Pyrogallarenes as alkali metal receptors: the role of cation–π interactions in complexation†

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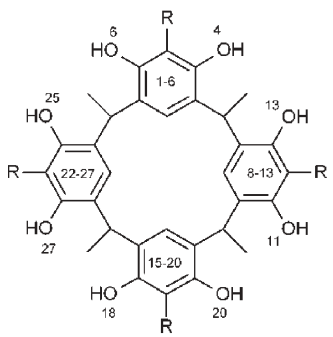
Crystallization studies of *C*-methyl pyrogallarene with potassium, rubidium and caesium bromides or chlorides resulted in a hydrogen bonded molecular cage in which the alkali metal cations are η^6 coordinated to aromatic rings *via* strong cation–π interactions.

Research for the receptors capable of complexing target cations, either metals or organic, is a subject of wide interest in the field of molecular recognition. Because of their chemical and biological relevance, special attention has been paid to the cation–π interactions of alkali metal ions.[1–4] Examples of artificial ligands for such studies include lariat ethers with aromatic sidearms,[2] calixarene derivatives,[3] and uranyl salophen ligands.[4]

Pyrogallarenes **1** and resorcinarenes **2** (Scheme 1) are well-known receptors for small alkyl ammonium cations, where CH–π and cation–π interactions are observed between the aromatic parts of the receptor and the cation.[5–10] Cations are usually enclosed within the cavity of the receptor forming open 1 : 1 inclusion complexes[8,9] or closed 1 : $2^{6–9}$ or 1 : 6^5 capsules. Complexation has been observed in the gas phase,[7–9] in solution[5,8] and in the solid state.[6–10] Although few theoretical and mass spectrometric,[11] as well as extraction,[12] studies have shown the possible affinity of resorcinarene type hosts towards alkali metal cations, especially towards Cs^+, no evidence of complexation in solution or in the solid state nor of the nature of the interactions causing the complexation, has been obtained so far. Herein we report the first X-ray crystal structures of pyrogallarene **1** complexes with K^+, Rb^+ and Cs^+,‡ in which very strong cation–π interactions are established.



1 R = OH
2 R = H

Scheme 1 Structural formula and relevant crystallographic numbering of *C*-methyl pyrogallarene **1** and *C*-methyl resorcinarene **2**.

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Cocrystallization of **1** with a series of alkali metal bromides and chlorides from Na^+ to Cs^+ was carried out in mixtures of **1** and alkali metal salt in proportions 1 : 1 dissolved in MeOH or MeOH/H_2O (1.5–3.0 ml).

Slow evaporation (several days) at ambient temperature gave good quality single crystals in the cases of caesium and potassium bromides and rubidium chloride.

KBr forms a 1 : 1 complex with receptor **1**, which is, however, best described as a continuous chain of 1 : 1 assemblies, in which each K^+ is coordinated between two facing receptor molecules (Fig. 1 and Fig. 2). These two receptors are hydrogen bonded to each other with six hydrogen bonds of length d(D···A) = 2.75–3.09 Å, and form a tightly closed cage, which prevents all interaction between the cation and the counteranion. The cation is connected to four hydroxyl oxygens, two from each receptor. The coordinative distances fall within the typical range of K^+···O coordination, being 2.76–2.85 Å. Most importantly, the cation is η^6 coordinated to two aromatic rings, *i.e.* completely "sandwiched" between the opposite hosts (distances for K^+···centroid of the aromatic ring are 2.79 and 2.90 Å), which assume a boat conformation. The boat conformation is the requirement for this type of very strong complexation by cation–π interactions. If the complexation took place inside the cavity of the host in a crown conformation, as was assumed in the earlier theoretical studies of alkali metal complexes of resorcinarenes,[8] the cation–π interactions would not be optimal η^6 coordination, and also the simultaneous coordination to the hydroxyls would be prohibited or at least more difficult.

The complexes **1**·RbCl and **1**·CsBr crystallize with very close unit cells and isomorphous structures. In contrast to the structure of **1**·KBr, each cation is coordinated altogether to six oxygens, two from each of three different hosts, creating a pseudo-crown ether[13] environment for the cation. Additionally, Rb^+ and Cs^+ are coordinated to halide anions, and to only one aromatic ring of **1** *via* η^6 coordination. This indicates that electrostatic interactions may play a bigger role in the complexation of Cs^+ and Rb^+ than in the case of K^+, although it must be remembered that packing effects caused by the different sizes of ions also contribute to the structural differences. Distances of Rb^+ and Cs^+ coordinative bonds are 2.92–3.43 Å for Rb^+···O, 3.08–3.47 Å for Cs^+···O, 3.49 Å for Rb^+···Cl^-, 3.63 Å for Cs^+···Br^-, 3.17 Å for Rb^+···centroid of the aromatic ring and 3.27 Å for Cs^+···centroid of the aromatic ring.†

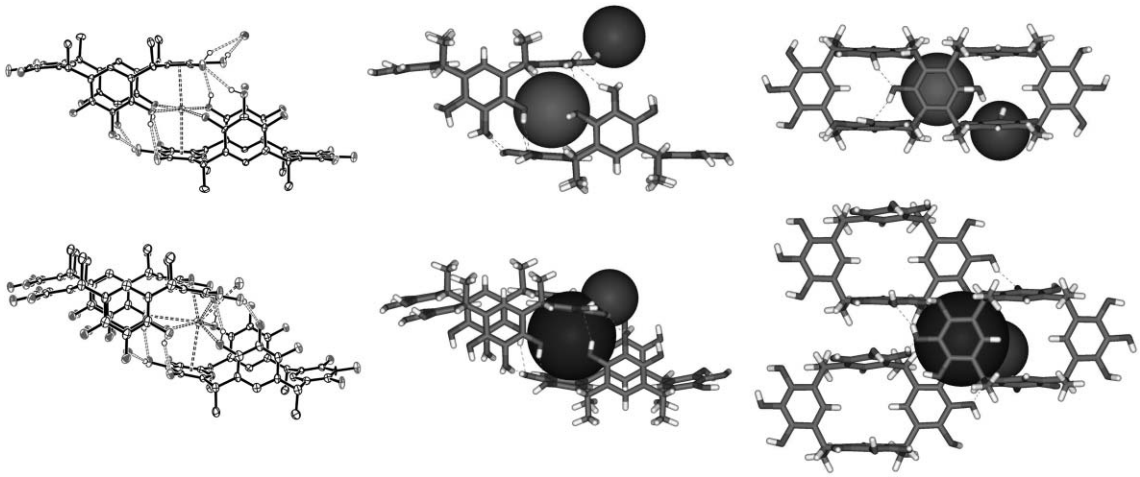

Fig. 1 Crystal structure of the KBr complex of **1** (top) and CsBr complex of **1** (bottom), which is isomorphous to the RbCl complex, drawn as Ortep plots (50% probability level) and as VDW/stick presentations. In Ortep plots cation···π and cation···O interactions and hydrogen bonds are shown as dashed lines. Non-hydrogen bonding hydrogens and solvent molecules are omitted for clarity.

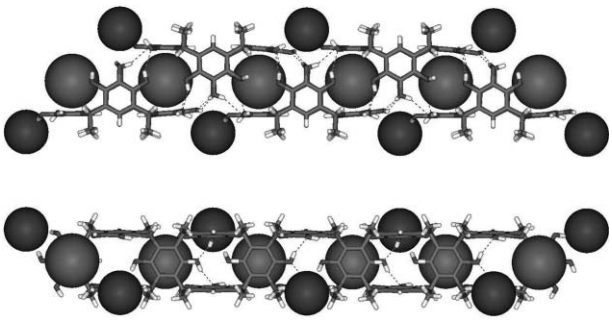

Fig. 2 Crystal packing of **1**·KBr. Side view (top) and top view (bottom).

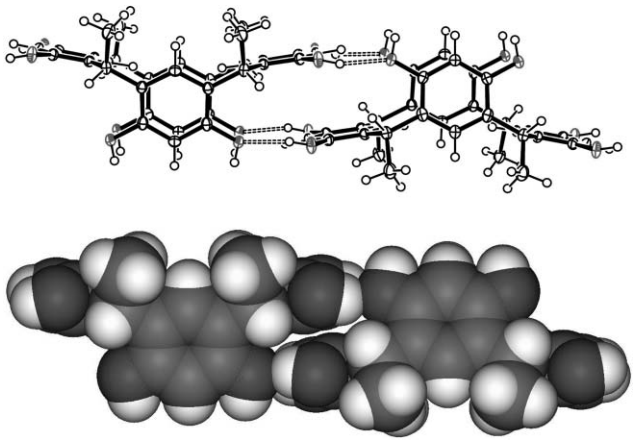

Fig. 3 No complexation of any alkali metal is observed with resorcinarene **2**. Instead, the molecules are directly hydrogen bonded to each other.

All of the complexes, **1**·KBr, **1**·RbCl and **1**·CsBr, include nearly optimal cation–π interaction, where the cation approaches the ring centroid along the normal to the carbon plane in η^6 coordination mode, as shown by theoretical studies[1] and X-ray crystal studies with simple aromatics such as benzene.[14] Center geometries are not common when the cation is coordinated to the aromatic parts of the structures of more elaborate receptors, and where other weak interactions contribute to the complexation like in the case of uranyl salophen receptors[4] and calixarenes.[3]

As a comparison for the pyrogallarene structures, several analogous cocrystallization attempts were carried out on receptor **2** (Scheme 1) with alkali metal salts in MeOH, EtOH, MeOH/H_2O and EtOH/H_2O solutions. All these attempts resulted in either powder precipitate or crystallization of salt free receptor.§ To our surprise, the structure of the salt free receptor was not the expected crown-like conformation with solvent inclusion, but a structure of *C*-methyl resorcinarene **2** in a clear boat conformation (Fig. 3), in which all usually crown conformation stabilising intramolecular hydrogen bonds are replaced by intermolecular hydrogen bonds to solvents or neighbouring resorcinarenes, thus connecting them into a continuous chain, which resembles somewhat the chain of pyrogallarenes **1** in a potassium complex (Fig. 2). However, in the case of resorcinarene **2**, the intermolecular hydrogen bonding (d(D···A) = 2.77 Å) directs the resorcinarenes so close to each other that no room is left above the aromatic ring for alkali metal inclusion, and instead, close intermolecular π···π contact between the opposing aromatic rings is observed (centroid to centroid distance is 3.78 Å and the closest distance between aromatic carbons 3.33 Å). In the case of **2**, close π···π contact is probably favoured by the lack of extra hydrogen bonds between additional hydroxyl groups at 2-positions, which stabilize the molecular cage in the potassium complex of pyrogallarene **1**. This indicates that resorcinarene **2** may not have as strong a tendency to complex alkali metals as pyrogallarenes **1**, and therefore, the additional hydroxyl groups at the 2-position of **1** play a crucial role in the complexation, or at least in complex organisation in the solid state.

Preliminary NMR studies of the complexation in solution showed no host–guest complexation between **1** and KBr, RbCl or CsBr in MeOH-d_4. The reason for this is most probably the competing interactions of solvent and hydroxyl groups of the host as well as the solvation effect of cations, which is generally very strong compared to cation–π interactions. Another reason for the rarity of the experimental evidence of cation–π interactions of alkali metal cations in solution is counter ion separation, which is also difficult to offset by weak cation–π interactions. In some cases

more lipophilic solvent and anions with a more delocalized charge are possible ways to overcome these problems.[2,4]

Although the mass spectrometric, theoretical[11] and extraction studies[12] showed the selectivity of resorcinarenes and pyrogallarenes towards caesium, no explanation to support this was found in the solid state, hence the structures of Rb^+ and Cs^+ proved to be isomorphous with similar interactions between the cation and the receptor. Also, based on the cation–π interactions of potassium with two aromatic rings inside the strongly hydrogen bonded cage of two pyrogallarenes, one may assume that, at least in the solid state, the complexation of potassium by pyrogallarene **1** is very close to optimal interaction and complexation. Further studies on alkali metal complexation and their interactions with resorcinarene type hosts in solution, in the gas phase and in the solid state are underway.

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Notes and references

‡ Crystal data for $C_{32}H_{32}O_{12}\cdot KBr\cdot 5CH_3OH$, M = 887.80, monoclinic, a = 13.1714(6), b = 16.3264(8), c = 18.3847(8) Å, β = 93.276(3)°, V = 3947.0(3) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 1.222 mm^{-1}, 18719 reflections measured, 7308 unique (R_{int} = 0.104) which were used in all calculations. The final $R1$ and $wR2$ were 0.087 and 0.138 for observed data. Crystal data for $C_{32}H_{32}O_{12}\cdot RbCl\cdot 2.5CH_3OH\cdot 0.5H_2O$, M = 818.61, monoclinic, a = 9.2378(2), b = 22.9315(5), c = 17.3511(3) Å, β = 94.206(2)°, V = 3665.7(1) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 1.494 mm^{-1}, 19708 reflections measured, 6734 unique (R_{int} = 0.075) which were used in all calculations. The final $R1$ and $wR2$ were 0.073 and 0.139 for observed data. Crystal data for $C_{32}H_{32}O_{12}\cdot CsBr\cdot 2.5CH_3OH\cdot 0.75H_2O$, M = 914.26, monoclinic, a = 9.3414(1), b = 23.2823(4), c = 17.4432(3) Å, β = 93.767(1)°, V = 3785.5(1) Å^3, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 2.103 mm^{-1}, 21695 reflections measured, 7011 unique (R_{int} = 0.048) which were used in all calculations. The final $R1$ and $wR2$ were 0.077 and 0.161 for observed data.

§ Crystal data for $C_{32}H_{32}O_8\cdot 3CH_3OH\cdot 5H_2O$, M = 730.78, orthorhombic, a = 10.4761(3), b = 16.4356(4), c = 20.9672(5) Å, V = 3610.2(2) Å^3, space group $Pnam$ (no. 62), Z = 4, μ(Mo-Kα) = 0.105 mm^{-1}, 15091 reflections measured, 3064 unique (R_{int} = 0.091) which were used in all calculations. The final $R1$ and $wR2$ were 0.064 and 0.145 for observed data. CCDC 288486–288489. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515143kSee supplementary material for crystallographic details.

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