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Self-assembly of an organo-palladium molecular basket that encapsulates cobalticarborane anion in water

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ABSTRACT

Two $[M_3L_3]^{6+}$-type organo-palladium(II) macrocyclic host molecules, $\{[(phen)Pd]_3(4,7\text{-}phen)_3\}(NO_3)_6$, $\mathbf{1}\cdot 6NO_3^-$; $\{[(dtod\text{-}phen)Pd]_3(4,7\text{-}phen)_3\}(NO_3)_6$, $\mathbf{2}\cdot 6NO_3^-$, (where M = (4,7-phen)Pd, (dtod-phen)Pd; 4,7-phen = 4,7-phenanthroline (**L**), phen = 1,10-phenanthroline, dtod-phen = 5,6-di(1′,4′,7′,10′-tetraoxododecanoxy)-1,10-phenanthroline), have been synthesized by metal-directed self-assembly in aqueous solution. These basket-shaped hosts bearing *syn*, *syn*, *syn* orientations and their anion complexes, have been fully characterized by ^1H NMR, cold-spray ionization mass spectrometry (CSI-MS) and in the case of basket-shaped host $\mathbf{1}*PF_6^-$ by X-ray single-crystal diffraction analysis. On the basis of anion binding structure within the cavity of **1**, the molecule basket **2** possessing a hydrophobic inner cavity expanded with hydrophilic polyethyleneglycol chains was successfully designed for encapsulating one giant anion $[(C_2B_9H_{11})_2Co]^-$ in water and the host–guest interaction was studied by ^1H NMR titration and CSI-MS.

Introduction

Supramolecular chemistry of anions (i.e., anion coordination chemistry) has drawn increasing interest due to the importance of anions in areas as diverse as environmental monitoring, biology, medicine, catalysis, and so on [1,2]. In particular, anion complexing and sensing in aqueous solution are still a significant challenge as a result of the high free energies of hydration of most anions, although a numerous number of supramolecular systems for selective anion guests and sensors in organic solvents have been developed successfully [3]. Recently, much effort has been concentrated on the design and construction of well-defined supramolecular self-assemblies with appropriate dimensionality and size [4], highly positive charge, binding sites, which are capable of their selective recognition and sensing for anionic guests via hydrogen bonding and/or electrostatic interaction in water [5]. Cationic metal–organic coordination supramolecular species, such as molecular triangles [6], squares and rectangles [7], pentagons and hexagons [8], grids, catenanes, nanotubes and polytubes, as promising candidates for anion receptors are attracting more and more attention in recent years.

Since 2003, we have successfully developed a series of metal–organic container molecules that show promise toward anion complexation, anion switching and recognition by a cavity-tunable modular self-assembly approach in aqueous media [9]. These open molecular containers with *cone*-conformer were controlling self-assembled by reaction of 4,7-phenanthroline, imidazolate, poly-pyrazolate as linkers with palladium(II), platinum(II) diimine complexes as corners in water. In order to expand the inner cavity and to improve the functionality of such metal–organic container molecular, the 1,10-phenanthroline-crown ether secondary ligands were introduced to coordinated Pd(II) and Pt(II) complexes as building blocks to self-assemble with 4,7-phenanthroline (**L**) into bowl-like container molecules.

Based on our previous works on the self-assembly of metal–organic container molecules through mono- or dimetal complexes $M(bpy)(NO_3)_2$ or $M(phen)(NO_3)_2$ (M = Pd or Pt, bpy = 2, 2′-bipyridine, phen = 1,10-phenanthroline) to react with bridging ligands **L** in the water, we successfully synthesized two novel $[M_3L_3]^{6+}$-type metallomacrocyclic molecules that show encapsulation of anions in water (Fig. 1). These supramolecular assemblies have been intensively studied by NMR spectroscopy, ESI-MS and CSI-MS [10]. Complex $\mathbf{1}*PF_6^-$ anions have also been characterized by X-ray crystallographic analysis in the solid state [11].

Experimental

As shown in Scheme 1, the treatment of $[(dtod\text{-}phen)Pd](NO_3)_2$ with a solution containing one equivalent of **L** in water at room temperature over several minutes gives rise to the self-assembly of the molecular basket $[Pd_3(dtod\text{-}phen)_3L_3](NO_3)_6$ ($\mathbf{2}\cdot 6NO_3^-$) in quantitative yield.

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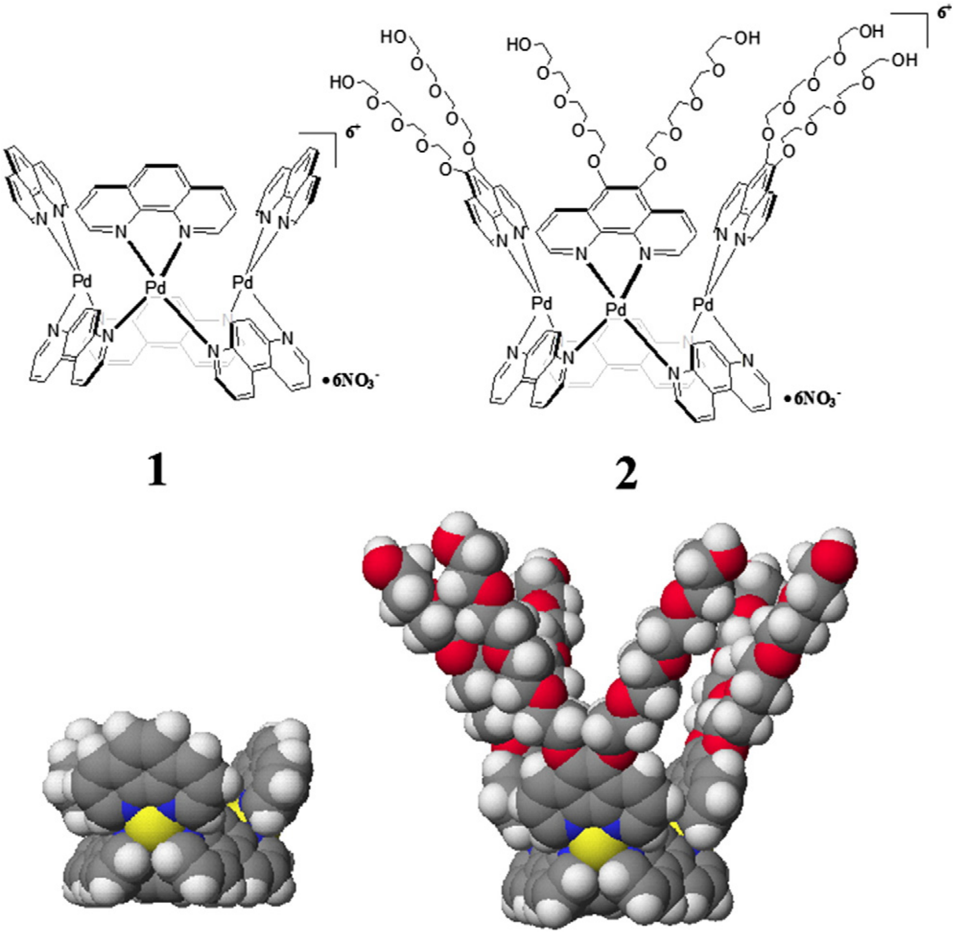
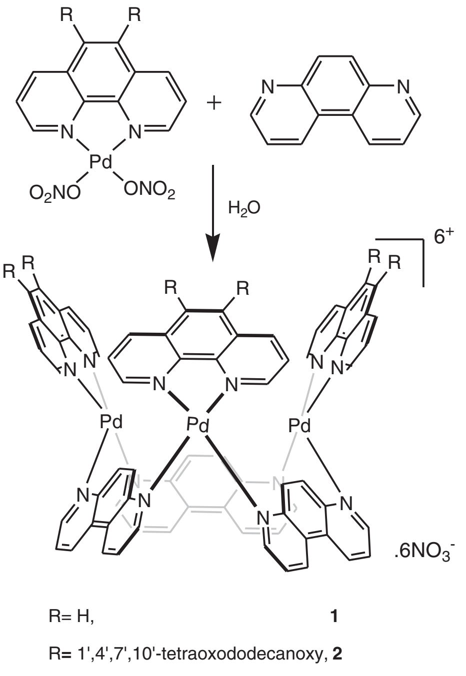


Fig. 1. The $[M_3L_3]^{6+}$-type metallo-macrocyclic structures of the molecular baskets **1**·$6NO_3^-$ and **2**·$6NO_3^-$ (the space-filling diagrams calculated using the CAChe 6.1.1 program).

Similarly, the complex **1**·$6NO_3^-$ was prepared by the method that employed for the complex **2**·$6NO_3^-$, only replaced [(dtod-phen)Pd]$(NO_3)_2$ with [(phen)Pd]$(NO_3)_2$ [10].



Scheme 1. Self-assembly of the molecular baskets **1**·$6NO_3^-$ and **2**·$6NO_3^-$.

Results and discussion

A series of $[M_3L_3]^{6+}$-type basket-like supramolecular species have been self-assembled by the reaction of monometallic complexes containing Pd or Pt with bridging ligands **L** in aqueous solution. In order to extend the inner cavity, hydrophilic polyethyleneglycol chains were introduced at 5,6-position of 1,10-phenanthroline coordination corners to construct basket-shaped metallomacrocycle **2**·$6NO_3^-$ as host molecule for anion encapsulation. Analysis by ^1H NMR spectroscopy of **2**·$6NO_3^-$ in its deuterated aqueous solutions clearly shows a dispersed array of well-defined resonance and suggests the self-assembly of [(dtod-phen)Pd]$(NO_3)_2$ and **L** to form a single product. As shown in Fig. 2, all of the signals in the spectrum can be ascribed to the protons of **L**-H, phen-H and polyethyleneglycol-H, respectively (e.g., for **L**-H, $\delta = 10.49$, 9.05, 7.68 and 7.43 ppm, for phen-H, $\delta = 10.02$, 9.62 and 8.24 ppm, for polyethyleneglycol-H, $\delta = 3.71$–3.55 ppm). Significantly, the integrations of **L**-H and phen-H are present in a 1:1 ratio in the self-assembly product, which are marked with letters and numbers, respectively. The formation of complex **2**·$6NO_3^-$ was further supported by cold-spray ionization mass spectrometry (CSI-MS) in water: the mass to charge ratio (*m/z*) peaks at 1400.1, 669.4 and 523.1 are assigned to $[\mathbf{2}\cdot6NO_3^- -2NO_3^-]^{2+}$, $[\mathbf{2}\cdot6NO_3^- -4NO_3^-]^{4+}$ and $[\mathbf{2}\cdot6NO_3^- -5NO_3^-]^{5+}$, respectively. Similarly, all of the signals in the ^1H NMR spectrum of the complex **1** could be respectively ascribed to two kinds of protons, namely, **L**-H and phen-H (e.g., for L-H, $\delta = 10.26$, 8.63, 7.46 and 7.28 ppm, for phen-H, $\delta = 10.02$, 9.43, 8.05 and 7.79 ppm). A signal corresponding to the complex **1**·$6NO_3^-$ was also observed in the gas phase via ESI-MS analysis ($[\mathbf{1}\cdot6NO_3^- -2NO_3^-]^{2+}$, *m/z* 824.0). Based on the results described above, the ^1H NMR and ESI-MS (CSI-MS) data are fully consistent with the structures of the molecular baskets **1**·$6NO_3^-$ and **2**·$6NO_3^-$.