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Encapsulation of Triphenylene Derivatives in the Hexanuclear Arene Ruthenium Metallo-Prismatic Cage $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ (tpt = 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine, dhbq = 2,5-dihydroxy-1,4-benzoquinonato)

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Dedicated to Professor Heinrich Nöth on the Occasion of his 80th Birthday

Abstract. A large cationic triangular metallo-prism, $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ $(\mathbf{1})^{6+}$, incorporating *p*-cymene ruthenium building blocks, bridged by 2,5-dihydroxy-1,4-benzoquinonato (dhbq) ligands, and connected by two 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits, allows the permanent encapsulation of the triphenylene derivatives hexahydroxytriphenylene, $C_{18}H_6(OH)_6$ and hexamethoxytriphenylene, $C_{18}H_6(OMe)_6$. These two cationic carceplex systems $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ have been isolated as their triflate salts. The molecular structure of these systems has been established by one-dimensional ^{1}H ROESY NMR experiments as well as by the single-crystal structure analysis of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$.

Keywords: Arenes; Carceplex; Encapsulation; Ruthenium; Supramolecular chemistry

Introduction

Combining the "molecular clip" strategy developed by *Stang* [1] and the "molecular panelling" strategy developed by *Fujita* [2], we recently synthesised a series of cationic triangular metallo-prisms (M = Rh, Ir, Ru) connected by 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt) subunits, which contain bridging chloro [3], oxalato [4] and 2,5-dihydroxy-1,4-benzoquinonato (dhbq) [5] ligands. Despite a large metal-metal distance in the oxalato-bridged system (M-M separation ≈ 5.5 Å) [4], inclusion of a guest molecule has not been observed in these cages. Only in the large cationic cage $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ $(\mathbf{1})^{6+}$ (Ru-Ru separation = 7.9 Å), encapsulation of square-planar complexes $M(acac)_2$ [M = Pd, Pt; acac = acetylacetato] was achieved in good yield by adding 1 eq. of the complex during the synthesis of **1** [5].

Herein we report the synthesis and characterization of two new carceplex systems in which hexahydroxytriphenylene, $C_{18}H_6(OH)_6$, and hexamethoxytriphenylene, $C_{18}H_6(OMe)_6$, are permanently encapsulated in the cationic triangular metallo-prism, $[Ru_6(p\text{-}Pr^iC_6H_4Me)_6(tpt)_2(dhbq)_3]^{6+}$ $(\mathbf{1})^{6+}$. The molecular structures of $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ are established by one-dimensional ROESY ^{1}H NMR experiments. The single-crystal structure analysis of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$ is presented as well.

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Experimental Section

General Remarks

All organic solvents were degassed and saturated with nitrogen prior to use. Hexahydroxytriphenylene and hexamethoxytriphenylene were purchased from TCI Europe N.V. and used as received. 2,4,6-Tris(pyridin-4-yl)-1,3,5-triazine (tpt) [6] and $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ [5] were prepared according to published methods. The ^{1}H, $^{13}C\{^1H\}$, and ROESY NMR spectra were recorded on a Bruker AMX 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FTIR 1720 X spectrometer. Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland).

Synthesis of $[C_{18}H_6(OH)_6\subset\mathbf{1}][O_3SCF_3]_6$

A mixture of $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ (60 mg, 0.09 mmol) and $Ag(O_3SCF_3)$ (47 mg, 0.18 mmol) in MeOH (20 mL) is stirred at room temperature for 2 hours, then filtered. To the red filtrate tpt (18 mg, 0.06 mmol) and $C_{18}H_6(OH)_6$ (10 mg, 0.03 mmol) are added. The mixture is stirred at room temperature for 24 hours, and then the solvent is removed under vacuum. The residue is dissolved in dichloromethane (20 mL) and filtered. The dark red solution is concentrated (3 mL), and diethyl ether is slowly added to precipitate the red solid. Yield 80 mg, (76 %). Anal. Calcd for $C_{138}H_{126}N_{12}O_{30}F_{18}S_6Ru_6$: C, 46.39; H, 3.55; N, 4.70. Found: C, 42.26; H, 3.87; N, 4.52 %.

^{1}H NMR (400 MHz, CD_3CN): δ = 8.31 (d, 12H, H_α), 7.93 (d, 12H, H_β), 6.65 (s, 6H, H_g), 6.08 (s, 6H, H_q), 5.88 (d, 12H, H_{ar}), 5.62 (d, 12H, H_{ar}),

5.46 (s, 6H, H_{OH}), 2.84 (sept, 6H, CH), 2.08 (s, 18H, CH_3), 1.36 (d, 36H, CH_3); **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN): δ = 186.0, 168.5, 154.2, 144.4, 143.6, 124.7, 122.4, 118.4, 109.1, 104.8, 102.8, 100.3, 84.8, 82.6, 32.1, 22.5, 18.2; **IR** (cm^{-1}): 1715(s), 1526(s), 1445(m), 1361(s), 1219(s), 1091(s), 829(s).

Synthesis of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$

It is prepared following an analogous procedure as described above using $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ (60 mg, 0.09 mmol), $Ag(O_3SCF_3)$ (47 mg, 0.18 mmol), tpt (18 mg, 0.06 mmol) and $C_{18}H_6(OMe)_6$ (13 mg, 0.03 mmol). Yield 90 mg, (83 %). Anal. Calcd for $C_{144}H_{138}N_{12}O_{30}F_{18}S_6Ru_6$: C, 47.29; H, 3.80; N, 4.60. Found: C, 47.34; H, 3.92; N, 4.22.

^{1}H NMR (400 MHz, CD_3CN): δ = 8.24 (d, 12H, H_α), 8.06 (d, 12H, H_β), 6.71 (s, 6H, H_g), 6.13 (s, 6H, H_q), 5.85 (d, 12H, H_{ar}), 5.59 (d, 12H, H_{ar}), 3.41 (s, 18H, H_{OMe}), 2.82 (sept, 6H, CH), 2.18 (s, 18H, CH_3), 1.31 (d, 36H, CH_3); **^{13}C {^{1}H} NMR** (100 MHz, CD_3CN): δ = 185.7, 168.7, 153.9, 147.4, 144.1, 124.7, 121.9, 118.4, 105.2, 104.8, 103.0, 100.0, 84.6, 82.6, 54.0, 32.1, 22.5, 18.1; **IR** (cm^{-1}): 1703(s), 1527(s), 1362(s), 1204(s), 1091(s), 906(s).

One-Dimensional ROESY Experiments

The 1-D ^{1}H ROESY experiments have been recorded using the MP-ROESY mixing sequence, which has shown its effectiveness with regard to TOCSY transfer suppression and cross-relaxation peak intensity enhancement [7]. The mixing time of the experiments has been kept short (100ms) to avoid spin diffusion and so that the linear approximation remains valid [8].

X-ray Crystallographic Study

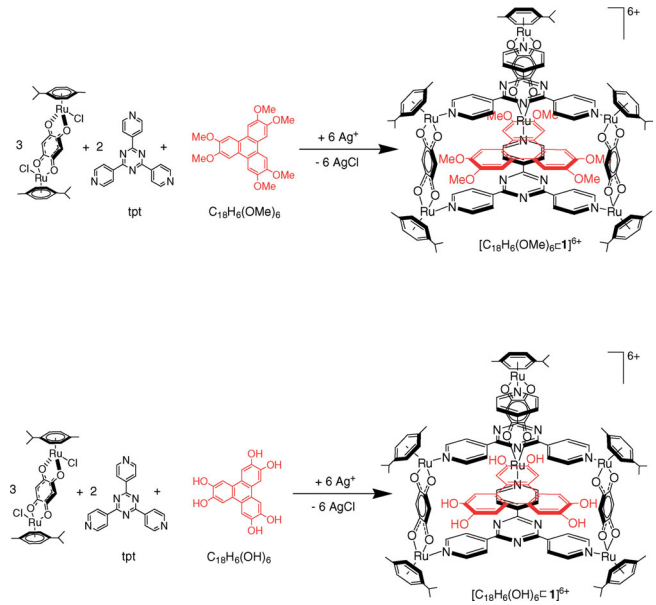
Red crystals of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$ suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$ in an acetone/benzene solution. *Crystal data for* $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6\cdot 1.5\ C_6H_6$; $C_{156}H_{150}F_{18}N_{12}O_{36}Ru_6S_6$, trigonal space group $R\bar{3}c$ (No. 167), cell parameters a = 19.376(1), b = 19.376(1), c = 78.784(6) Å, V = 25614(3) Å^3, T = 173(2) K, Z = 6, D_c = 1.521 g cm^{-3}, $F(000)$ 11880, λ (Mo Kα) = 0.71073 Å, 5356 reflections measured, 2623 unique (R_{int} = 0.0845) which were used in all calculations. The structure was solved by direct method (SHELXS-97) [9] and refined (SHELXL-97) [10] by full-matrix least-squares methods on F^2 with 620 parameters. R_1 = 0.0849 ($I > 2\sigma(I)$) and wR_2 = 0.2580, GOF = 0.908; max./min. residual density 1.158/−1.046 eÅ^{-3}. Figure 3 was drawn with ORTEP [11] while Figure 4 with POV-Ray [12].

CCDC 675474 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via **www.ccdc.cam.ac.uk/data_request/cif**.

Results and Discussion

Synthesis

The hexametallic cation $[\mathbf{1}]^{6+}$ is prepared according to a two-step strategy in which the dinuclear 2,5-dihydroxy-1,4-benzoquinonato (dhbq) complex $[Ru_2(p\text{-}Pr^iC_6H_4Me)_2(dhbq)Cl_2]$ is used as a bi-metallic connector [5]. If one equivalent of hexahydroxytriphenylene, $C_{18}H_6(OH)_6$ or hexamethoxytriphenylene, $C_{18}H_6(OMe)_6$ is added to the reaction mixture, the cationic carceplex systems $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ are obtained, see Scheme 1. These complexes are isolated in good yield and characterized as their triflate salts, $[C_{18}H_6(OH)_6\subset\mathbf{1}][O_3SCF_3]_6$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$, respectively.



Scheme 1 Synthesis and molecular representation of $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$.

NMR Studies

The formation of these carceplex systems can easily be monitored by ^{1}H NMR spectroscopy, as shown in Figure 1. The ^{1}H NMR spectra of $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ show a well organized structure with a quite simple set of signals which is attributed to cage **1** and the triphenylene moiety. However, unlike the empty cage **1**, where the H_α and H_β are found in the expected

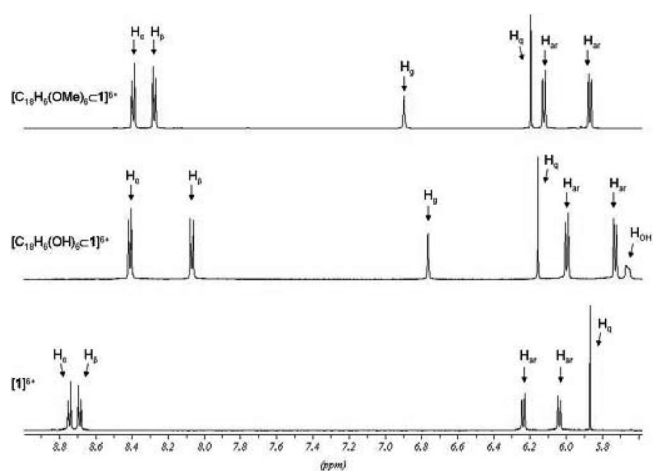


Figure 1 Aromatic region of the ^{1}H NMR spectra (acetonitrile-d_3) of $[\mathbf{1}]^{6+}$, $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$.

positions, 8.75 and 8.68 ppm (acetonitrile-d_3), upon encapsulation of an aromatic molecule the H_α and H_β signals are strongly shifted upfield. Moreover, the protons (H_q) of the dhbq bridging ligands are shifted downfield, while the signals of the aromatic protons (H_{ar}) of the *p*-cymene ligand remain almost unchanged upon insertion of the triphenylene moiety. Similarly, the protons of the methyl and isopropyl groups of the *p*-cymene ligand are not affected by the presence of the aromatic molecule within the cavity of **1**. In $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$, the signal of the methoxy groups is shifted upfield by 0.7 ppm, as compared to free $C_{18}H_6(OMe)_6$ in acetonitrile-d_3.

One-dimensional ^{1}H ROESY NMR experiments confirm the spatial proximity of the different components of **1** and the encapsulated molecule. Indeed, for $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$, intense well-resolved cross-peaks are observed between the protons of the encapsulated molecule (H_g and H_{OH}) and the protons (H_q, H_α and H_β) of the cage molecule, see Figure 2. The strong interactions between the encapsulated molecule and the cationic cage $[\mathbf{1}]^{6+}$ suggest an eclipsed conformation of the tpt-triphenylene-tpt arrangement. This is in agreement with the conformation observed in the prismatic cage $[C_{18}H_6(OMe)_6\subset Pt_6(NH_2CH_2CH_2NH_2)_6(tpt)_2(C_4H_4N_2)_3]^{12+}$ encapsulating a hexamethoxytriphenylene molecule [2a]. Similarly, in $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$, intense cross-peaks are observed between the protons of the encapsulated guest molecule (H_g and H_{OMe}) and the protons of the different connecting components of the cage molecule (H_q, H_α and H_β). An estimation of the different host-guest H···H separations have been established from the NMR data and are given in Table 1 along with the corresponding X-ray data for $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$. The H···H distances found by NMR are in good agreement with the values found by X-ray analysis, the differences being due to the mobility in solution and to the precision of the methods used.

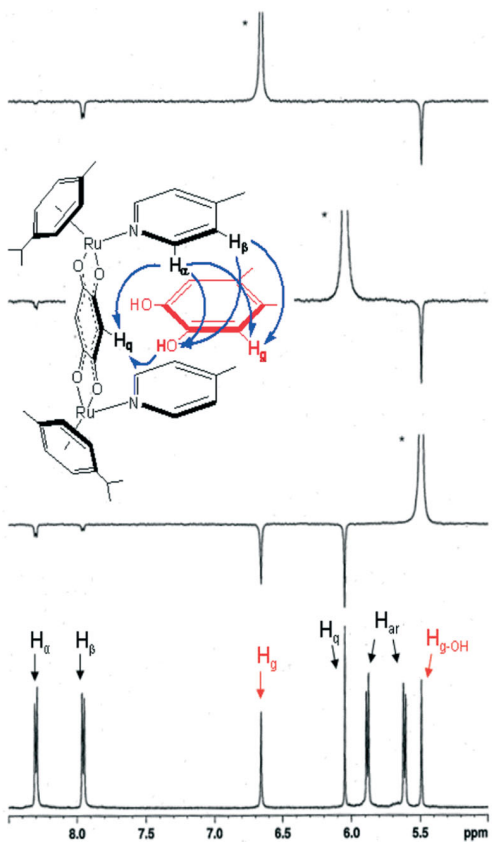


Figure 2 One-dimensional ROESY (400 MHz) spectrum in acetonitrile-d_3 and schematic representation of the corresponding cross-peaks observed in the system $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$.

Table 1 Estimated H···H separations of $[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ and $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ from NMR and X-ray data.

	$[C_{18}H_6(OH)_6\subset\mathbf{1}]^{6+}$ NMR data [a]	$[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ NMR data [a]	$[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$ X-ray data
H_g-H_α	4.0 Å	3.9 Å	4.47 Å
H_g-H_β	2.9 Å	3.0 Å	3.33 Å
H_q-H_α	3.9 Å	3.3 Å	4.22 Å
H_q-H_{OH}	2.7 Å	–	–
H_α-H_{OH}	3.1 Å	–	–
H_β-H_{OH}	3.4 Å	–	–
H_q-H_{OMe}	–	2.9 Å	2.45 Å
H_α-H_{OMe}	–	3.1 Å	2.96 Å
H_β-H_{OMe}	–	3.2 Å	3.00 Å

[a] Calculated with the formula $r_{ij} = r_{ref}\,(c_{ref}{*}a_{ref}/c_{ij}{*}a_{ij})^{1/6}$, where a_{ij} is the ROE cross-peak area and r_{ij} is the interproton distance of the two protons i and j; r_{ref} and a_{ref} are the reference distance and cross peak intensity between the aromatic protons H_α and H_β (distance set to 2.3 Å): c_{ref} and c_{ij} are the correction factors to correct the offset dependence relative to the transmitter centre [13].

Crystal Structure

Single-crystals of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6$ suitable for X-ray analysis were obtained by the slow diffusion of benzene in an acetone solution of the salt. The crystal structure of $[C_{18}H_6(OMe)_6\subset\mathbf{1}][O_3SCF_3]_6\cdot 1.5\ C_6H_6$ shows, apart from slightly disordered triflate anions, a perfectly eclipsed conformation of the cation (trigonal space group $R\bar{3}c$) and strong parallel π-stacking interactions between the aromatic rings of the tpt subunits and the $C_{18}H_6(OMe)_6$ encapsulated molecule, see Figure 3.

It is clear from the van der Waals representation of the carceplex system that the hexamethoxytriphenylene is permanently encapsulated in **1**, see Figure 4. The interplanar separation observed between the central aromatic moieties (3.29 Å), is shorter than the theoretical value calculated for this stacking mode [14], confirming strong π-stacking interaction between the triazine rings and the central aromatic ring of the triphenylene moiety. The empty spaces left between the cationic hexanuclear cages are filled with $[O_3SCF_3]^-$ anions and benzene solvent molecules.

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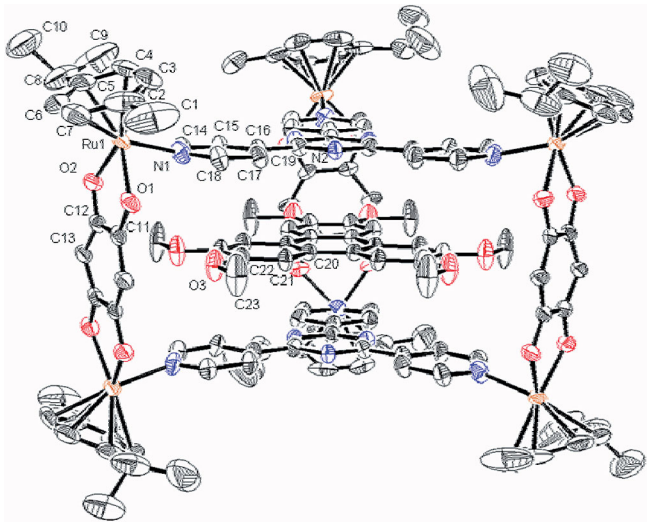

Figure 3 ORTEP drawing of cation $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$, at 35 % probability level, with hydrogen atoms, benzene molecules and $[O_3SCF_3]^-$ anions being omitted for clarity. Selected bond lengths/Å and angles/°: Ru(1)-Ru(1)^i 7.857(1), Ru(1)-N(1) 2.114(9), Ru(1)-O(1) 2.078(7), Ru(1)-O(2) 2.080(6); O(1)-Ru(1)-O(2) 78.1(3), O(1)-Ru(1)-N(1) 86.2(3), O(2)-Ru(1)-N(1) 85.9(3) i = 1/3 + x − y, 2/3 − y, 1/6−z.

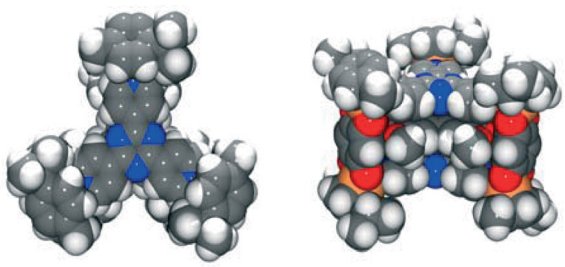

Figure 4 Top and side view representations of $[C_{18}H_6(OMe)_6\subset\mathbf{1}]^{6+}$, anions and benzene molecules being omitted for clarity.

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