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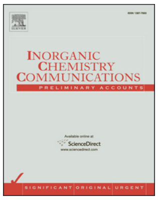

Short communication

Self-assembly of a Pd-based molecular bowl as anion receptor featured by multiple C—H···anion hydrogen bonds

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ABSTRACT

The self-assembly of (tmen)Pd$(NO_3)_2$ (where tmen = N^1, N^1, N^2, N^2-tetramethylethane-1,2-diamine) and 4,7-phenanthroline rigid ligand (**L**) in aqueous solution affords positively charged $[Pd_3L_3]^{6+}$ Pd-based molecular bowls (**1a**·$6NO_3^-$ and **1b**·$6BF_4^-$). Their structures were characterized by ^{1}H NMR, electrospray ionization mass spectrometry and single-crystal X-ray diffraction analysis. Interestingly, X-ray diffraction analysis of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ revealed that an anion was bound inside the cavity of the bowl-shaped structure by multiple C—H···O hydrogen bonds in **1a**·$6NO_3^-$, while multiple C—H···F hydrogen bonds in **1b**·$6BF_4^-$. The interactions between $[Pd_3L_3]^{6+}$ molecular bowl and a variety of anions were investigated via NMR titration and fluorescent studies, respectively.

1. Introduction

In current supramolecular chemistry field, designing of novel anion receptors have drawn considerable attention, due to their potential applications in the areas of physiology, medicine, synthetic chemistry, biology, materials development, sensing and waste remediation [1–4]. Recently, chemists have made great efforts on the construction of self-assembled anion receptors [5–9], such as caged, macrocyclic, calixarenes-like structure, and so on [10–12]. In particular, although a numerous number of anion receptors for highly anion binding, sensing and recognition by C—H···anion hydrogen bond have been developed successfully [13–16], self-assembled Pd-based molecular bowl featured by multiple C—H···anion hydrogen bonds utilized to interact with anion has been rarely reported.

Since 2003, we have developed a series of positively charged metal-organic complexes through cavity-tunable self-assembly approaches, such as molecular clips, bowls, crowns, baskets, hats and cages, which show very large potential applications toward the complexation of inorganic anions [17–25]. Herein, we employed 4,7-phenanthroline (phen) heterocycle as linker (**L**), which can be considered hydrogen-bonding bridges, and metal complex (tmen)Pd$(NO_3)_2$ (tmen = N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine) as constructing unit to synthesize and characterize $[Pd_3L_3]^{6+}$-type molecular bowl via the solution self-assembly (Scheme 1). These Pd-based metal-organic bowls **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ were characterized by ^{1}H and ^{13}C NMR spectroscopy, element analysis, ESI-MS and crystal X-ray diffraction methods. Anion-binding properties for Pd-based molecular bowl were investigated via NMR titration and fluorescence studies.

2. Results and discussion

2.1. Self-assembly and characterization of $[Pd_3L_3]^{6+}$-type molecular bowls

As shown in Scheme 1, addition of palladium(II) nitrate precursor [(tmen)Pd]$(NO_3)_2$ to a suspension of 1 equivalent of 4,7-phenanthroline rigid ligand (**L**) in H_2O/acetone (2:1 v/v), we successfully synthesized the complex **1a**·$6NO_3^-$ with a bowl-shaped conformation in quantitative yield. Subsequent addition of an excess of $NaBF_4$ to its aqueous solution afforded complex **1b**·$6BF_4^-$. Analysis by NMR spectra of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ clearly shows a dispersed array of well-defined resonance and suggests 1:1 (tmen)Pd^{2+} to 4,7-phenanthroline rigid ligand complexes were formed (Figs. S2–S5). As shown in Fig. 1, all of the signals in the spectrum can be ascribed to the protons of **L**-H and tmen-H respectively (e.g., for **L**-H, δ = 10.41, 10.01, 9.29 and 8.02 ppm, for tmen-H, δ = 3.26, 2.74 and 2.55 ppm). Surprisingly, the resonance signals at approximately δ = 2.74 and 2.55 ppm are assigned to the H^f and H^g of tmen, which theoretically should display only one signal (Fig. S1), indicating two different environments of CH_3 protons that cannot be averaged. These proton signals clearly revealed that $[Pd_3L_3]^{6+}$ of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ were highly symmetric and keep cone conformation, which was confirmed by the single-crystal X-ray diffraction analyses of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$.

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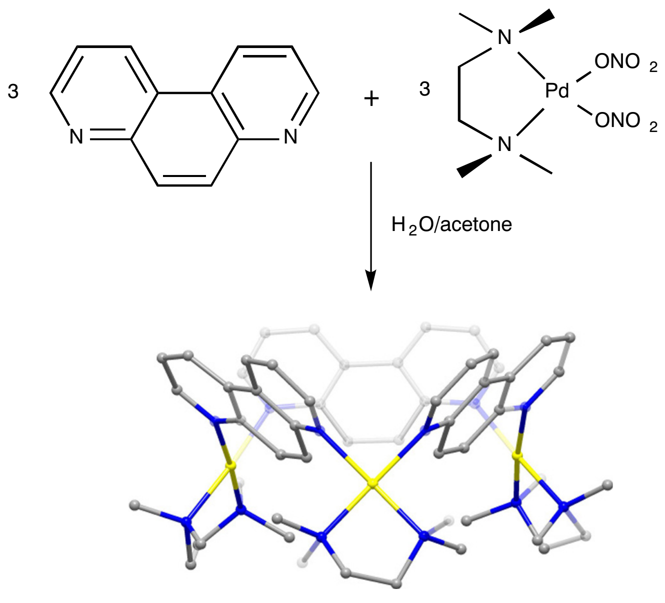

Scheme. 1. Schematic showing the self-assembly of the bowl-shaped host molecule **1a**·$6NO_3^-$ (counterions and hydrogen atoms are omitted).

The formation of the $[Pd_3L_3]^{6+}$-type molecular bowl in solution was further supported by ESI mass spectrometry (ESI-MS). ESI-MS spectra of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ in a methanol solution allowed the unambiguous assignment of $[(tmen)Pd_3L_3]$. As shown in Fig. 2 and Fig. S6, the multiply charged molecular ions of **1a**·$6NO_3^-$ and **1b**·$6BF_4^-$ were observed at *m/z* 332.82 ([**1a**·$2NO_3^-$ - $4CH_3]^{4+}$) and 777.68 ([**1b**·$4BF_4^-$ - $2CH_3]^{2+}$), respectively.

2.2. Crystal structures of the $[Pd_3L_3]^{6+}$-type molecular bowls

Structures of the molecular cations of **1a** and **1b** determined by X-ray diffraction are depicted in Figs. 3–4 and S7. Selected bond lengths and bond angles are listed in Tables S1–S2. Two complexes display similar connectivities.

Complex **1a**·$6NO_3^-$ crystallizes in the trigonal space group R3c. The crystal structure analysis for **1a**·$6NO_3^-$ reveals the formation of a bowl-shaped structure made up of three ligands connected with three half-protected Pd(II) atoms. The three Pd atoms build up an almost equilateral triangle with Pd···Pd distances of 7.86 Å, 7.86 Å and 7.86 Å. The dimensions of the bowl are as follows: 8.19 Å, 8.19 Å and 8.19 Å

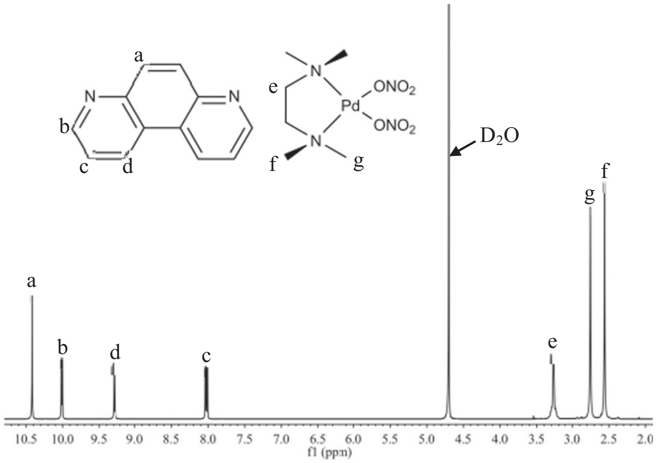

Fig. 1. ^1H NMR spectrum of bowl-shaped molecular structure **1a**·$6NO_3^-$ (400 MHz, D_2O, 298 k).

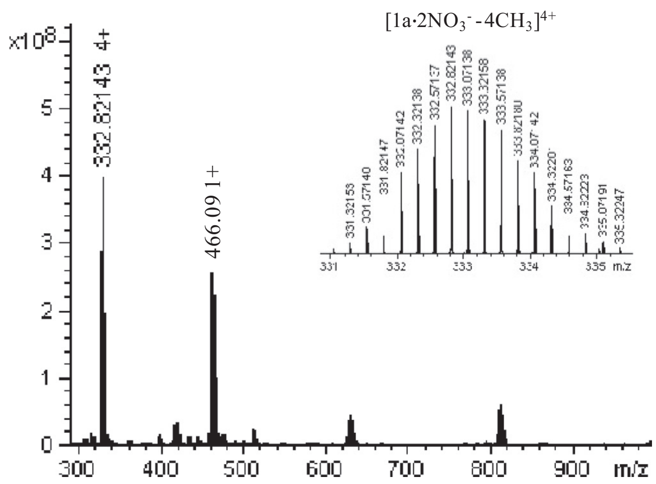

Fig. 2. ESI-MS spectra of **1a**·$6NO_3^-$ in methanol; the inset shows the isotopic distribution of the species [**1a**·$2NO_3^-$ - $4CH_3]^{4+}$, and peaks at 466.09 of $[L + (tmen)PdNO_3]^+$.

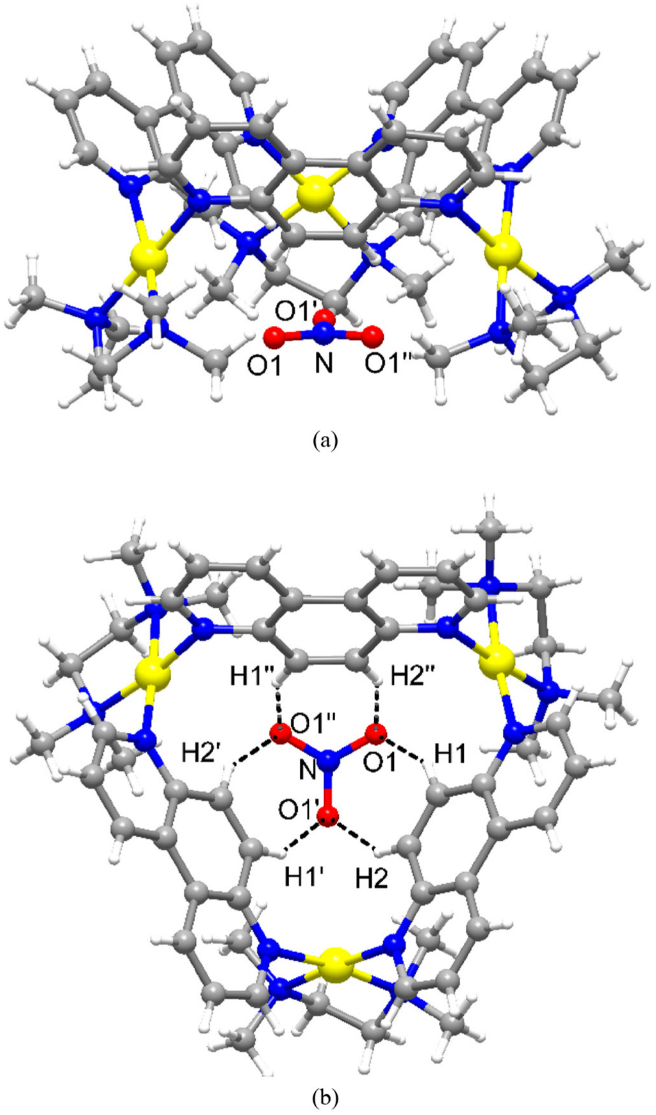

Fig. 3. The molecular structure of **1a**·$6NO_3^-$ (a, side view; b, top view). Nonbonding anions and solvent molecules are omitted for clarity (red for O, yellow for Pd, blue for N, gray for C and white for H). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)