Ionic dimeric pyrogallol[4]arene capsules†

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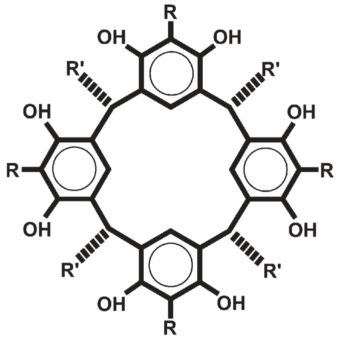
Received (in Cambridge, UK) 9th May 2007, Accepted 11th July 2007
First published as an Advance Article on the web 26th July 2007
DOI: 10.1039/b707009h

Ionic capsules based on dimeric arrangements of pyrogallol[4]arenes have been structurally authenticated and suggest that there is a degree of flexibility in capsule formation with further potential for multiple guest encapsulation and manipulation in such arrangements.

Gaining control over the self-assembly of molecular building blocks such as calixarenes, as well as the controlled incorporation of metal ions in multi-component capsule-like architectures, is a significant challenge that has attracted much interest in recent times.[1] The *p*-sulfonatocalix[*n*]arenes (where *n* = 4,5,6,8) have been studied extensively for this purpose and have afforded numerous supramolecular motifs based on molecular/ionic capsules that include 'Russian dolls', 2-D and 3-D coordination polymers, amino acid complexes, or capsules containing multiple guests, for example.[2,3] In relation to this, the assembly of *p*-sulfonatocalix[4]arene can be tailored such that twelve assemble at the vertices of a cuboctahedron, with neighbouring cuboctahedra packing in the solid state through such 'Russian doll' links in a *pseudo*-cubic close packed manner.[3b] Other pertinent examples include capsule-like arrangements formed with modified cyclotriveratrylenes (CTV) and silver halocarbaboranes,[4] non-covalent ionic capsules based on mixtures of charged calixarenes,[5] and metal resorcin[4]arene capsules.[6]



R = H, R' = Me, CMRC; R = OH, R' = C_nH_{2n+1}, PgC_n;
R = OH, R' = $(CH_2)_4Cl$, PgC_4Cl, **1**; R = OH, R' = $(CH_2)_5CH_3$, PgC_6, **2**.

Fig. 1 Structure of *C*-methylresorcin[4]arene, the *C*-alkylpyrogallol[4]arenes, *C*-chlorobutylpyrogallol[4]arene (**1**) and *C*-hexylpyrogallol[4]arene (**2**).

Six *C*-methylresorcin[4]arenes (CMRC, Fig. 1) have been shown to self-assemble with eight structural water molecules (through hydrogen bonding) as a hexameric nano-capsule, as identified through X-ray diffraction studies.[7] The related *C*-alkylpyrogallol[4]arenes (PgC's, Fig. 1) self-assemble without structural water molecules to form similar hydrogen-bonded nano-capsules,[8] and these assemblies are capable of hosting multiple guest species that can relay information about the nature of the interior void when studied using fluorescence spectroscopy.[9,10] A number of our recent studies with PgC's have focused on the assembly of metal–organic nano-capsules.[11] Addition of copper or gallium nitrate to solutions of particular functionalised PgC's results in the formation of hexameric analogues with 'upper rim' OH hydrogen atoms replaced by metal centres.[11*a–c*] When zinc nitrate is reacted with PgC_3 in the presence of pyridine, the components were found to assemble into a dimeric capsule 'stitched' together by an octanuclear zinc coordination belt.[11*d*] In relation to these studies, alkali metal interaction with calixarene π-systems has also been of interest in recent times.[12,13] Nissinen and co-workers have shown that *C*-methylpyrogallol[4]arene (PgC_1) can act as an alkali metal receptor for potassium, rubidium, and caesium bromides and chlorides.[13] Their studies found the host to adopt a boat conformation as a requirement for strong cation–π interactions between the metals and the aromatic rings of PgC_1. As both *C*-alkylresorcin[4]arenes and *C*-alkylpyrogallol[4]arenes have been shown to form non-covalent dimeric capsules under various conditions,[14] we employed an alkali metal in order to study the potential of these systems to form metal–organic (or rather ionic) nano-capsules with the possibility of more easily 'anchoring' useful guest species within capsular assemblies based on metal coordination to both pyrogallol[4]arene and guest.

Herein, we report a structural study on two complexes formed (in water and acetonitrile) between caesium chloride and PgC's with very different 'lower rim' character (PgC_4Cl, **1**, and PgC_6, **2**). These studies afforded two related dimeric capsules, one head-to-head and one offset (**1·CsCl** and **2·CsCl** respectively), that are facilitated by varied coordination of caesium to the 'upper rim' oxygen atoms and in one case to the aromatic ring of the host. Acetonitrile molecules occupy the cavities of the hosts in both arrangements, and in the head-to-head capsule (**1·CsCl**), the guest solvent is also bound to the caesium centre through the C–N triple bond.

Crystals suitable for X-ray diffraction studies were obtained for each assembly from addition of an aqueous CsCl solution to an acetonitrile–water solution of **1** or **2**, followed by standing and/or slow evaporation.‡ For **1·CsCl**, the crystals were in a monoclinic cell and the solution was performed in space group $P2_1/c$. The asymmetric unit, as shown in Fig. 2A, comprises one PgC_4Cl and one caesium that is coordinated to three water molecules, one

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† Electronic supplementary information (ESI) available: Full tables of bond distances with ESD's in relation to metal coordination sphere. Extended packing structures for **1·CsCl** and **2·CsCl**. See DOI: 10.1039/b707009h

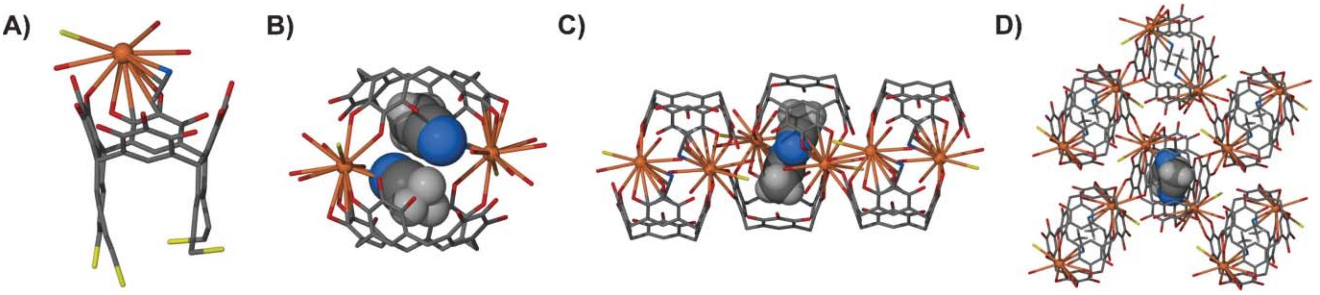

Fig. 2 Views of complex **1·CsCl**. (A) The asymmetric unit showing the coordination of Cs cation to the aromatic ring and 'upper rim' OH groups of **1**, the triple C–N bond of the guest MeCN molecule, waters of crystallisation and the chloride anion. (B) A head-to-head capsule with MeCN molecules in space-filling representation. (C) Side view of the extended structure showing neighbouring capsules joined by Cs coordination (some MeCN guest molecules in space-filling representation). (D) Orthogonal view of the extended structure relative to (C).

acetonitrile and a chloride counterion. Within this unit, the metal is coordinated to three of the PgC_4Cl 'upper rim' oxygen atoms as well as part of one aromatic ring with typical Cs–O and Cs–C distances in the ranges of 3.207–3.354 and 3.586–3.661 Å respectively (Fig. 2A). In addition, the Cs centre is coordinated to the C–N triple bond of the acetonitrile molecule (Cs–N and Cs–C distances of 3.228 and 3.875 Å respectively), three water molecules (Cs–O bond distances in the range of 3.344–3.609 Å), and the chloride that is positioned at the periphery of the capsule (Cs–Cl bond distance of 3.5732 Å). The methyl group of the acetonitrile guest molecule resides in the cavity of the PgC_4Cl with two $CH\cdots\pi$ interactions between the methyl group and aromatic rings of the host with CH···aromatic centroid distances of 2.555 and 2.609 Å.

Symmetry expansion of the asymmetric unit affords a layered network of head-to-head dimeric capsules (Fig. 2) that is facilitated by additional coordination of the Cs centre to four symmetry equivalent 'upper rim' oxygen atoms; two are from the head-to-head molecule of **1** (Fig. 2B, upper left hand side) while the remaining two are from a neighbouring molecule of **1** (Fig. 2C, middle left hand side), Cs–O distances of which lie in the range of 3.072–3.393 Å.† In addition to this, there are six hydrogen bonds from 'upper rim' hydroxyl groups of neighbouring molecules of **1** or water molecules to the chloride acceptor at the capsule periphery, the OH···Cl distances of which lie in the range of 2.243–2.514 Å (Fig. S1†).

In relation to the present contribution, we have recently identified a number of dimeric capsule arrangements (that also encapsulate two acetonitrile molecules) for several *C*-alkylpyrogallol[4]arenes that are formed when the molecules are crystallised from a water–acetonitrile mixture.[14c] Comparison of the dimeric arrangement of acetonitrile molecules in **1·CsCl** shows this to be somewhat reminiscent of these assemblies, although the metal–guest coordination in the present case appears to force the molecules to occupy more central positions within the cavity generated by the direct head-to-head motif. This is evidenced from the distance between the quaternary carbons of the two guests in **1·CsCl** being ~3.6 Å, compared with a typical distance of ~4.3 Å in the aforementioned 'metal-free' cases. The layered network of head-to-head capsules in **1·CsCl** packs in the expected manner to form a bi-layer type arrangement which is similar to those from a number of reported examples for the *C*-alkylpyrogallol[4]arenes,[14d] in addition to when **1** is crystallised from either methanol or ethyl acetate (Fig. S2–S4†).[15]

For **2·CsCl**, crystals were of triclinic symmetry and the structural solution was performed in the space group $P\bar{1}$. The asymmetric unit, as shown in Fig. 3A, is composed of one PgC_6, one caesium, one coordinated chloride and a non-coordinated acetonitrile molecule. Within the asymmetric unit, the caesium centre is bound to two 'upper rim' PgC_6 oxygen atoms (Cs–O distances of 3.392 and 3.567 Å) and the chloride counterion (Cs–Cl distance of 3.512 Å), as shown in Fig. 2B–D. The methyl group of the acetonitrile guest resides in the cavity of the PgC_6, forming two $CH\cdots\pi$ interactions between the methyl group and aromatic rings of the host with CH···aromatic centroid distances of 2.562 and 2.974 Å.

Symmetry expansion of the asymmetric unit affords a layered network, similar to that in **1·CsCl**, although the metal coordination and capsule conformation are slightly different (Fig. 2B–D). The capsule arrangement is offset and the crystallographically

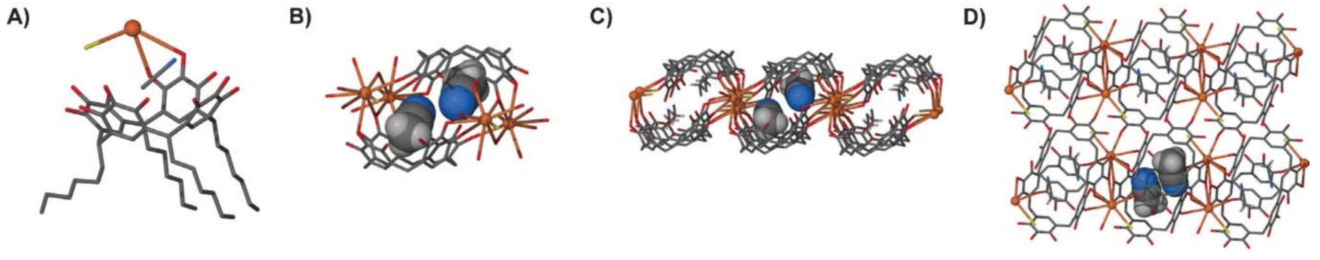

Fig. 3 Views of complex **2·CsCl**. (A) The asymmetric unit showing the coordination of Cs cation to the 'upper rim' OH groups of **2** and the chloride anion. (B) A skewed capsule with MeCN molecules in space-filling representation. (C) Side view of the extended structure showing neighbouring capsules joined by Cs coordination (some MeCN guest molecules in space-filling representation). (D) Orthogonal view of the extended structure relative to (C).

unique caesium centre is found to coordinate to six neighbouring PgC_6 'upper rim' oxygen atoms from symmetry equivalent molecules of **2**, one from the capsule and three from neighbouring capsules, with Cs–O distances in the range of 3.085–3.756 Å (Fig. 2D).† A result of this coordination is that the oxygen atoms of the two molecules of **2** in each capsule are bound to a total of six caesium centres. In addition, the offset nature of the capsule generates two 'voids' in the capsule seam that are filled by the chloride counterions that act as hydrogen bond acceptors to hydroxy groups of molecules of **2**; there are a total of four OH···Cl interactions with distances in the range of 2.139–2.483 Å (Fig. S5†). Notably there are no waters of crystallisation in **2·CsCl**, despite the complex formation being performed in an acetonitrile–water mixture. This suggests that each pyrogallol[4]-arene may dictate the inclusion or exclusion of water in the resulting complexes, in addition to the fact that a number of interesting architectures could be identified with further study.

When the nature of the extended structure is further examined, the 'lower rim' *C*-hexyl chains of the pyrogallol[4]arenes are, for all but one, found to interdigitate in order to maximise van der Waals interactions in a fashion typical for bi-layer arrangements of *O*-alkylcalix[4]arenes,[16] resorcin[4]arenes, or pyrogallol[4]arenes.[14] The fourth chain is bent away from the base of the PgC_6 in order to fill voids in the bi-layer structure, as shown in Fig. S6.† The offset capsule in **2·CsCl** is similar to the dimeric offset capsule formed in the 'metal-free' case of PgC_6 formed in acetonitrile and water, and features of the two capsular structures are found to be rather similar. In the 'metal-free' capsule, one of the four chains bends away from the base of the PgC_6 in a similar fashion to that in **2·CsCl**, and the distance between the quaternary carbons of the included acetonitrile molecules is ~4.2 Å which is comparable to the distance of ~4.6 Å for **2·CsCl**. Furthermore, there is a water of crystallisation in the 'metal-free' structure[14d] that occupies a position very similar to that of the caesium centre in **2·CsCl** (for a comparison see Fig. S7–S8†), suggesting some retention of structural nature upon alkali metal inclusion.

In summary, we have described two different capsular assemblies that are formed from the addition of aqueous caesium chloride to water–acetonitrile solutions of two pyrogallol[4]arenes that have different 'lower rim' character. The behaviour of the metal centre in each structure is somewhat in contrast to that observed by Nissinen and co-workers in partly related assemblies that show PgC_1 to adopt a boat conformation in the presence of CsCl. These studies suggest that a number of important supramolecular motifs may exist for these systems depending on the particular choice of pyrogallol[4]arene (*i.e.* change in alkyl chain length), solvent/co-crystallising agent and metal salt, especially considering the observed correlation between 'metal-free' and 'alkali metal-included' arrangements. Our studies in this area continue with a view to controlling the encapsulation of potentially useful species for the assembly of larger superstructures, for performing reactions in the solid state for example, or for using these capsule like assemblies as intermediates for other 'metal-based' or 'mixed metal' systems.

Notes and references

‡ **1** and **2** were synthesised using literature procedures. In a general experiment, excess caesium chloride (3 equiv.) in H_2O (2 ml) was added to a 1 : 1 MeCN : H_2O solution of **1** or **2**. For **1**, standing over a number of hours afforded very large colourless crystals, while for **2**, slow evaporation of the resulting solution was necessary. **Crystal data for 1·CsCl·MeCN·3H$_2$O**: $C_{46}H_{61}Cl_5Cs_1N_1O_{15}$, M = 1178.12, monoclinic, a = 21.015(10), b = 13.189(6), c = 18.318(9) Å, β = 101.325(8)°, U = 4978(4) Å^3, T = 173(2) K, space group $P2_1/c$, Z = 4, Mo-Kα radiation (wavelength λ = 0.71073 Å), GOF = 1.003, agreement index $R1$ = 0.0618, 33 974 reflections measured, 10 987 unique (R_{int} = 0.0913) which were used in all calculations. The final w$R2$ was 0.1579 (all data); CCDC 646396. **Crystal data for 2·CsCl·MeCN**: $C_{54}H_{75}Cl_1Cs_1N_1O_{12}$, M = 1098.51, triclinic, a = 11.035(6), b = 12.678(7), c = 21.853(12) Å, α = 105.604(9), β = 98.632(10), γ = 95.176(9)°, U = 2884(3) Å^3, T = 173(2) K, space group $P\bar{1}$, Z = 2, Mo-Kα radiation (wavelength λ = 0.71073 Å), GOF = 1.019, agreement index $R1$ = 0.0775, 12 582 reflections measured, 10 542 unique (R_{int} = 0.0552) which were used in all calculations. The final w$R2$ was 0.2185 (all data); CCDC 646397. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b707009h

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