

Coordination-Driven Self-Assembly of Truncated Tetrahedra Capable of Encapsulating 1,3,5-Triphenylbenzene

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The design and synthesis of coordinative truncated tetrahedra is described. The coordination-driven self-assembly of a truncated tetrahedron was achieved using 90° organoplatinum acceptors and a hexapyridyl ligand with six-fold symmetry under mild conditions. This tetrahedron can act as a host toward 1,3,5-triphenylbenzene. The truncated tetrahedral structures and the host–guest complex were identified using multinuclear (³¹P and ¹H) NMR spectroscopy, electrospray ionization mass spectrometry, X-ray crystallography, and pulsed-field-gradient spin–echo NMR, along with computational simulations.

Coordination-driven self-assembly is a successful methodology for preparing three-dimensional (3-D) supramolecular

structures.¹ During the past two decades, a variety of novel 3-D coordinative structures of high complexity, high symmetry, and well-defined size and shape, such as tetrahedra, cubes, double squares, cuboctahedra, adamantanoids, dodecahedra, and a sphere, have been developed.² By virtue of their robust structural backbone and well-defined 3-D cavity, 3-D coordinative supramolecules have been used in a variety of applications such as guest encapsulation, gas storage, catalysis, and drug delivery.³ With further exo/endo functionalization,⁴ 3-D supramolecules are endowed with a variety of novel properties, like 3-D dendrimers, a nanoscale fluorodroplet, and confined polymerization.⁵ Among these 3-D supramolecules, because of their unique structural features and fascinating host–guest properties, tetrahedral structures represent one of the most widely studied systems, as witnessed by the impressive results of Raymond et al.⁶ and Fujita et al.⁷ However, the design of tetrahedral structures is still limited.^{6–8}

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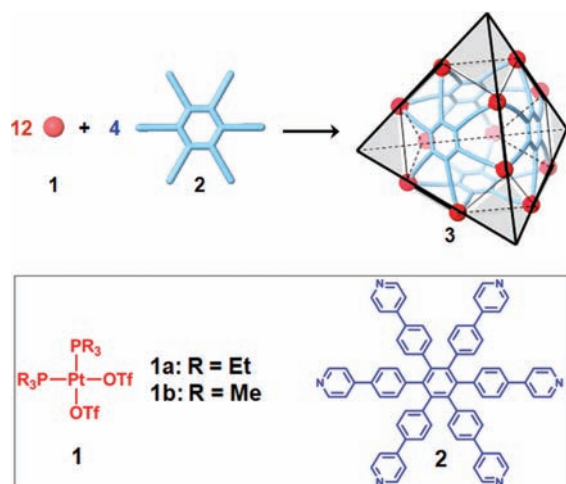
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Scheme 1. Graphical Representation of the [12 + 4] Self-Assembly of 90° Organoplatinum Acceptors **1** and Hexapyridyl Ligand **2** into a Truncated Tetrahedron **3**



The homoleptic self-assembly of a hexapyridyl ligand and a 90° acceptor should form a tetrahedral structure, where the hexadentate ligand acts as faces and the organoplatinum acceptors are the connectors at the corners, as shown in Scheme 1. We therefore carried out the self-assembly of the hexapyridyl donor **2**⁹ with the 90° organoplatinum acceptors **1**, resulting in a truncated tetrahedron in quantitative yield. The structures were characterized by multinuclear (³¹P and ¹H) NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), pulsed-field-gradient spin-echo (PGSE) NMR, and X-ray crystallography. Furthermore, it was found that truncated tetrahedron **3b** is able to encapsulate 1,3,5-triphenylbenzene in an aqueous acetone solution. This host-guest complex was characterized by NMR spectroscopy and ESI-MS as well as computational simulations.

When 90° organoplatinum acceptor **1** and hexapyridyl donor **2**⁹ were mixed in a 3:1 ratio in an acetone-*d*₆/CD₃NO₂ (7:3, v/v) solution for **3a** and an aqueous acetone solution (1:1, v/v) for **3b**, self-assembly of truncated tetrahedra **3** was obtained after 16 h of heating at 80 °C. The assemblies **3** can be quantitatively isolated via ion exchange with KPF₆.

In the ³¹P{¹H} NMR spectra (Figure 1) of **3**, only one singlet each at 0.92 ppm (**3a**) and −28.2 ppm (**3b**) with concomitant ¹⁹⁵Pt satellites can be found, respectively, for the coordinated platinum centers. Likewise, the ¹H NMR spectra (see the Supporting Information) also exhibit sharp signals for the pyridyl protons of **3** ($\delta_{\text{Py}\alpha\text{-H}} = 8.91$ ppm and $\delta_{\text{Py}\beta\text{-H}} = 7.44$ ppm for **3a**; $\delta_{\text{Py}\alpha\text{-H}} = 8.68$ ppm and $\delta_{\text{Py}\beta\text{-H}} = 7.48$ ppm for **3b**), with approximately 0.1 ppm ($H_{\text{Py}\beta}$) and 0.2–4 ppm ($H_{\text{Py}\alpha}$) downfield shifts due to the loss of electron density upon coordination with the platinum centers. Signals corresponding to the phenyl protons on the donors are split into two sets of doublets, presumably caused by the difference between the exterior and interior of the cage structure. In the ESI-MS spectra of **3** (see the Supporting Information), peaks corresponding to [**3a** − 5PF₆]⁵⁺ and [**3a** − 6PF₆]⁶⁺ can be found at *m/z* 2383.1 and 1961.9, as are those for **3b** at *m/z* 2197.0 [**3b** − 5OTf]⁵⁺ and *m/z* 1806.2 [**3b** − 6OTf]⁶⁺. These signals are

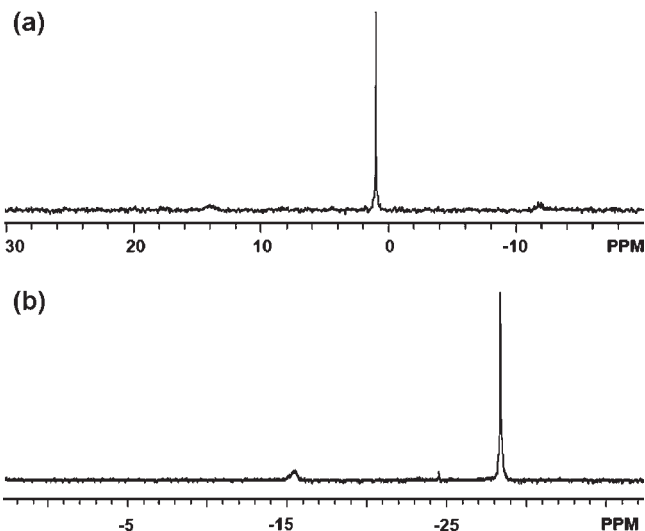


Figure 1. ³¹P{¹H} NMR spectra (121.4 MHz) of truncated tetrahedra **3a** in acetone-*d*₆/CD₃NO₂ (a) and **3b** in acetone-*d*₆/D₂O (b).

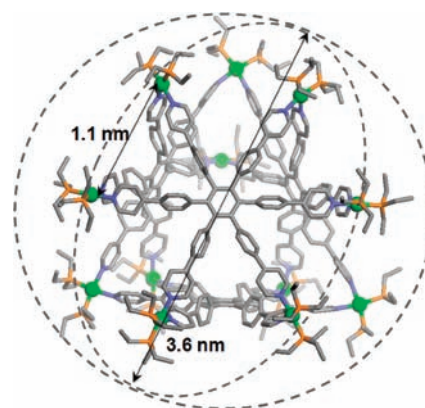


Figure 2. Crystal structure of truncated tetrahedron **3a**. Color code: Pt, green; C, gray; N, blue; P, orange. Protons, solvent, and PF₆[−] are omitted for clarity.

isotopically resolved and are in agreement with their theoretical distributions.

The structure of **3** was unambiguously determined by X-ray diffraction analysis using synchrotron radiation. X-ray-quality crystals of **3a** were obtained by the slow diffusion of pentane into the acetone solution of **3a**. As shown in Figures 2 and S4 in the Supporting Information, the structure has a truncated tetrahedral shape with a diameter of 3.6 nm and bears a 1.0 nm cavity core. The shortest Pt–Pt distance is 1.1 nm. The PF₆[−] anions are found to be surrounding the structure but not in the cavity, and the shortest Pt–F distance was measured to be 0.48 nm. As seen in Table S3 in the Supporting Information, the Pt atoms in the structure are coordinating with two PEt₃ and two N atoms from the pyridine moieties in a distorted square-planar geometry. The mean values from the square-planar Pt^{II} are N–Pt–N 80.6°, P–Pt–P 98.2°, N–Pt–P 90.6°, Pt–P 2.28 Å, and Pt–N 2.09 Å, respectively.

PGSE NMR measurements were also used to characterize the structures in solution. Using the translational self-diffusion coefficient measured by PGSE NMR in conjunction with the Stokes–Einstein equation, the “effective size” of the overall assembly in acetone-*d*₆ was obtained: 3.35 ± 0.15 nm for **3a**

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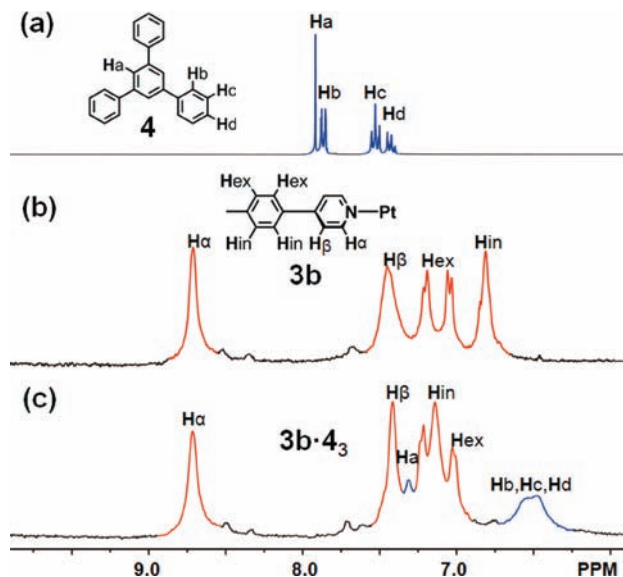


Figure 3. Partial ^1H NMR spectra (300 MHz) of “free” **4** in acetone- d_6 (a), **3b** in acetone- $d_6/\text{D}_2\text{O}$ (b), and the encapsulated complex **3b**·**4**₃ in acetone- $d_6/\text{D}_2\text{O}$ (c).

and 3.23 ± 0.21 nm for **3b**, which are in good agreement with that of the crystal structure.

The host–guest properties of **3** were also studied. According to the symmetry and size of the host, 1,3,5-triphenylbenzene (**4**) was chosen for the investigation. The experiment was carried out by mixing **1b** and **2** in a 3:1 ratio with excess **4** in an aqueous acetone solution (1:1, v/v). After 16 h of heating at 70 °C, the encapsulated complex **3b**·**4**₃ was formed.

The singlet at -28.2 ppm with concomitant ^{195}Pt satellites in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (see the Supporting Information) and the identifiable peaks ($\delta = 8.76$ ppm, $\text{H}_{\text{Py}\alpha\text{-3b}}$; $\delta = 7.36$ ppm, $\text{H}_{\text{Py}\beta\text{-3b}}$; $\delta = 6.94$ ppm, $\text{H}_{\text{phenyl-3b}}$) in the ^1H NMR spectra (Figure 3c) show the formation of a truncated tetrahedron. By comparison of the ^1H NMR spectra of **4** (acetone- d_6), **3b** (1:1 acetone- $d_6/\text{D}_2\text{O}$), and **3b**·**4**₃ (1:1 acetone- $d_6/\text{D}_2\text{O}$) in Figure 3, signals are found at 7.25 ppm ($\Delta\delta = -0.6$ ppm, $\text{H}_{\text{phenyl-4}}$), 7.06 ppm ($\Delta\delta = 0.24$ ppm, $\text{H}_{\text{phenyl-3b}}$), and 6.35 ppm ($\Delta\delta = -1.0$ – 1.8 ppm, $\text{H}_{\text{phenyl-4}}$), indicating that the **4** is encapsulated in the truncated tetrahedron **3b**, and integration of the peaks at 8.76 ppm ($\text{H}_{\text{Py}\alpha\text{-3b}}$) and 6.35 ppm ($\text{H}_{\text{phenyl-4}}$) suggests that three guest molecules are encapsulated in each cage. In the ESI-MS spectra (see the Supporting Information), isotopically resolved signals at m/z 2380.8 [**3b**·**4**₃ – 5OTf] $^{5+}$ and m/z 1959.3 [**3b**·**4**₃ – 6OTf] $^{6+}$ confirm the complex **3b**·**4**₃. Elemental analysis (see the Supporting Information) of the isolated complex is also consistent with the composition of **3b**·**4**₃.

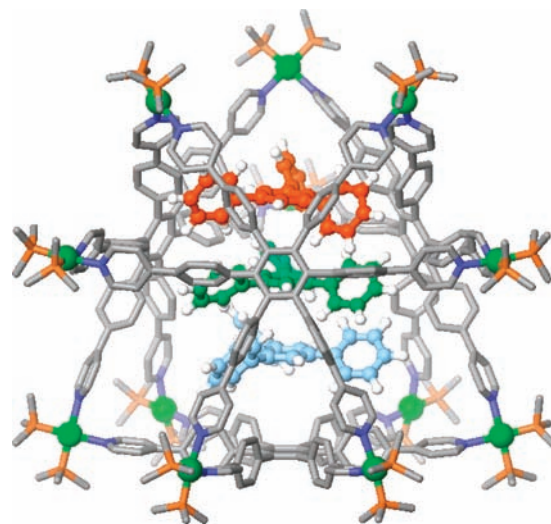


Figure 4. Computational model (MMFF) of the encapsulated complex **3b**·**4**₃ (for clarity, the three guest molecules are labeled as blue, green, and orange).

While X-ray-quality crystals for **3b**·**4**₃ were not obtained, a computational simulation was used to gain insight into the structural features of the encapsulated complex **3b**·**4**₃.¹⁰ A molecular dynamics simulation using a molecular mechanics force field (MMFF), 300 K, in the gas phase was used to equilibrate each supramolecule, and the output of the simulation was then minimized to full convergence. As shown in Figure 4, in the model of **3b**·**4**₃, three molecules of **4** are stacked within the cavity of **3b**. The distance between these guests is about 4.3 Å, and that between the guest and the interior of the cage is 3.6–4.3 Å.

In conclusion, we report the facile synthesis of a new type of 3-D truncated tetrahedra via coordination-driven self-assembly, where the highly symmetrical hexapyridyl ligand acts as the faces and 90° organoplatinum acceptors are connectors at the edges. These truncated tetrahedra show a unique 3-D nanoscale pore, and preliminary studies indicate that the nanocavity is able to encapsulate 1,3,5-triphenylbenzene.

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Supporting Information Available: X-ray crystallographic data in CIF format and experimental details for the synthesis and characterization of supramolecules **3** and the host–guest study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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