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A Double-Walled Hexagonal Supermolecule Assembled by Guest Binding

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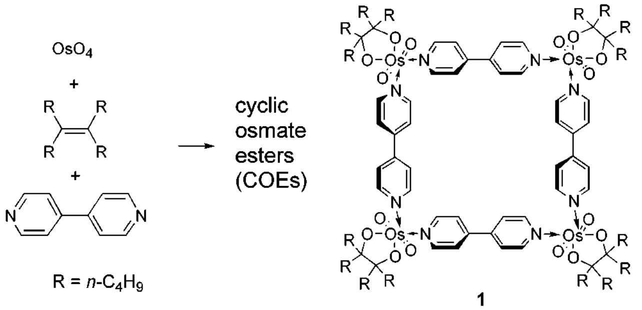
The transition metal−ligand interaction has been one of the most powerful tools to construct various sophisticated supermolecules such as macrocycles[1,2] and cages,[1,3] owing to its strength and directionality. We recently described that discrete mono- and dinuclear macrocycles could be spontaneously assembled from a mixture of osmium tetroxide, olefin, and bispyridyl ligand.[4] In this assembling motif, the octahedral coordination center is generated in situ during the assembly process, unlike most other systems which require extra steps for the preparation of the metal center with the desired geometry and properties. Furthermore, the macrocycles are electrically neutral so that molecular recognition based on hydrogen bonds can be studied without interference by otherwise existing counterions. Herein we report the first example of double-walled hexanuclear hexagon formed by spontaneous reorganization of osmate ester-based macrocycles in the presence of naphthalene-2,6-diol.[5]

Addition of osmium tetroxide (∼1 equiv, 0.1 M in toluene) to a toluene solution of 1:1 bipyridine and 5,6-dibutyl-5-decene[6] resulted in brown precipitates within a few minutes at room temperature (Scheme 1).[7] A strong infrared band of the product appeared at 830 cm^{-1}, diagnostic of the trans $O{=}Os{=}O$ bond of the octahedral dioxoosmate ester complex which results from the reaction between osmium tetroxide and olefin and concomitant coordination of two pyridyl moieties in a cis relationship.[8] The ^{1}H NMR spectrum showed two sets of doublets at 8.95 and 7.66 ppm corresponding to the α- and *β*-pyridyl protons of the product, respectively, both of which were shifted downfield ($\Delta\delta = 0.1-0.2$ ppm) relative to the free ligand. Elemental analysis, along with ^{1}H NMR integration,[9] revealed a 1:1:1 stoichiometry of three components; OsO$_4$, bipyridine and 5,6-dibutyl-5-decene. All of these data are consistent with the symmetrical cyclic structure, for example **1**, of the osmate ester product. Vapor pressure osmometry (VPO) was used to determine the size of this macrocyclic product in CHCl$_3$ at 313 K.[10,11] The molecular weights measured by VPO (Supporting Information) depend on the concentration of the sample. As the concentration increases from 8 to 27 g/kg (solute/solvent), the molecular weights were gradually increased from 2200 to 3200 (2651 for square **1**), using benzil as the standard. This concentration dependence of the molecular weight may be explained if the product exists as an equilibrium mixture of various cyclic osmate esters (COEs), reminiscent of a dynamic combinatorial library.[12] At lower concentrations the relative population of smaller macrocycles is increased, while at higher concentrations larger macrocycles or aggregates increase.[13] More evidences for an equilibrium mixture of COEs in solution were obtained from ^{1}H NMR studies: (a) chemical shifts of the α- and *β*-bipyridyl protons are slightly concentration-dependent ($\Delta\delta$ 0.06−0.08 ppm over concentrations 0.5−50 mM), and (b) signals for α- and *β*-bipyridyl protons split into more sets of doublets below 0 °C, possibly due to a slow interconversion between cyclic osmate esters on the NMR time scale (Supporting Information).

Scheme 1



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Molecular modeling studies suggested that the COEs could bind 2,6-naphthalenediol (**2**) by hydrogen-bonding and aromatic stacking interactions as shown in Scheme 2. This possibility was first examined by solid−liquid extractions. The COEs efficiently dissolves 2,6- (**2**) and 2,7-naphthalenediol (**3**), which are otherwise sparingly soluble in CDCl$_3$, but negligibly dissolves *p*-dihydroxybenzene (**5**) possessing a smaller spacer between the two hydroxyl

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(5) For discrete hexagonal assemblies, see: Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Baker, G. R.; Cush, R.; Russo, P. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3717−3720 and also see ref 1c. For self-assembly of macrocyclic molecular necklaces by coordinate bonds and hydrogen bonds, see: Roh, S.-G.; Park, K.-M.; Park, G.-J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 638−640 and references are therein.

(6) A symmetrical tetra-substituted olefin 5,6-dibutyl-5-decene was used to (i) prevent the generation of asymmetric centers unnecessary to this study, (ii) enhance the solubility of the product in organic solvents, and (iii) increase the stability of the osmate ester on contact with protic solvents.[8a] For the synthesis of tetra-substituted olefins, see: *Synthesis* **1989**, 883−897.

(7) The reaction proceeded quantitatively, but the isolated yield was 80−95%.

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(9) Although osmium tetroxide, olefin, and bipyridine are mixed in molar ratios of 0.5:0.5:1 and 1.5:1.5:1, ^{1}H NMR integrations of the resulting precipitates gave a 1:1 molar ratio of bipyridine and olefin.

(10) The mass spectral analysis afforded no structural information on the product, showing only small fragments with $m/z < 10^3$, even under mild ionization conditions (FAB, MALDI, and ESI), due to the presence of labile Os−N and Os−O−C (*tertiary*) bonds of the neutral product.

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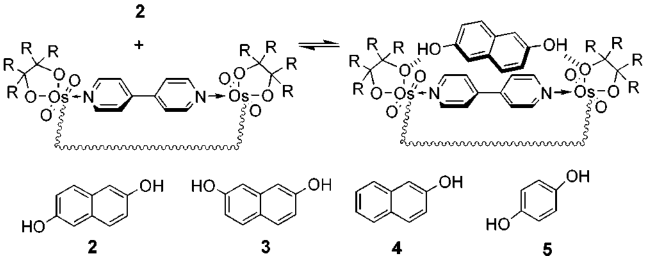
Scheme 2



groups. Approximately 1 equiv of either diol **2** or **3** was dissolved relative to the bipyridine in the COEs based on the ^{1}H NMR integrations.

To obtain more quantitative information on the binding events, ^{1}H NMR titration experiments were performed by adding the COE solution to the diol stock solution in $CDCl_3$ at 297 K.[14] The OH resonances of diols **2** and **3** shifted considerably downfield ($\Delta\delta$ > 3 ppm) and the aromatic signals shifted upfield ($\Delta\delta = 0.4-0.6$ ppm), indicative of complex formation by aromatic stacking interactions as well as hydrogen bonds. The titration curves were analyzed by nonlinear least-squares fitting methods,[4b,15] assuming the independent binding of the diol on each side of the COE,[16] and nicely fit to the expression of a 1:1 (diol/side of COE) binding isotherm (Supporting Information). The Job plots[17] also indicate that the maximum complexation occurs at a 1:1 molar ratio. The association constants were 4.5×10^3 and 1.9×10^3 M^{-1} for diols **2** and **3**, respectively, but only 1.1×10^2 M^{-1} for 2-naphthol (**4**). This large difference ($\Delta\Delta G \approx 2.2$ kcal/mol) in the binding energy between di- and monohydroxyl guests clearly suggests that two hydroxyl groups in **2** and **3** simultaneously hydrogen bonded to the osmate oxygen atoms in such a way to bridge each corner of the COE, as shown in Scheme 2.[18]

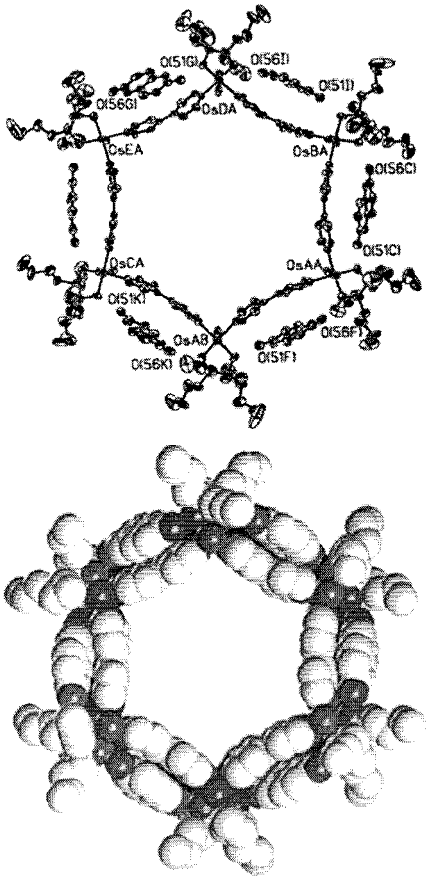


Figure 1. Ortep plot (top) and CPK representation (bottom) of X-ray crystal structure of the complex between COE and **2**.

The structure of the complex between COE and **2** was determined by single-crystal X-ray diffraction analysis,[19] affording a surprising double-walled hexagonal structure (Figure 1). As expected, one 2,6-naphthalenediol was bound to each side of the COE by two hydrogen bonds as well as face-to-face aromatic stacking forces. The hydrogen bonding distance (O···O) is 2.69 ± 0.01 Å and the interplanar distance between bipyridyl and naphthyl surfaces is 3.4 ± 0.2 Å. More interestingly, each inner side of the hexagon composed of Os−bipyridine−Os is significantly concave, along with a slight bending of the bipyridine in the crystal structure of the complex. This is presumably responsible for the formation of the supramolecular hexagon despite a nearly 90° N−Os−N bond angle at each corner (88.1°).

In conclusion, we have described the self-assembly of an Os (VI)-based supermolecule by the combination of chemical reaction (osmylation), coordination, hydrogen bond, and aryl stacking between all 24 individual components. The guest molecule may control the size and shape of the supermolecule in a way to balance and maximize the intermolecular interactions between components. Current work is aiming at finding guests that can induce different supramolecular assemblies.

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Supporting Information Available: Physical and spectroscopic properties, concentration- and temperature-dependent ^{1}H NMR spectra of the COEs, VPO experiments, binding studies, and X-ray crystal data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Initial concentrations of the COE and diol stock solutions for titration experiments were 10 mM and 1−2 mM, respectively. The former was calculated on the basis of the molecular weight of one side (bipyridine·OsO_4·olefin)$_1$ of the COE.

(15) Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375−387.

(16) This also assumes the binding constant does not vary with the geometry of the different sized COEs in solution. By expressing the binding per side of the COE, we do not need to know the distribution of COEs in solution, only total number of sides of the COEs.

(17) Corners, K. A. *Binding Constants*; John Wiely & Sons: New York, 1984; p 24.

(18) Due to the complicated equilibria between COEs and 2,6-dyhydroxynaphthalene, the structure of the complex in solution is not conclusive at this moment, although we tried numerous methods to identify it including VPO and temperature-dependent ^{1}H NMR experiments in the presence of 2,6-dihydroxynaphthalene.

(19) Single crystals were obtained by a slow diffusion of *n*-hexane to a $CHCl_3$/acetone solution of COEs and **2** and by standing the resulting solution for 2 weeks at room temperature. Crystal data: Rhombohedral, *R*-3; $a = 32.218(5)$ Å, $b = 32.218(5)$ Å, $c = 21.581(4)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 19399(6)$ Å^3; $z = 18$; $D_{calcd} = 1.392$ g cm^{-3}; $F(000) = 8280$; λ (Mo Kα) = 0.71073 Å; temp, 293(2) K.; crystal size $0.16 \times 0.14 \times 0.12$ mm; reflections collected/unique, 38652/6253 (R (int) = 0.2097); final R indices ($I > 2\sigma(I)$) $R = 0.1172$, $R_w = 0.2323$; R indices (all data) $R = 0.2240$, $R_w = 0.2897$.