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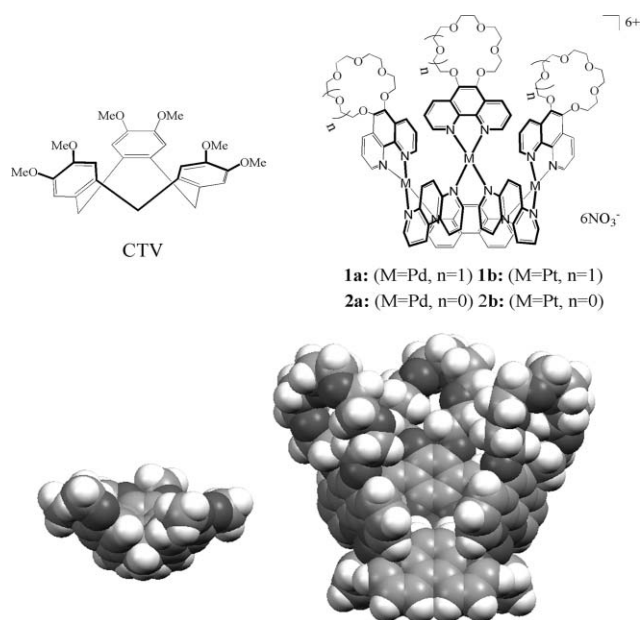
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**A [3 + 3] modular self-assembly gives rise to the formation of basket-shaped, crown ether-functionalized, nano-sized trimetallo-macrocycles, which function as structural analogues of cyclotrimeratrylenes (CTV).**

The construction of container molecules remains an interesting topic in supramolecular chemistry, particularly bowl-shaped molecules, such as calixarenes and cyclotrimeratrylenes (CTV), because of their potential applications in molecular encapsulation, catalysis, assembly and self-assembly, *etc.*<sup>1</sup> Over the last decade, numerous well-defined metal-organic container molecules with high symmetries (*regular* polygons and polyhedra such as molecular squares, molecular grids, tetrahedral cages, *etc.*) have been established by metal-directed molecular self-assembly.<sup>2</sup> However, only a few examples with low-symmetries (*irregular assemblies*)<sup>2c</sup> like bowl-shaped metallo-organic entities have been reported, which have attracted particular attention because they are capable of behaving as structural analogues of calixarenes or CTV.<sup>3-6</sup> Recently, we have succeeded in the self-assembly of such *irregular* metallo-organic container molecules with calixarene features, such as molecular bowls, crowns and capsules.<sup>7,8</sup> It should be noted that we have developed a cavity-tunable modular self-assembly approach,<sup>7,8a</sup> which has provided a scaffold for design and architecture of structurally and functionally new metallo-organic container molecules. In order to enlarge the cavity and to modify the functionality of such metal-organic frameworks, herein we introduced the 1,10-phenanthroline-crown ethers ligand<sup>9</sup> coordinated Pd(II) and Pt(II) complexes as building blocks to self-assemble with 4,7-phenanthroline (L) into basket-like container molecules as shown in Scheme 1.

The treatment of [Pd(NO<sub>3</sub>)<sub>2</sub>(phen-crown-6)] with a solution containing one equivalent of L in D<sub>2</sub>O at room temperature over several minutes leads to formation of [{Pd(phen-crown-6)}<sub>3</sub>L<sub>3</sub>](NO<sub>3</sub>)<sub>6</sub> (**1a**) in quantitative yield. The <sup>1</sup>H NMR spectrum shown in Fig. 1 revealed the presence in solution of a symmetrical structure and is consistent with a single product. Integration of the signals indicates a 1 : 1 ratio of metal-coordination-complex fragment to L, and this is supported by elemental



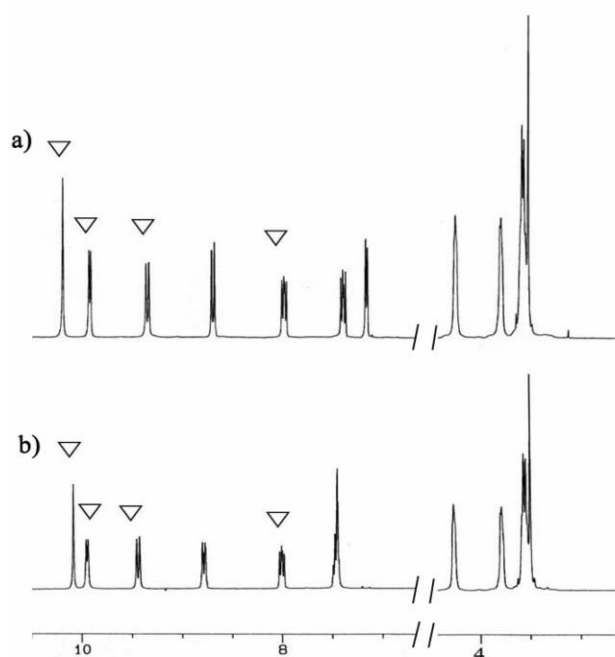
**Scheme 1** CTV and its inorganic analogues: self-assembling molecular baskets (the CPK diagrams calculated using the CAChe 6.1.1 program<sup>10</sup>).

analyses. The resonance signals labelled  $\Delta$  correspond to the ligand L. The Pt analogue, [{Pt(phen-crown-6)}<sub>3</sub>L<sub>3</sub>](NO<sub>3</sub>)<sub>6</sub> (**1b**) was obtained at elevated temperature (100 °C, 36 h) by a similar route to that of **1a**, and the spectra of **1b** are similar to those of **1a**. Therefore, **1b** possesses the same structure as **1a**, that is, a trimetal-centre molecular basket with a charge of 6+.

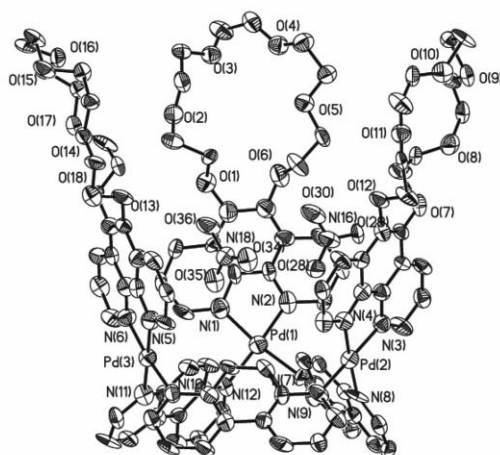
The formation of the proposed molecular basket **1a** (and **1b**) was further supported by cold spray ionization mass spectrometry (CSI-MS)<sup>11</sup>: [**1a** - 2NO<sub>3</sub>]<sup>2+</sup> (1175.6), [**1a** - 3NO<sub>3</sub>]<sup>3+</sup> (763.1), [**1b** - 2NO<sub>3</sub>]<sup>2+</sup> (1308.4) and [**1b** - 4NO<sub>3</sub>]<sup>4+</sup> (623.2).

A single crystal of **1a** was obtained by slow evaporation of its aqueous solution. The X-ray crystallographic analysis<sup>‡</sup> confirms the molecular basket structure of **1a** (Fig. 2). It is interesting that the two kinds of modules make up two different cavities, one is hydrophobic, while the other is hydrophilic due to the crown ether modified rims. The three Pd atoms lie on a nearly perfect equilateral triangle with Pd...Pd distances of

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental section; <sup>1</sup>H NMR spectra of **1a**, **1b**, **2a**, **2b**; CSI-MS spectra of **1a**, **1b**, **2a**, **2b**; crystallography: experimental and refinement. See <http://www.rsc.org/suppdata/dt/b5/b504639d/>



**Fig. 1** Self-assembly of **1a** and **1b**. a)  $^1\text{H}$  NMR spectrum of **1a**, b)  $^1\text{H}$  NMR spectrum of **1b**.



**Fig. 2** ORTEP drawing of **1a** encapsulating two  $\text{NO}_3^-$  anions within the upper cavity (50% probability ellipsoids. The free counter anions as well as solvent molecules and hydrogen atoms have been removed for clarity).

7.65(1), 7.54(7) and 7.64(3) Å. The three rigid modules of **L** make up the lower cavity (below the tri-Pd triangle) exhibiting hydrophobic character and they are bridged by three square-planar coordination modules  $[\text{Pd}(\text{phen-crown-6})]$  in a *syn, syn, syn* orientation. The dimensions of the resultant bowl are as follows: 8.40(1), 8.34(3) and 8.38(2) Å in rim lengths (*i.e.* the distances between the midpoint of the 1,10 position of **L**); 3.6(2) Å in depth; dihedral angles between **L** and the tri-Pd triangular plane: 52.9, 49.6, 54.5°.

The upper cavity (above the tri-Pd triangle consisting of the three square planar  $\text{Pd}(\text{phen-crown-6})$  modules) has a cavity size as follows: 11.69(2), 11.78(1) and 16.17(2) Å in rim lengths; 12.74(3) Å in depth; dihedral angles between the square planar modules and the tri-Pd triangular plane: 81.4, 73.6 and 77.2°. The upper cavity, which possess the more open and larger and deeper void space than the lower cavity, is expected to exhibit more important receptor chemistry. Remarkably, two nitrate anions (N16–O28–O29–O30 and N18–O34–O35–O36) are encapsulated within the upper hydrophilic cavity of the basket. On the contrary, there are no nitrates located inside the

lower cavity, a similar phenomenon was previously observed in the case of a molecular crown,<sup>8a</sup> due to the hydrophobic properties of the aromatic module constructed cavities.

By analogy, starting from  $[\text{Pd}(\text{NO}_3)_2(\text{phen-crown-5})]$  or  $[\text{Pt}(\text{NO}_3)_2(\text{phen-crown-5})]$  and **L**, a similar self-assembly was successfully achieved which was confirmed by  $^1\text{H}$  NMR, and CSI-MS spectroscopy as well as molecular modeling. In the CSI-MS spectra for **2a** in methanol, the peaks appearing at 719.0 and 1109.5 can be assigned to  $[\mathbf{2a} - 3\text{NO}_3^-]^{3+}$ ,  $[\mathbf{2a} - 2\text{NO}_3^-]^{2+}$ , respectively. Similarly, in the CSI-MS spectra for **2b** in methanol, the peaks presenting at 459.8, 590.2, 807.6 and 1242.4 are attributed to  $[\mathbf{2b} - 5\text{NO}_3^-]^{5+}$ ,  $[\mathbf{2b} - 4\text{NO}_3^-]^{4+}$ ,  $[\mathbf{2b} - 3\text{NO}_3^-]^{3+}$ , and  $[\mathbf{2b} - 2\text{NO}_3^-]^{2+}$ , respectively.

The ability of such a CTV-linked container molecule to include aromatic carboxylate anions<sup>12</sup> (such as benzoic acid sodium salt, *p*-toluic acid sodium salt and *p*-anisic acid sodium salt) in its cavity has been studied by means of  $^1\text{H}$  NMR spectroscopy. A significant upfield shift was observed for the aromatic protons of the anion of benzoic acid in  $\text{D}_2\text{O}$  upon complexation with an equimolecular amount of **1a** ( $\Delta\delta = -0.24$ ,  $-0.30$  and  $-0.42$  for  $\text{H}_2$ ,  $\text{H}_3$  and  $\text{H}_4$ ). However, compared with the anion receptor chemistry exhibited by  $[\{\text{Pd}(\text{en})\}_3\text{L}_3](\text{NO}_3)_6$ ,<sup>8a</sup> **1a** does not show important interactions with  $\text{SO}_4^{2-}$  in aqueous solution. In fact, the  $^1\text{H}$  NMR monitoring experiments showed that the addition of an excess quantity of  $\text{SO}_4^{2-}$  to a solution of **1a** does not lead to any significant chemical shift. Additionally, the formation of 1 : 1 host–guest complex  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  to **1a** was tentatively studied by NMR titration.

In summary, we have described self-assembling molecular baskets with novel crown-ether functionalized nano-cavities. Further investigation will be directed toward their potentials as sensors for binding large cluster anions (such as cobalticarborene, polyoxometalate anions, *etc.*) or for multiple recognition of cations and anions.

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## Notes and references

† Crystal data for **1a**:  $\text{C}_{102}\text{H}_{114}\text{N}_{18}\text{O}_{42}\text{Pd}_3$ ,  $M = 2583.31$ ; triclinic, space group  $P\bar{1}$ ,  $a = 17.182(3)$ ,  $b = 17.856(4)$ ,  $c = 23.319(5)$  Å,  $\alpha = 103.37(3)^\circ$ ,  $\beta = 91.54(3)^\circ$ ,  $\gamma = 105.97(3)^\circ$ ,  $V = 6660(3)$  Å<sup>3</sup>,  $D_c = 1.288$  g cm<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 2652$ ,  $\mu(\text{Mo-K}\alpha) = 0.482$  mm<sup>-1</sup>,  $\lambda = 0.71073$  Å,  $2\theta_{\text{max}} = 52^\circ$ , 47324 reflections measured, 18658 observed reflections ( $I > 2\sigma(I)$ ). Number of parameters 1585,  $R_1 = 0.0558$ ,  $wR_2 = 0.1159$ , GOF = 1.03. CCDC reference number 267395. See <http://www.rsc.org/suppdata/dt/b5/b504639d/> for crystallographic data in CIF or other electronic format.

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