

Inclusion of methano[60]fullerene derivatives in cavitand-based coordination cages

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Abstract—The X-ray study of self-assembled coordination cage **1**, constituted of two tetrapyrrolyl-substituted resorcin[4]arene cavitands coupled through four square-planar palladium complexes is reported. The coordination cage, embracing an internal cavity of ca. 840 Å³, reveals to have the right size for the inclusion of large molecules such as fullerenes. Cage **1** forms 1:1 complexes with methano[60]fullerene derivatives **3** and **4** bearing a dimethyl and a diethyl malonate addend, respectively. Evidence for inclusion complexation was provided by ¹H NMR spectroscopic studies and ESI-MS investigations, which unambiguously showed the formation of 1:1 fullerene–cage complexes. The association constants (K_a) were experimentally determined to be ca. 150 M⁻¹ at 298 K in CD₂Cl₂. In both complexes **1·3** and **1·4**, the malonate residue is threaded through one of the four lateral portals, as clearly shown by docking simulations.

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1. Introduction

Current materials-oriented science is characterized by the vigorous exploration of new efficient chemical methods for the development of new nano-sized architectures in which functional molecules possessing unique optical and electrochemical properties can be selectively hosted.^{1–3} The ability of the supramolecular approach to confine and stabilize molecular species by specific weak intermolecular interactions in both solid and liquid phase makes it particularly attractive for engineering many potential molecule-based applications ranging from sensors to nanotechnology.^{4,5} Metal-directed self-assembly has been widely employed to engineer two- and three-dimensional structures showing internal cavities capable of trapping molecules.^{6–10} In this respect, cavitand-based coordination cages^{11–16} are increasingly attracting attention as one of the most promising classes of molecular hosts due to the versatile properties of the cavitand scaffold in terms of preorganization, geometry, and synthetic modularity.¹⁷

π -Conjugated molecules such as fullerenes with tunable electronic properties are appealing building blocks for the construction of functional materials possessing exceptional electrochemical and photophysical properties. With the availability of macroscopic quantities of these all-carbon compounds, large efforts have been geared toward discovering rapid and efficient methods for their purification¹⁸ and subsequent inclusion in photosynthetic,^{19,20} photonic,^{21,22} and molecular electronics devices.^{23,24} Numerous examples of fullerene-containing complexes have appeared in the literature, in which the host molecules consist mainly of macrocyclic molecules, such as calixarenes,^{25–28} resorcinarenes,^{29,30} cyclotrimeratrylenes,³¹ cyclodextrins,^{32,33} porphyrins,³⁴ and cyclic [6]paraphenylene-acetylene,³⁵ which spontaneously form complexes in the presence of C₆₀ or C₇₀. Consequently, the preparation of specific preorganized³⁶ receptors containing two or more covalently-linked macrocycles, exploiting a high selectivity toward fullerenes binding, were also explored.³⁷ In this respect, Fukazawa and co-workers prepared the first covalently-linked biscalix[5]arene fullerene receptor, with association constants ranging from 76 to 163 × 10³ M⁻¹ at 298 K in toluene.³⁸ Recently, Saigo, Aida, and co-workers reported a series of cyclophane-type metal-porphyrin dimers that encapsulate fullerenes in organic solvents (with fast host–guest exchange on the NMR time scale)

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and in the solid state, showing exceptionally high association constants (ca. $2.4 \times 10^7 \text{ M}^{-1}$ for C_{60} in benzene at 298 K) as a consequence of the strong charge-transfer interaction between the two electron-rich tetrapyrrolic macrocycles and the electron-deficient fullerene sphere. Parallel studies were also reported by Reed, Boyd, and co-workers, who engineered fashionable jaw-like hosts as fullerene binders.^{39,40} Consecutive to these works, several other papers have been reported for the construction of porphyrin-based receptors for fullerenes showing a variety of stimulating features. Thus a dendritic porphyrin receptor with a pronounced allosteric effect in the binding of three C_{60} molecules⁴¹ and a bisporphyrin receptor that can be reversibly switched by complexation with metals were described by Shinkai and co-workers.⁴² However, more rarely the encapsulation of fullerenes in self-assembled cages has been employed.^{43–45} Shinkai *et al.*, reported for the first time a 1:1 complex between a C_{60} molecule and a homooxocalix[3]arene dimer cross-linked by three Pd(II) complexes.^{43,46} Very recently, Claessens and Torres described the encapsulation of C_{60} in an isomeric mixture of C_3 -symmetric coordination cages constituted by two pyridine-bearing subphthalocyanine ligands connected by three metal complexes.⁴⁷

In this work, we describe the self-assembly, crystal structure, and fullerene inclusion properties of cavitand-based coordination cage **1** composed of two tetrapyrridyl-substituted cavitands connected through four square-planar palladium complexes.

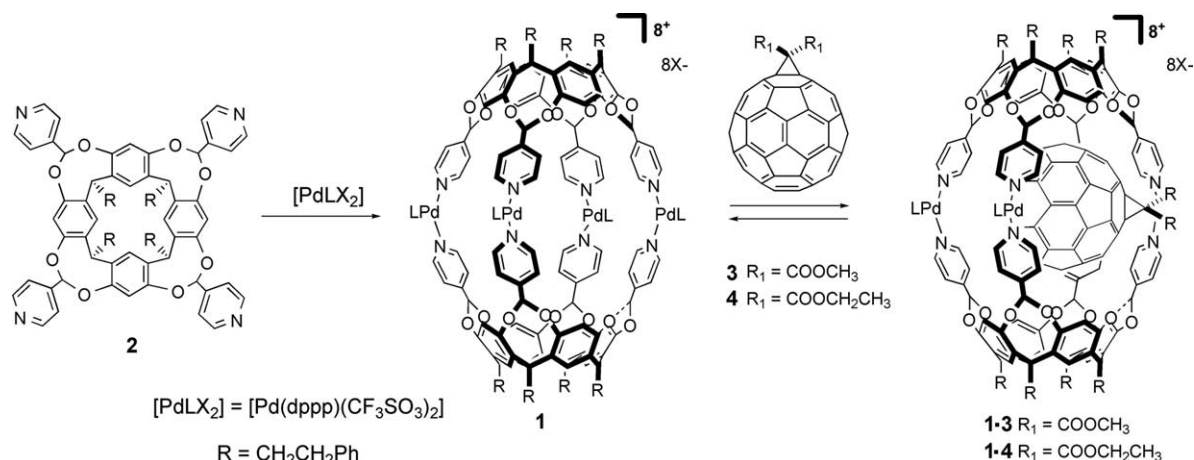
2. Results and discussion

Self-assembly of cavitand ligand **2** into molecular cage **1** was carried out as outlined in Scheme 1, following the protocol reported in the literature.⁴⁸ The typical procedure for the cage preparation is based on the mixing of cavitand ligand **2** with a metal precursor, such as $[\text{Pd}(\text{dppp})(\text{CF}_3\text{SO}_3)_2]$, in a 1:2 molar ratio at room temperature in chlorinated solvents or acetone, affording cage **1** in quantitative yield. The ^1H NMR spectrum showed the formation of a new set of proton resonances, indicative of the presence of a single compound. The downfield shift of the pyridine protons

ortho to the nitrogen is indicative of coordination to the Pd ions, whereas the upfield shift of the OCHO protons, pointing inside the cavity, is diagnostic of the cage formation.⁴⁸ The high symmetry of compound **1** in solution was also confirmed by the ^{31}P NMR spectra, which featured a sharp singlet indicating the equivalence of the eight phosphorous atoms.

A small crystal of coordination cage **1**, suitable for X-ray diffraction, was obtained by slow evaporation of a solution of **1** in acetone. The electron density maps and the refinement of the structure revealed the presence of one octa-cationic coordination cage in the triclinic unit cell, intramolecularly related by a crystallographic symmetry center. The molecular structure, depicted in Figure 1, nicely reveals the presence of four square-planar Pd(II) complexes in the equatorial region connecting two cavitand units (equatorial distance between two successive Pd(II) ions is 12.3 Å). The coordination cage shows a pseudo C_{2h} symmetry in the solid state, which increases to D_{2h} if the terminal (3-phenyl)propyl substituents are excluded.

All Pd(II) metal ions form tetra-coordinated species, with the $\text{N}(\text{Py})\text{--Pd--N}(\text{Py})$ and $\text{P}(\text{dppp})\text{--Pd--P}(\text{dppp})$ angles ranging from 85.9 to 87.5° and from 91.1 to 91.9°, respectively, indicating a small distortion in the square-planar coordination geometry at the Pd(II) metal centers. The positive charges of the four Pd(II) metal centers are counterbalanced by eight CF_3SO_3^- anions, of which four are crystallographically independent. All CF_3SO_3^- ions are disordered at least along two directions. Six CF_3SO_3^- counterions closely surround the cage (Fig. 2a), of which four are in close contact with the Pd(II) metal ions (Pd–O distance 3.0 Å) and two hosted within the two hindered portals between two Pd(II) centers (shortest Pd–O distance = 4.3 Å). Of the two remaining CF_3SO_3^- molecules, one is located outside the cage in a crystallographic center of symmetry and one is confined within the capsule cavity. Both sites are at half occupancy. The latter observation contrasts with the ^{19}F NMR measurements obtained in solution, which clearly showed no permanent inclusion of CF_3SO_3^- anions inside the cage cavity.⁴⁸ The lateral portals are wide enough to allow a fast exchange of the counterions with the bulk solvent.⁴⁹ Eleven acetone molecules (5.5



Scheme 1. Schematic representation of the coordination cage formation and the complexation of **1** with methano[60]fullerene derivatives **3** and **4**. dppp: 1,1'-bis(diphenylphosphino)propane.

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