

      F2 - Processing parameters
SI                    1024
SF             500.1300000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

F2PHI                7.398 ppm
F2HI               3699.72 Hz
F1PLO                9.600 ppm
F1LO               4801.25 Hz
F1PHI                7.398 ppm
F1HI               3699.72 Hz
F2PPMCM            0.14683 ppm/cm
F2HZCM            73.43491 Hz/cm
F1PPMCM            0.14688 ppm/cm
F1HZCM            73.43491 Hz/cm
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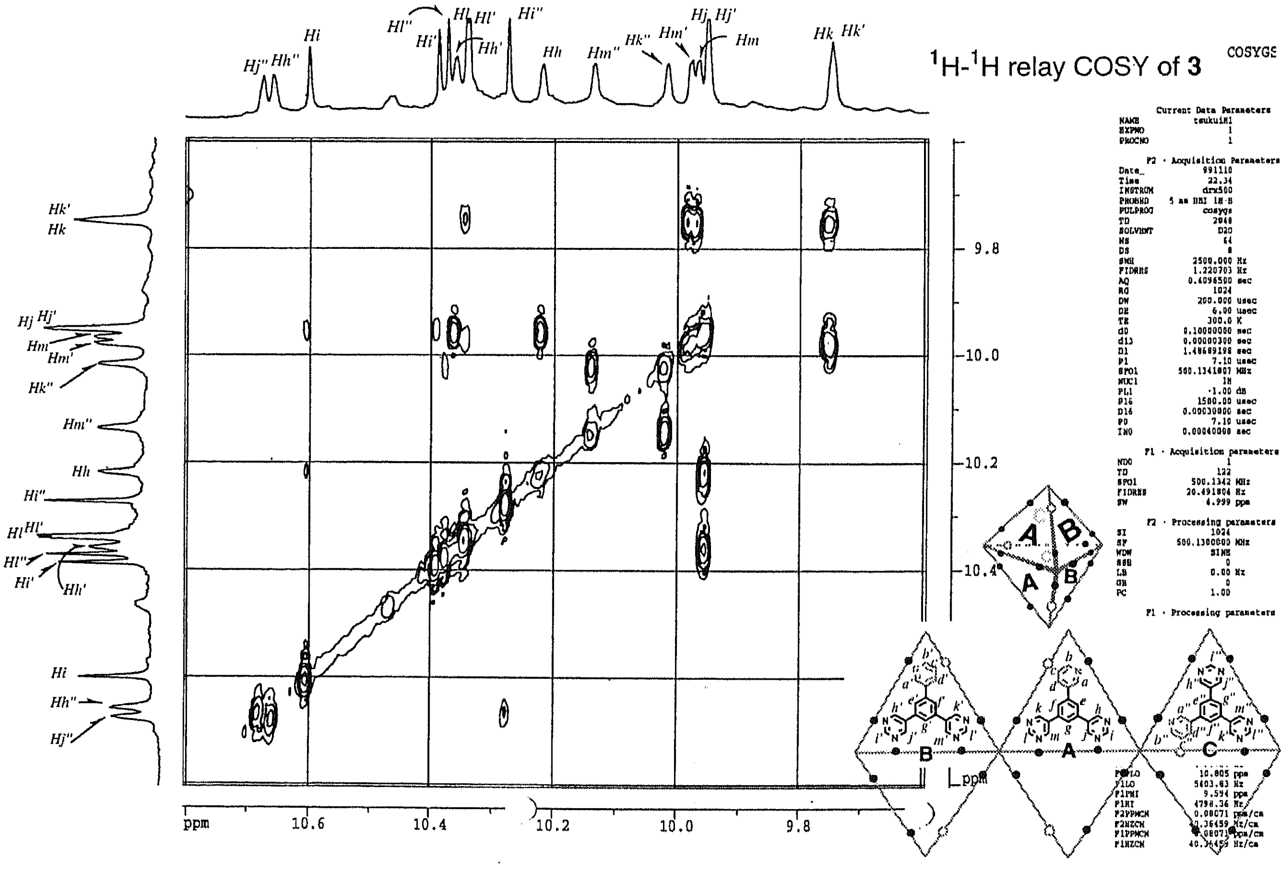

^{1}H-^{1}H relay COSY of **3**

COSYGS

```
        Current Data Parameters
NAME              tsukuiH1
EXPNO                    1
PROCNO                   1

      F2 - Acquisition Parameters
Date_               991110
Time                 22.34
INSTRUM             drx500
PROBHD     5 mm DBI 1H-B
PULPROG             cosygs
TD                    2048
SOLVENT                D2O
NS                      64
DS                       8
SWH               2500.000 Hz
FIDRES            1.220703 Hz
AQ               0.4096500 sec
RG                    1024
DW                 200.000 usec
DE                    6.00 usec
TE                   300.0 K
d0              0.10000000 sec
d13             0.00000300 sec
D1              1.48689198 sec
P1                    7.10 usec
SFO1           500.1341807 MHz
NUC1                    1H
PL1                  -1.00 dB
P16                1500.00 usec
D16             0.00030000 sec
P0                    7.10 usec
IN0             0.00040000 sec

      F1 - Acquisition parameters
ND0                      1
TD                     122
SFO1              500.1342 MHz
FIDRES           20.491804 Hz
SW                   4.999 ppm

      F2 - Processing parameters
SI                    1024
SF             500.1300000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters

F1PLO               10.805 ppm
F1LO               5403.83 Hz
F1PHI                9.594 ppm
F1HI               4798.36 Hz
F2PPMCM            0.08071 ppm/cm
F2HZCM            40.36459 Hz/cm
F1PPMCM            0.08071 ppm/cm
F1HZCM            40.36459 Hz/cm
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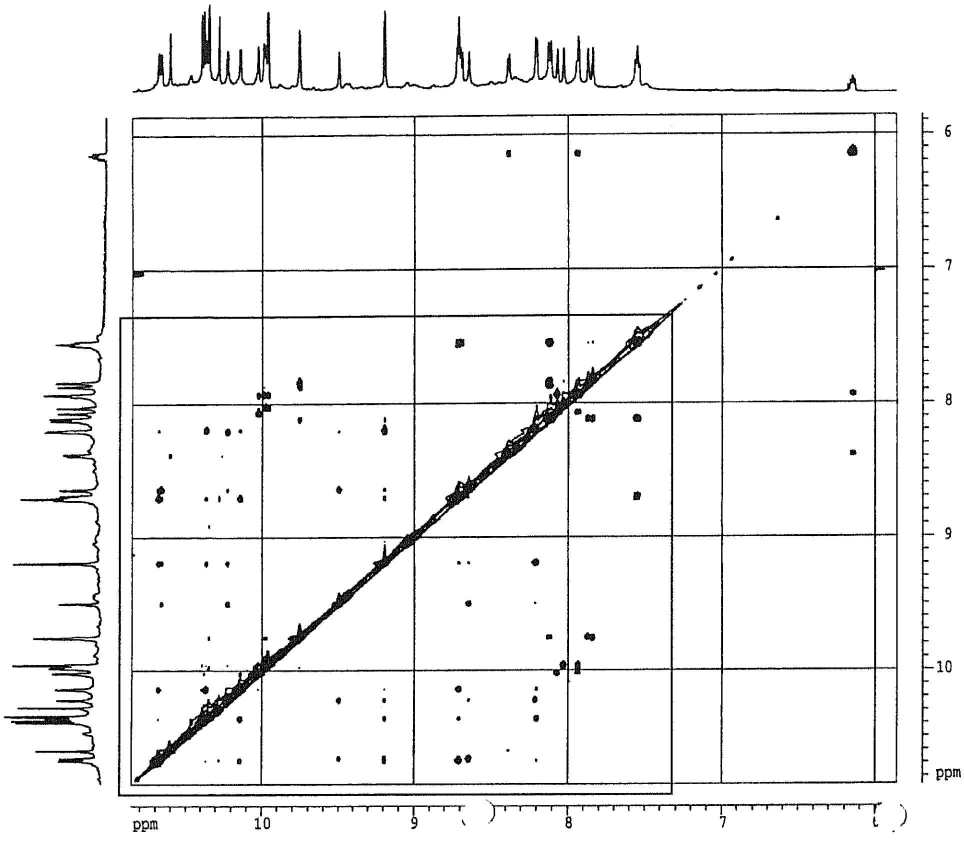
NOESY of 3



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EXPNO                    1
PROCNO                   1

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PULPROG           noesygptp
TD                    2048
SOLVENT                D2O
NS                      16
DS                       4
SWH            2500.000 Hz
FIDRES         1.220703 Hz
AQ            0.4096500 sec
RG                      64
DW              200.000 usec
DE                 6.00 usec
TE                300.0 K
d0           0.00000300 sec
D16          0.00030000 sec
D8           0.30000001 sec
P16             1500.00 usec
d20          0.14820001 sec
D1           2.00000000 sec
P1                 7.10 usec
SFO1        500.1341807 MHz
NUC1                    1H
PL1               -1.00 dB
GPX1               0.00 %
GPY1               0.00 %
GPZ1              40.00 %
GPNAM1            sine.100
P2                14.20 usec
GPX2               0.00 %
GPY2               0.00 %
GPZ2             -40.00 %
GPNAM2            sine.100
IN0          0.00020000 sec

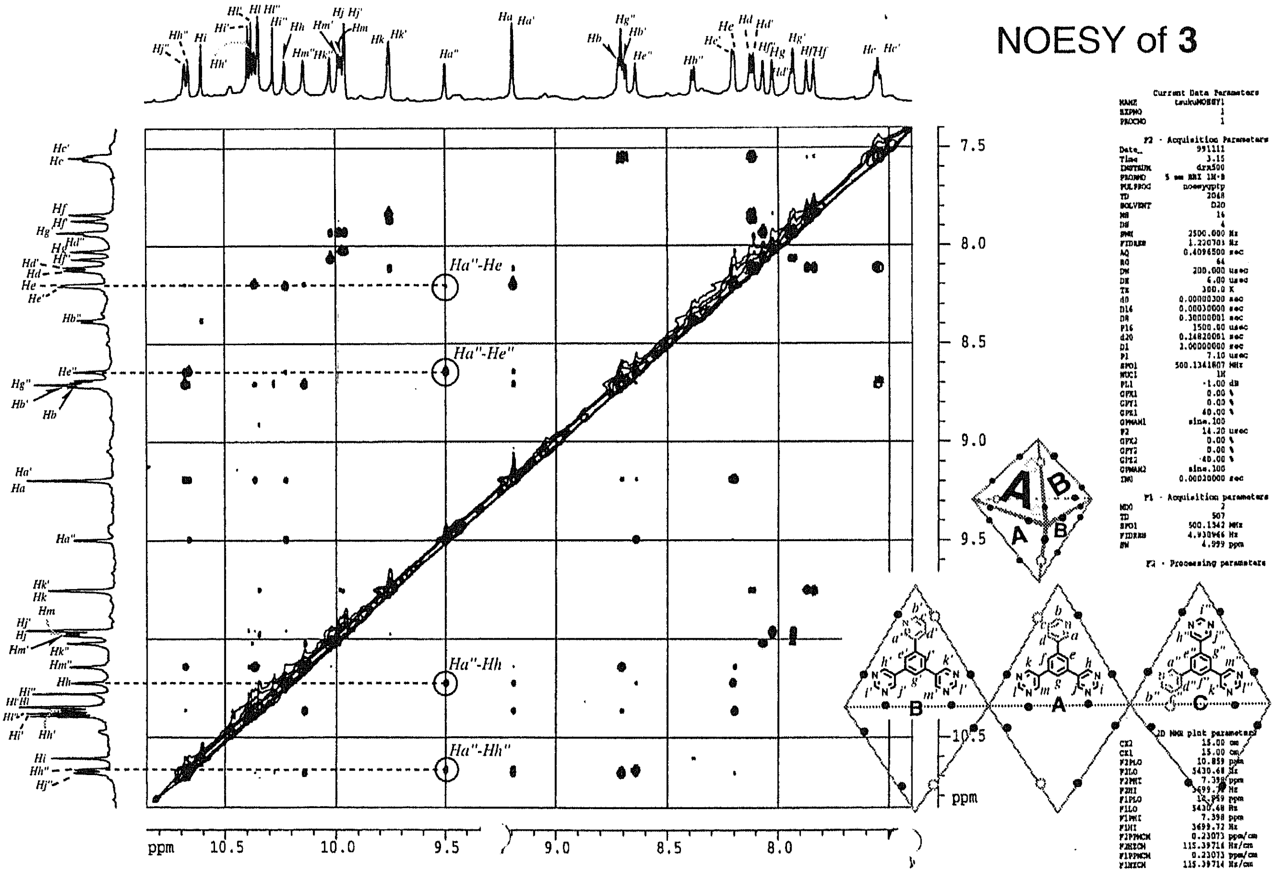
     F1 - Acquisition parameters
ND0                      2
TD                     510
SFO1           500.1342 MHz
FIDRES         4.901961 Hz
SW                4.999 ppm

     F2 - Processing parameters
SI                    1024
SF          500.1300000 MHz
WDW                 QSINE
SSB                      2
LB                 0.00 Hz
GB                       0
PC                    1.40

     F1 - Processing parameters
SI                    1024
MC2                   TPPI
SF          500.1300000 MHz
WDW                 QSINE
SSB                      2
LB                 0.00 Hz
GB                       0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO             10.859 ppm
F2LO             5430.68 Hz
F2PHI              5.860 ppm
F2HI             2930.68 Hz
F1PLO             10.859 ppm
F1LO             5430.68 Hz
F1PHI              5.860 ppm
F1HI             2930.68 Hz
F2PPMCM          0.33325 ppm/cm
F2HZCM         166.66666 Hz/cm
F1PPMCM          0.33325 ppm/cm
F1HZCM         166.66666 Hz/cm
```

NOESY of 3



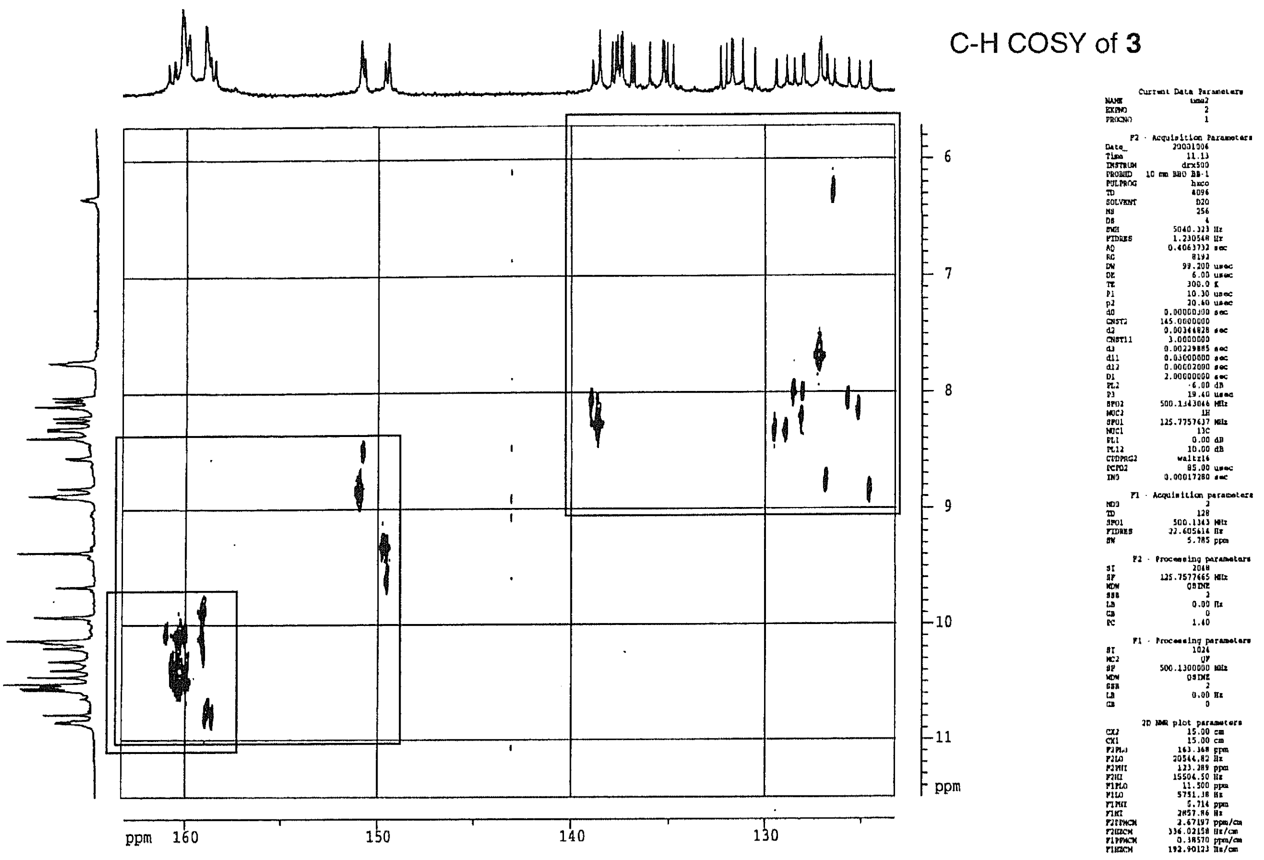
```
        Current Data Parameters
NAME           tsukuNOESY1
EXPNO                    1
PROCNO                   1

     F2 - Acquisition Parameters
Date_               991111
Time                  3.15
INSTRUM             drx500
PROBHD    5 mm BBI 1H-B
PULPROG           noesygptp
TD                    2048
SOLVENT                D2O
NS                      16
DS                       4
SWH            2500.000 Hz
FIDRES         1.220703 Hz
AQ            0.4096500 sec
RG                      64
DW              200.000 usec
DE                 6.00 usec
TE                300.0 K
d0           0.00000300 sec
D16          0.00030000 sec
D8           0.30000001 sec
P16             1500.00 usec
d20          0.14820001 sec
D1           2.00000000 sec
P1                 7.10 usec
SFO1        500.1341807 MHz
NUC1                    1H
PL1               -1.00 dB
GPX1               0.00 %
GPY1               0.00 %
GPZ1              40.00 %
GPNAM1            sine.100
P2                14.20 usec
GPX2               0.00 %
GPY2               0.00 %
GPZ2             -40.00 %
GPNAM2            sine.100
IN0          0.00020000 sec

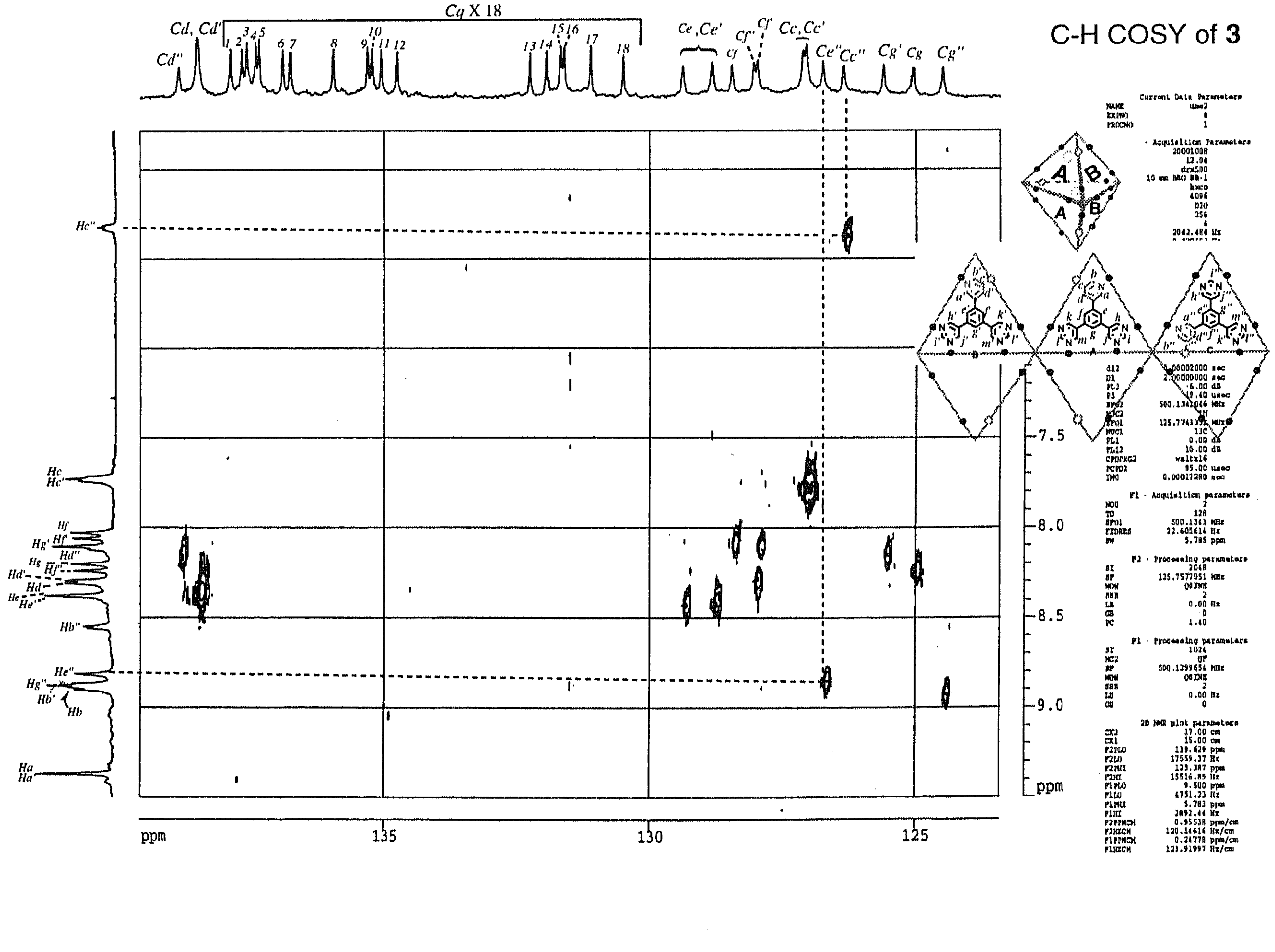
     F1 - Acquisition parameters
ND0                      2
TD                     507
SFO1           500.1342 MHz
FIDRES         4.930966 Hz
SW                4.999 ppm

     F2 - Processing parameters

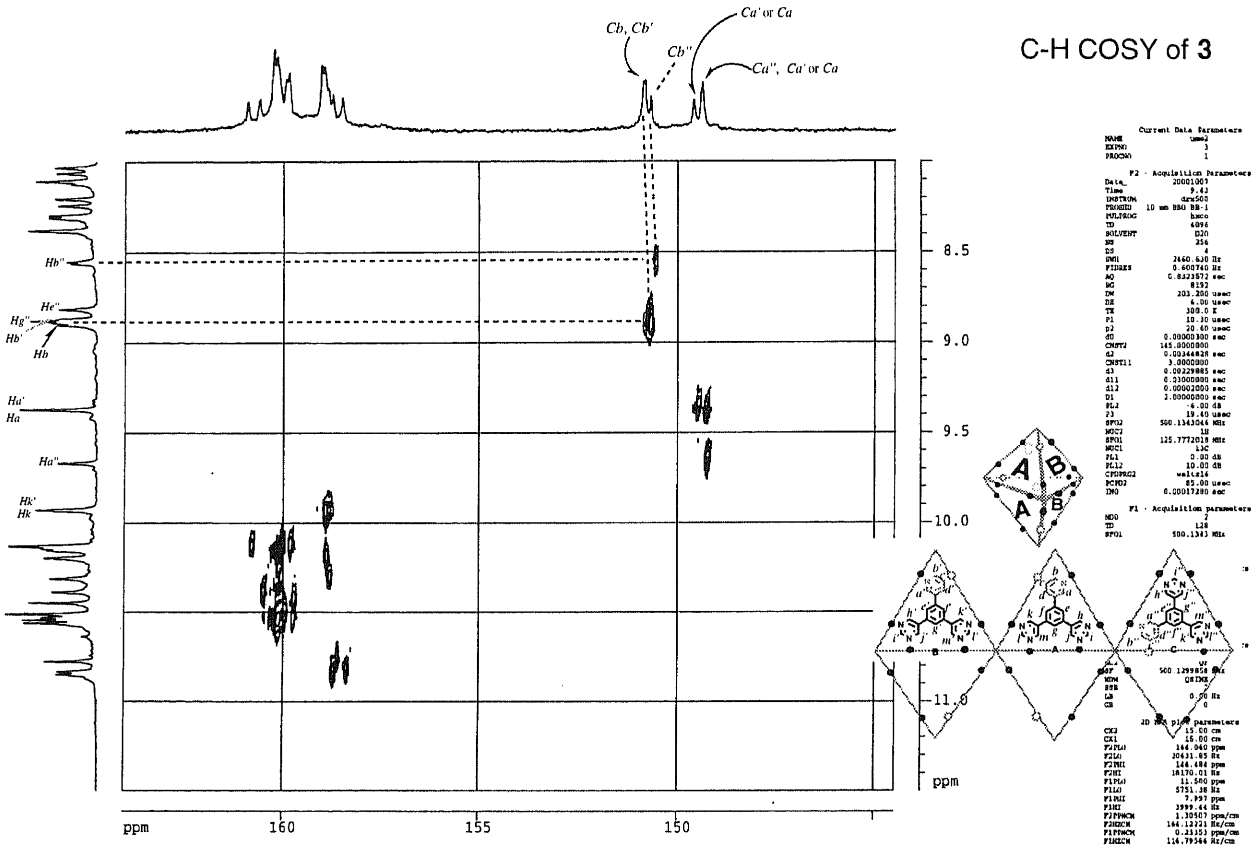
        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO             10.859 ppm
F2LO             5430.68 Hz
F2PHI              7.398 ppm
F2HI             3699.72 Hz
F1PLO             10.859 ppm
F1LO             5430.68 Hz
F1PHI              7.398 ppm
F1HI             3699.72 Hz
F2PPMCM          0.23073 ppm/cm
F2HZCM         115.39714 Hz/cm
F1PPMCM          0.23073 ppm/cm
F1HZCM         115.39714 Hz/cm
```



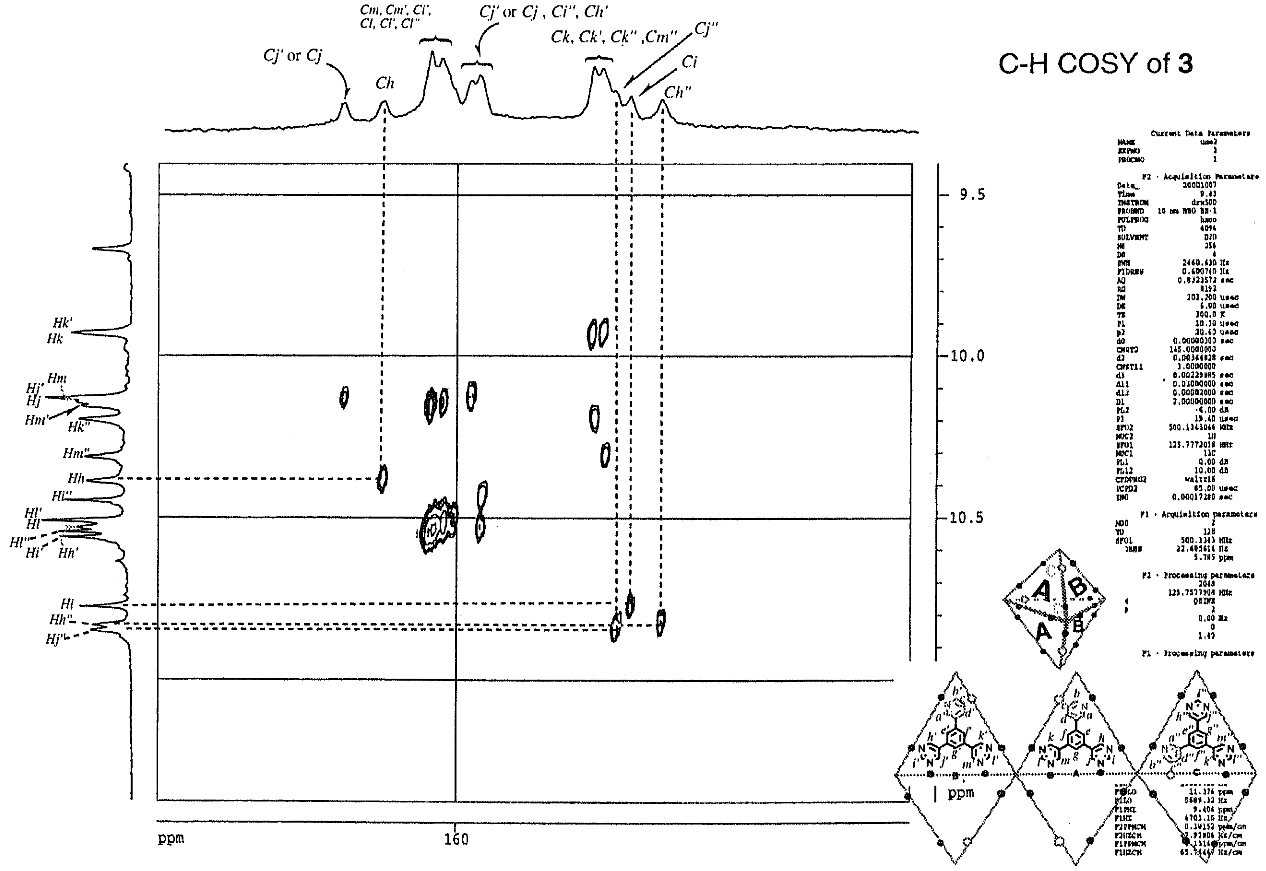
C-H COSY of **3**



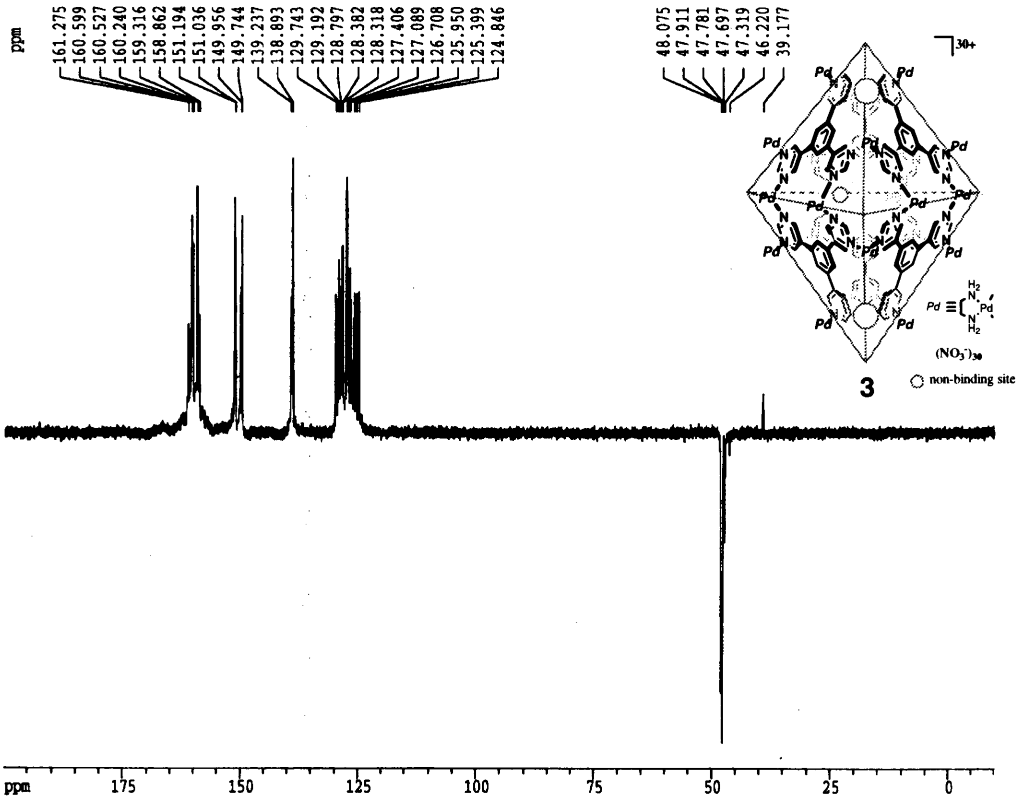
C-H COSY of **3**



C-H COSY of **3**



C-H COSY of **3**



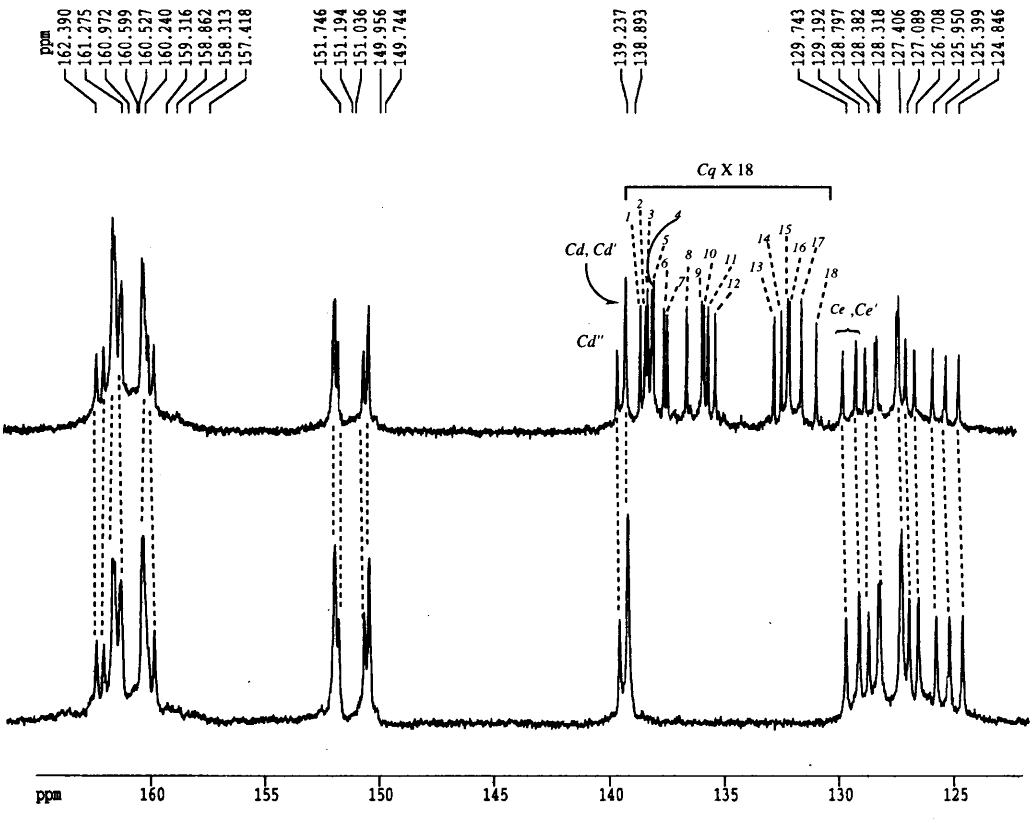
```
Current Data Parameters
NAME                 ume2
EXPNO                   1
```

DEPT of 3

```
TIME                11.47
INSTRUM            drx500
PROBHD   10 mm BBO BB-1
PULPROG          dept135
TD                  65536
SOLVENT               D2O
NS                  30000
DS                      4
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8258036 sec
RG                   8192
DW                 12.600 usec
DE                   6.00 usec
TE                  300.0 K
P1                  10.30 usec
p2                  20.60 usec
P3                  19.40 usec
p4                  38.80 usec
CNST2         145.0000000
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001311 sec
D1             2.00000000 sec
PL2                 -6.00 dB
SFO2          500.1320005 MHz
NUC2                   1H
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB
PL12                10.00 dB
CPDPRG2           waltz16
PCPD2               85.00 usec

F2 - Processing parameters
SI                  32768
SF            125.7577390 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               200.000 ppm
F1               25151.55 Hz
F2P               -10.000 ppm
F2               -1257.58 Hz
PPMCM            10.50000 ppm/cm
HZCM           1320.45618 Hz/cm
```



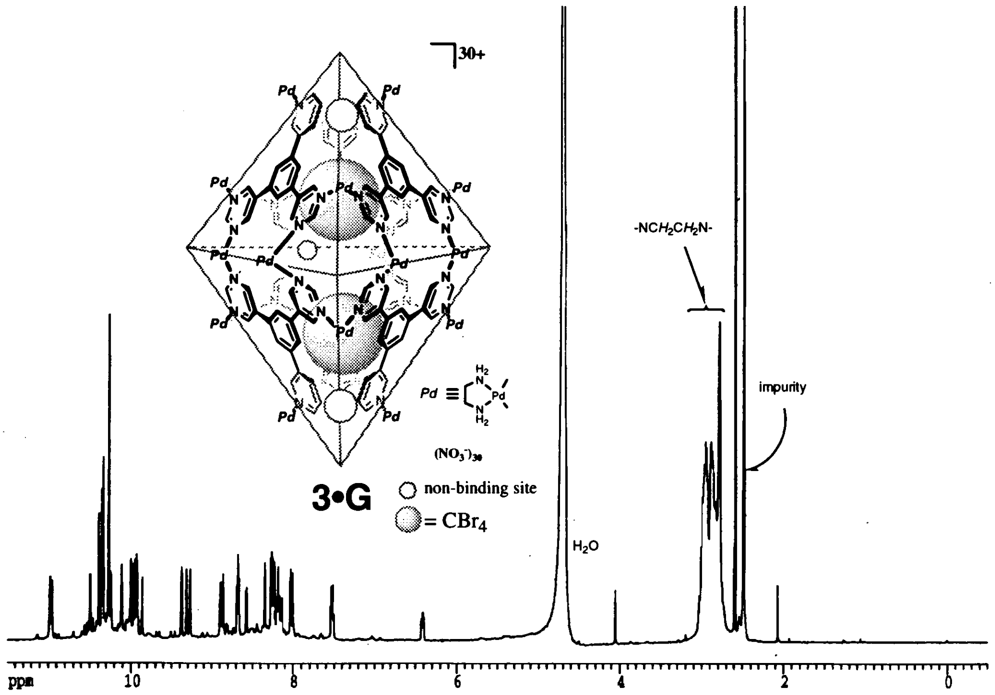
```
Current Data Parameters
```

DEPT of 3

```
F2 - Acquisition Parameters
Date_            20001005
Time                11.47
INSTRUM            drx500
PROBHD   10 mm BBO BB-1
PULPROG          dept135
TD                  65536
SOLVENT             CDCl3
NS                  30000
DS                      4
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8258036 sec
RG                   8192
DW                 12.600 usec
DE                   6.00 usec
TE                  300.0 K
P1                  10.30 usec
p2                  20.60 usec
P3                  19.40 usec
p4                  38.80 usec
CNST2         145.0000000
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001311 sec
D1             2.00000000 sec
PL2                 -6.00 dB
SFO2          500.1320005 MHz
NUC2                   1H
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB
PL12                10.00 dB
CPDPRG2           waltz16
PCPD2               85.00 usec

F2 - Processing parameters
SI                  32768
SF            125.7577390 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               165.000 ppm
F1               20750.03 Hz
F2P               122.000 ppm
F2               15342.44 Hz
PPMCM             2.15000 ppm/cm
HZCM            270.37912 Hz/cm
```



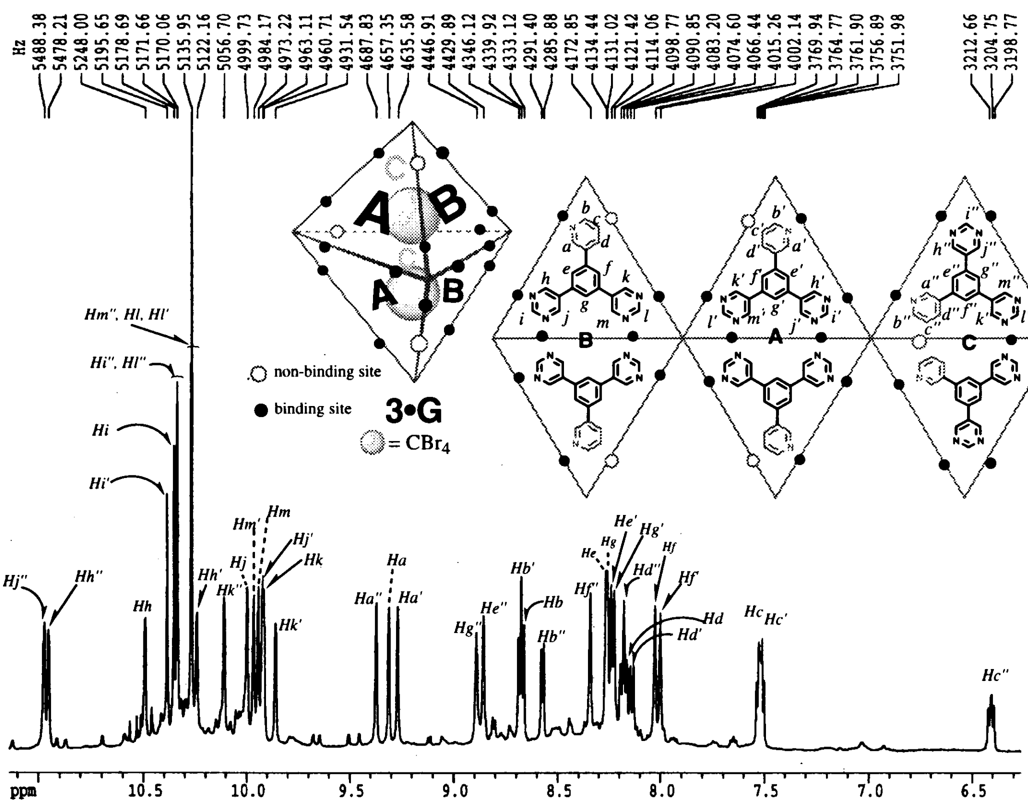
```
Current Data Parameters
NAME          tsukuiH7
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           991207
Time              3.46
INSTRUM         drx500
PROBHD   5 mm BBI 1H-B
PULPROG           zg30
TD               32768
SOLVENT            D2O
NS                  16
DS                   2
SWH          10330.578 Hz
FIDRES        0.315264 Hz
AQ           1.5860212 sec
RG                  57
DW              48.400 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec
P1                7.10 usec
SFO1       500.1330885 MHz
NUC1                1H
PL1              -1.00 dB

F2 - Processing parameters
SI               16384
SF         500.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
F1P             11.500 ppm
F1             5751.50 Hz
F2P             -0.500 ppm
F2             -250.07 Hz
PPMCM          0.60000 ppm/cm
HZCM         300.07800 Hz/cm
```

^{1}H NMR of **3•G**



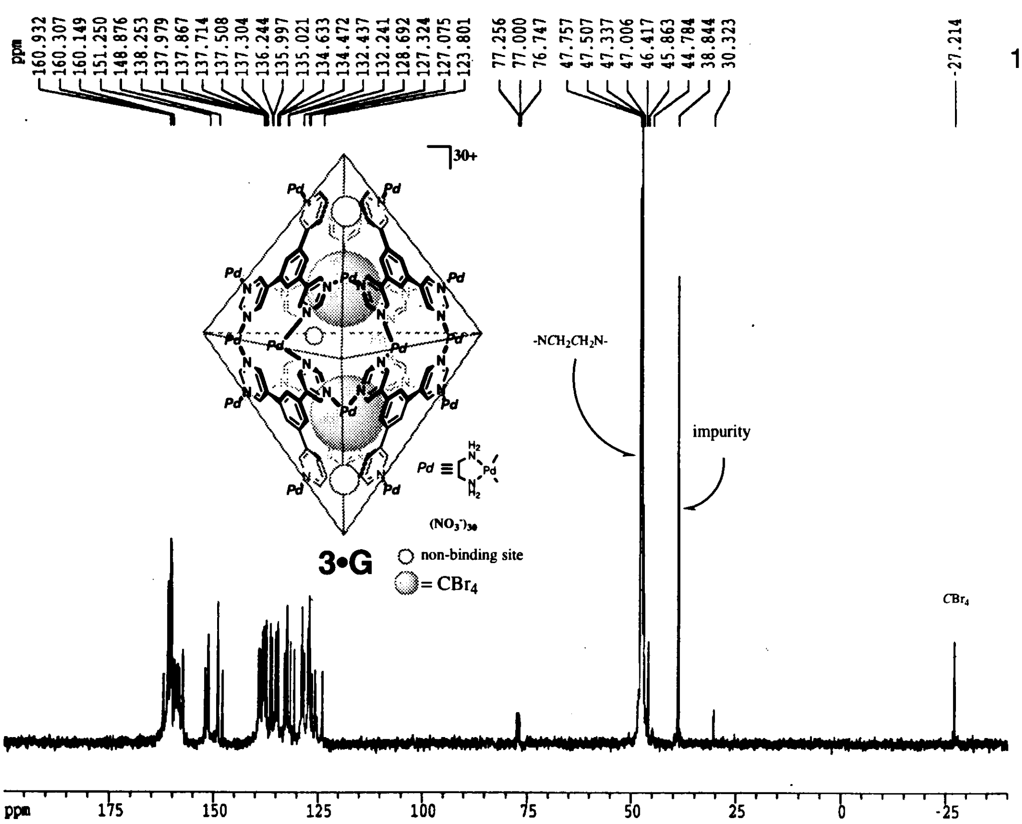
```
Current Data Parameters
NAME          tsukuiH7
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           991207
Time              3.46
INSTRUM         drx500
PROBHD   5 mm BBI 1H-B
PULPROG           zg30
TD               32768
SOLVENT            D2O
NS                  16
DS                   2
SWH          10330.578 Hz
FIDRES        0.315264 Hz
AQ           1.5860212 sec
RG                  57
DW              48.400 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec
P1                7.10 usec
SFO1       500.1330885 MHz
NUC1                1H
PL1              -1.00 dB

F2 - Processing parameters
SI               16384
SF         500.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
F1P             11.143 ppm
F1             5573.01 Hz
F2P              6.266 ppm
F2             3133.71 Hz
PPMCM          0.24387 ppm/cm
HZCM         121.96480 Hz/cm
```

^{1}H NMR of **3•G**



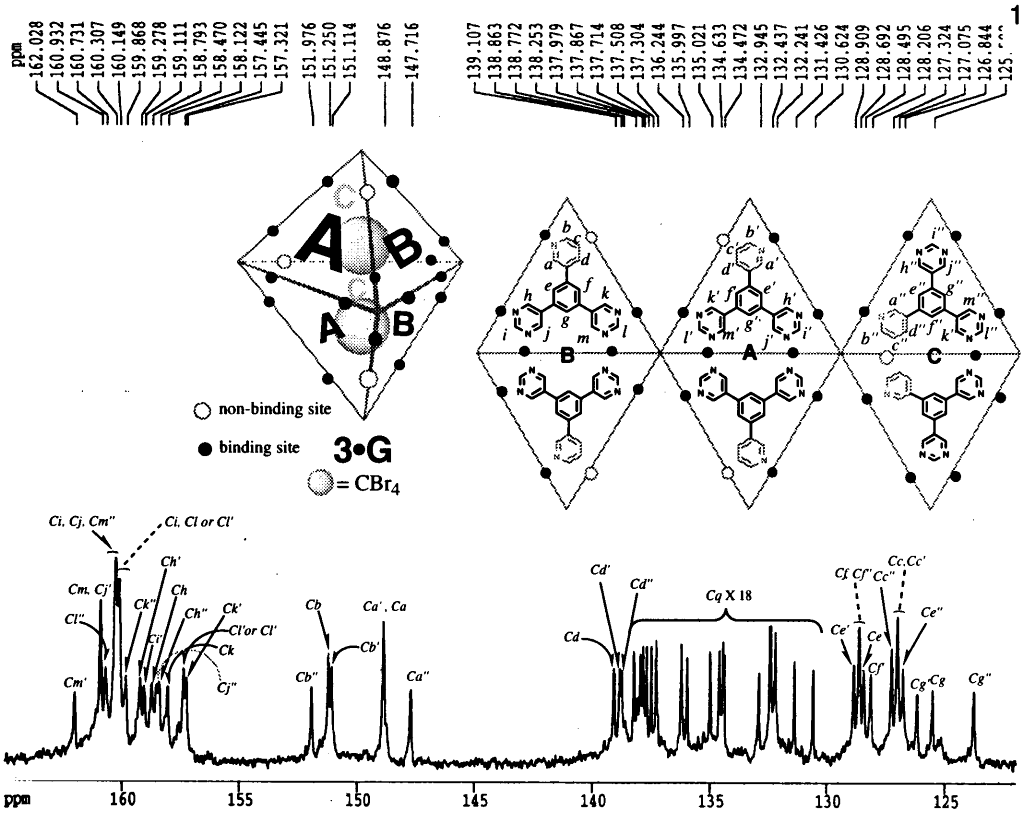
```
Current Data Parameters
NAME                 ume3
EXPNO                   3
```

^{13}C NMR of **3•G**

```
Time                17.03
INSTRUM            drx500
PROBHD    10 mm BBO BB-1
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                  20924
DS                      2
SWH             44642.855 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                 3649.1
DW                 11.200 usec
DE                   6.00 usec
TE                  300.0 K
d11            0.03000000 sec
d12            0.00002000 sec
PL13                18.00 dB
D1             2.00000000 sec
CPDPRG2          waltz16
PCPD2               85.00 usec
SFO2          500.1320005 MHz
NUC2                   1H
PL2                 -6.00 dB
PL12                10.00 dB
P1                  10.30 usec
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB

F2 - Processing parameters
SI                  32768
SF            125.7577842 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               200.000 ppm
F1               25151.55 Hz
F2P               -40.000 ppm
F2               -5030.31 Hz
PPMCM            12.00000 ppm/cm
HZCM           1509.09338 Hz/cm
```

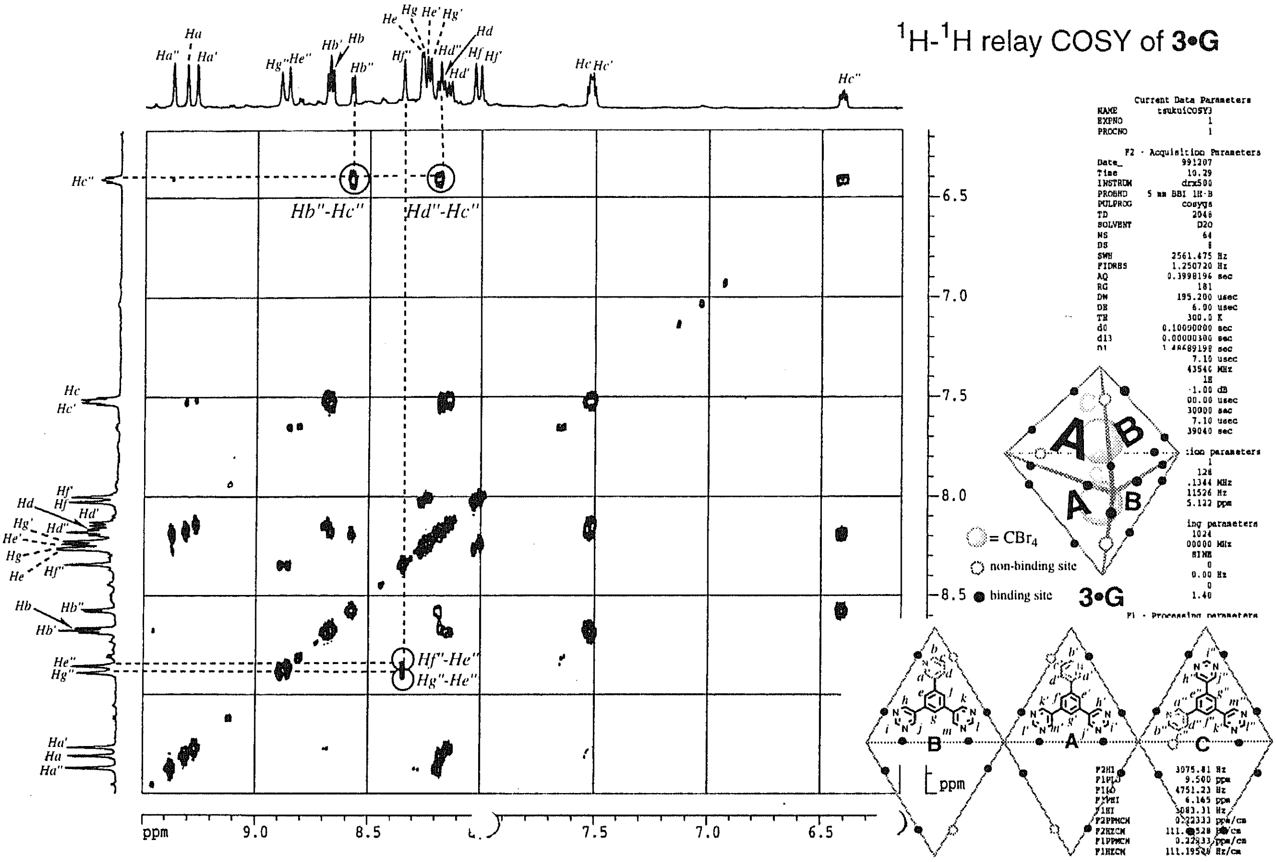


^{13}C NMR of **3•G**

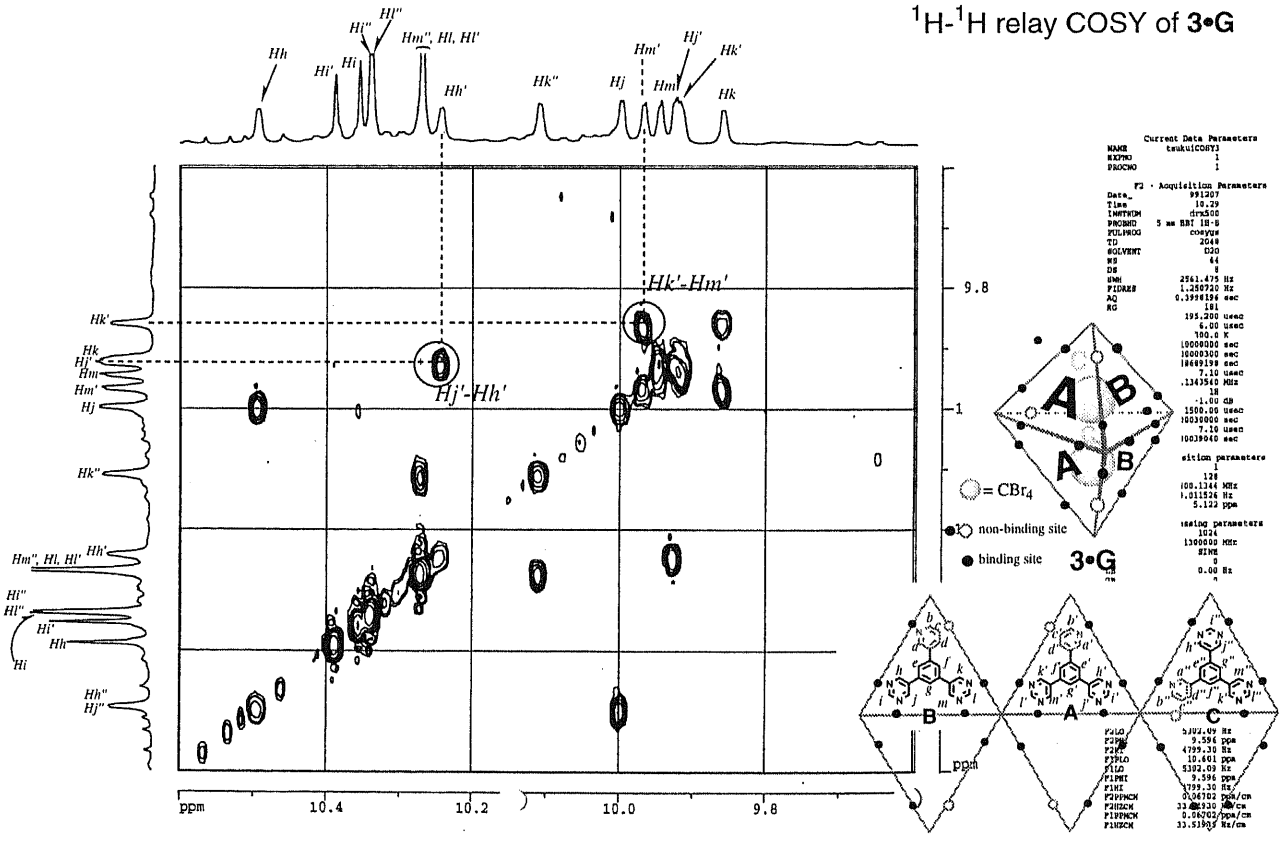
```
F2 - Acquisition Parameters
Date_            20001015
Time                17.03
INSTRUM            drx500
PROBHD    10 mm BBO BB-1
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                  20924
DS                      2
SWH             44642.855 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                 3649.1
DW                 11.200 usec
DE                   6.00 usec
TE                  300.0 K
d11            0.03000000 sec
d12            0.00002000 sec
PL13                18.00 dB
D1             2.00000000 sec
CPDPRG2          waltz16
PCPD2               85.00 usec
SFO2          500.1320005 MHz
NUC2                   1H
PL2                 -6.00 dB
PL12                10.00 dB
P1                  10.30 usec
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB

F2 - Processing parameters
SI                  32768
SF            125.7577842 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40

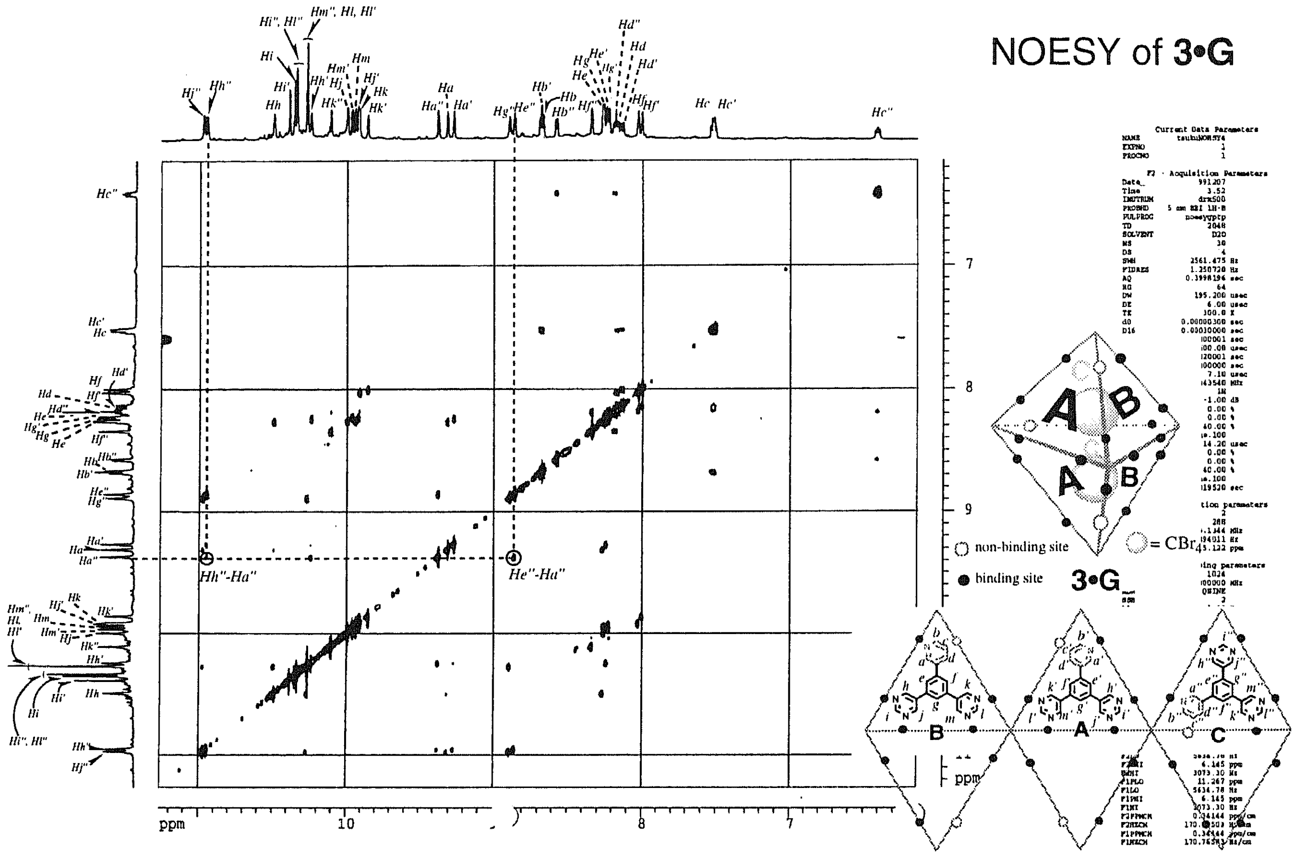
1D NMR plot parameters
CX                  20.00 cm
F1P               165.000 ppm
F1               20750.03 Hz
F2P               122.000 ppm
F2               15342.45 Hz
PPMCM             2.15000 ppm/cm
HZCM            270.37924 Hz/cm
```



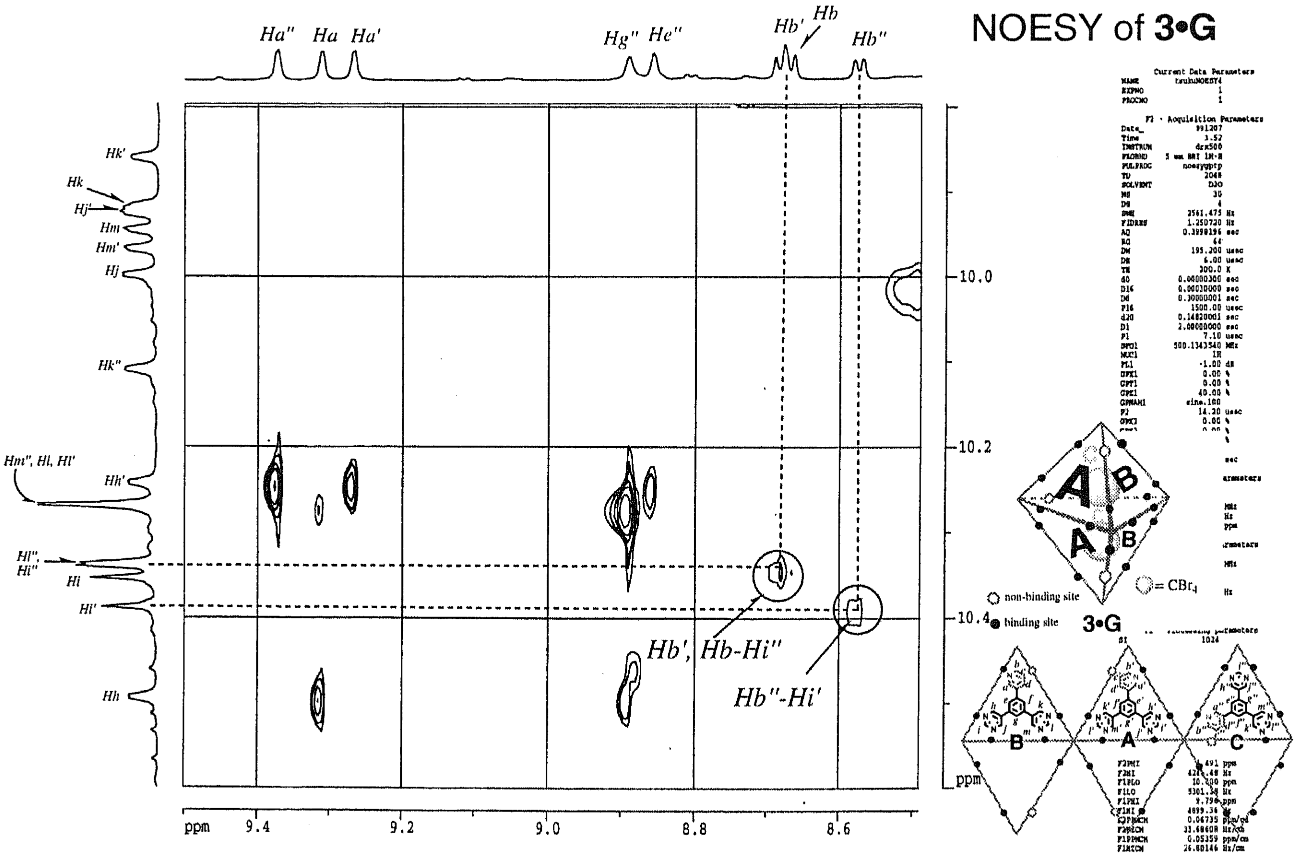
^1H-^1H relay COSY of **3•G**



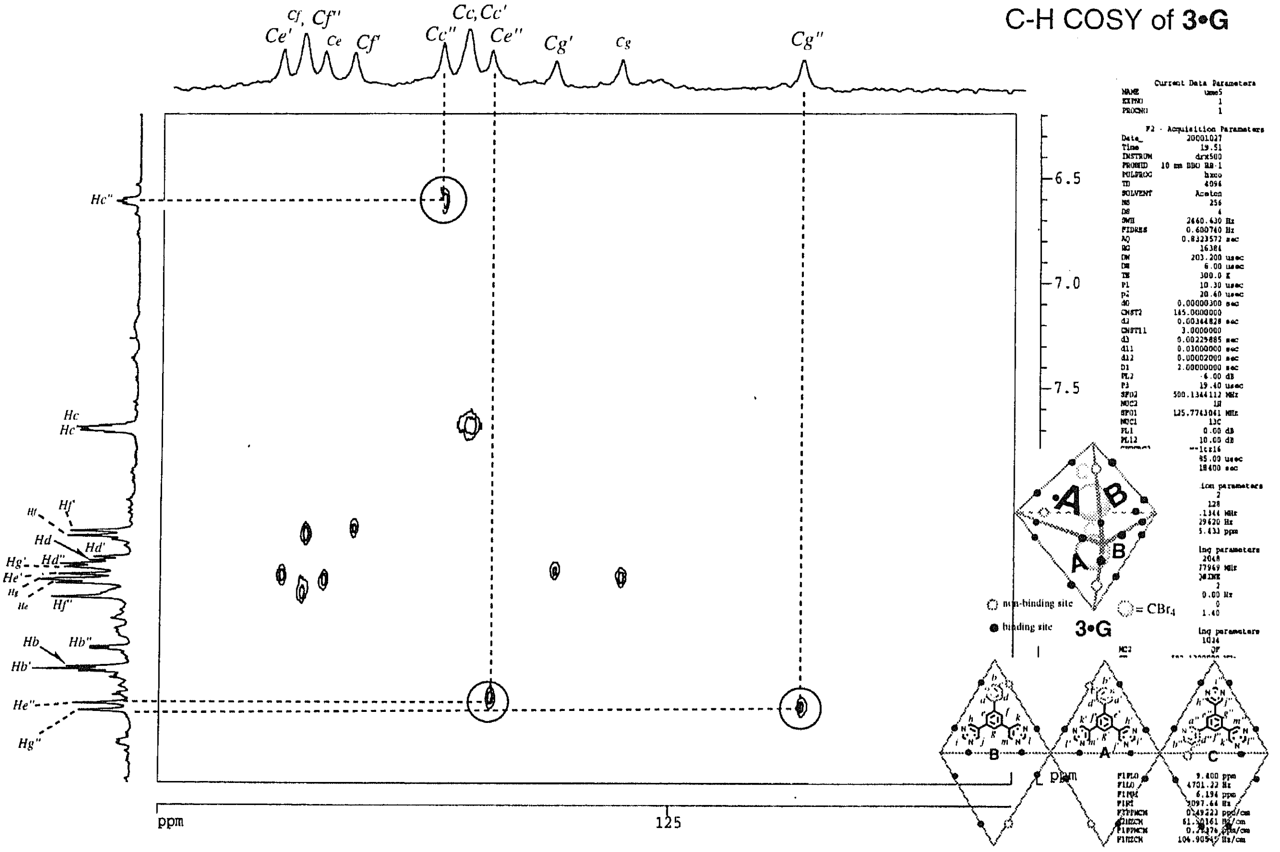
^1H-^1H relay COSY of **3•G**



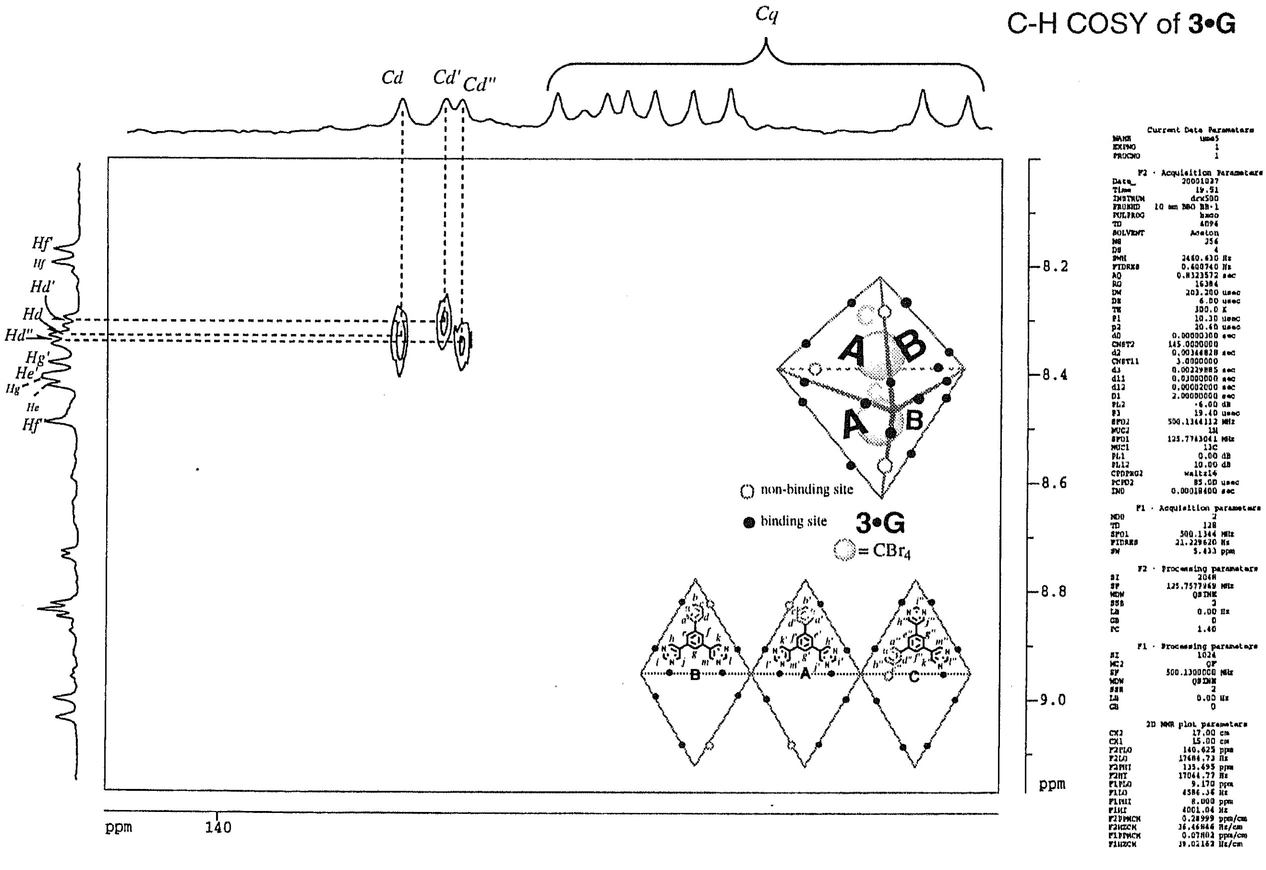
NOESY of **3•G**



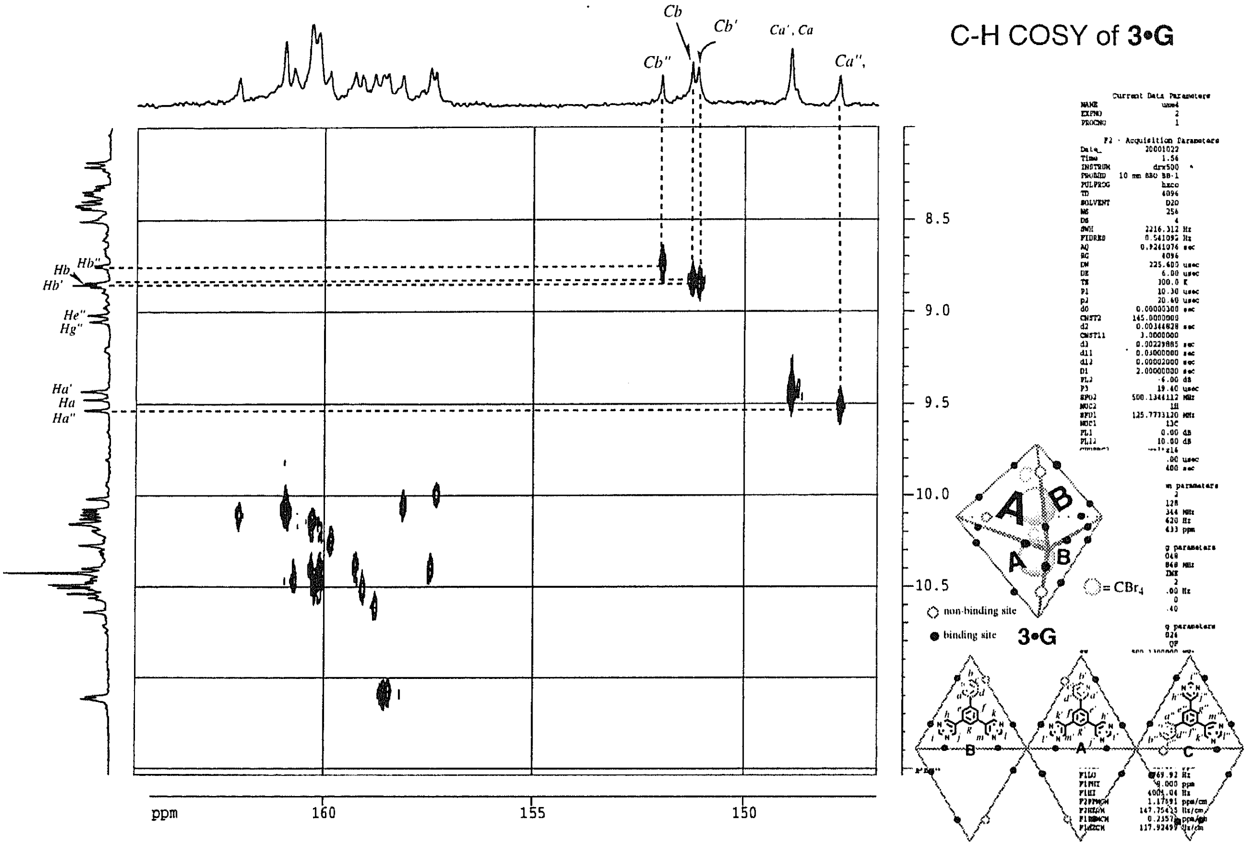
NOESY of **3•G**

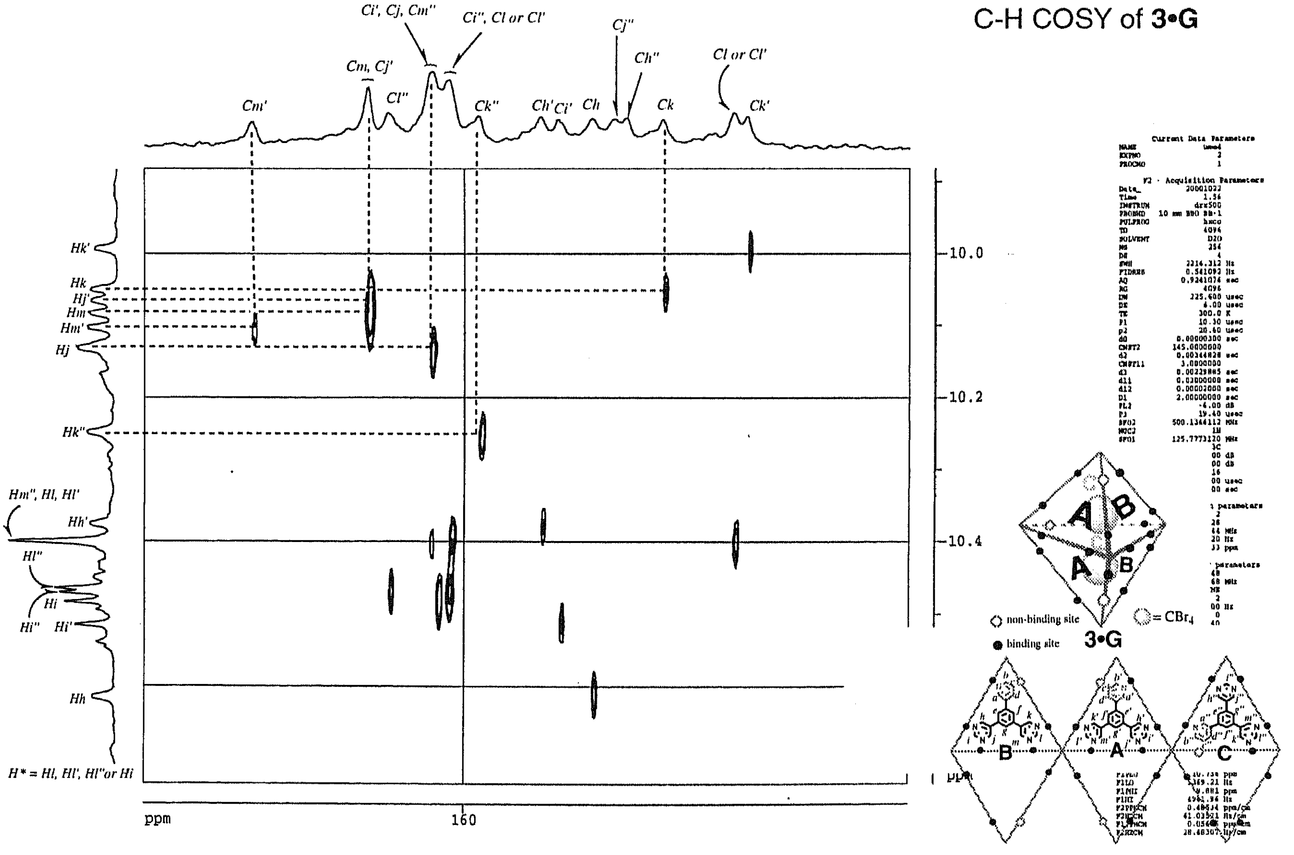


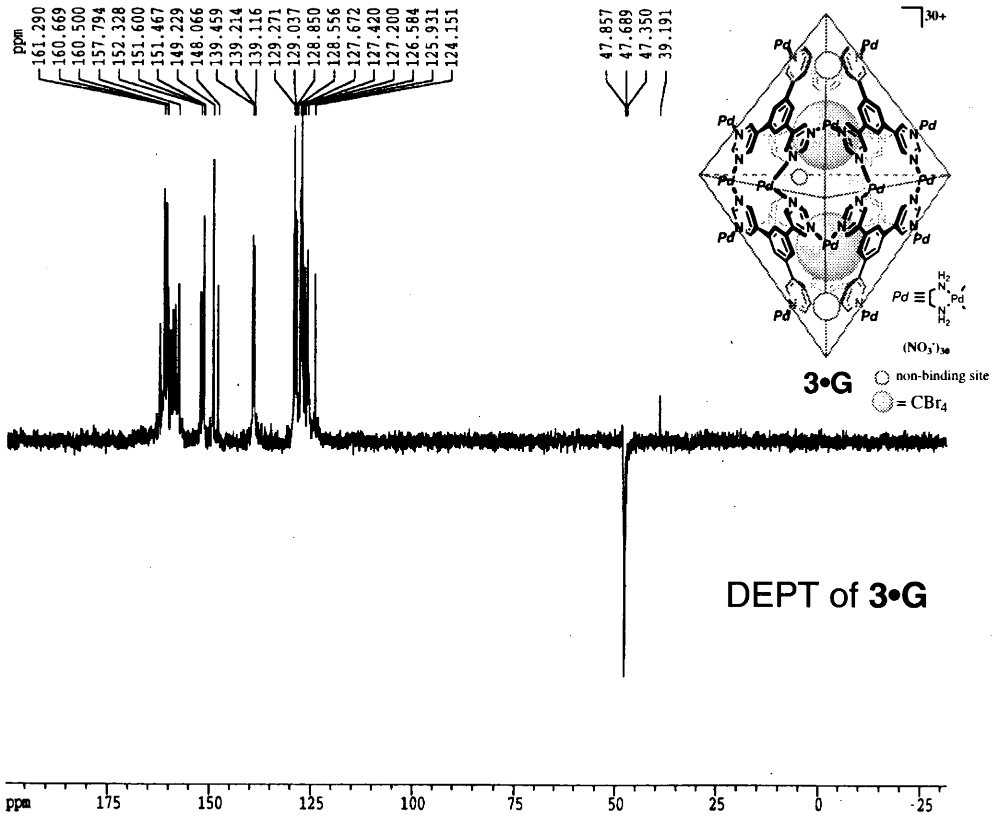
C-H COSY of **3•G**



C-H COSY of **3•G**


C-H COSY of **3•G**


C-H COSY of **3•G**



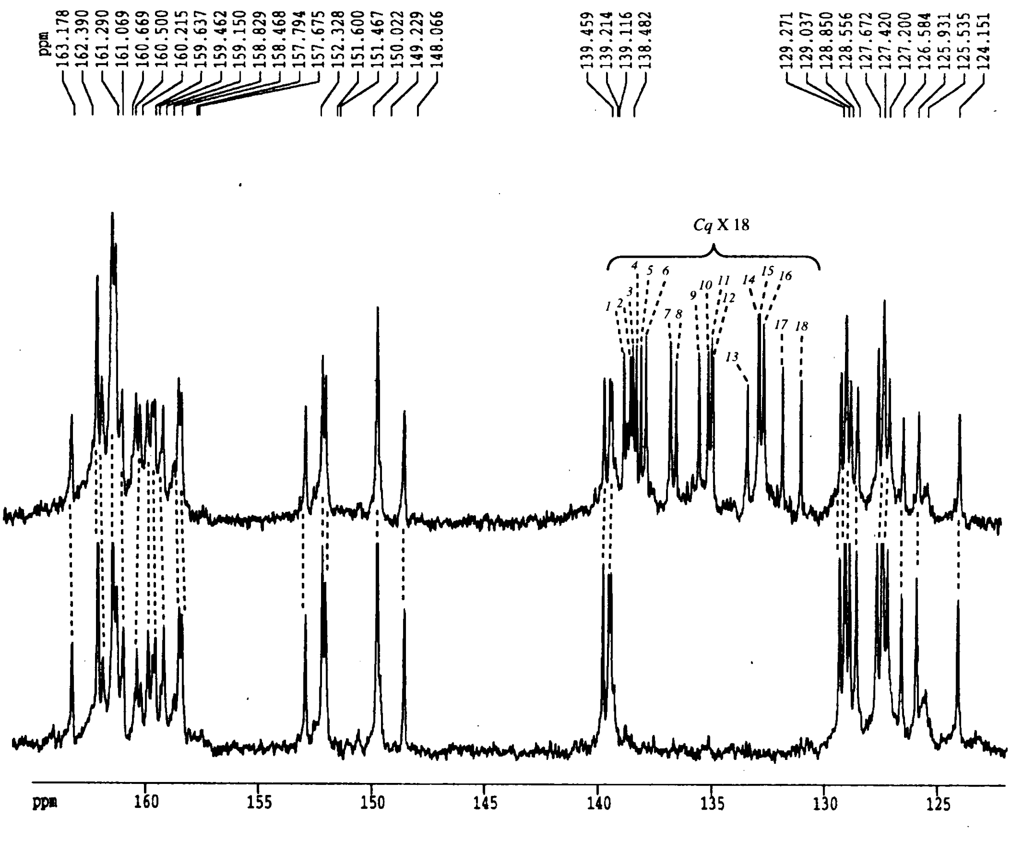
DEPT of 3•G

```
Current Data Parameters
NAME                  ume3
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20001015
Time                 13.48
INSTRUM             drx500
PROBHD   10 mm BBO BB-1
PULPROG           dept135
TD                   65536
SOLVENT                D2O
NS                    6386
DS                       4
SWH              39682.539 Hz
FIDRES            0.605507 Hz
AQ               0.8258036 sec
RG                   16384
DW                  12.600 usec
DE                    6.00 usec
TE                   300.0 K
P1                   10.30 usec
p2                   20.60 usec
P3                   19.40 usec
p4                   38.80 usec
CNST2          145.0000000
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001311 sec
D1              2.00000000 sec
PL2                  -6.00 dB
SFO2           500.1320005 MHz
NUC2                    1H
SFO1           125.7736214 MHz
NUC1                   13C
PL1                   0.00 dB
PL12                 10.00 dB
CPDPRG2            waltz16
PCPD2                85.00 usec

F2 - Processing parameters
SI                   32768
SF             125.7577390 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                200.000 ppm
F1                25151.54 Hz
F2P                -40.000 ppm
F2                -5030.31 Hz
PPMCM             12.00000 ppm/cm
HZCM            1509.09277 Hz/cm
```



DEPT of 3•G

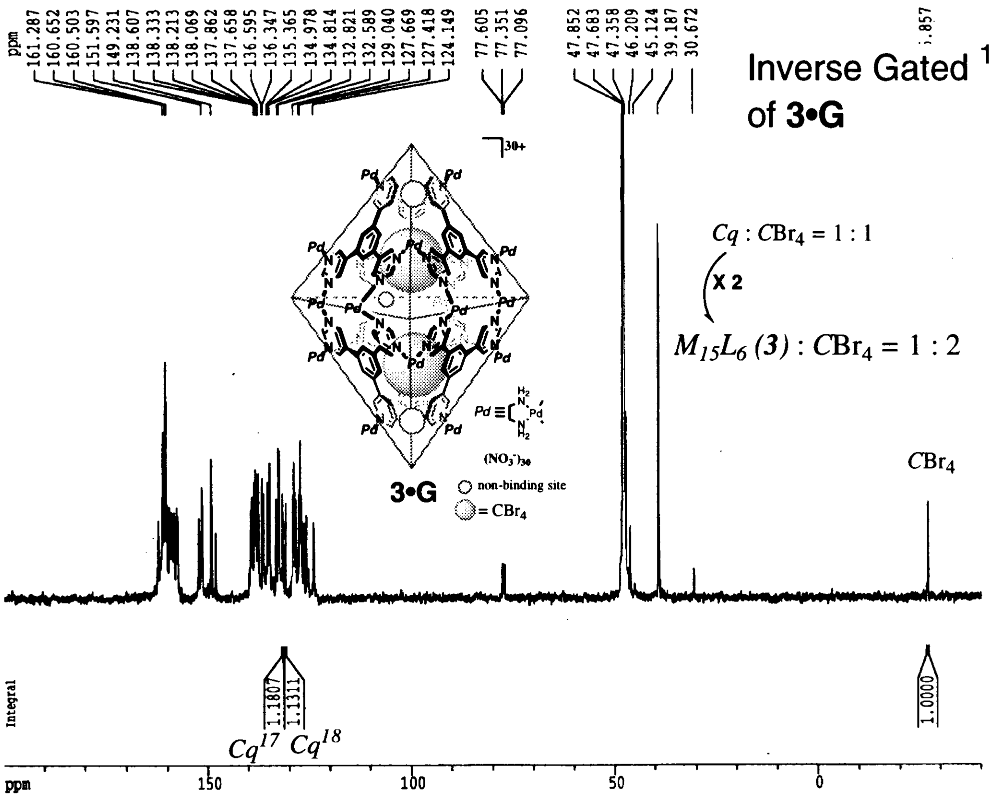
```
Current Data Parameters
NAME                  ume3
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
TD                   65536
SOLVENT                D2O
NS                    6386
DS                       4
SWH              39682.539 Hz
FIDRES            0.605507 Hz
AQ               0.8258036 sec
RG                   16384
DW                  12.600 usec
DE                    6.00 usec
TE                   300.0 K
P1                   10.30 usec
p2                   20.60 usec
P3                   19.40 usec
p4                   38.80 usec
CNST2          145.0000000
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001311 sec
D1              2.00000000 sec
PL2                  -6.00 dB
SFO2           500.1320005 MHz
NUC2                    1H
SFO1           125.7736214 MHz
NUC1                   13C
PL1                   0.00 dB
PL12                 10.00 dB
CPDPRG2            waltz16
PCPD2                85.00 usec

F2 - Processing parameters
SI                   32768
SF             125.7577390 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                165.000 ppm
F1                20750.03 Hz
F2P                122.000 ppm
F2                15342.44 Hz
PPMCM              2.15000 ppm/cm
HZCM             270.37912 Hz/cm
```

Inverse Gated ^{1}H-Decoupling of **3•G**



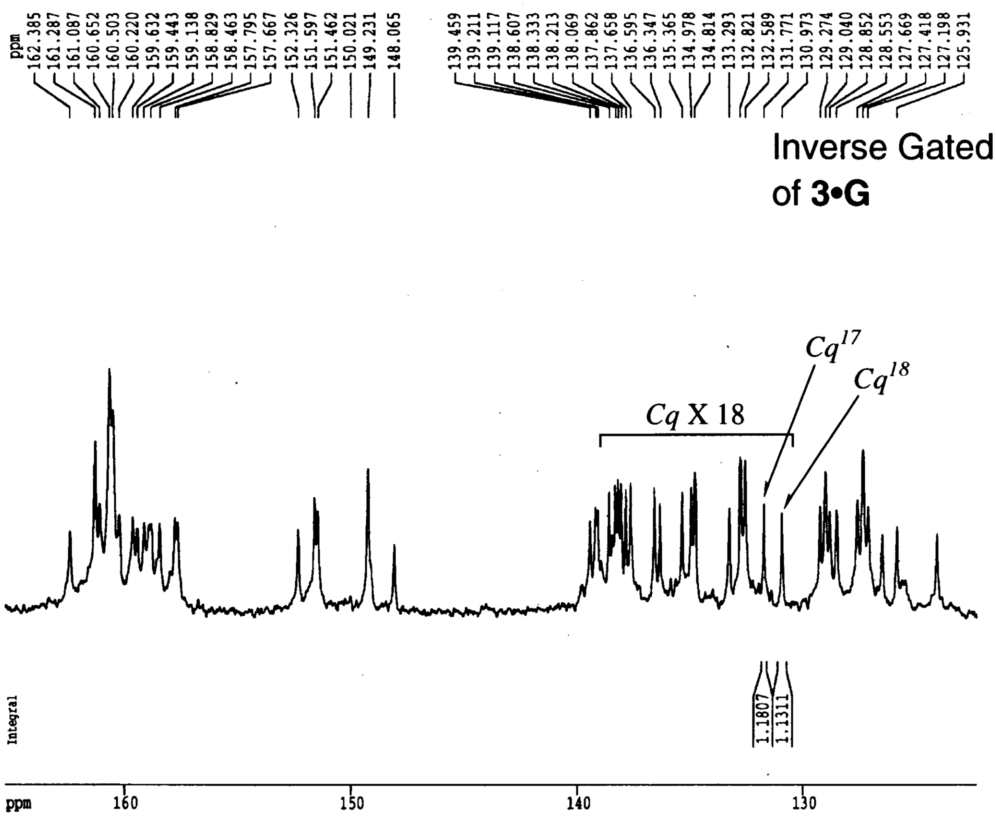
```
Current Data Parameters
NAME                 ume3
EXPNO                   1
PROCNO                  1

TD                  65536
SOLVENT               D2O
NS                  27701
DS                      2
SWH             43478.262 Hz
FIDRES           0.663426 Hz
AQ              0.7537140 sec
RG                 3649.1
DW                 11.500 usec
DE                   6.00 usec
TE                  300.0 K
d11            0.03000000 sec
PL12                10.00 dB
D1             2.00000000 sec
P1                  10.30 usec
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB
CPDPRG2           waltz16
PCPD2               85.00 usec
SFO2          500.1320005 MHz
NUC2                   1H
PL2                 -6.00 dB

F2 - Processing parameters
SI                  32768
SF            125.7577390 MHz
WDW                    EM
SSB                     0
LB                   5.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               200.000 ppm
F1               25151.54 Hz
F2P               -40.000 ppm
F2               -5030.31 Hz
PPMCM            12.00000 ppm/cm
HZCM           1509.09277 Hz/cm
```

Inverse Gated ^{1}H-Decoupling of **3•G**



```
Current Data Parameters
NAME                 ume3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20001014
Time                14.41
INSTRUM            drx500

SWH             43478.262 Hz
FIDRES           0.663426 Hz
AQ              0.7537140 sec
RG                 3649.1
DW                 11.500 usec
DE                   6.00 usec
TE                  300.0 K
d11            0.03000000 sec
PL12                10.00 dB
D1             2.00000000 sec
P1                  10.30 usec
SFO1          125.7736214 MHz
NUC1                  13C
PL1                  0.00 dB
CPDPRG2           waltz16
PCPD2               85.00 usec
SFO2          500.1320005 MHz
NUC2                   1H
PL2                 -6.00 dB

F2 - Processing parameters
SI                  32768
SF            125.7577390 MHz
WDW                    EM
SSB                     0
LB                   5.00 Hz
GB                      0
PC                   1.40

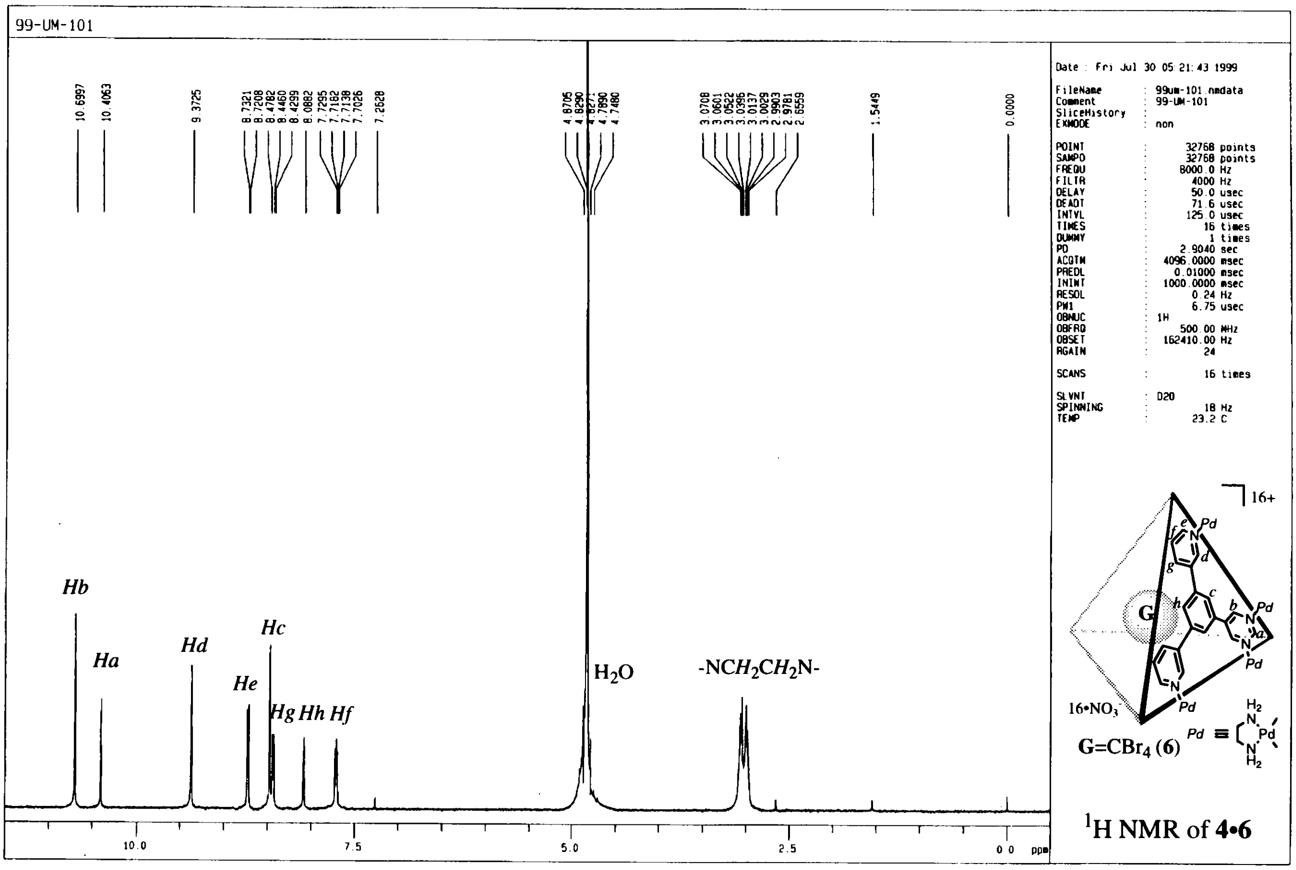
1D NMR plot parameters
CX                  20.00 cm
F1P               165.204 ppm
F1               20775.74 Hz
F2P               122.379 ppm
F2               15390.13 Hz
PPMCM             2.14126 ppm/cm
HZCM            269.28055 Hz/cm
```

X-ray crystallographic data of $M_{15}L_6$

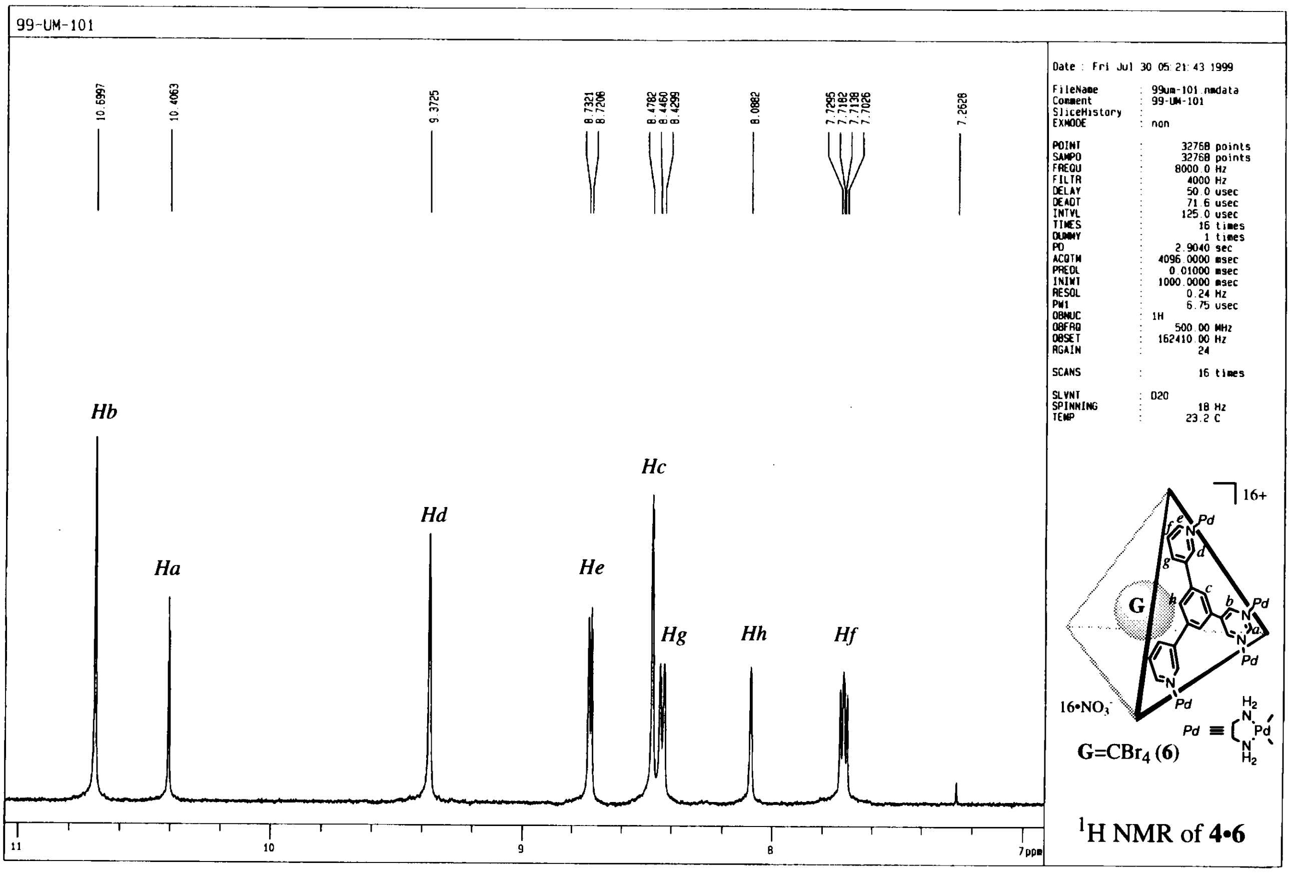
Experimental Details

Table 1. Crystal data and structure refinement for $M_{15}L_6$.

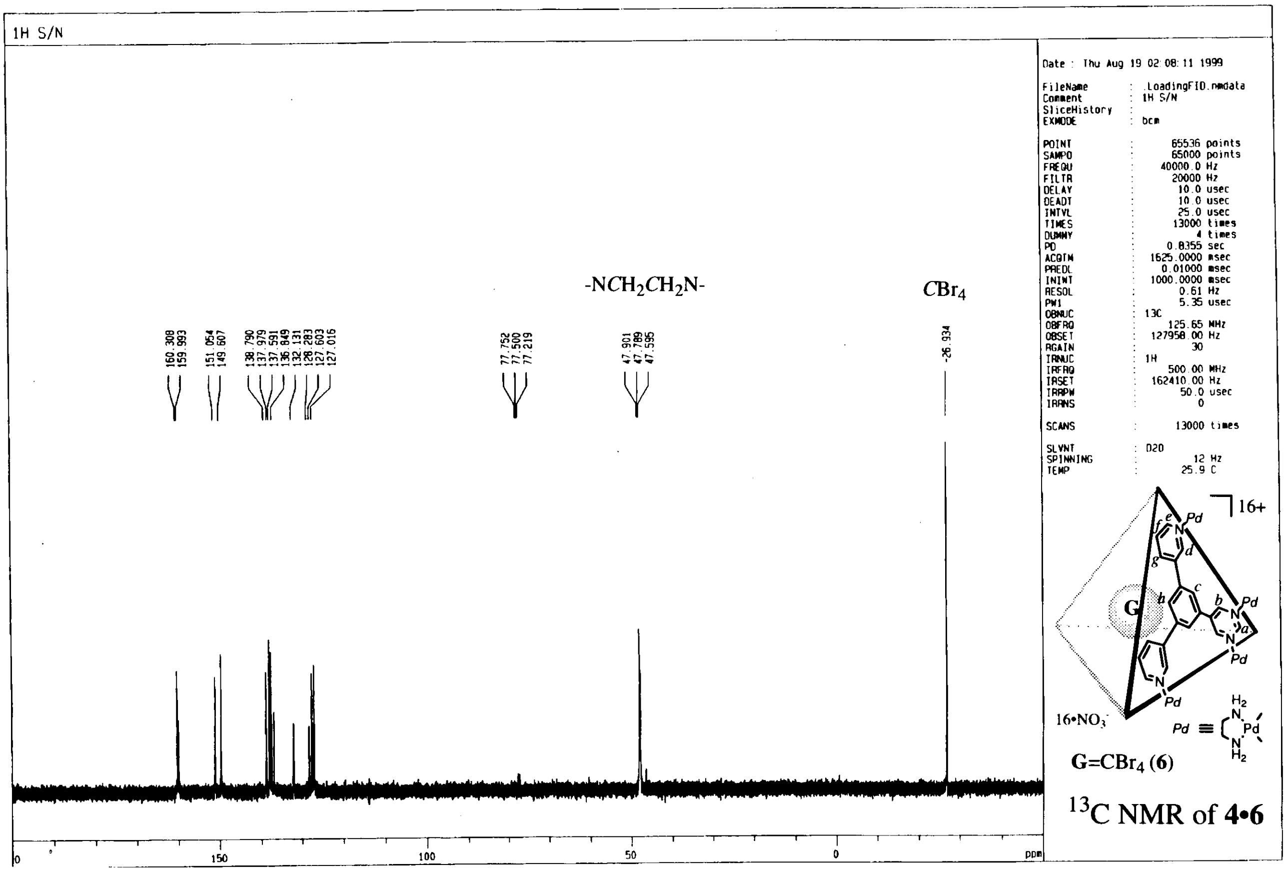
Identification code	nk107t	
Empirical formula	C145.50 H319 N90 O149 Pd15	
Formula weight	7309.91	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 26.503(3) Å	α= 85.468(2)°.
	b = 30.887(3) Å	β= 85.735(2)°.
	c = 35.743(4) Å	γ = 89.850(2)°.
Volume	29086(6) Å^3	
Z	4	
Density (calculated)	1.669 Mg/m^3	
Absorption coefficient	1.016 mm^{-1}	
F(000)	14816	
Crystal size	0.20 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.15 to 28.12°.	
Index ranges	-27<=h<=34, -40<=k<=38, -47<=l<=33	
Reflections collected	189592	
Independent reflections	131409 [R(int) = 0.0749]	
Completeness to theta = 28.12°	92.5 %	
Max. and min. transmission	0.8625 and 0.8226	
Refinement method	Full-matrix-block least-squares on F^2	
Data / restraints / parameters	131409 / 9020 / 6859	
Goodness-of-fit on F^2	1.160	
Final R indices [I>2sigma(I)]	R1 = 0.0867, wR2 = 0.2189	
R indices (all data)	R1 = 0.2137, wR2 = 0.2681	
Largest diff. peak and hole	2.717 and -5.982 e.Å^{-3}	



^{1}H NMR of **4•6**



^{1}H NMR of **4•6**



```
Date : Thu Aug 19 02:08:11 1999

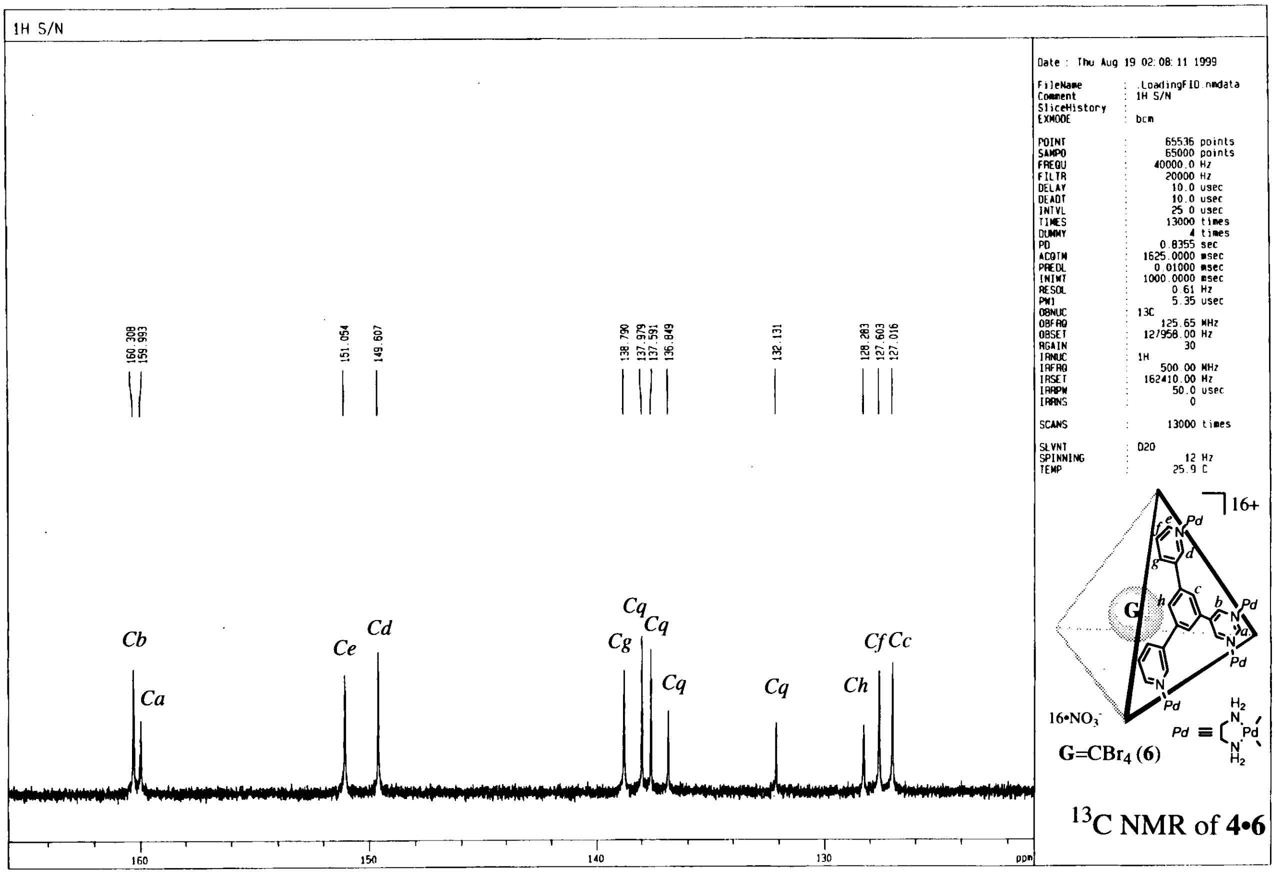
FileName      : .LoadingFID.nmdata
Comment       : 1H S/N
SliceHistory  :
EXMODE        : bcm

POINT         :      65536 points
SAMPO         :      65000 points
FREQU         :    40000.0 Hz
FILTR         :      20000 Hz
DELAY         :       10.0 usec
DEADT         :       10.0 usec
INTVL         :       25.0 usec
TIMES         :      13000 times
DUMMY         :          4 times
PD            :     0.8355 sec
ACQTM         :  1625.0000 msec
PREDL         :    0.01000 msec
ININT         :  1000.0000 msec
RESOL         :       0.61 Hz
PW1           :       5.35 usec
OBNUC         : 13C
OBFRQ         :     125.65 MHz
OBSET         :  127958.00 Hz
RGAIN         :         30
IRNUC         : 1H
IRFRQ         :     500.00 MHz
IRSET         :  162410.00 Hz
IRRPW         :       50.0 usec
IRRNS         :          0

SCANS         :      13000 times

SLVNT         : D2O
SPINNING      :         12 Hz
TEMP          :       25.9 C
```

^{13}C NMR of **4•6**



```
Date : Thu Aug 19 02:08:11 1999

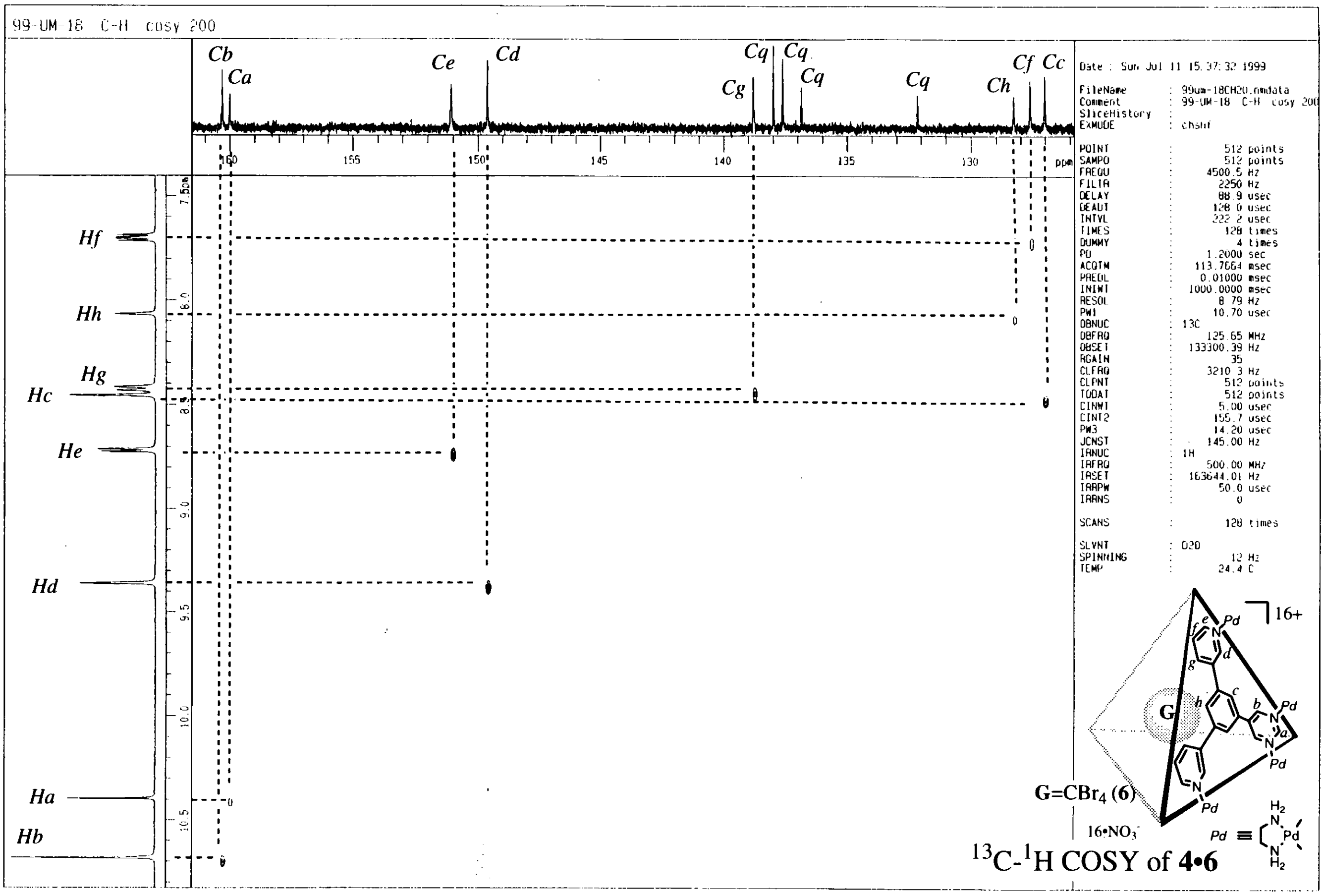
FileName      : .LoadingFID.nmdata
Comment       : 1H S/N
SliceHistory  :
EXMODE        : bcm

POINT         :      65536 points
SAMPO         :      65000 points
FREQU         :    40000.0 Hz
FILTR         :      20000 Hz
DELAY         :       10.0 usec
DEADT         :       10.0 usec
INTVL         :       25.0 usec
TIMES         :      13000 times
DUMMY         :          4 times
PD            :     0.8355 sec
ACQTM         :  1625.0000 msec
PREDL         :    0.01000 msec
ININT         :  1000.0000 msec
RESOL         :       0.61 Hz
PW1           :       5.35 usec
OBNUC         : 13C
OBFRQ         :     125.65 MHz
OBSET         :  127958.00 Hz
RGAIN         :         30
IRNUC         : 1H
IRFRQ         :     500.00 MHz
IRSET         :  162410.00 Hz
IRRPW         :       50.0 usec
IRRNS         :          0

SCANS         :      13000 times

SLVNT         : D2O
SPINNING      :         12 Hz
TEMP          :       25.9 C
```

^{13}C NMR of **4•6**



```
Date : Sun Jul 11 15:37:32 1999

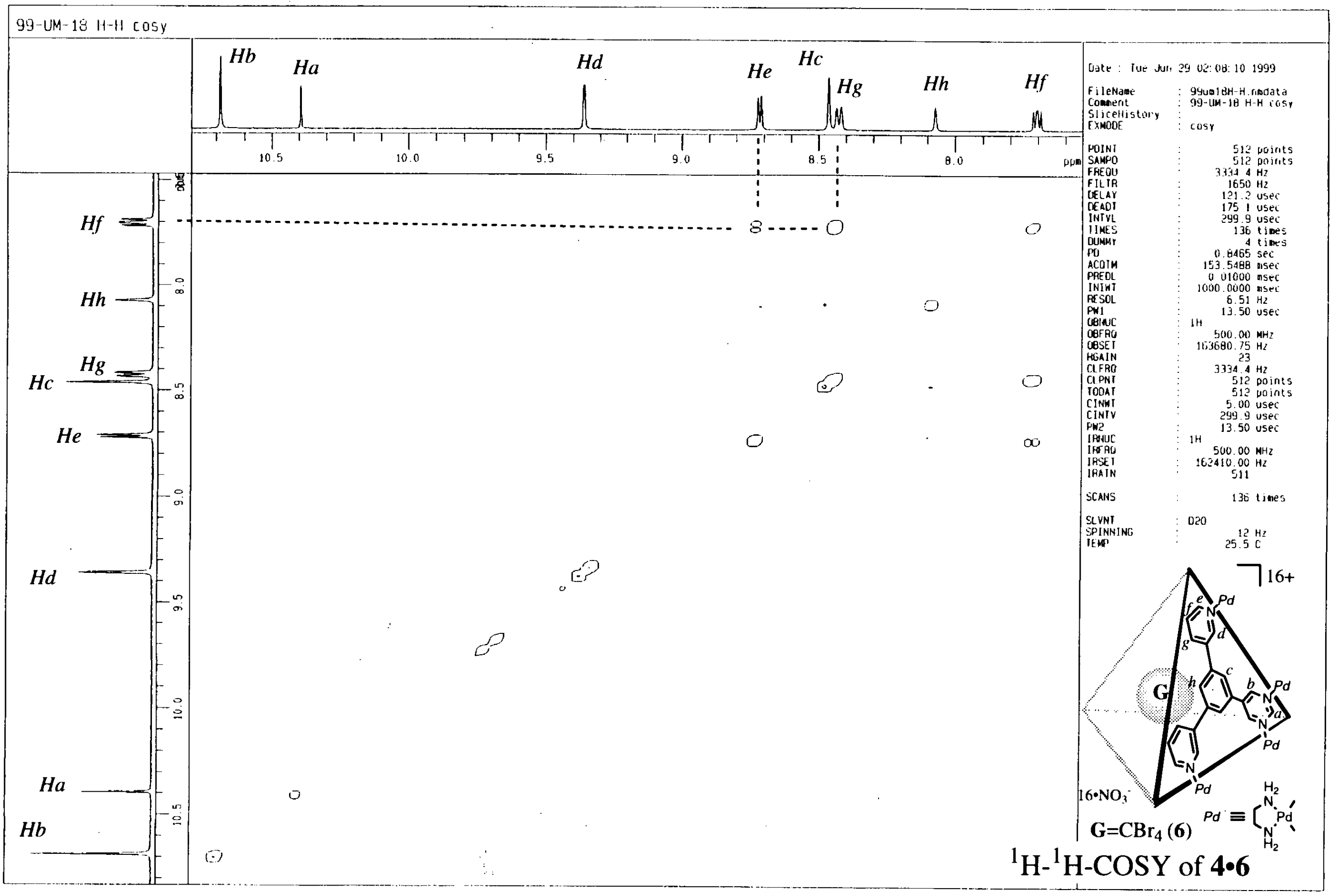
FileName        : 99um-18CH20.nmdata
Comment         : 99-UM-18  C-H  cosy 200
SliceHistory    :
EXMODE          : chshf

POINT           :        512 points
SAMPO           :        512 points
FREQU           :     4500.5 Hz
FILTR           :       2250 Hz
DELAY           :       88.9 usec
DEADT           :      128.0 usec
INTVL           :      222.2 usec
TIMES           :        128 times
DUMMY           :          4 times
PD              :     1.2000 sec
ACQTM           :   113.7664 msec
PREDL           :    0.01000 msec
ININT           :  1000.0000 msec
RESOL           :       8.79 Hz
PW1             :      10.70 usec
OBNUC           : 13C
OBFRQ           :     125.65 MHz
OBSET           :  133300.39 Hz
RGAIN           :         35
CLFRQ           :     3210.3 Hz
CLPNT           :        512 points
TODAT           :        512 points
CINWT           :       5.00 usec
CINT2           :      155.7 usec
PW3             :      14.20 usec
JCNST           :     145.00 Hz
IRNUC           : 1H
IRFRQ           :     500.00 MHz
IRSET           :  163644.01 Hz
IRRPW           :       50.0 usec
IRRNS           :          0

SCANS           :        128 times

SLVNT           : D2O
SPINNING        :         12 Hz
TEMP            :       24.4 C
```

^{13}C-^{1}H COSY of **4•6**



```
Date : Tue Jun 29 02:08:10 1999

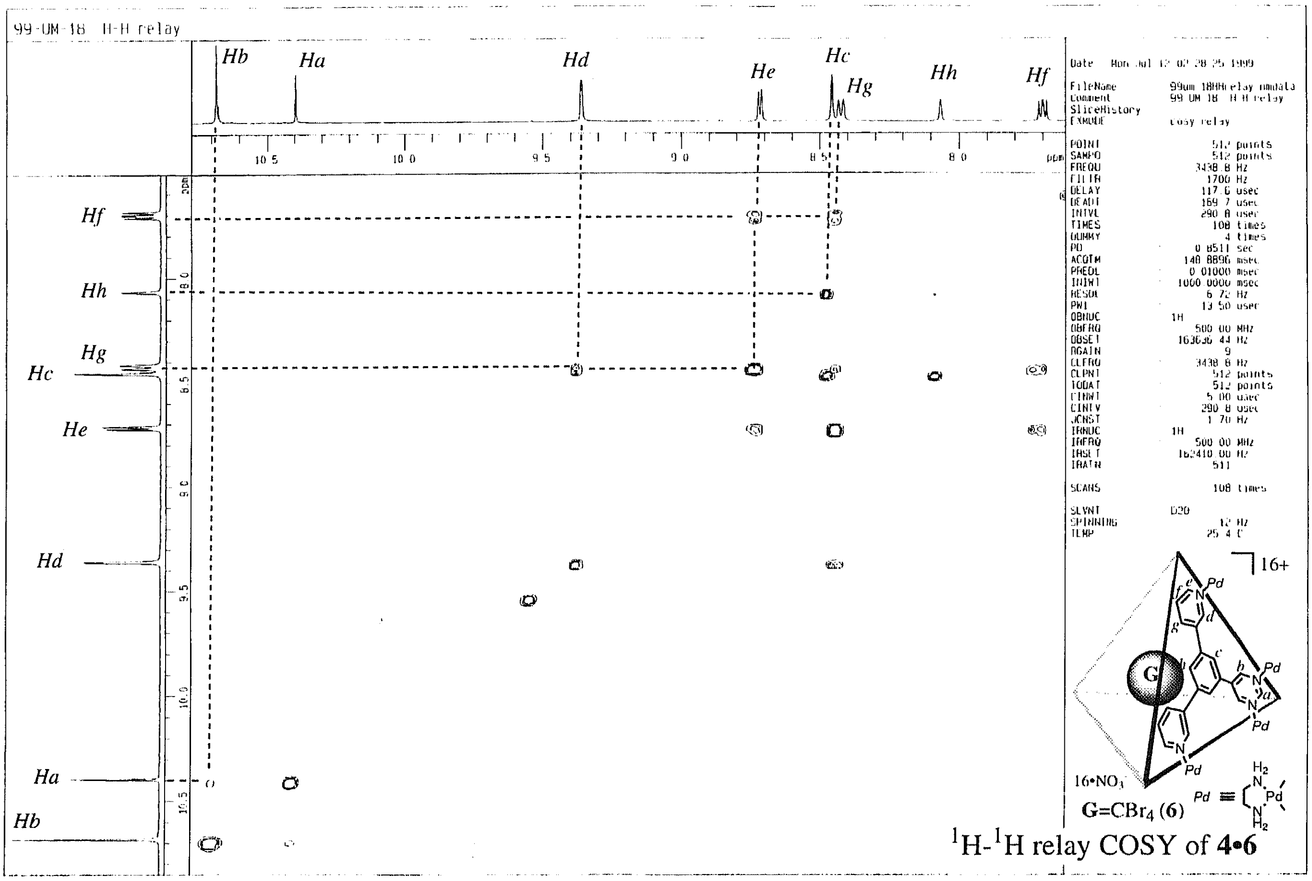
FileName        : 99um18H-H.nmdata
Comment         : 99-UM-18 H-H cosy
SliceHistory    :
EXMODE          : cosy

POINT           :        512 points
SAMPO           :        512 points
FREQU           :     3334.4 Hz
FILTR           :       1650 Hz
DELAY           :      121.2 usec
DEADT           :      175.1 usec
INTVL           :      299.9 usec
TIMES           :        136 times
DUMMY           :          4 times
PD              :     0.8465 sec
ACQTM           :   153.5488 msec
PREDL           :    0.01000 msec
ININT           :  1000.0000 msec
RESOL           :       6.51 Hz
PW1             :      13.50 usec
OBNUC           : 1H
OBFRQ           :     500.00 MHz
OBSET           :  163680.75 Hz
HGAIN           :         23
CLFRQ           :     3334.4 Hz
CLPNT           :        512 points
TODAT           :        512 points
CINWT           :       5.00 usec
CINTV           :      299.9 usec
PW2             :      13.50 usec
IRNUC           : 1H
IRFRQ           :     500.00 MHz
IRSET           :  162410.00 Hz
IRAIN           :        511

SCANS           :        136 times

SLVNT           : D2O
SPINNING        :         12 Hz
TEMP            :       25.5 C
```

^{1}H-^{1}H-COSY of **4•6**



```
Date      Mon Jul 12 02 28 25 1999

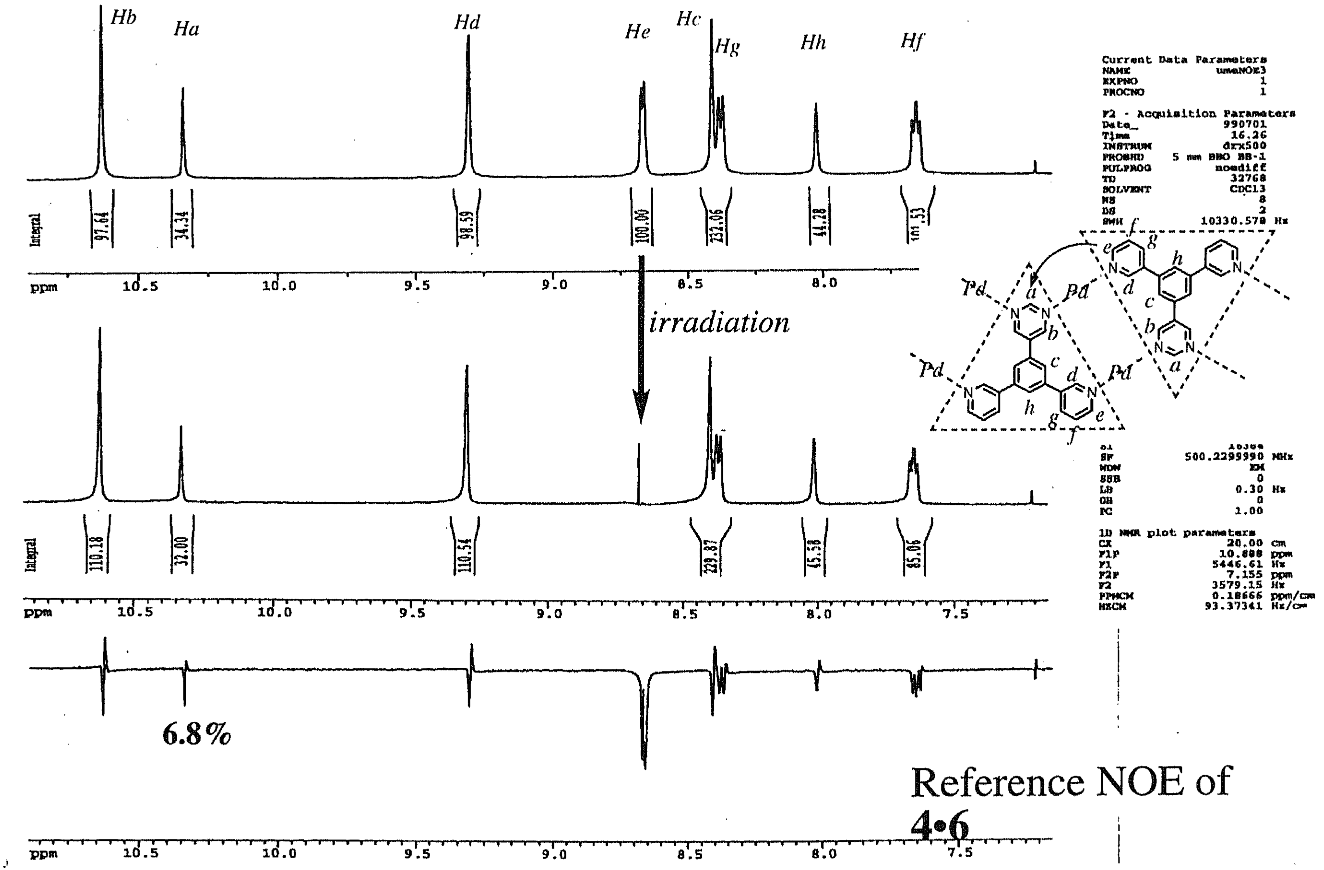
FileName          99um 18HHrelay nmdata
Comment           99 UM 18  H H relay
SliceHistory
EXMODE            cosy relay

POINT                   512 points
SAMPO                   512 points
FREQU                3438.8 Hz
FILTR                  1700 Hz
DELAY                 117.6 usec
DEADT                 169.7 usec
INTVL                 290.8 usec
TIMES                   108 times
DUMMY                     4 times
PD                   0.8511 sec
ACQTM              140.8896 msec
PREDL               0.01000 msec
INIWT             1000.0000 msec
RESOL                  6.72 Hz
PW1                   13.50 usec
OBNUC             1H
OBFRQ                500.00 MHz
OBSET             163636.44 Hz
RGAIN                     9
CLFRQ                3438.8 Hz
CLPNT                   512 points
TODAT                   512 points
CINWT                  5.00 usec
CINTV                 290.8 usec
JCNST                  1.70 Hz
IRNUC             1H
IRFRQ                500.00 MHz
IRSET             162410.00 Hz
IRATN                   511

SCANS                   108 times

SLVNT             D2O
SPINNING                 12 Hz
TEMP                   25.4 C
```

^1H-^1H relay COSY of **4•6**



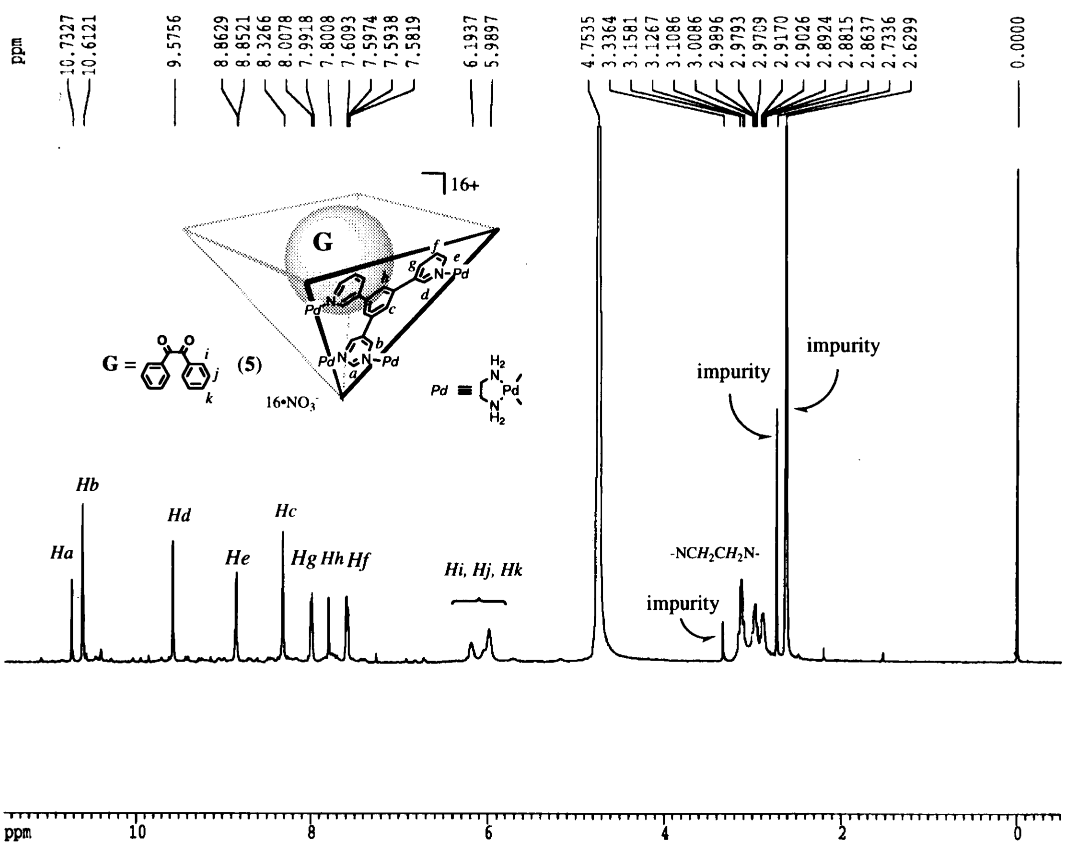
```
Current Data Parameters
NAME                umeNOE3
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_                990701
Time                  16.26
INSTRUM              drx500
PROBHD      5 mm BBO BB-1
PULPROG            noediff
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        2
SWH              10330.578 Hz
```

```
SI                    16384
SF              500.2299990 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
F1P                  10.888 ppm
F1                  5446.61 Hz
F2P                   7.155 ppm
F2                  3579.15 Hz
PPMCM               0.18666 ppm/cm
HZCM               93.37341 Hz/cm
```

Reference NOE of **4•6**



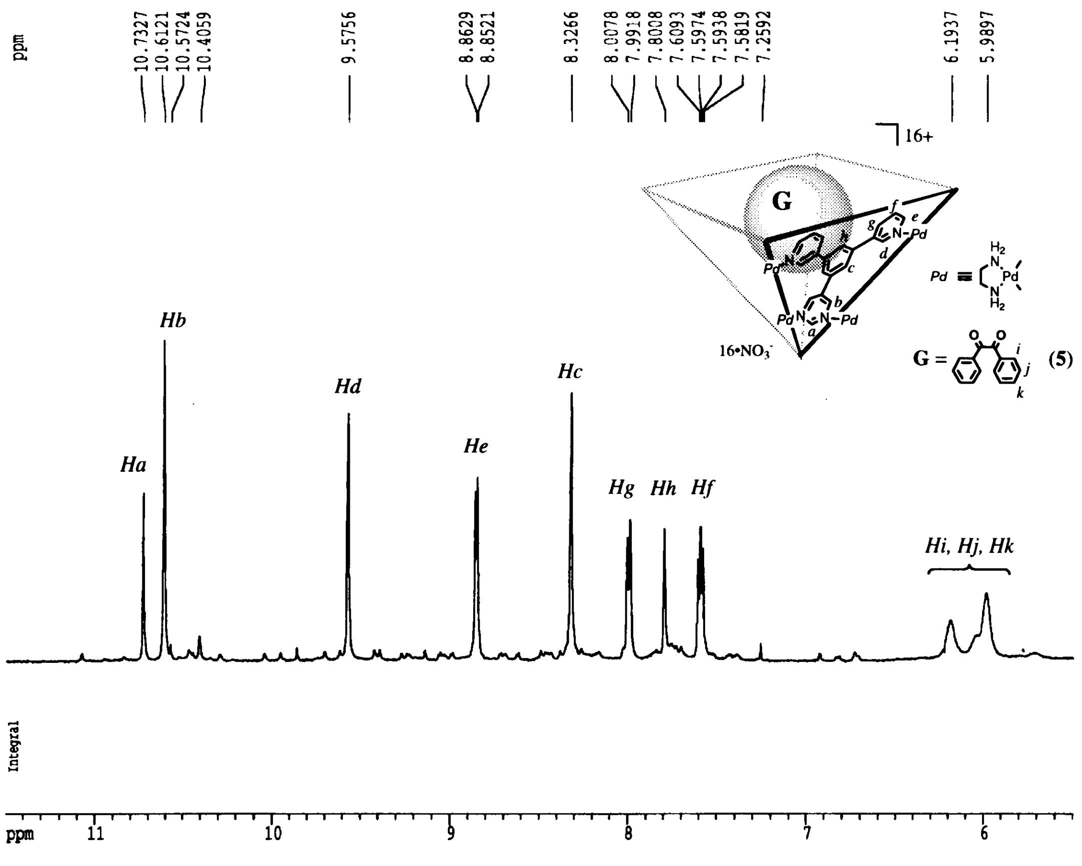
```
Current Data Parameters
NAME              341-H1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20000317
Time               15.20
INSTRUM           drx500
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    32
DS                     2
SWH            10330.578
FIDRES          0.315264
AQ             1.5860212
RG                   362
DW                48.400
DE                  6.00
TE                 300.0
D1            1.00000000
P1                  8.40
SFO1         500.1330885
NUC1                  1H
PL1                -4.00

F2 - Processing paramete
SI                 16384
SF           500.1299744
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00
F1P               11.500
F1               5751.49
F2P               -0.500
F2               -250.06
PPMCM            0.60000
HZCM           300.07797
```

^{1}H NMR of **3•5**



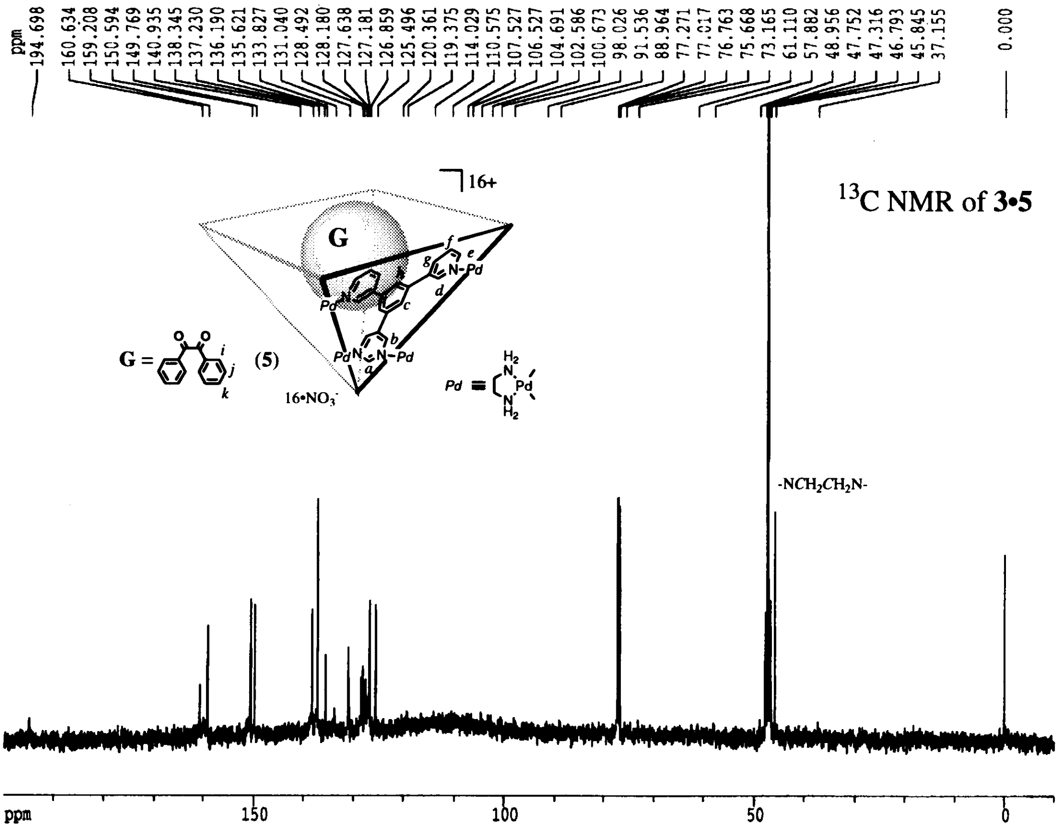
```
Current Data Parameters
NAME              341-H1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20000317
Time               15.20
INSTRUM           drx500
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    32
DS                     2
SWH            10330.578
FIDRES          0.315264
AQ             1.5860212
RG                   362
DW                48.400
DE                  6.00
TE                 300.0
D1            1.00000000
P1                  8.40
SFO1         500.1330885
NUC1                  1H
PL1                -4.00

F2 - Processing paramete
SI                 16384
SF           500.1299744
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00
F1P               11.500
F1               5751.49
F2P                5.500
F2               2750.71
PPMCM            0.30000
HZCM           150.03899
```

^{1}H NMR of **3•5**

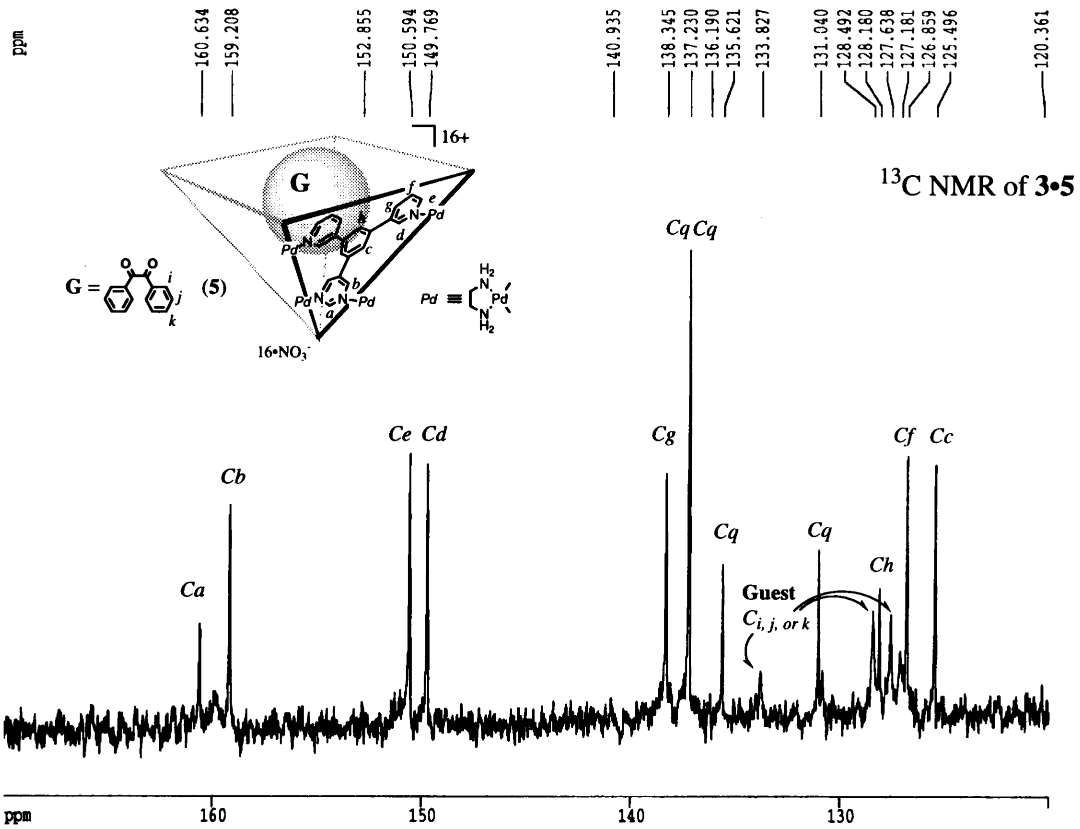


```
Current Data Parameters
NAME              341-13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Paramete
Date_            20000316
Time                22.16
INSTRUM            drx500
PROBHD     5 mm BBO BB-1
PULPROG           zgpg30
TD                  65536
SOLVENT               D2O
NS                  39650
DS                      2
SWH            39682.539 H
FIDRES          0.605507 H
AQ             0.8258036 s
RG                   8192
DW                 12.600 u
DE                   6.00 u
TE                  300.0 K
d11           0.03000000 s
d12           0.00002000 s
PL13               120.00 d
D1            2.00000000 s
CPDPRG2           waltz16
PCPD2               81.00 u
SFO2         500.1320005 M
NUC2                   1H
PL2                 -4.00 d
PL12                16.00 d
P1                   6.40 u
SFO1         125.7736214 M
NUC1                  13C
PL1                  2.00 d

F2 - Processing parameter
SI                  32768
SF           125.7577764 M
WDW                    EM
SSB                     0
LB                   3.00 H
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 c
F1P               200.000 p
F1               25151.55 H
F2P               -10.000 p
F2               -1257.58 H
PPMCM            10.50000 p
HZCM           1320.45667 H
```



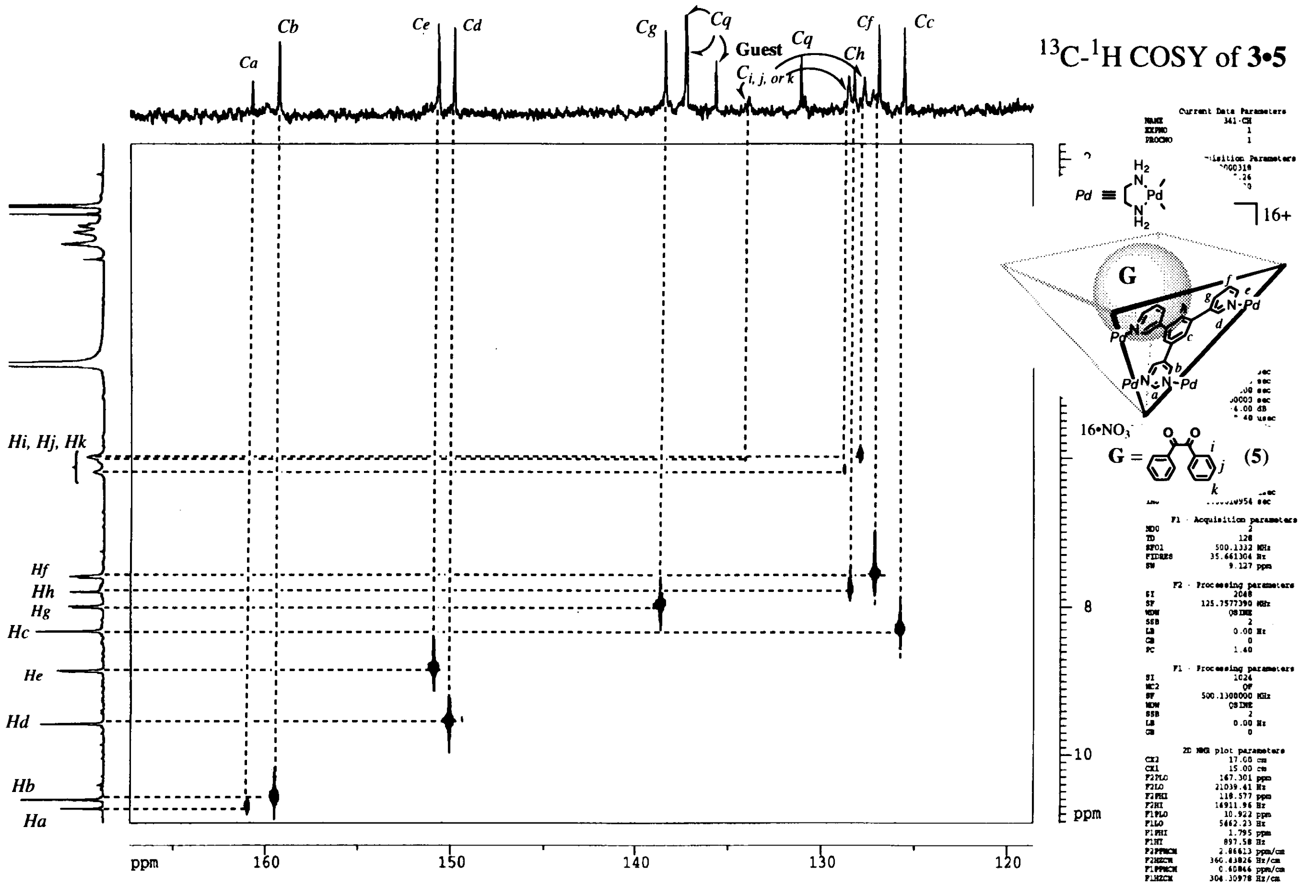
```
Current Data Parameters
NAME              341-13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parametei
Date_            20000316
Time                22.16
INSTRUM            drx500
PROBHD     5 mm BBO BB-1
PULPROG           zgpg30
TD                  65536
SOLVENT               D2O
NS                  39650
DS                      2
SWH            39682.539 H
FIDRES          0.605507 H
AQ             0.8258036 s
RG                   8192
DW                 12.600 u
DE                   6.00 u
TE                  300.0 K
d11           0.03000000 s
d12           0.00002000 s
PL13               120.00 d
D1            2.00000000 s
CPDPRG2           waltz16
PCPD2               81.00 u
SFO2         500.1320005 M
NUC2                   1H
PL2                 -4.00 d
PL12                16.00 d
P1                   6.40 u
SFO1         125.7736214 M
NUC1                  13C
PL1                  2.00 d

F2 - Processing parameter
SI                  32768
SF           125.7577764 M
WDW                    EM
SSB                     0
LB                   3.00 H
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 c
F1P               170.000 p
F1               21378.82 H
F2P               120.000 p
F2               15090.93 H
PPMCM             2.50000 p
HZCM            314.39444 H
```

^{13}C-^{1}H COSY of **3•5**



```
Current Data Parameters
NAME             341-CH
EXPNO                 1
PROCNO                1

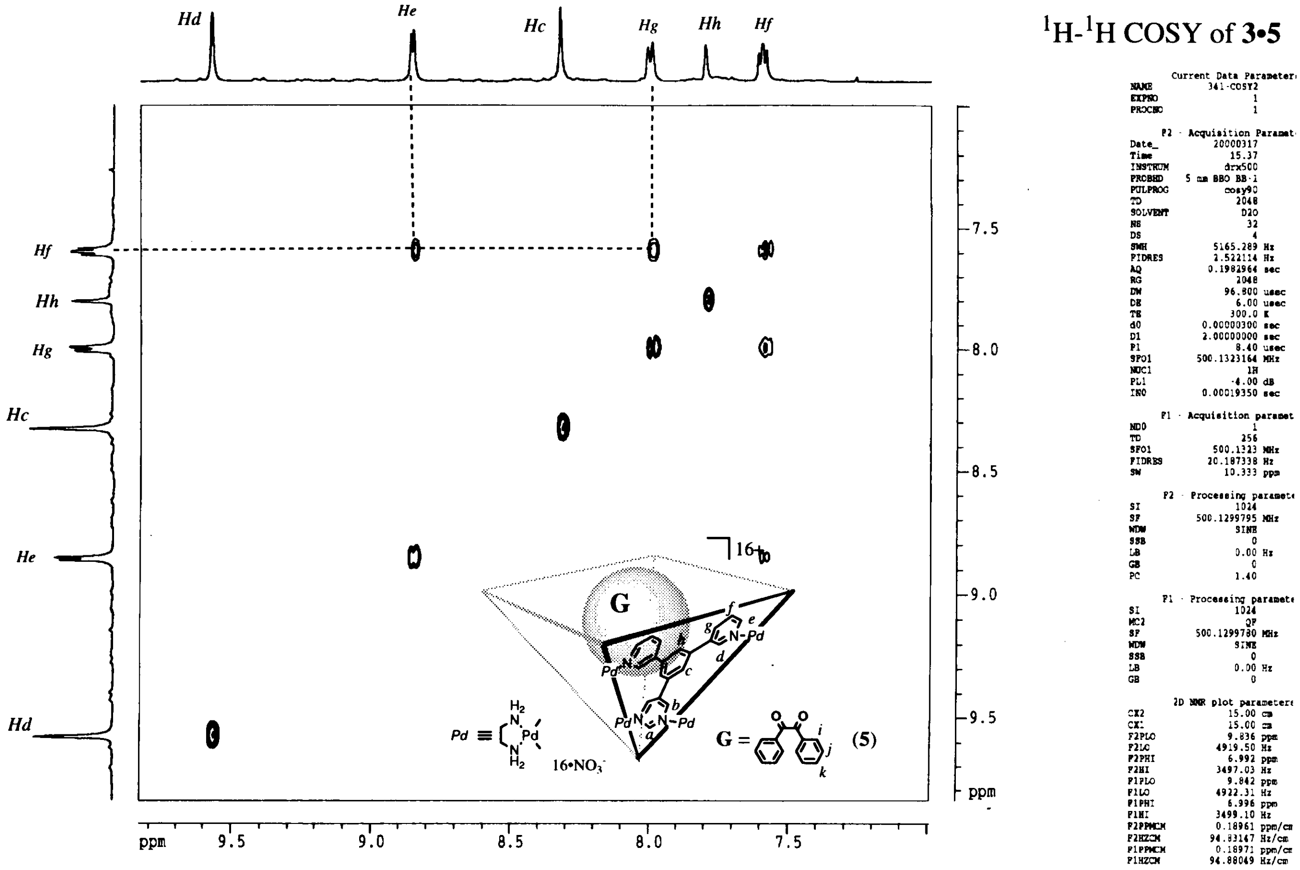
     F1 - Acquisition parameters
ND0                   2
TD                  128
SFO1        500.1332 MHz
FIDRES     35.661304 Hz
SW             9.127 ppm

     F2 - Processing parameters
SI                 2048
SF       125.7577390 MHz
WDW              QSINE
SSB                   2
LB              0.00 Hz
GB                    0
PC                 1.40

     F1 - Processing parameters
SI                 1024
MC2                  QF
SF       500.1300000 MHz
WDW              QSINE
SSB                   2
LB              0.00 Hz
GB                    0

     2D NMR plot parameters
CX2            17.00 cm
CX1            15.00 cm
F2PLO        167.301 ppm
F2LO        21039.41 Hz
F2PHI        118.577 ppm
F2HI        14911.96 Hz
F1PLO         10.922 ppm
F1LO         5462.23 Hz
F1PHI          1.795 ppm
F1HI          897.58 Hz
F2PPMCM      2.86613 ppm/cm
F2HZCM     360.43826 Hz/cm
F1PPMCM      0.60846 ppm/cm
F1HZCM     304.30978 Hz/cm
```

^{1}H-^{1}H COSY of **3•5**



```
Current Data Parameters
NAME           341-COSY2
EXPNO                 1
PROCNO                1

     F2 - Acquisition Paramet
Date_          20000317
Time              15.37
INSTRUM          drx500
PROBHD    5 mm BBO BB-1
PULPROG          cosy90
TD                 2048
SOLVENT             D2O
NS                   32
DS                    4
SWH            5165.289 Hz
FIDRES         2.522114 Hz
AQ            0.1982964 sec
RG                 2048
DW               96.800 usec
DE                 6.00 usec
TE                300.0 K
d0           0.00000300 sec
D1           2.00000000 sec
P1                 8.40 usec
SFO1        500.1323164 MHz
NUC1                 1H
PL1               -4.00 dB
IN0          0.00019350 sec

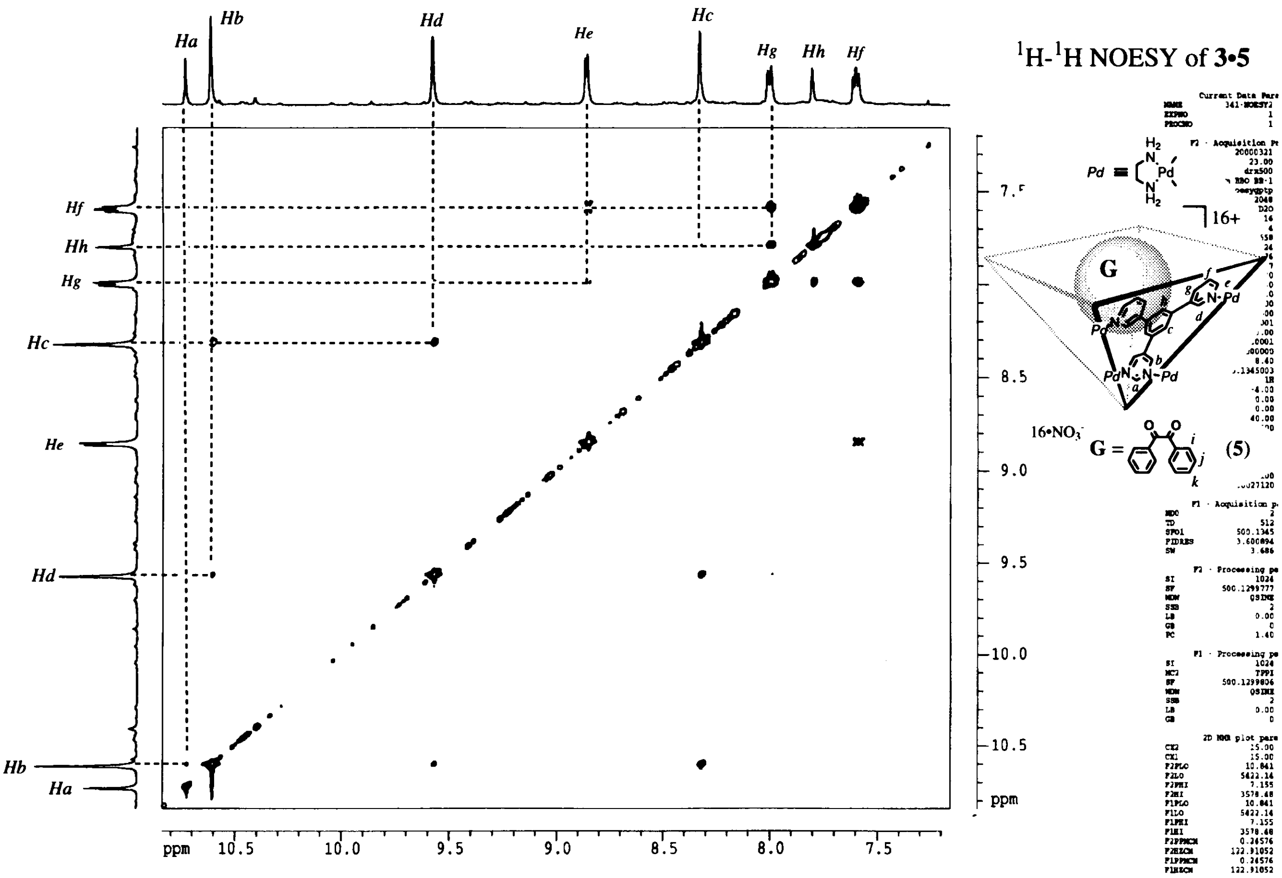
     F1 - Acquisition paramet
ND0                   1
TD                  256
SFO1           500.1323 MHz
FIDRES        20.187338 Hz
SW               10.333 ppm

     F2 - Processing paramete
SI                 1024
SF          500.1299795 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40

     F1 - Processing paramete
SI                 1024
MC2                  QF
SF          500.1299780 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

     2D NMR plot parametere
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.836 ppm
F2LO            4919.50 Hz
F2PHI             6.992 ppm
F2HI            3497.03 Hz
F1PLO             9.842 ppm
F1LO            4922.31 Hz
F1PHI             6.996 ppm
F1HI            3499.10 Hz
F2PPMCM         0.18961 ppm/cm
F2HZCM         94.83147 Hz/cm
F1PPMCM         0.18971 ppm/cm
F1HZCM         94.88049 Hz/cm
```

¹H-¹H NOESY of 3•5



```
                 Current Data Pare
NAME             341-NOESY2
EXPNO                     1
PROCNO                    1

           F2 - Acquisition Pa
                   20000321
                      23.00
                     drx500
                 BBO BB-1
                  oesygptp
                       2048
                        D2O
                         16
                          4
                        558
                         24
                         .00
                       .0001
                      00000
                       8.40
                   .1345003
                         1H
                      -4.00
                       0.00
                       0.00
                      40.00
                         00
                         00
                   .0027120

           F1 - Acquisition p
ND0                       2
TD                      512
SFO1               500.1345
FIDRES             3.600894
SW                    3.686

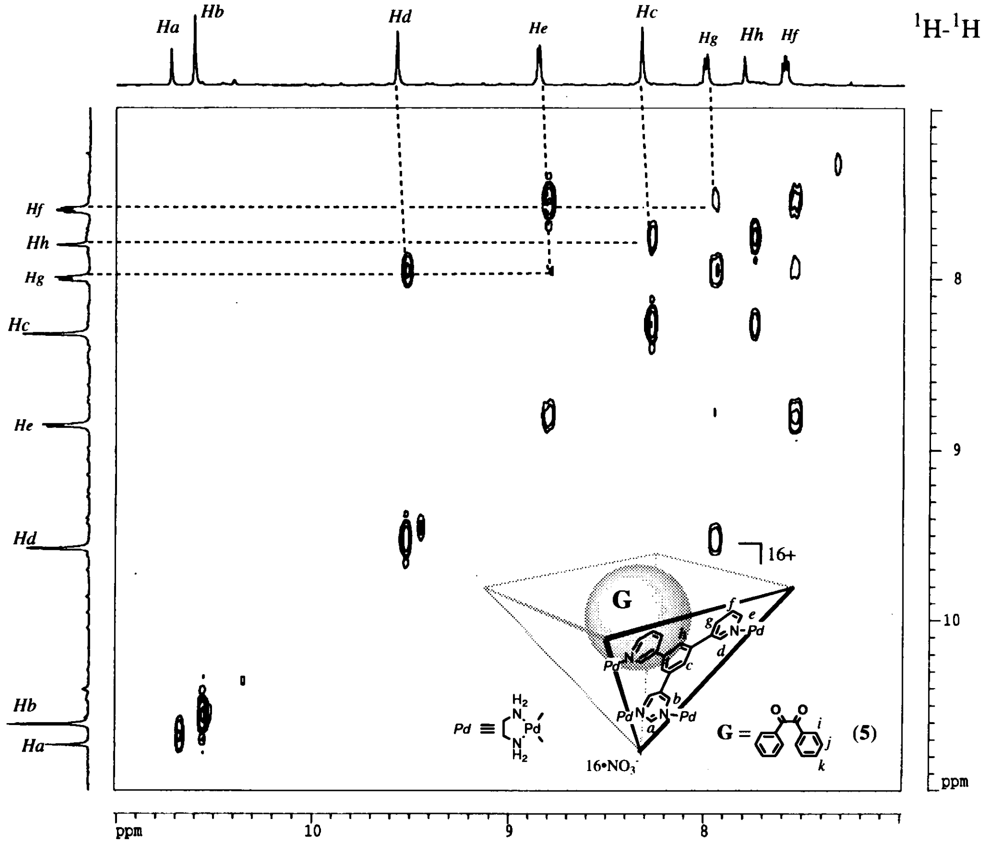
           F2 - Processing pa
SI                     1024
SF              500.1299777
WDW                   QSINE
SSB                       2
LB                     0.00
GB                        0
PC                     1.40

           F1 - Processing pa
SI                     1024
MC2                    TPPI
SF              500.1299806
WDW                   QSINE
SSB                       2
LB                     0.00
GB                        0

           2D NMR plot para
CX2                   15.00
CX1                   15.00
F2PLO                10.841
F2LO                5422.14
F2PHI                 7.155
F2HI                3578.48
F1PLO                10.841
F1LO                5422.14
F1PHI                 7.155
F1HI                3578.48
F2PPMCM             0.24576
F2HZCM            122.91052
F1PPMCM             0.24576
F1HZCM            122.91052
```

¹H-¹H relay COSY of 3•5

COSYGS



```
        Current Data Parameters
NAME             341-NOESY
EXPNO                    1
PROCNO                   1

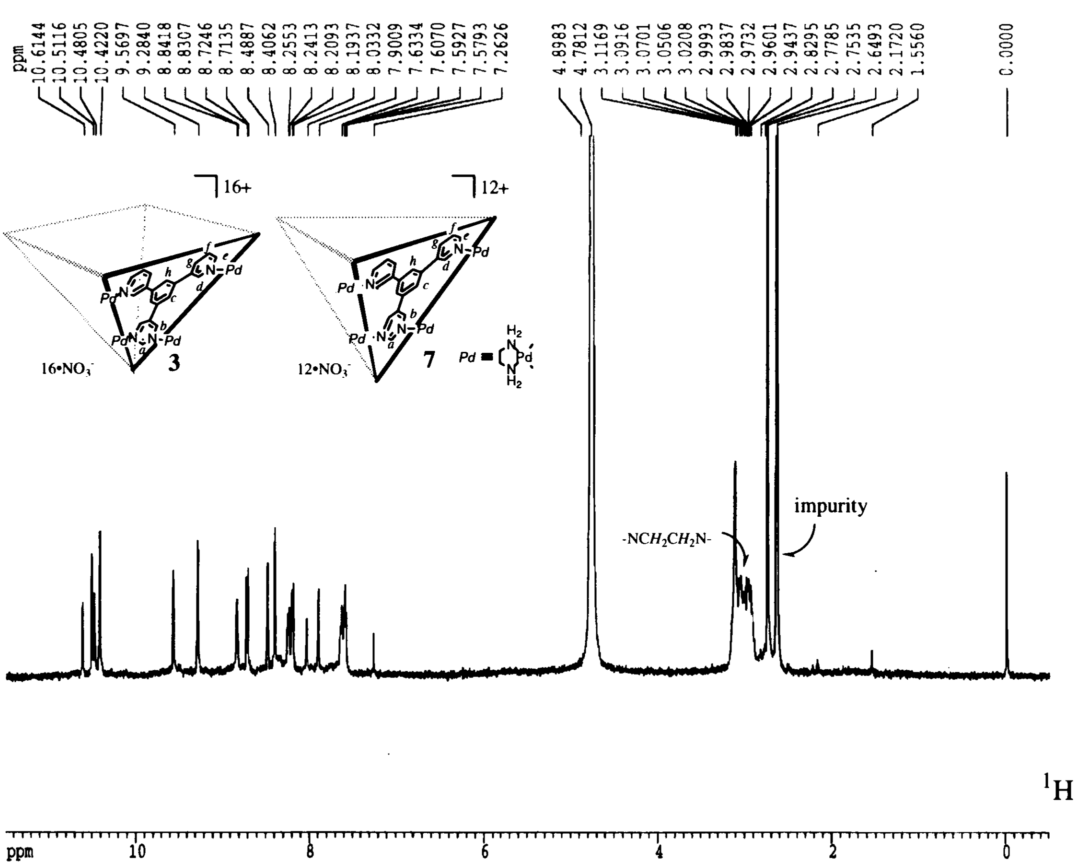
     F2 - Acquisition Parameters
Date_             20000317
Time                  4.31
INSTRUM             drx500
PROBHD      5 mm BBO BB-1
PULPROG             cosygs
TD                    2048
SOLVENT               DMSO
NS                     256
DS                       8
SWH               6666.667 Hz
FIDRES            3.255208 Hz
AQ               0.1536500 sec
RG                    6502
DW                  75.000 usec
DE                    6.00 usec
TE                   300.0 K
d0              0.10000000 sec
d13             0.00000300 sec
D1              1.48689198 sec
P1                    8.40 usec
SFO1           500.1330069 MHz
NUC1                    1H
PL1                  -4.00 dB
P16                1500.00 usec
D16             0.00030000 sec
P0                    8.40 usec
IN0             0.00014990 sec

     F1 - Acquisition parameters
ND0                      1
TD                      88
SFO1               500.133 MHz
FIDRES           75.808113 Hz
SW                  13.339 ppm

     F2 - Processing parameters
SI                    1024
SF             500.1300000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40

     F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

       2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO               11.011 ppm
F2LO               5506.88 Hz
F2PHI                6.989 ppm
F2HI               3495.16 Hz
F1PLO               11.001 ppm
F1LO               5502.03 Hz
F1PHI                6.989 ppm
F1HI               3495.48 Hz
F2PPMCM            0.26816 ppm/cm
F2HZCM           134.11459 Hz/cm
F1PPMCM            0.26747 ppm/cm
F1HZCM           133.76973 Hz/cm
```



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EXPNO                  2
PROCNO                 1

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Time               23.43
INSTRUM           drx500
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    32
DS                     2
SWH            10330.578
FIDRES          0.315264
AQ             1.5860212
RG                 912.3
DW                48.400
DE                  6.00
TE                 300.0
D1            1.00000000
P1                  7.10
SFO1         500.1330885
NUC1                  1H
PL1                -1.00

F2 - Processing paramete
SI                 16384
SF           500.1299608
WDW                   EM
SSB                    0
LB                  0.30
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00
F1P               11.500
F1               5751.49
F2P               -0.500
F2               -250.06
PPMCM            0.60000
HZCM           300.07797
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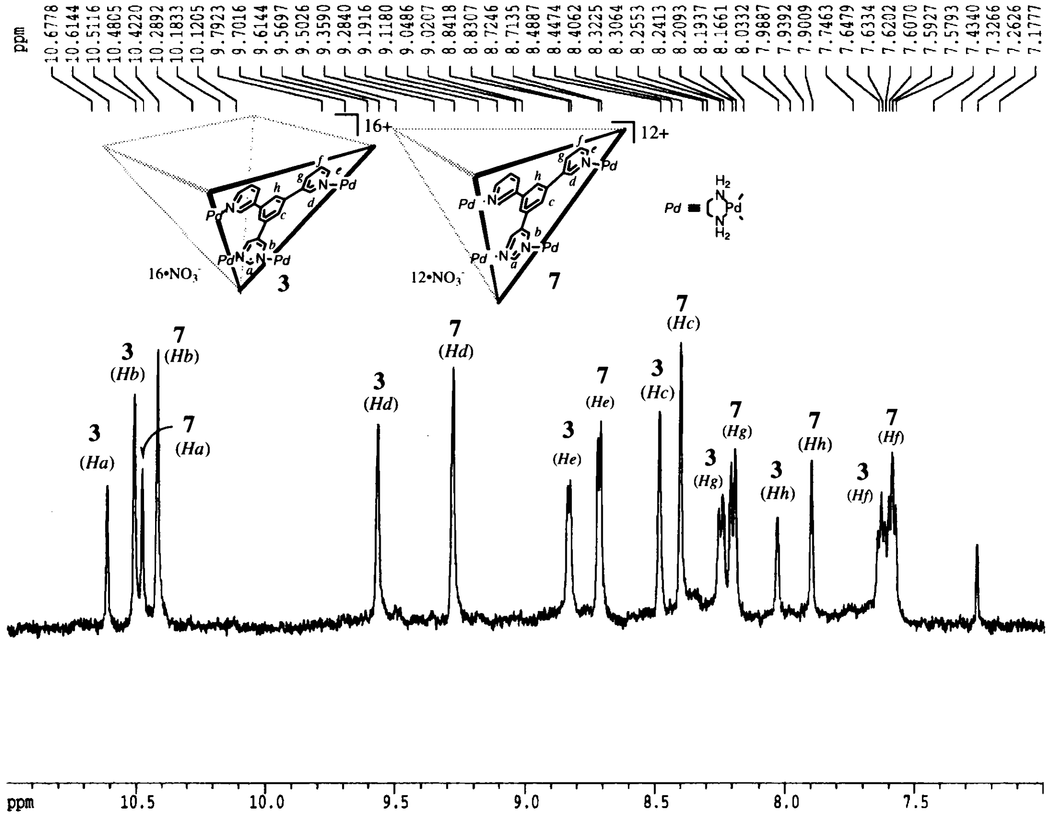
^{1}H NMR of **3** and **7**



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Current Data Parameters
NAME                 416
EXPNO                  2
PROCNO                 1

F2 - Acquisition Paramete
Date_           20000323
Time               23.43
INSTRUM           drx500
PROBHD   5 mm BBO BB-1
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    32
DS                     2
SWH          10330.578 H
FIDRES        0.315264 H
AQ           1.5860212 s
RG                 912.3
DW              48.400 u
DE                6.00 u
TE               300.0 K
D1          1.00000000 s
P1                7.10 u
SFO1       500.1330885 M
NUC1                  1H
PL1              -1.00 d

F2 - Processing parameter
SI                 16384
SF         500.1299608 M
WDW                   EM
SSB                    0
LB                0.30 H
GB                     0
PC                  1.00

1D NMR plot parameters
CX               20.00 c
F1P             11.000 p
F1             5501.43 H
F2P              7.000 p
F2             3500.91 H
PPMCM          0.20000 p
HZCM         100.02599 H
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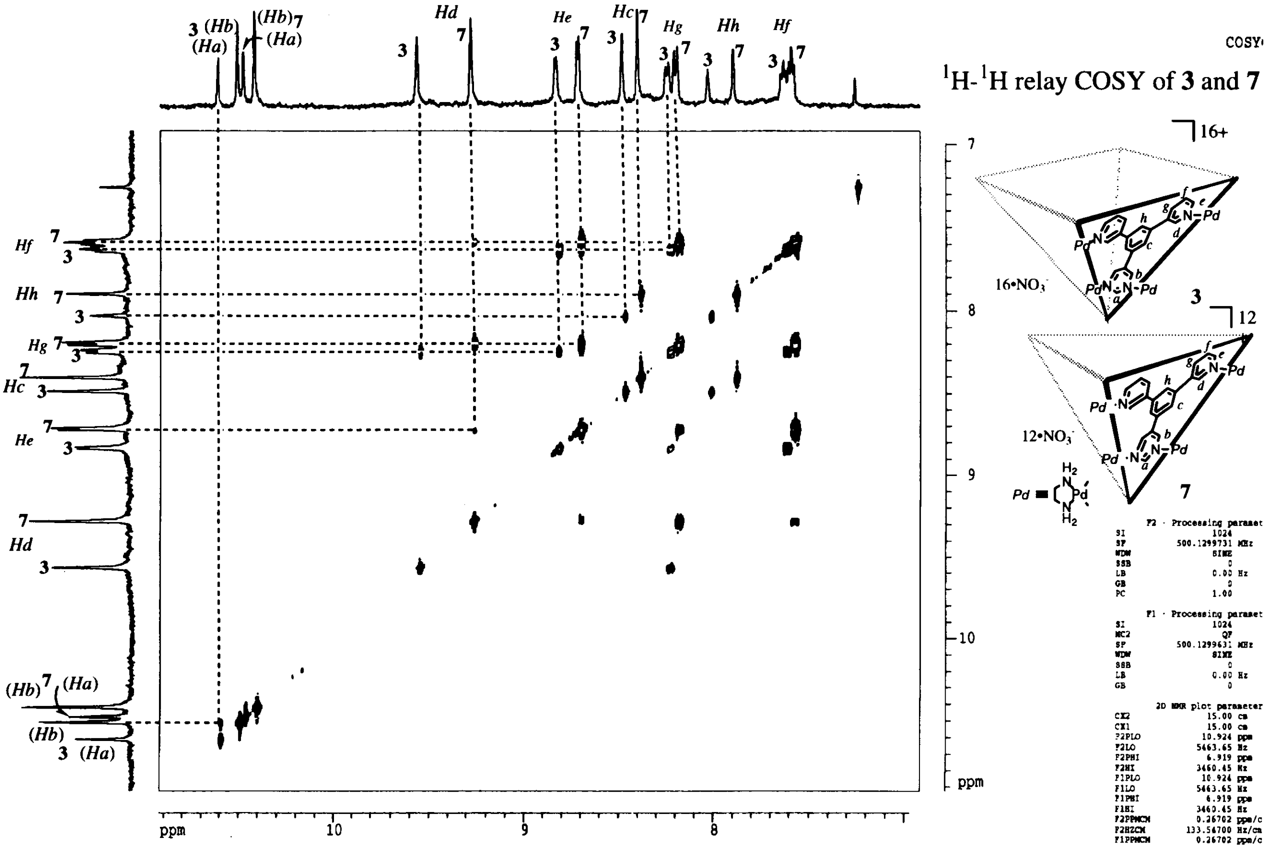
^{1}H NMR of **3** and **7**



^{1}H-^{1}H relay COSY of **3** and **7**

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        F2 - Processing paramet
SI                    1024
SF             500.1299731 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

        F1 - Processing paramet
SI                    1024
MC2                     QF
SF             500.1299631 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

          2D NMR plot parameter
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO               10.924 ppm
F2LO               5463.65 Hz
F2PHI                6.919 ppm
F2HI               3460.45 Hz
F1PLO               10.924 ppm
F1LO               5463.65 Hz
F1PHI                6.919 ppm
F1HI               3460.45 Hz
F2PPMCM            0.26702 ppm/c
F2HZCM           133.54700 Hz/cm
F1PPMCM            0.26702 ppm/c
F1HZCM           133.54700 Hz/cm
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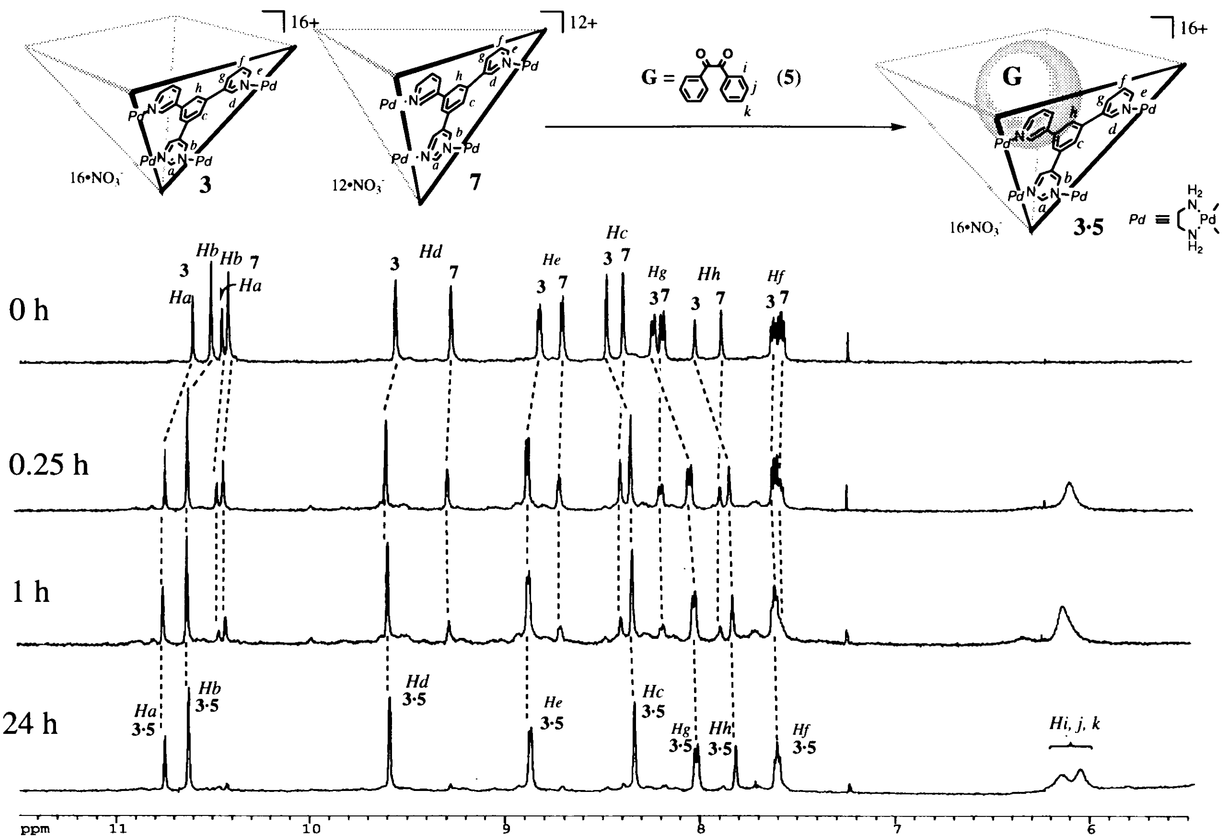
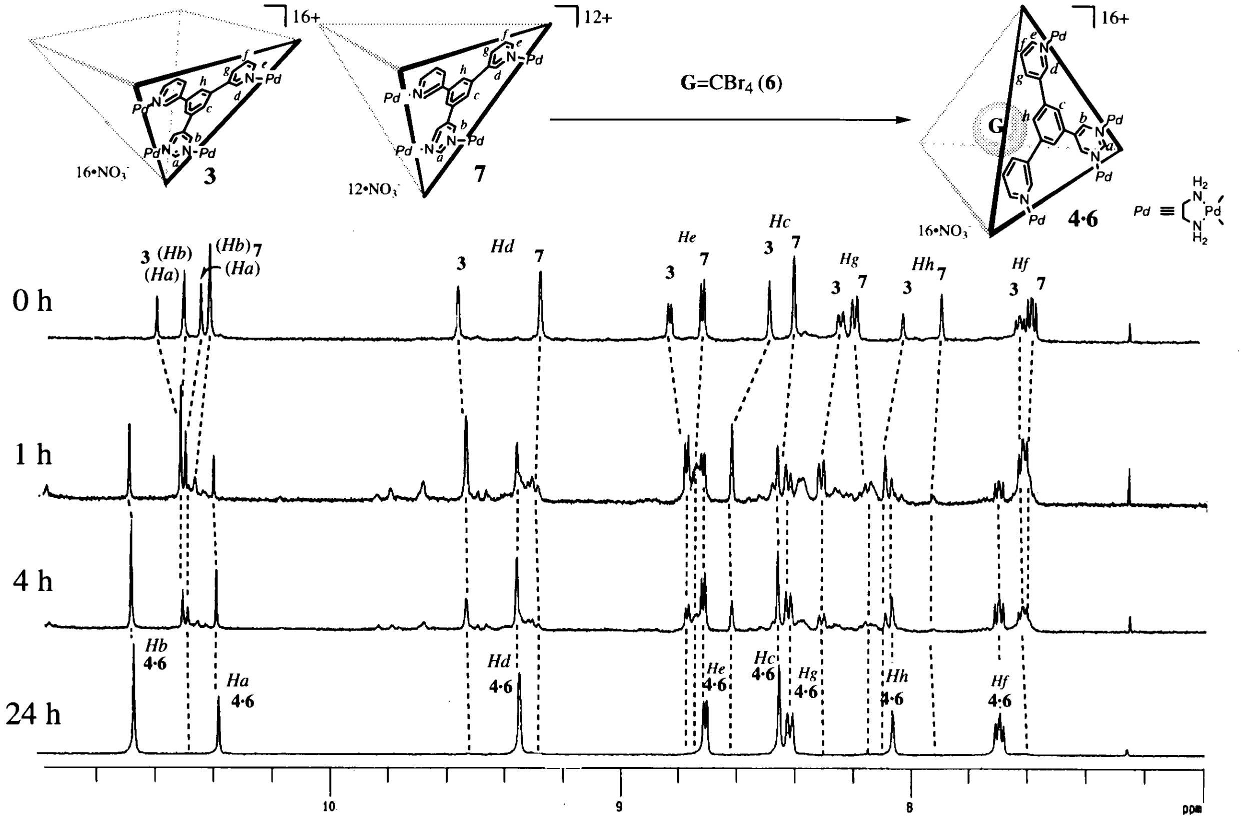


The ^{1}H NMR observation of the reorganization structure from mixture open cones **3**, **7** to **3·5**.



The ^{1}H NMR observation of the reorganization structure from mixture open cones **3**, **7** to **4·6**.

```
[ Mass Spectrum ]
Data  : 000308-383-010                  Date : 08-Mar-2000 18:30
Sample:
Note : -
Inlet : Direct                          Ion Mode : ESI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 24.89 min          Scan# : (1,159)
BP : m/z 802.9534       Int.   : 36.78
Output m/z range : 454.0059 to 1172.1068       Cut Level : 0.00 %
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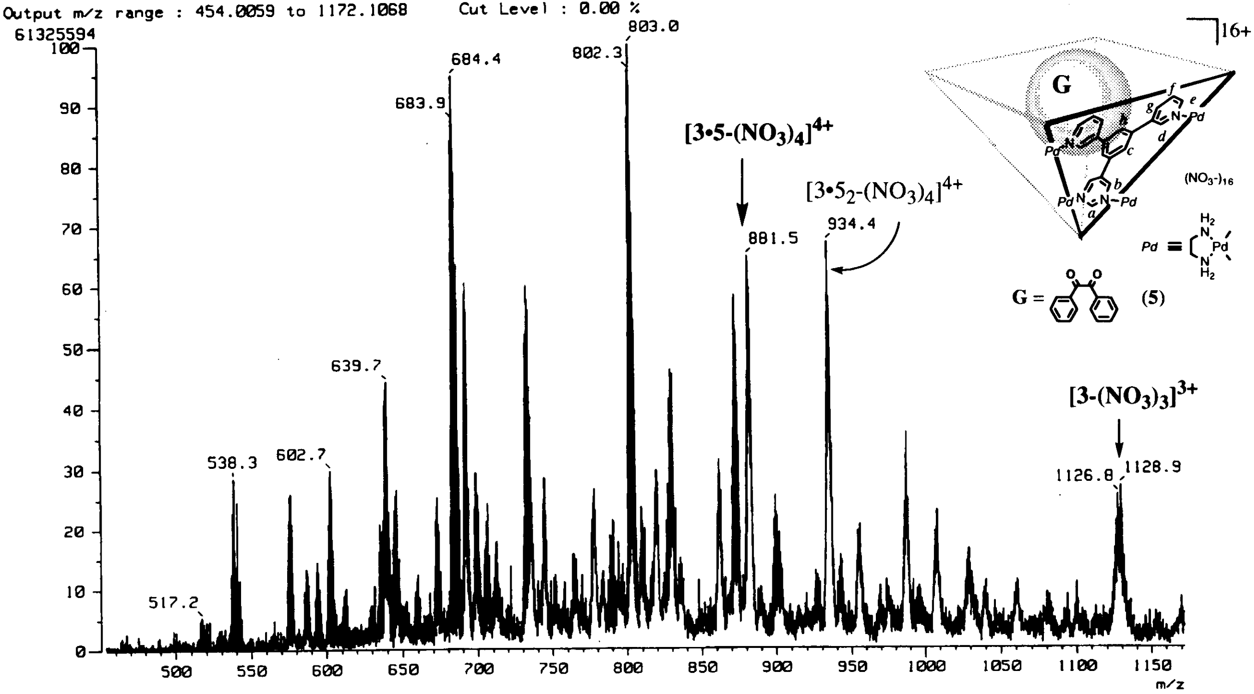
ESI-MS of **3•5**

$C_{110}H_{130}N_{48}O_{50}Pd_8$

FW 3775.90



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[ Mass Spectrum ]
Data  : 000308-383-010                  Date : 08-Mar-2000 18:30
Sample:
Note : -
Inlet : Direct                          Ion Mode : ESI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 24.89 min          Scan# : (1,159)
BP : m/z 802.9534       Int.   : 36.78
Output m/z range : 874.4463 to 888.1032        Cut Level : 0.00 %
 39731282
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ESI-MS of **3•5**

$C_{110}H_{130}N_{48}O_{50}Pd_8$

FW 3775.90

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3509.1971   0.0839
3510.1969   0.1991
3511.1967   0.4438
3512.1966   0.9289 *
3513.1965   1.8241 *
3514.1964   3.3613 **
3515.1963   5.8194 ***
3516.1962   9.4966 ******
3517.1962  14.6597 *********
3518.1962  21.4879 *************
3519.1962  29.9962 ******************
3520.1962  40.0041 ************************
3521.1962  51.0905 *******************************
3522.1963  62.6477 **************************************
3523.1964  73.8774 *********************************************
3524.1964  83.9677 ****************************************************
3525.1965  92.0688 *********************************************************
3526.1967  97.5830 ************************************************************
3527.1968 100.0000 *************************************************************
3528.1970  99.2870 *************************************************************
3529.1971  95.4417 ***********************************************************
3530.1973  89.0604 *******************************************************
3531.1975  80.5040 **************************************************
3532.1977  70.7651 *******************************************
3533.1980  60.2316 *************************************
3534.1982  49.9539 *******************************
3535.1985  40.0447 *************************
3536.1988  31.3652 *******************
3537.1992  23.6636 ***************
3538.1994  17.5059 **********
3539.1999  12.4139 *******
3540.2001   8.6628 *****
3541.2007   5.7654 ***
3542.2010   3.7834 **
3543.2015   2.3593 *
3544.2019   1.4488 *
3545.2026   0.8444
3546.2030   0.4821
3547.2037   0.2615
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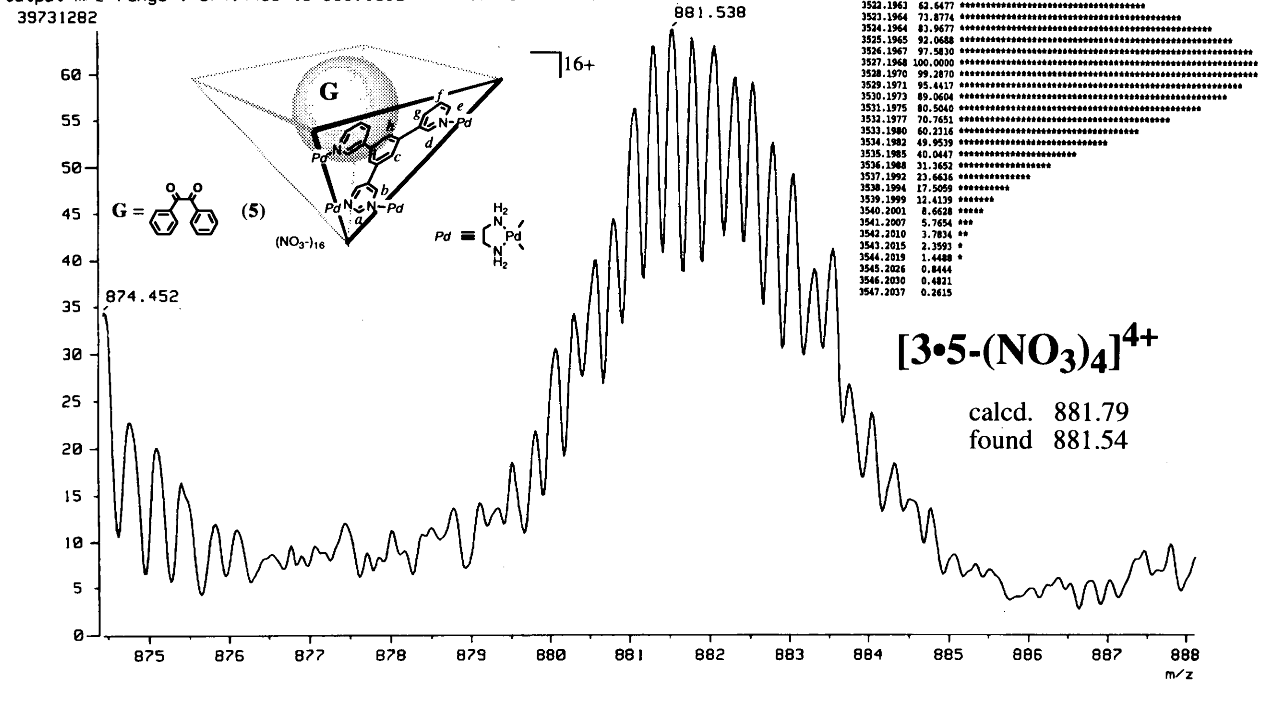


$[3•5-(NO_3)_4]^{4+}$

calcd. 881.79
found 881.54

X-ray crystallographic data of **4•6**

Experimental Details

Table 1. Crystal data and structure refinement.

Empirical formula	C97 H120 Br4 N48 O72 Pd8	
Formula weight	4281.25	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 40.32(3) Å	α= 90°.
	b = 15.767(9) Å	β= 127.36(2)°.
	c = 30.83(2) Å	γ = 90°.
Volume	15583(18) $Å^3$	
Z	4	
Density (calculated)	1.825 Mg/m^3	
Absorption coefficient	2.037 mm^{-1}	
F(000)	8488	
Crystal size	0.20 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.27 to 28.73°.	
Index ranges	-45<=h<=52, -19<=k<=19, -40<=l<=41	
Reflections collected	39507	
Independent reflections	17874 [R(int) = 0.1019]	
Completeness to theta = 28.73°	88.5 %	
Max. and min. transmission	0.7498 and 0.6861	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17874 / 0 / 1050	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0720, wR2 = 0.1850	
R indices (all data)	R1 = 0.1157, wR2 = 0.2034	
Largest diff. peak and hole	1.790 and -1.688 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
Pd(1)	1787(1)	4162(1)	8015(1)	30(1)
Pd(2)	937(1)	8282(1)	10156(1)	30(1)
Pd(3)	2257(1)	5082(1)	10133(1)	31(1)
Pd(4)	-800(1)	7515(1)	9148(1)	31(1)
C(100)	0	3731(8)	2500	50(3)
Br(2)	-89(1)	3012(1)	2926(1)	80(1)
Br(1)	478(1)	4432(1)	2965(1)	78(1)
C(11A)	1037(2)	8307(4)	7709(3)	30(1)
C(12A)	876(2)	8676(4)	7957(3)	33(2)
C(13A)	940(2)	8317(4)	8414(3)	30(1)
C(14A)	1169(2)	7572(4)	8624(3)	30(1)
C(15A)	1339(2)	7194(4)	8392(3)	29(1)
C(16A)	1273(2)	7561(4)	7935(2)	28(1)
N(21A)	826(2)	8382(4)	6359(2)	31(1)
C(21A)	953(2)	8661(4)	7210(3)	31(1)
C(22A)	900(2)	8112(4)	6822(3)	32(2)
C(23A)	799(3)	9229(5)	6266(3)	40(2)
C(24A)	834(3)	9816(5)	6621(3)	44(2)
C(25A)	920(2)	9530(4)	7108(3)	38(2)
N(31A)	728(2)	8766(4)	9418(2)	32(1)
C(31A)	745(2)	8699(4)	8657(3)	31(1)
C(32A)	905(2)	8492(4)	9190(3)	29(1)
C(33A)	397(2)	9283(5)	9147(3)	39(2)
C(34A)	239(3)	9539(5)	8636(3)	46(2)
C(35A)	407(3)	9228(5)	8376(3)	42(2)
N(41A)	1801(2)	5078(4)	8502(2)	33(1)
N(42A)	2019(2)	5474(4)	9367(2)	31(1)
C(41A)	1586(2)	6410(4)	8624(3)	29(1)
C(42A)	1591(2)	5786(4)	8299(3)	32(1)
C(43A)	2017(2)	4934(5)	9033(3)	38(2)
C(44A)	1813(2)	6210(4)	9171(3)	32(2)
C(11B)	-98(2)	4196(4)	8380(3)	32(1)
C(12B)	292(2)	3859(5)	8616(3)	37(2)
C(13B)	639(2)	4235(4)	9071(3)	31(1)
C(14B)	599(2)	4963(4)	9290(3)	31(1)
C(16B)	-139(2)	4960(4)	8582(3)	31(1)
C(15B)	211(2)	5324(4)	9047(3)	31(1)
N(21B)	-1218(2)	3749(4)	7229(2)	32(1)
C(21B)	-477(2)	3816(4)	7874(3)	31(1)
C(22B)	-877(2)	4056(4)	7681(3)	36(2)
C(23B)	-1181(3)	3177(5)	6940(3)	44(2)
C(24B)	-796(3)	2885(6)	7104(4)	54(2)
C(25B)	-446(3)	3203(6)	7576(3)	50(2)
N(31B)	1793(2)	4188(4)	9784(2)	35(1)
C(31B)	1068(2)	3895(4)	9309(3)	31(1)
C(32B)	1403(2)	4439(4)	9556(3)	32(2)
C(33B)	1866(2)	3377(5)	9756(3)	37(2)
C(34B)	1552(2)	2788(5)	9506(3)	39(2)
C(35B)	1146(3)	3036(5)	9289(3)	40(2)
N(41B)	-235(2)	7100(4)	9363(2)	29(1)
N(42B)	457(2)	7426(4)	9761(2)	31(1)
C(41B)	162(2)	6132(4)	9258(3)	29(1)
C(42B)	-204(2)	6371(4)	9168(3)	31(1)
C(43B)	94(2)	7591(5)	9664(3)	37(2)
C(44B)	492(2)	6700(4)	9558(3)	32(1)
N(1A)	2339(2)	4545(4)	8210(3)	41(2)
N(2A)	1811(2)	3291(4)	7558(3)	45(2)

Table 2. continued

C(1A)	2406(3)	4111(6)	7831(4)	56(2)
C(2A)	2249(3)	3227(6)	7746(4)	55(2)
N(1B)	1411(2)	9122(4)	10572(3)	41(1)
N(2B)	1182(2)	7803(4)	10908(3)	49(2)
C(1B)	1588(3)	9085(6)	11155(4)	61(2)
C(2B)	1596(3)	8196(6)	11298(4)	63(3)
N(1C)	2730(2)	5932(5)	10510(3)	50(2)
N(2C)	2478(2)	4741(4)	10893(2)	45(2)
C(1C)	2893(4)	5981(7)	11080(3)	72(3)
C(2C)	2906(3)	5120(7)	11273(3)	70(3)
N(1D)	-825(2)	6643(4)	9615(3)	48(2)
N(2D)	-1369(2)	7859(5)	8933(3)	49(2)
C(1D)	-1244(4)	6609(11)	9470(5)	104(5)
C(2D)	-1508(4)	7185(8)	9102(9)	129(8)
N(100)	2317(3)	7604(6)	4066(3)	67(2)
O(101)	2087(3)	8096(6)	4079(5)	107(3)
O(102)	2567(2)	7866(5)	3988(3)	74(2)
O(103)	2311(5)	6872(6)	4152(6)	143(5)
N(200)	3064(3)	3253(7)	7527(3)	66(2)
O(201)	2833(5)	3393(9)	7046(4)	164(6)
O(202)	3140(3)	2507(6)	7700(4)	106(3)
O(203)	3221(2)	3852(5)	7850(3)	72(2)
N(300)	3715(2)	768(4)	8106(3)	43(2)
O(301)	3847(2)	746(6)	8582(3)	82(2)
O(302)	3369(2)	531(5)	7760(3)	77(2)
O(303)	3949(2)	1012(4)	7989(2)	46(1)
N(400)	1496(6)	325(10)	9491(7)	122(6)
O(401)	1201(5)	811(9)	9425(6)	155(6)
O(402)	1768(8)	121(13)	9916(7)	260(14)
O(403)	1465(4)	95(8)	9077(6)	135(4)
N(500)	1557(4)	6437(7)	10214(5)	92(3)
O(501)	1933(5)	6436(18)	10489(7)	269(12)
O(502)	1432(5)	6095(19)	10531(8)	264(12)
O(503)	1360(2)	6525(4)	9743(3)	61(2)
N(600)	7(6)	-281(9)	4923(5)	48(4)
O(601)	204(5)	-878(9)	4928(7)	71(4)
O(602)	239(4)	433(5)	5060(5)	120(4)
N(700)	2170(4)	8102(9)	10382(5)	89(3)
O(701)	2080(7)	8430(20)	10606(10)	330(18)
O(702)	1906(6)	8042(13)	9903(7)	222(10)
O(703)	2452(5)	7863(10)	10468(11)	242(13)
N(800)	-119(5)	2247(19)	5778(7)	208(13)
O(801)	53(9)	2680(30)	5629(10)	390(30)
O(802)	-517(4)	2079(9)	5567(5)	137(4)
O(803)	93(4)	1821(10)	6270(5)	150(5)
N(900)	198(10)	4430(30)	5315(12)	136(13)
O(901)	312(7)	5151(10)	5192(8)	195(10)
O(902)	400(13)	3770(13)	5610(12)	173(15)
O(1W)	998(3)	-756(5)	5210(4)	95(3)
O(2W)	2017(8)	5523(12)	1406(7)	276(13)
O(3W)	1102(4)	-922(7)	3088(5)	140(4)
O(4W)	-399(4)	1582(6)	6616(5)	141(5)
O(5W)	1940(3)	578(6)	7464(4)	99(3)
O(6W)	1257(6)	3848(6)	6450(4)	229(11)
O(7W)	2761(4)	991(8)	8026(6)	142(4)
O(8W)	2368(3)	6378(6)	8243(4)	117(4)
O(9W)	1976(3)	1143(6)	785(4)	105(3)
O(10W)	1497(3)	1622(5)	7640(3)	85(2)
O(11W)	-250(5)	748(9)	7478(7)	171(6)
O(12W)	895(3)	2037(7)	6564(4)	117(3)

Table 3. Bond lengths [Å].

atom atom	length	atom atom	length
Pd(1)-N(2A)	2.011(6)	C(21B)-C(25B)	1.389(10)
Pd(1)-N(1A)	2.016(6)	C(21B)-C(22B)	1.391(10)
Pd(1)-N(21B)#1	2.038(6)	C(23B)-C(24B)	1.387(12)
Pd(1)-N(41A)	2.058(5)	C(24B)-C(25B)	1.368(11)
Pd(2)-N(1B)	2.021(6)	N(31B)-C(33B)	1.328(9)
Pd(2)-N(2B)	2.034(7)	N(31B)-C(32B)	1.337(9)
Pd(2)-N(31A)	2.036(6)	C(31B)-C(32B)	1.375(10)
Pd(2)-N(42B)	2.046(6)	C(31B)-C(35B)	1.400(10)
Pd(3)-N(2C)	2.010(6)	C(33B)-C(34B)	1.370(11)
Pd(3)-N(1C)	2.024(7)	C(34B)-C(35B)	1.397(11)
Pd(3)-N(42A)	2.032(5)	N(41B)-C(43B)	1.314(9)
Pd(3)-N(31B)	2.048(6)	N(41B)-C(42B)	1.338(9)
Pd(4)-N(21A)#1	2.032(6)	N(42B)-C(43B)	1.330(10)
Pd(4)-N(2D)	2.037(7)	N(42B)-C(44B)	1.352(8)
Pd(4)-N(1D)	2.037(6)	C(41B)-C(42B)	1.378(10)
Pd(4)-N(41B)	2.055(6)	C(41B)-C(44B)	1.392(9)
C(100)-Br(1)#2	1.907(7)	N(1A)-C(1A)	1.513(10)
C(100)-Br(1)	1.907(7)	N(2A)-C(2A)	1.492(11)
C(100)-Br(2)	1.927(7)	C(1A)-C(2A)	1.487(13)
C(100)-Br(2)#2	1.927(7)	N(1B)-C(1B)	1.481(11)
C(11A)-C(12A)	1.392(9)	N(2B)-C(2B)	1.477(12)
C(11A)-C(16A)	1.404(9)	C(1B)-C(2B)	1.463(13)
C(11A)-C(21A)	1.471(9)	N(1C)-C(1C)	1.457(11)
C(12A)-C(13A)	1.390(9)	N(2C)-C(2C)	1.502(12)
C(13A)-C(14A)	1.388(9)	C(1C)-C(2C)	1.471(13)
C(13A)-C(31A)	1.502(9)	N(1D)-C(1D)	1.463(13)
C(14A)-C(15A)	1.392(9)	N(2D)-C(2D)	1.438(15)
C(15A)-C(16A)	1.393(8)	C(1D)-C(2D)	1.336(18)
C(15A)-C(41A)	1.472(9)	N(100)-O(103)	1.188(12)
N(21A)-C(22A)	1.337(8)	N(100)-O(101)	1.228(12)
N(21A)-C(23A)	1.356(9)	N(100)-O(102)	1.242(11)
N(21A)-Pd(4)#1	2.032(6)	N(200)-O(201)	1.199(12)
C(21A)-C(22A)	1.385(9)	N(200)-O(203)	1.232(11)
C(21A)-C(25A)	1.393(10)	N(200)-O(202)	1.252(12)
C(23A)-C(24A)	1.373(11)	N(300)-O(302)	1.193(9)
C(24A)-C(25A)	1.396(10)	N(300)-O(301)	1.220(9)
N(31A)-C(33A)	1.337(9)	N(300)-O(303)	1.256(9)
N(31A)-C(32A)	1.342(8)	N(400)-O(402)	1.13(2)
C(31A)-C(35A)	1.368(10)	N(400)-O(403)	1.261(16)
C(31A)-C(32A)	1.393(9)	N(400)-O(401)	1.32(2)
C(33A)-C(34A)	1.356(11)	N(500)-O(503)	1.166(13)
C(34A)-C(35A)	1.415(10)	N(500)-O(501)	1.208(17)
N(41A)-C(42A)	1.308(9)	N(500)-O(502)	1.45(3)
N(41A)-C(43A)	1.328(9)	N(600)-N(600)#3	1.02(3)
N(42A)-C(43A)	1.332(9)	N(600)-O(602)#3	1.052(18)
N(42A)-C(44A)	1.339(9)	N(600)-O(601)	1.225(19)
C(41A)-C(44A)	1.380(9)	N(600)-O(602)	1.357(19)
C(41A)-C(42A)	1.415(9)	O(602)-N(600)#3	1.052(18)
C(11B)-C(12B)	1.377(10)	N(700)-O(703)	1.068(16)
C(11B)-C(16B)	1.412(9)	N(700)-O(701)	1.089(18)
C(11B)-C(21B)	1.494(9)	N(700)-O(702)	1.190(18)
C(12B)-C(13B)	1.377(10)	O(702)-O(703)	1.82(2)
C(13B)-C(14B)	1.389(9)	N(800)-O(801)	1.24(4)
C(13B)-C(31B)	1.509(10)	N(800)-O(802)	1.34(2)
C(14B)-C(15B)	1.383(10)	N(800)-O(803)	1.38(3)
C(16B)-C(15B)	1.386(9)	N(900)-O(902)	1.29(5)
C(15B)-C(41B)	1.495(9)	N(900)-O(901)	1.36(4)
N(21B)-C(22B)	1.320(9)	N(900)-O(901)#4	1.79(4)
N(21B)-C(23B)	1.339(9)	O(901)-N(900)#4	1.79(4)
N(21B)-Pd(1)#1	2.038(6)		

Table 4. Bond angles [°].

atom atom atom	angle
N(2A)-Pd(1)-N(1A)	84.2(3)
N(2A)-Pd(1)-N(21B)#1	92.6(3)
N(1A)-Pd(1)-N(21B)#1	176.3(2)
N(2A)-Pd(1)-N(41A)	176.2(3)
N(1A)-Pd(1)-N(41A)	92.0(3)
N(21B)#1-Pd(1)-N(41A)	91.2(2)
N(1B)-Pd(2)-N(2B)	84.4(3)
N(1B)-Pd(2)-N(31A)	93.0(3)
N(2B)-Pd(2)-N(31A)	176.5(3)
N(1B)-Pd(2)-N(42B)	177.9(2)
N(2B)-Pd(2)-N(42B)	93.7(3)
N(31A)-Pd(2)-N(42B)	88.9(2)
N(2C)-Pd(3)-N(1C)	84.8(3)
N(2C)-Pd(3)-N(42A)	177.2(3)
N(1C)-Pd(3)-N(42A)	94.7(3)
N(2C)-Pd(3)-N(31B)	92.6(3)
N(1C)-Pd(3)-N(31B)	177.3(3)
N(42A)-Pd(3)-N(31B)	87.9(2)
N(21A)#1-Pd(4)-N(2D)	92.8(3)
N(21A)#1-Pd(4)-N(1D)	175.4(3)
N(2D)-Pd(4)-N(1D)	83.1(3)
N(21A)#1-Pd(4)-N(41B)	89.5(2)
N(2D)-Pd(4)-N(41B)	176.9(3)
N(1D)-Pd(4)-N(41B)	94.5(3)
Br(1)#2-C(100)-Br(1)	109.1(6)
Br(1)#2-C(100)-Br(2)	109.48(8)
Br(1)-C(100)-Br(2)	110.42(8)
Br(1)#2-C(100)-Br(2)#2	110.42(8)
Br(1)-C(100)-Br(2)#2	109.47(8)
Br(2)-C(100)-Br(2)#2	107.9(6)
C(12A)-C(11A)-C(16A)	118.8(6)
C(12A)-C(11A)-C(21A)	121.7(6)
C(16A)-C(11A)-C(21A)	119.5(6)
C(13A)-C(12A)-C(11A)	121.6(6)
C(14A)-C(13A)-C(12A)	118.7(6)
C(14A)-C(13A)-C(31A)	120.4(6)
C(12A)-C(13A)-C(31A)	120.8(6)
C(13A)-C(14A)-C(15A)	121.2(6)
C(14A)-C(15A)-C(16A)	119.5(6)
C(14A)-C(15A)-C(41A)	120.6(6)
C(16A)-C(15A)-C(41A)	119.9(6)
C(15A)-C(16A)-C(11A)	120.3(6)
C(22A)-N(21A)-C(23A)	118.4(6)
C(22A)-N(21A)-Pd(4)#1	118.8(5)
C(23A)-N(21A)-Pd(4)#1	122.6(4)
C(22A)-C(21A)-C(25A)	118.3(6)
C(22A)-C(21A)-C(11A)	118.9(6)
C(25A)-C(21A)-C(11A)	122.7(6)
N(21A)-C(22A)-C(21A)	122.8(6)
N(21A)-C(23A)-C(24A)	122.6(6)
C(23A)-C(24A)-C(25A)	118.5(7)
C(21A)-C(25A)-C(24A)	119.3(7)
C(33A)-N(31A)-C(32A)	121.0(6)
C(33A)-N(31A)-Pd(2)	120.4(5)
C(32A)-N(31A)-Pd(2)	118.3(5)
C(35A)-C(31A)-C(32A)	117.5(6)
C(35A)-C(31A)-C(13A)	123.3(6)
C(32A)-C(31A)-C(13A)	119.2(6)
N(31A)-C(32A)-C(31A)	122.0(6)
N(31A)-C(33A)-C(34A)	119.7(7)
C(33A)-C(34A)-C(35A)	120.4(7)
C(31A)-C(35A)-C(34A)	119.2(7)
C(42A)-N(41A)-C(43A)	119.0(6)
C(42A)-N(41A)-Pd(1)	121.8(4)
C(43A)-N(41A)-Pd(1)	119.2(5)
C(43A)-N(42A)-C(44A)	119.7(6)
C(43A)-N(42A)-Pd(3)	118.7(5)
C(44A)-N(42A)-Pd(3)	121.0(4)
C(44A)-C(41A)-C(42A)	115.0(6)
C(44A)-C(41A)-C(15A)	122.5(6)
C(42A)-C(41A)-C(15A)	122.4(6)
N(41A)-C(42A)-C(41A)	122.6(6)
N(41A)-C(43A)-N(42A)	122.4(7)
N(42A)-C(44A)-C(41A)	121.2(6)
C(12B)-C(11B)-C(16B)	119.8(6)
C(12B)-C(11B)-C(21B)	120.9(6)
C(16B)-C(11B)-C(21B)	118.9(6)
C(13B)-C(12B)-C(11B)	120.1(6)
C(12B)-C(13B)-C(14B)	120.3(6)
C(12B)-C(13B)-C(31B)	119.9(6)
C(14B)-C(13B)-C(31B)	119.6(6)
C(15B)-C(14B)-C(13B)	120.3(6)
C(15B)-C(16B)-C(11B)	119.5(6)
C(14B)-C(15B)-C(16B)	119.7(6)
C(14B)-C(15B)-C(41B)	121.3(6)
C(16B)-C(15B)-C(41B)	118.9(6)
C(22B)-N(21B)-C(23B)	119.0(6)
C(22B)-N(21B)-Pd(1)#1	119.4(5)
C(23B)-N(21B)-Pd(1)#1	121.6(5)
C(25B)-C(21B)-C(22B)	117.0(6)
C(25B)-C(21B)-C(11B)	121.5(7)
C(22B)-C(21B)-C(11B)	121.5(6)
N(21B)-C(22B)-C(21B)	123.1(6)
N(21B)-C(23B)-C(24B)	122.2(7)
C(25B)-C(24B)-C(23B)	118.1(7)
C(24B)-C(25B)-C(21B)	120.6(8)
C(33B)-N(31B)-C(32B)	119.2(7)
C(33B)-N(31B)-Pd(3)	121.9(5)
C(32B)-N(31B)-Pd(3)	118.8(5)
C(32B)-C(31B)-C(35B)	117.1(7)

Table 4. continue

atom atom atom	angle	atom atom atom	angle
C(32B)-C(31B)-C(13B)	119.9(6)	O(103)-N(100)-O(101)	119.2(11)
C(35B)-C(31B)-C(13B)	123.0(7)	O(103)-N(100)-O(102)	119.6(12)
N(31B)-C(32B)-C(31B)	123.7(6)	O(101)-N(100)-O(102)	121.1(9)
N(31B)-C(33B)-C(34B)	121.6(7)	O(201)-N(200)-O(203)	119.4(11)
C(33B)-C(34B)-C(35B)	119.6(7)	O(201)-N(200)-O(202)	120.4(12)
C(34B)-C(35B)-C(31B)	118.7(7)	O(203)-N(200)-O(202)	120.2(9)
C(43B)-N(41B)-C(42B)	119.5(6)	O(302)-N(300)-O(301)	119.0(8)
C(43B)-N(41B)-Pd(4)	119.1(5)	O(302)-N(300)-O(303)	121.1(7)
C(42B)-N(41B)-Pd(4)	121.1(5)	O(301)-N(300)-O(303)	119.9(7)
C(43B)-N(42B)-C(44B)	118.1(6)	O(402)-N(400)-O(403)	121(2)
C(43B)-N(42B)-Pd(2)	121.3(5)	O(402)-N(400)-O(401)	119.7(17)
C(44B)-N(42B)-Pd(2)	120.4(5)	O(403)-N(400)-O(401)	119(2)
C(42B)-C(41B)-C(44B)	115.6(6)	O(503)-N(500)-O(501)	119.4(17)
C(42B)-C(41B)-C(15B)	123.5(6)	O(503)-N(500)-O(502)	129.2(13)
C(44B)-C(41B)-C(15B)	120.8(6)	O(501)-N(500)-O(502)	109.2(16)
N(41B)-C(42B)-C(41B)	121.7(7)	N(600)#3-N(600)-O(602)#3	82(2)
N(41B)-C(43B)-N(42B)	123.1(7)	N(600)#3-N(600)-O(601)	151(3)
N(42B)-C(44B)-C(41B)	121.7(6)	O(602)#3-N(600)-O(601)	116.6(15)
C(1A)-N(1A)-Pd(1)	108.5(5)	N(600)#3-N(600)-O(602)	50.1(15)
C(2A)-N(2A)-Pd(1)	108.9(5)	O(602)#3-N(600)-O(602)	131.8(15)
C(2A)-C(1A)-N(1A)	107.7(7)	O(601)-N(600)-O(602)	108.3(16)
C(1A)-C(2A)-N(2A)	106.3(7)	N(600)#3-O(602)-N(600)	48.2(15)
C(1B)-N(1B)-Pd(2)	108.4(5)	O(703)-N(700)-O(701)	137(2)
C(2B)-N(2B)-Pd(2)	107.4(5)	O(703)-N(700)-O(702)	107(2)
C(2B)-C(1B)-N(1B)	108.1(7)	O(701)-N(700)-O(702)	116(2)
C(1B)-C(2B)-N(2B)	110.5(8)	N(700)-O(702)-O(703)	34.1(11)
C(1C)-N(1C)-Pd(3)	107.9(6)	N(700)-O(703)-O(702)	38.7(12)
C(2C)-N(2C)-Pd(3)	106.9(5)	O(801)-N(800)-O(802)	135(3)
N(1C)-C(1C)-C(2C)	108.6(8)	O(801)-N(800)-O(803)	124(2)
C(1C)-C(2C)-N(2C)	108.0(8)	O(802)-N(800)-O(803)	101(2)
C(1D)-N(1D)-Pd(4)	110.6(6)	O(902)-N(900)-O(901)	134(3)
C(2D)-N(2D)-Pd(4)	107.2(6)	O(902)-N(900)-O(901)#4	144(3)
C(2D)-C(1D)-N(1D)	114.4(9)	O(901)-N(900)-O(901)#4	82(3)
C(1D)-C(2D)-N(2D)	121.6(10)	N(900)-O(901)-N(900)#4	98(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+3/2 #2 -x,y,-z+1/2 #3 -x,-y,-z+1
#4 -x,-y+1,-z+1

Table 5. Anisotropic displacement parameters (Å^{2}x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

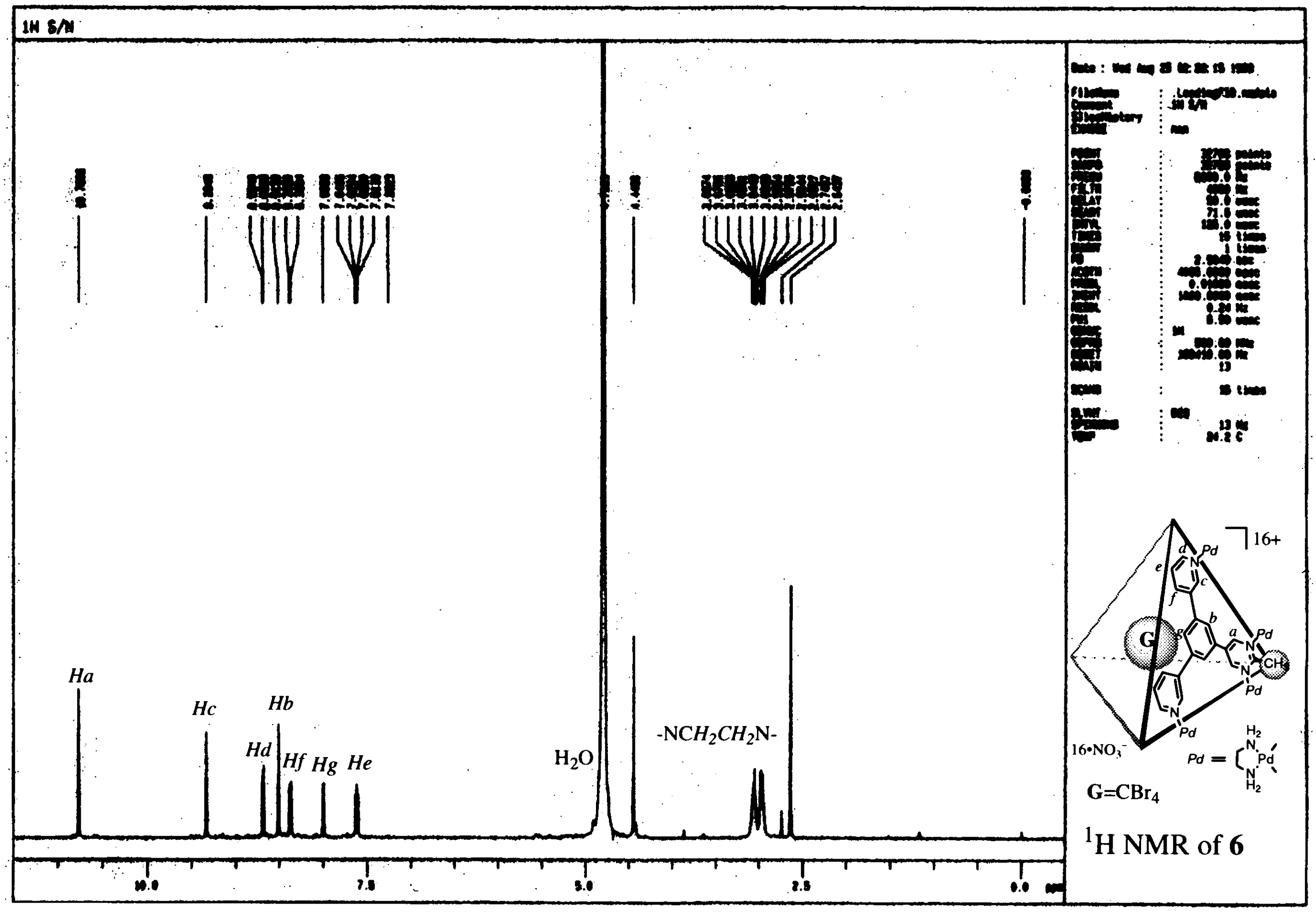
atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	33(1)	29(1)	30(1)	-1(1)	20(1)	5(1)
Pd(2)	40(1)	26(1)	29(1)	-6(1)	24(1)	-3(1)
Pd(3)	35(1)	30(1)	24(1)	3(1)	15(1)	2(1)
Pd(4)	39(1)	35(1)	26(1)	1(1)	23(1)	6(1)
C(100)	47(6)	42(7)	62(7)	0	34(6)	0
Br(2)	109(1)	60(1)	82(1)	5(1)	63(1)	-14(1)
Br(1)	73(1)	59(1)	97(1)	-16(1)	49(1)	-17(1)
C(11A)	44(4)	23(3)	27(3)	1(2)	25(3)	4(3)
C(12A)	42(4)	25(3)	34(3)	6(3)	24(3)	6(3)
C(13A)	36(3)	33(4)	27(3)	-1(3)	22(3)	4(3)
C(14A)	41(4)	27(3)	25(3)	2(2)	22(3)	5(3)
C(15A)	40(4)	29(3)	27(3)	1(3)	25(3)	-1(3)
C(16A)	35(3)	32(4)	25(3)	-2(2)	22(3)	-1(3)
N(21A)	43(3)	28(3)	34(3)	-2(2)	29(3)	-7(3)
C(21A)	36(4)	31(4)	29(3)	0(3)	21(3)	-1(3)
C(22A)	47(4)	31(4)	25(3)	-1(3)	26(3)	-6(3)
C(23A)	59(5)	32(4)	40(4)	3(3)	37(4)	-8(4)
C(24A)	71(6)	24(4)	51(4)	5(3)	45(4)	-2(4)
C(25A)	55(5)	22(4)	40(4)	-1(3)	30(4)	-5(3)
N(31A)	38(3)	27(3)	37(3)	-1(2)	26(3)	3(2)
C(31A)	41(4)	30(4)	28(3)	-5(3)	24(3)	0(3)
C(32A)	41(4)	24(3)	30(3)	-6(2)	25(3)	-4(3)
C(33A)	48(4)	38(4)	43(4)	1(3)	35(4)	7(3)
C(34A)	58(5)	47(5)	47(4)	7(4)	39(4)	20(4)
C(35A)	54(5)	44(4)	32(3)	1(3)	29(3)	10(4)
N(41A)	43(3)	26(3)	27(3)	-3(2)	20(3)	7(3)
N(42A)	35(3)	33(3)	24(3)	5(2)	17(2)	6(2)
C(41A)	33(3)	32(4)	27(3)	1(3)	20(3)	5(3)
C(42A)	37(4)	35(4)	28(3)	2(3)	23(3)	5(3)
C(43A)	42(4)	38(4)	28(3)	3(3)	18(3)	6(3)
C(44A)	37(4)	35(4)	24(3)	-2(3)	19(3)	8(3)
C(11B)	35(4)	28(4)	36(3)	-7(3)	24(3)	-8(3)
C(12B)	46(4)	29(4)	43(4)	-7(3)	30(4)	-3(3)
C(13B)	36(4)	27(3)	31(3)	-2(3)	22(3)	3(3)
C(14B)	31(3)	33(4)	31(3)	-7(3)	19(3)	-3(3)
C(16B)	31(3)	32(4)	29(3)	-8(3)	18(3)	1(3)
C(15B)	43(4)	22(3)	32(3)	-1(3)	25(3)	2(3)
N(21B)	36(3)	33(3)	37(3)	-6(2)	26(3)	-4(3)
C(21B)	38(4)	28(4)	35(3)	-8(3)	26(3)	-5(3)
C(22B)	50(4)	27(4)	37(4)	-8(3)	30(3)	-9(3)
C(23B)	49(4)	46(5)	43(4)	-21(3)	31(4)	-14(4)
C(24B)	55(5)	55(5)	52(5)	-31(4)	32(4)	-8(4)
C(25B)	41(4)	52(5)	50(5)	-22(4)	24(4)	0(4)
N(31B)	40(3)	33(3)	32(3)	-1(2)	22(3)	3(3)
C(31B)	36(4)	31(4)	30(3)	1(3)	23(3)	5(3)
C(32B)	42(4)	23(3)	34(3)	3(3)	24(3)	7(3)
C(33B)	38(4)	34(4)	38(4)	3(3)	21(3)	5(3)
C(34B)	44(4)	30(4)	49(4)	3(3)	31(4)	4(3)
C(35B)	50(4)	27(4)	42(4)	2(3)	27(4)	4(3)
N(41B)	34(3)	31(3)	23(2)	-2(2)	17(2)	5(2)
N(42B)	40(3)	25(3)	35(3)	-4(2)	26(3)	-1(2)
C(41B)	35(3)	25(3)	30(3)	0(2)	20(3)	3(3)
C(42B)	36(4)	33(4)	25(3)	1(3)	19(3)	1(3)
C(43B)	48(4)	30(4)	33(3)	1(3)	25(3)	3(3)
C(44B)	32(3)	31(4)	35(3)	-9(3)	21(3)	-3(3)
N(1A)	34(3)	41(4)	49(4)	-7(3)	26(3)	-2(3)
N(2A)	55(4)	39(4)	51(4)	-14(3)	37(3)	0(3)

Table 5. continue

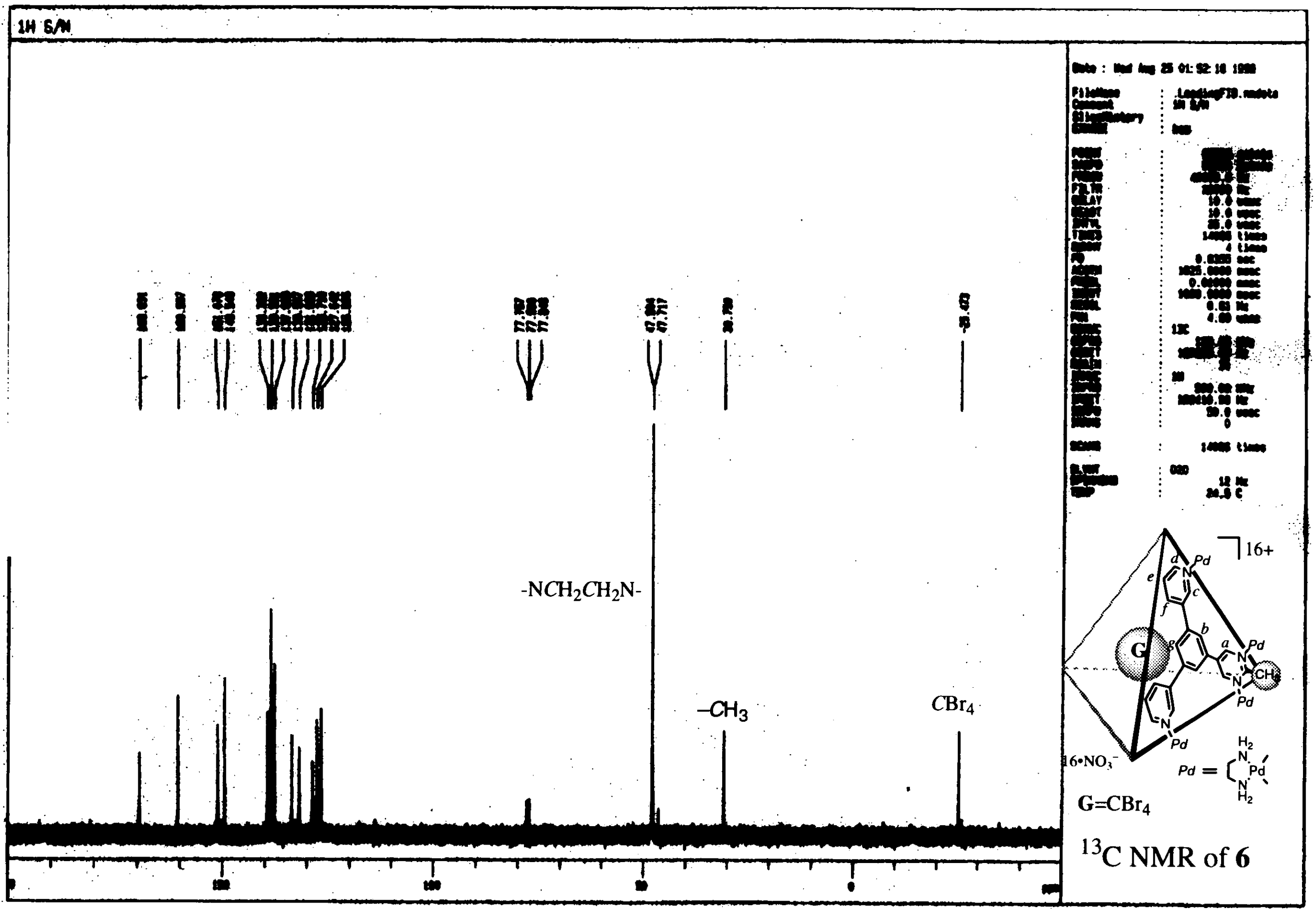
atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1A)	66(6)	56(6)	64(5)	-5(4)	50(5)	6(5)
C(2A)	64(6)	49(5)	64(6)	-11(4)	46(5)	6(4)
N(1B)	43(3)	35(3)	44(3)	-3(3)	25(3)	-6(3)
N(2B)	57(4)	41(4)	36(3)	-3(3)	22(3)	-10(3)
C(1B)	60(6)	58(6)	44(5)	-14(4)	21(4)	-17(5)
C(2B)	70(6)	62(6)	39(5)	2(4)	24(4)	-2(5)
N(1C)	45(4)	47(4)	37(3)	2(3)	15(3)	-9(3)
N(2C)	60(4)	39(4)	24(3)	8(3)	19(3)	8(3)
C(1C)	80(7)	66(6)	31(4)	-4(4)	14(4)	-32(5)
C(2C)	74(7)	73(7)	25(4)	6(4)	10(4)	-18(5)
N(1D)	70(5)	45(4)	46(4)	11(3)	45(4)	7(3)
N(2D)	39(4)	72(5)	42(4)	3(3)	28(3)	12(3)
C(1D)	69(7)	171(15)	95(9)	64(10)	61(7)	4(9)
C(2D)	95(10)	54(7)	290(30)	19(11)	145(15)	6(7)
N(100)	82(6)	59(6)	55(5)	-27(4)	39(5)	-32(5)
O(101)	110(7)	83(6)	180(11)	-2(6)	115(8)	-1(5)
O(102)	79(5)	66(5)	99(6)	-20(4)	65(5)	-18(4)
O(103)	260(15)	52(6)	208(13)	-14(6)	189(13)	-44(7)
N(200)	69(5)	83(7)	48(4)	8(4)	37(4)	3(5)
O(201)	222(14)	165(11)	58(6)	6(7)	61(8)	-3(11)
O(202)	126(8)	65(5)	82(6)	11(5)	40(6)	1(5)
O(203)	63(4)	79(5)	81(5)	4(4)	48(4)	11(4)
N(300)	43(4)	42(4)	37(3)	-7(3)	21(3)	-3(3)
O(301)	76(5)	119(7)	45(4)	-10(4)	35(4)	-31(5)
O(302)	64(4)	98(6)	56(4)	-17(4)	30(4)	-13(4)
O(303)	54(3)	43(3)	37(3)	1(2)	25(3)	1(3)
N(400)	181(15)	106(10)	133(12)	-71(10)	125(13)	-74(11)
O(401)	185(13)	142(11)	220(16)	-90(11)	165(13)	-69(10)
O(402)	380(30)	230(20)	90(10)	-21(12)	97(15)	80(20)
O(403)	175(12)	127(9)	166(12)	-25(8)	136(11)	-42(8)
N(500)	74(7)	84(7)	87(8)	-24(6)	32(6)	6(6)
O(501)	95(10)	460(30)	141(14)	67(19)	14(9)	-3(15)
O(502)	143(13)	460(40)	178(17)	-120(20)	91(13)	-92(18)
O(503)	68(4)	58(4)	60(4)	-11(3)	41(4)	-10(3)
N(600)	70(9)	49(11)	35(7)	13(7)	38(7)	6(9)
O(601)	68(9)	55(9)	92(11)	-1(7)	50(8)	-17(7)
O(602)	239(13)	57(5)	180(11)	4(6)	187(11)	-13(7)
N(700)	63(6)	129(10)	64(6)	-5(6)	33(5)	-8(7)
O(701)	290(30)	500(40)	270(30)	-60(30)	210(20)	160(30)
O(702)	180(15)	270(20)	146(14)	-5(14)	62(12)	-113(15)
O(703)	144(12)	133(12)	490(40)	110(16)	217(19)	41(10)
N(800)	71(9)	370(30)	85(10)	-111(15)	-2(8)	68(14)
O(801)	350(40)	750(70)	190(20)	-140(30)	220(30)	-200(40)
O(802)	142(10)	162(11)	96(8)	-16(8)	66(8)	26(9)
O(803)	110(9)	208(14)	99(8)	31(9)	46(7)	7(9)
N(900)	130(20)	210(40)	82(17)	-110(20)	69(18)	-70(20)
O(901)	340(30)	137(11)	222(19)	-120(12)	230(20)	-138(16)
O(902)	380(50)	61(12)	170(20)	2(14)	210(30)	-20(20)
O(1W)	125(7)	51(5)	82(6)	15(4)	48(5)	-6(5)
O(2W)	470(40)	200(17)	145(14)	-6(13)	178(19)	-80(20)
O(3W)	187(12)	106(8)	135(10)	29(7)	101(9)	-6(8)
O(4W)	238(14)	92(7)	170(11)	71(7)	163(11)	89(8)
O(5W)	125(7)	84(6)	99(7)	12(5)	73(6)	17(6)
O(6W)	420(30)	60(6)	70(7)	-5(5)	74(11)	7(10)
O(7W)	145(10)	144(10)	169(12)	-36(9)	111(9)	-18(8)
O(8W)	144(9)	67(5)	88(6)	-13(5)	42(6)	-10(6)
O(9W)	91(6)	104(7)	69(5)	19(5)	21(5)	-2(5)
O(10W)	126(7)	50(4)	82(5)	2(4)	65(5)	-1(4)
O(11W)	180(13)	134(10)	157(12)	19(9)	80(11)	31(9)
O(12W)	127(8)	138(9)	109(8)	16(7)	83(7)	-7(7)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

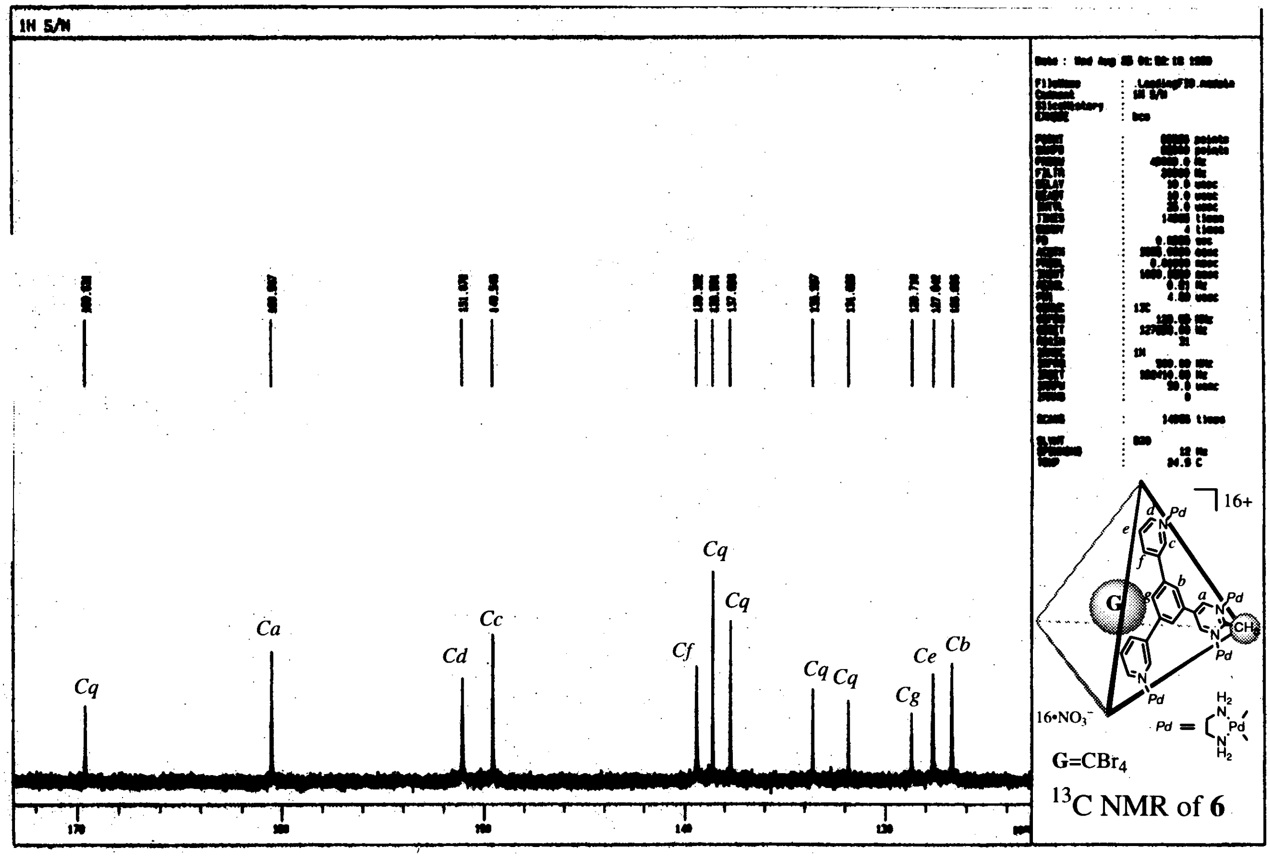
atom	x	y	z	U(eq)
H(12A)	720	9186	7810	40
H(14A)	1210	7316	8932	36
H(16A)	1389	7306	7775	34
H(22A)	917	7520	6887	39
H(23A)	755	9423	5943	48
H(24A)	801	10403	6536	53
H(25A)	955	9923	7366	46
H(32A)	1148	8147	9399	35
H(33A)	274	9469	9313	47
H(34A)	14	9931	8451	55
H(35A)	286	9384	8010	50
H(42A)	1436	5885	7918	38
H(43A)	2176	4428	9181	45
H(44A)	1823	6602	9413	38
H(12B)	321	3366	8465	45
H(14B)	839	5212	9608	38
H(16B)	-404	5222	8401	37
H(22B)	-906	4460	7885	43
H(23B)	-1427	2965	6611	52
H(24B)	-776	2476	6894	65
H(25B)	-179	3003	7702	60
H(32B)	1354	5026	9565	39
H(33B)	2143	3200	9912	45
H(34B)	1610	2213	9481	47
H(35B)	928	2631	9131	48
H(42B)	-440	6009	8961	37
H(43B)	72	8086	9819	44
H(44B)	749	6575	9622	38
H(1A1)	2339	5124	8174	49
H(1A2)	2551	4404	8566	49
H(2A1)	1724	2774	7592	54
H(2A2)	1637	3448	7197	54
H(1A3)	2252	4415	7478	67
H(1A4)	2706	4109	7994	67
H(2A3)	2422	2901	8090	66
H(2A4)	2257	2938	7467	66
H(1B1)	1614	8991	10532	49
H(1B2)	1315	9661	10438	49
H(2B1)	1011	7928	11003	58
H(2B2)	1207	7223	10908	58
H(1B3)	1874	9322	11384	73
H(1B4)	1414	9422	11219	73
H(2B3)	1677	8161	11671	76
H(2B4)	1806	7884	11292	76
H(1C1)	2937	5761	10486	60
H(1C2)	2635	6455	10347	60
H(2C1)	2307	4941	10973	55
H(2C2)	2492	4159	10925	55
H(1C3)	2712	6348	11116	86
H(1C4)	3177	6228	11302	86
H(2C3)	2991	5142	11649	84
H(2C4)	3112	4769	11277	84
H(1D1)	-754	6117	9565	57
H(1D2)	-635	6784	9978	57
H(2D1)	-1348	8357	9103	59
H(2D2)	-1554	7937	8562	59
H(1D3)	-1362	6037	9326	125
H(1D4)	-1222	6690	9805	125
H(2D3)	-1647	7455	9242	155
H(2D4)	-1727	6871	8768	155



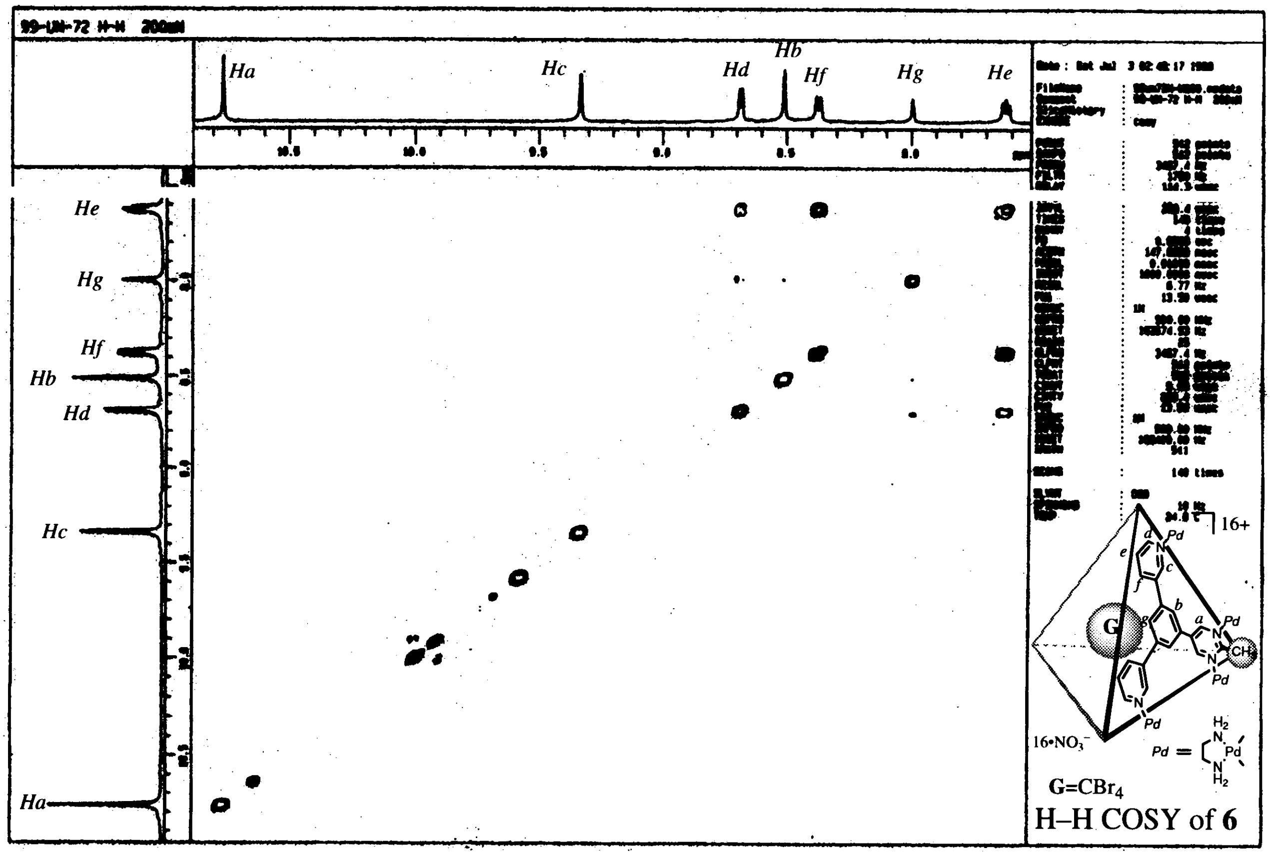
^{1}H NMR of **6**



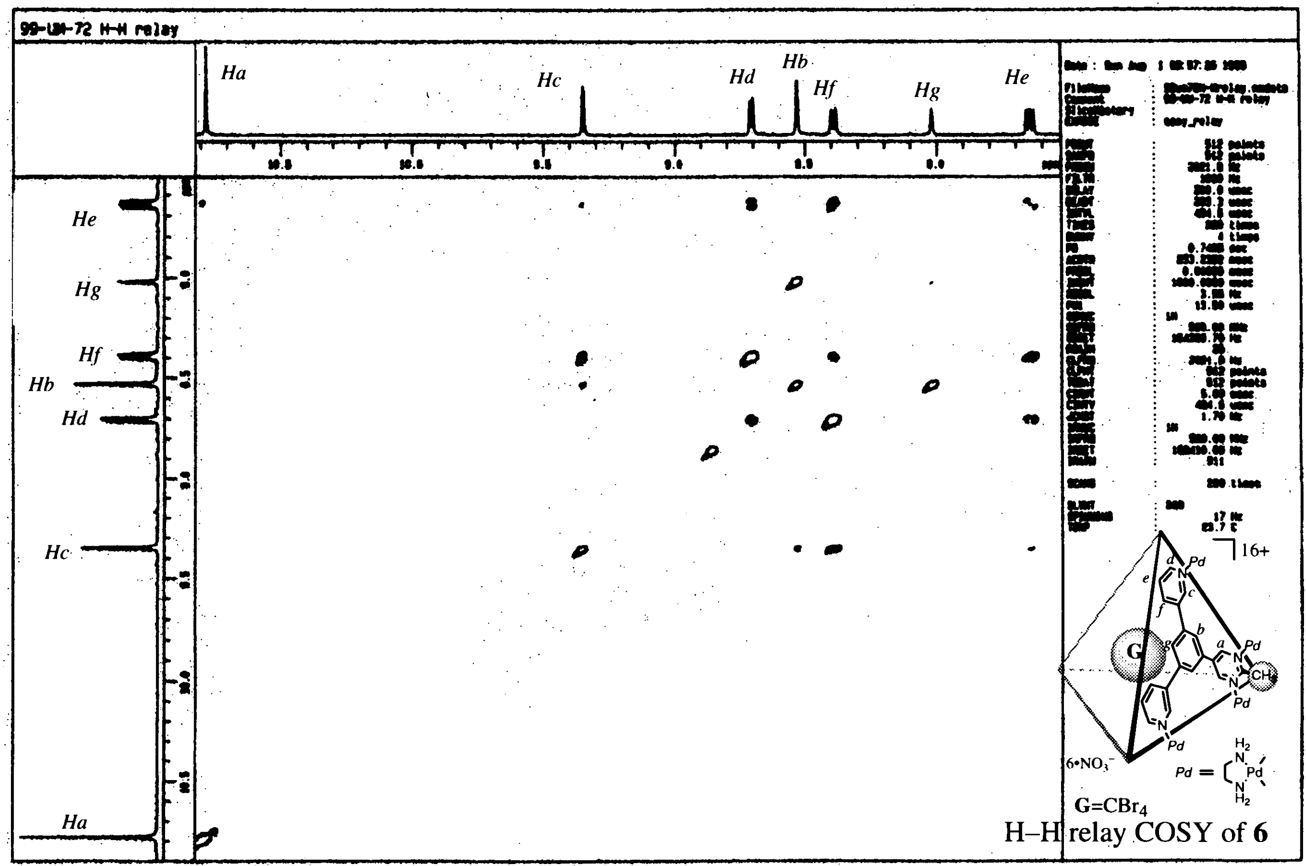
^{13}C NMR of **6**



^{13}C NMR of **6**



H–H COSY of **6**



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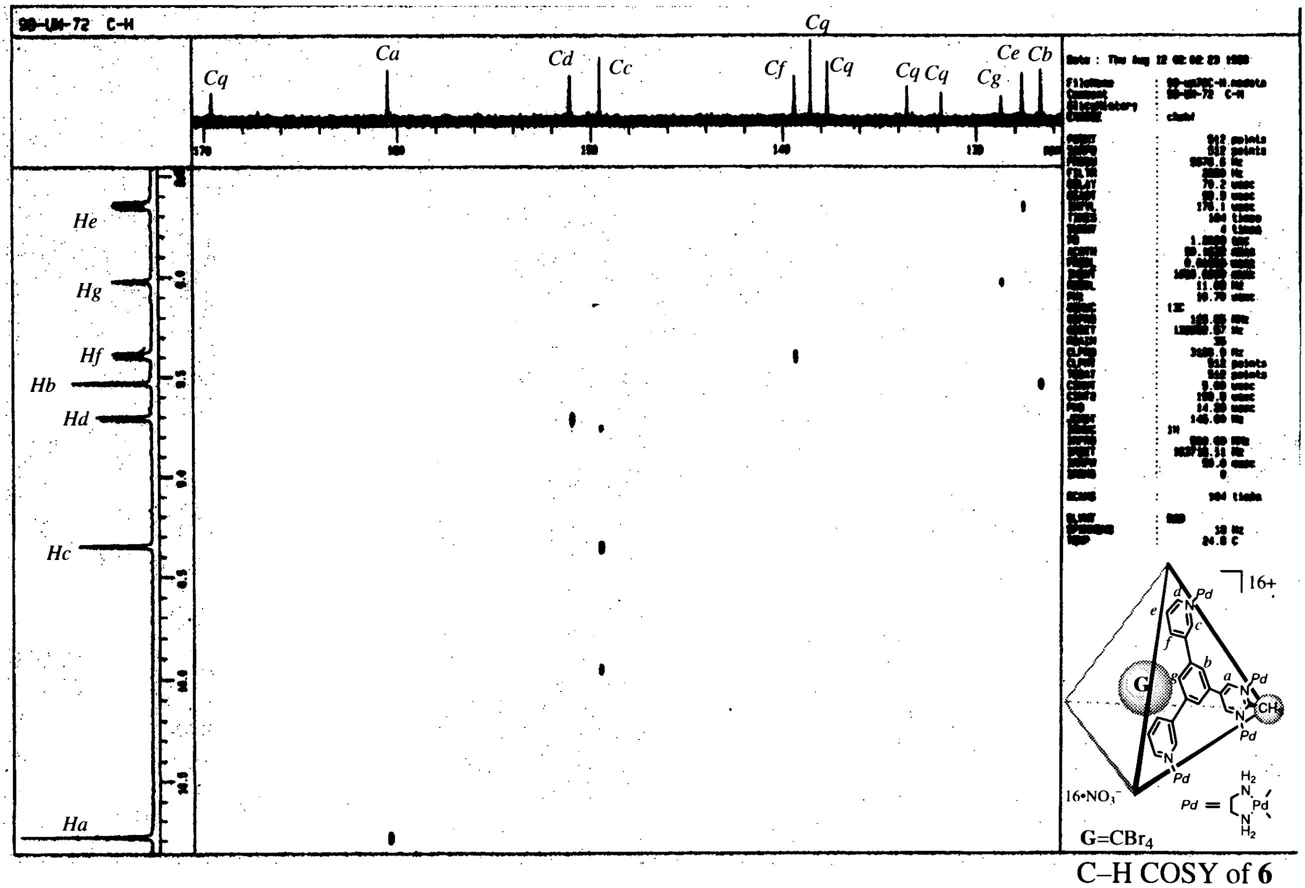

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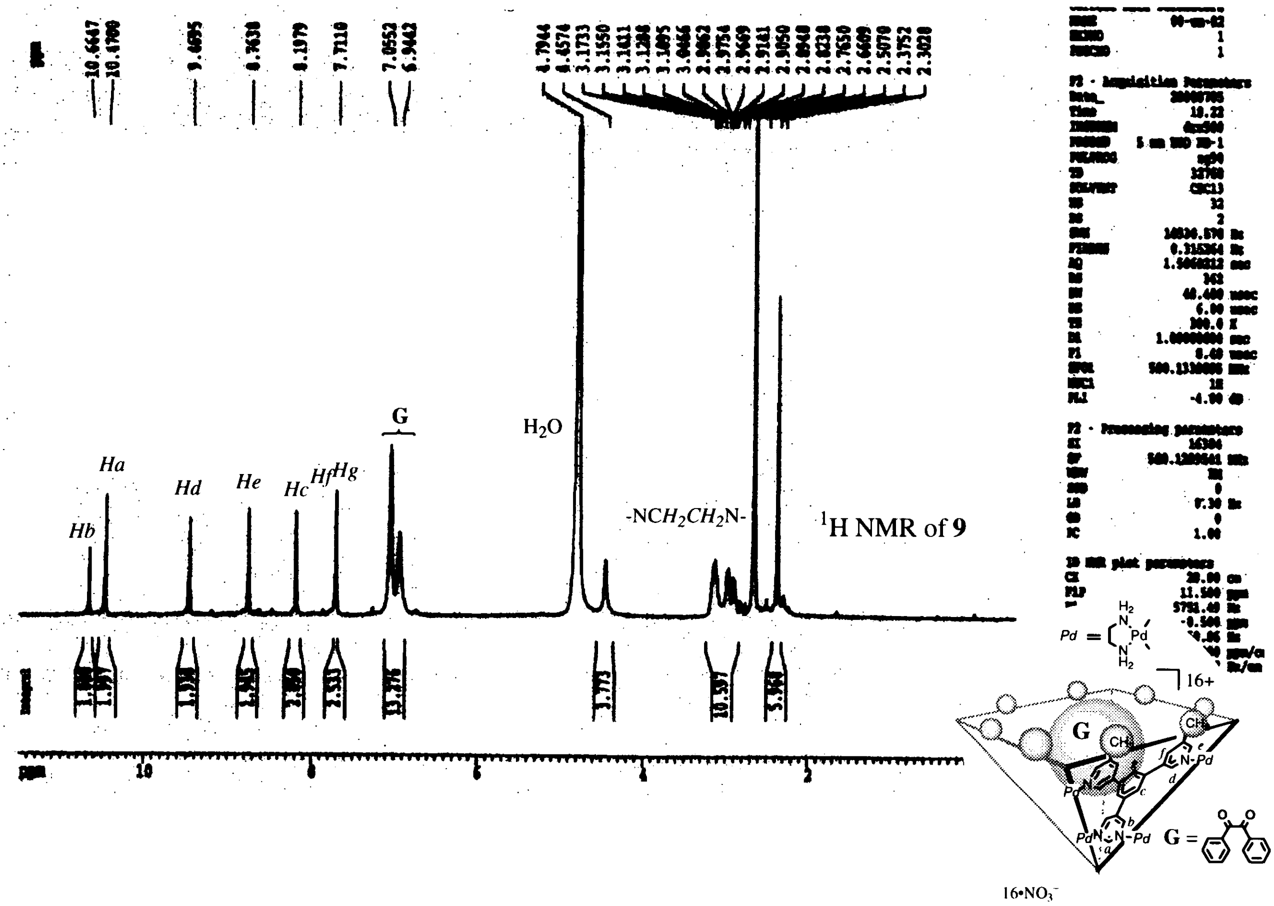
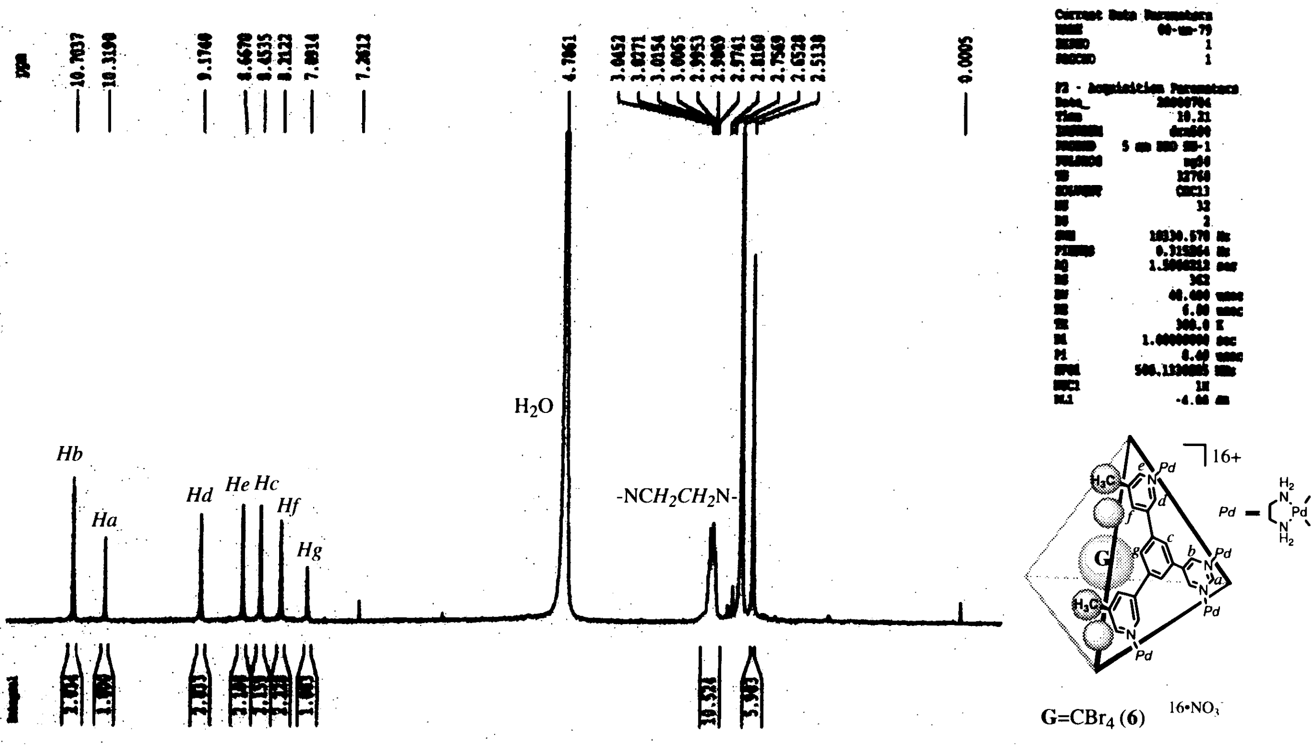


^{1}H NMR of **9**



^{1}H NMR of **8**

List of Publications

(1) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. A nanometre-sized hexahedral coordination capsule assembled from 24 components. *Nature* **1999**, *398*, 794–796.

(2) Umemoto, K.; Yamaguchi, K.; Fujita, M. Molecular Paneling *via* Coordination: Guest-Controlled Assembly of Open Cone and Tetrahedron Structures from Eight Metals and Four Ligands. *J. Am. Chem. Soc.* **2000**, *122*, 7150–7151.

(3) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. Molecular Paneling *via* Coordination. *Chem. Commun.*, **2001**, in press.

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