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A Pd_6 Molecular Cage via Multicomponent Self-Assembly Incorporating Both Neutral and Anionic Linkers

Arun Kumar Bar,[†] Golam Mostafa,[‡] and Partha Sarathi Mukherjee*[,†]

[†]*Inorganic and Physical Chemistry Department, Indian Institute of Sciences, Bangalore 560012, India, and*
[‡]*Department of Physics, Jadavpur University, Kolkata 32, India*

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A Pd_6 molecular cage $[\{(\mathrm{tmen})\mathrm{Pd}\}_6(\mathrm{bpy})_3(\mathrm{tma})_2](\mathrm{NO}_3)_6$ [**1**; where tmen = *N,N,N′,N′*-tetramethylethylene diamine, bpy = 4,4′-bipyridyl, and H_3tma = trimesic acid] was prepared via the template-free three-component self-assembly of a cis-blocked palladium(II) acceptor in combination with a tricarboxylate and a dipyridyl donor. Complex **1** represents the first example of a 3D palladium(II) cage of defined shape incorporating anionic and neutral linkers. Guest-induced exclusive formation of this cage was also monitored by an NMR study.

Coordination-driven self-assembly has emerged as a potential protocol to contrive discrete molecular architectures of defined shapes.[1] The structural advantage of the rigid square-planar coordination environment of palladium(II) and platinum(II) has long been utilized for the purpose of molecular architectures.[1,2] Generally, nitrogen-donor polypyridyl symmetrical linkers have been widely used with these metal ions except in a few examples where oxygen donors have also been used to form neutral 2D assemblies.[2a−c] Recently, ambidentate linkers containing both oxygen- and nitrogen-donor sites have also been utilized for the self-sorting of metallamacrocycles.[3] While two-component self-assembly is widely used, multicomponent assembly is still rare because this approach of designing a discrete supramolecule is expected to be unfavorable because of the greater loss of entropy resulting from their formation. Moreover, multicomponent self-assembly may generate a mixture of several possible structures. Only a few 3D cages are reported using a three-component self-assembly protocol but only in the presence of organic templates, and it was believed that host−guest interaction was essential to drive the formation of a discrete cage from several components. Previously reported multicomponent assemblies of these metal ions incorporated two or more different pyridyl-based neutral donors.[4] A multicomponent 3D architecture of platinum(II) or palladium(II) containing two different linkers with different donor atoms is not yet known.

Here we report the first example of the guest-free three-component self-assembly of a Pd_6 3D prism $[\{(\mathrm{tmen})\mathrm{Pd}\}_6(\mathrm{bpy})_3(\mathrm{tma})_2](\mathrm{NO}_3)_6$ [**1**; where tmen = *N,N,N′,N′*-tetramethylethylenediamine, bpy = 4,4′-bipyridyl, and H_3tma = trimesic acid] via both Pd−O and Pd−N bond coordination (Scheme 1).

Complex **1** represents a unique example of a discrete palladium(II) supramolecule composed of a cationic acceptor and both neutral (bpy) and anionic (tma) donors. Interestingly, template-assisted exclusive formation of this molecular prism ($\mathbf{1}\supset 2\mathrm{G}$) (G = 1,3,5-benzenetricarboxylic acid) is also achieved (Scheme 1).

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*To whom correspondence should be addressed. E-mail: psm@ipc.iisc.ernet.in. Tel: 91-80-2293-3352. Fax: 91-80-2360-1552.

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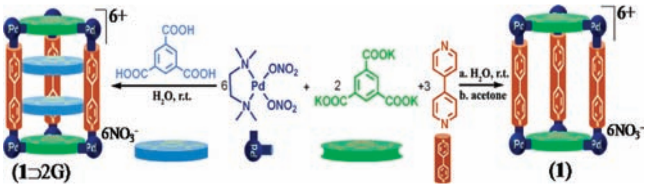
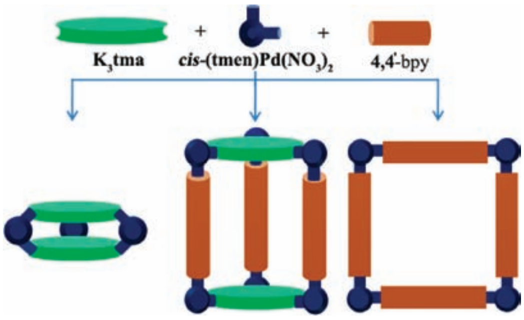
Scheme 1. Schematic Presentation of the Three-Component Self-Assembly of **1** and Selective Formation of Guest-Trapped Molecular Cage [**1**⊃2G]



Scheme 2. Possible Discrete Architectures from the Three-Component Self-Assembly of *cis*-(tmen)Pd$(NO_3)_2$, tma, and bpy



One can imagine the formation of several discrete structures upon treatment of a 90° acceptor with a mixture of tripodal and linear donors (Scheme 2). From an entropic point of view, the formation of a multicomponent prism is surprising.

Stirring a mixture of K_3tma and bpy with the acceptor *cis*-(tmen)Pd$(NO_3)_2$ in 2:3:6 molar ratio resulted in the formation of the first 3D palladium(II) cage of defined shape incorporating an oxygen-donor linker (Scheme 1). An immediate color change from yellow to cream color upon reaction and the complete consumption of the suspended particles after a while indicated the progress of the reaction. Treatment of the concentrated reaction mixture with cold acetone yielded **1** as a light-yellow solid along with a small amount of the known molecular square [{(tmen)Pd}$_4$(bpy)$_4$]$(NO_3)_8$ (**2**).[5] Fractional crystallization using acetone yielded pure **1**.

Evidence for the isolation of complex **1** can be seen in its NMR spectrum.[6] The protons of the pyridyl rings showed large downfield shifts with respect to the parent bipyridine, resulting from a loss of electron density upon coordination to palladium(II). The appearance of two doublets due to α- and *β*-pyridyl protons and a singlet corresponding to the phenyl protons of tma indicates isolation of a single and symmetrical product (Figure 1). Coordination of each (tmen)Pd^{2+} center with one carboxylate oxygen and a pyridyl nitrogen was further indicated by the appearance of two sets of CH_2 as well as CH_3 protons for tmen. Electrospray ionization mass spectrometry (ESI-MS) provided further support in favor of the formation of three-component cage **1**. Several peaks in the mass spectrum corresponding to $[\mathbf{1} - nNO_3^- - \text{tmen} + m\text{MeOH}/H_2O]^{n+}/n$ fragments were found (Supporting Information).

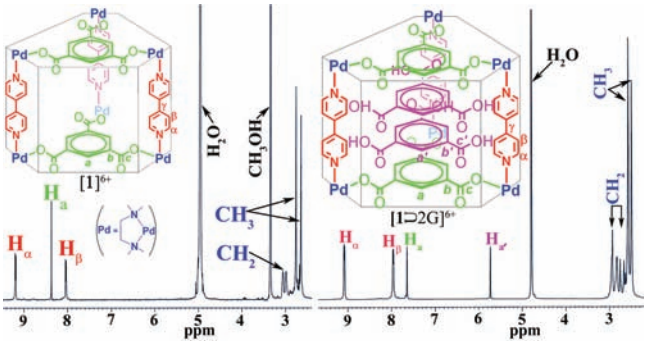


Figure 1. ^{1}H NMR spectra of **1** (left) recorded in CD_3OD and **1**⊃2G (right) recorded in D_2O at room temperature.

Variable-temperature ^{1}H NMR spectroscopic studies indicated the solution-state stability of **1** in the range of −40 to +40 °C (Supporting Information). Thermogravimetric analysis (TGA) evidenced the solid-state stability of **1** up to around a temperature of 210 °C. Moreover, the appearance of one set of α-/*β*-pyridyl protons even at −40 °C implied a low energy barrier for the Pd−N(pyridyl) bond rotation.

The presence of a large and uniform empty molecular interior surrounded by aromatic "floors" and "pillars" in **1** provides an excellent environment for an aromatic guest of suitable size. Its appropriate size and our anticipation for host−guest interaction by aromatic $\pi-\pi$ stacking prompted us to perform the reaction in the presence of H_3tma. The exclusive formation of the guest-encapsulated prism **1**⊃2G was achieved upon treatment of K_3tma, bpy, and H_3tma with *cis*-(tmen)Pd$(NO_3)_2$ in a 2:3:2:6 molar ratio. Along with a UV−vis spectroscopic analysis (Supporting Information), the appearance of a new singlet at δ 5.9 ppm as well as an integration correlation among the peaks in the ^{1}H NMR spectrum of **1**⊃2G confirms its formation and composition. In fact, the peaks in the ^{1}H NMR spectrum of the complex **1**⊃2G are assigned based on the heteronuclear (^{13}C−^{1}H) single quantum coherence (HSQC) NMR spectroscopic study (Supporting Information). Large upfield shifts of the phenyl protons of H_3tma (G) as well as of tma in **1**⊃2G are attributed to shielding of the aromatic protons owing to strong quadruple ("floor"···G···G···"ceiling") aromatic stacking. The diffusion-ordered (DOSY) NMR spectroscopic analysis (Supporting Information) yielded identical diffusion coefficients ($D = 5.0 \times 10^{-10}$ m^2 s^{-1}) for all of the signals derived from both the host and guest molecules, indicating the formation of a single adduct (**1**⊃2G).

Finally, formation of the template-free molecular prism **1** was unambiguously confirmed by single-crystal X-ray diffraction analysis. The single-crystal structure solution revealed that two tma groups form trigonally eclipsed "floor" and "ceiling" supported by three 4,4′-bpy "pillars", and each corner is occupied by a cis-blocked palladium ion (Figure 2).

The N_{tmen}−Pd−N_{tmen} (85−86°) as well as N_{py}−Pd−O_{tma} (88.1−88.6°) bite angles are slightly smaller than that expected for an ideal square-planar environment. The torsion angles between the pyridyl moieties of 4,4′-bpy range between 30 and 46° in the solid state. The length (11.10 Å) of the 4,4′-bpy pillars is almost equal to the distance (10.96 Å) between the centroids of the opposite phenyl ceiling/floor. The shortest Pd−Pd distance was measured to be 9.7 Å. A top view along the crystallographic *b* axis shows two types of porous channels (Figure 3). Intramolecular channels incorporate

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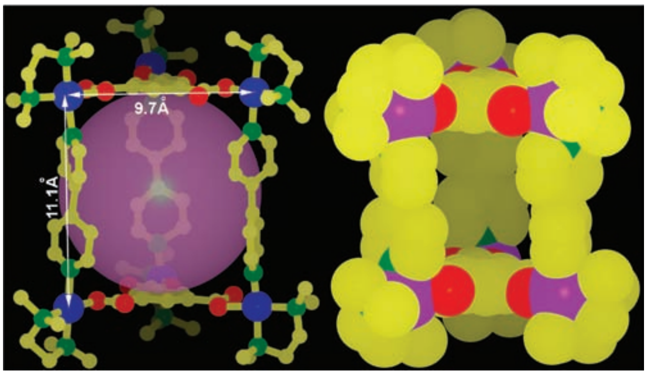

Figure 2. Ball-and-stick (left) and CPK (right) views of the single-crystal X-ray structure of **1**. Color code: blue/violet, Pd; green, N; red, O; yellow, C.

two diethyl ether molecules, three nitrate anions, and four assigned water molecules per cage **1**, while the intermolecular channels incorporate one diethyl ether molecule and three nitrate anions per cage **1**.

In conclusion, we report here the first example of the guest-free three-component self-assembly of a 3D palladium(II) structure of defined shape composed of both neutral pyridyl and anionic carboxylate donors. Isolation of the guest-free cage as well as guest-induced selective formation of the encapsulated cage $1 \supset 2G$ (G = H_3tma) were also achieved. Although oxygen donors are expected to be unsuitable for palladium(II) to form large structures because of unfavorable soft−hard interactions, the formation of **1** as well as its stability are probably due to an electrostatic interaction between palladium(II) and anionic carboxylate. Furthermore, the aromatic faces of the capping ligands in complex **1** enhance the efficacy of aromatic H_3tma encapsulation. The use of rigid polycarboxylates in conjunction with palladium(II) acceptors and the formation of interesting ionic/neutral ensembles including host−guest chemistry have the potential to considerably expand the range of directional bonding paradigms in self-assembly. Studies are underway to establish the full scope of this multicomponent assembly incorporating a carboxylate donor.

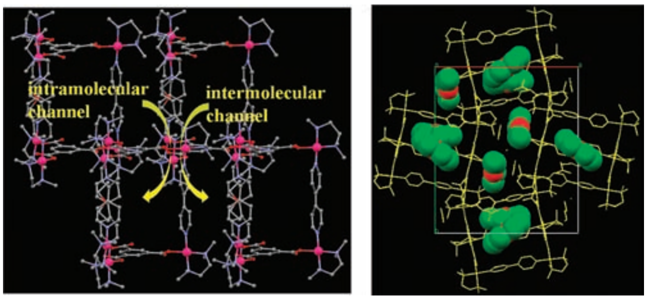

Figure 3. Solid-state packing diagram of **1** (left) viewed along the crystallographic *b* axis and positions of the diethyl ether molecules (space filled) and nitrate counteranions in the solid state of **1** (right) in the unit cell.

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Supporting Information Available: Experimental details, NMR, ESI-MS, and TGA spectra, and crystallographic information of **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.