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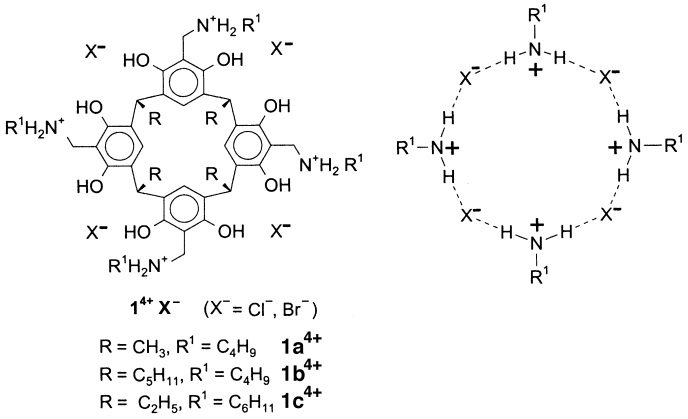
Hydrogen-Bonded Analogues of Cavitands**

Alexander Shivanyuk,* Thomas P. Spaniol, Kari Rissanen, Erkki Kolehmainen, and Volker Böhmer

Multiple hydrogen-bonding interactions are widely used for the design of hollow self-assembled structures capable of molecular encapsulation.[1] In particular, intermolecular hydrogen bonds between urea functions are responsible for the stability of dimeric calixarene capsules,[2] while the slow exchange of guests in self-folded caviplexes is caused by a seam of intramolecular hydogen bonds between amide groups.[3]

Herein we describe a novel type of self-assembled concave structures $\mathbf{1}^{4+} \cdot 4X^-$ in which the shallow socket of a resorcarene is extended by a cyclic hydrogen-bonded array of four halide ions and four ammonium ions attached to the wide rim of the macrocycle. We demonstrate also that $\mathbf{1}^{4+} \cdot 4Cl^-$, but not $\mathbf{1}^{4+} \cdot 4Br^-$, is able to complex certain alcohols in $CDCl_3$ through the formation of hydrogen bonds and inclusion into the π-basic resorcarene cavity.



$\mathbf{1}^{4+}\,X^-$ ($X^- = Cl^-, Br^-$)

R = CH_3, $R^1 = C_4H_9$ **1a**$^{4+}$
R = C_5H_{11}, $R^1 = C_4H_9$ **1b**$^{4+}$
R = C_2H_5, $R^1 = C_6H_{11}$ **1c**$^{4+}$

Condensation of resorcarenes[4] with primary amines and formaldehyde readily gives the corresponding tetrabenzoxazine derivatives.[5] The subsequent cleavage of the benzoxazine rings with HCl or HBr (*n*-butanol, 80 °C) yields the tetraammonium salts $\mathbf{1}^{4+} \cdot 4X^-$ ($X^- = Cl^-$,[6] Br^-) in 80 – 90 % yield.

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Single crystals of $\mathbf{1a}^{4+}\cdot 4\,Cl^-$ were obtained from MeCN/CH_2Cl_2.[7] In the crystalline state $\mathbf{1a}^{4+}$ adopts a slightly distorted cone conformation (Figure 1) which is stabilized

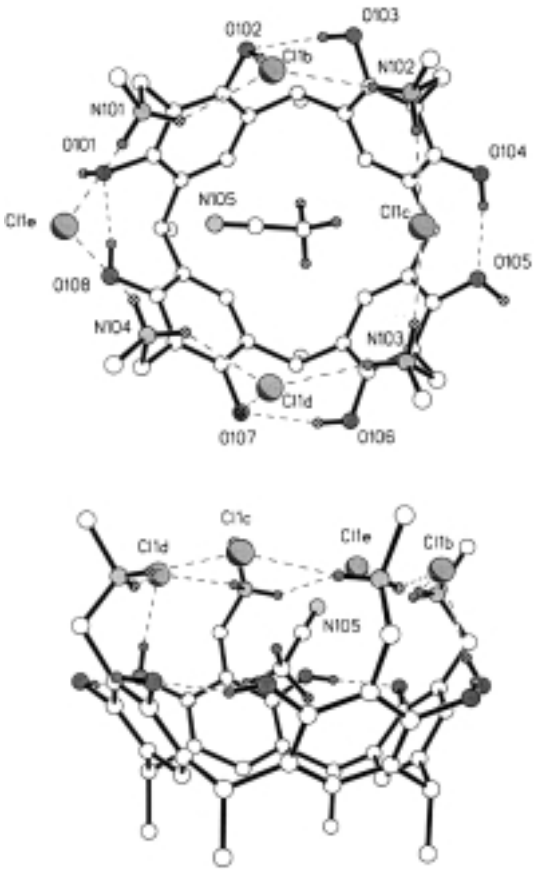

Figure 1. One of the two crystallographically independent $\mathbf{1a}^{4+}\cdot 4\,Cl^-$ complexes. Only the first carbon atoms of pendant butyl groups are shown, and the C-bound hydrogen atoms of the resorcarene molecule are omitted for clarity. Hydrogen bonds are indicated as dotted lines and heteroatoms are darkened. Top: top view; bottom: side view. Selected distances [Å]: N104-Cl1d 3.098(2), N104-Cl1e 3.211(2), N102-Cl1c 3.193(2), N102-Cl1b 3.230(2), N103-Cl1d 3.181(2), N103-Cl1c 3.227(2), N101-Cl1b 3.205(2), N101-Cl1e 3.277(2), O107-Cl1d 2.976(2); O106-O107 2.722(2), O104-O105 2.639(2), O103-O102 2.674(2), O108-O101 2.646(2), N101-N105 3.149(4), N104-N105 3.088(3).

by four intramolecular O–H···O–H hydrogen bonds. Each ammonium nitrogen atom forms two hydrogen bonds with two neighboring anions which results in a 16-membered $Cl^-\cdots H{-}N^+{-}H\cdots Cl^-$ array above the wide rim of the resorcarene molecule. In addition, two hydrogen bonds are found between the chloride ions and the resorcinol hydroxyl groups within the same $\mathbf{1a}^{4+}\cdot 4\,Cl^-$ unit while two other hydroxy groups form hydrogen bonds with chloride ions of the neighboring $\mathbf{1a}^{4+}\cdot 4\,Cl^-$ complexes. The structure of $\mathbf{1a}^{4+}\cdot 4\,Cl^-$ possesses a cavity of $8.4\times 8.3\times 5.3$ Å^3 in which one acetonitrile molecule is included. The distances between the nitrogen atom of the acetonitrile molecule (N105) and two neighboring ammonium nitrogen atoms (N101, N104) are rather short (Figure 1), probably because of ion–dipole and/or weak hydrogen-bonding interactions between the host and the guest. Thus, the shallow cavity of the resorcarene is significantly extended[8] by the cyclic hydrogen-bonded array of ammonium and chloride ions.

The ^{1}H NMR spectra of $\mathbf{1}^{4+}\cdot 4\,Cl^-$ (500 MHz, 303 K) in $CDCl_3$ show one set of sharp signals for the protons of the resorcarene skeleton, which is in accordance with a C_{4v}-symmetric structure. NOE and ^{1}H-^{15}N GHSQC experiments prove that the sharp singlet at $\delta = 9.5$ and the broadened resonance at $\delta = 7.8$ (Figure 2a) correspond to the protons of

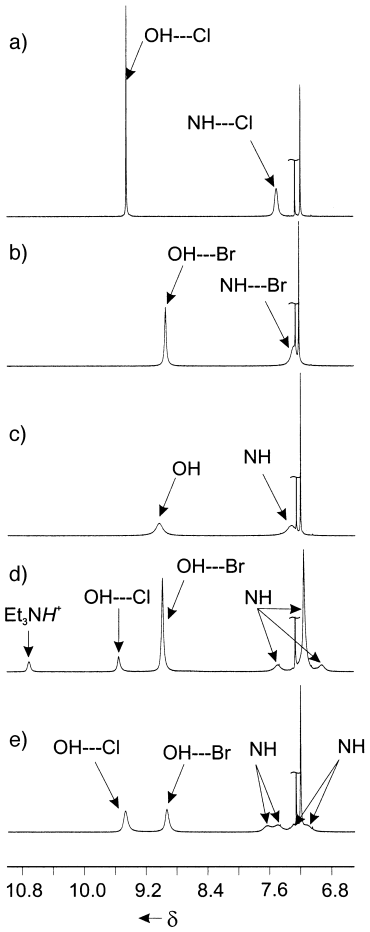

Figure 2. The lowfield region of the ^{1}H NMR spectra ($[\mathbf{1c}^{4+}\cdot 4\,Cl^-] = [\mathbf{1c}^{4+}\cdot 4\,Br^-] = 10^{-2}$ M, $CDCl_3$, 500 MHz). The residual signal of $CHCl_3$ is shortened: a) $\mathbf{1c}^{4+}\cdot 4\,Cl^-$ at 303 K; b) $\mathbf{1a}^{4+}\cdot 4\,Br^-$ at 303 K; c) $\mathbf{1a}^{4+}\cdot 4\,Br^- + Et_3NH^+Cl^-$ at 303 K; d) $\mathbf{1a}^{4+}\cdot 4\,Br^- + Et_3NH^+Cl^-$ at 223 K; e) $\mathbf{1c}^{4+}\cdot 4Cl^- + \mathbf{1c}^{4+}\cdot 4\,Br^-$ at 303 K.

OH and NH_2^+ groups, respectively. The unusually high chemical shift for the OH protons can be explained by the hydrogen bonds to the Cl^- ions which are also observed in the crystalline state. The ^{1}H NMR spectra of $\mathbf{1}^{4+}\cdot 4\,Br^-$ are similar to those of the chloride analogues (Figure 2b), which suggests that the two complexes have the same structure. The OH resonance of $\mathbf{1c}^{4+}\cdot 4\,Br^-$ is shifted upfield by $\Delta\delta = 0.5$ relative to the corresponding signal in $\mathbf{1c}^{4+}\cdot 4\,Cl^-$. This shift is probably a consequence of the weaker basicity (and hence the lower hydrogen-bonding ability) of the bromide ion. The ^{1}H NMR spectra of $\mathbf{1c}^{4+}\cdot 4\,X^-$ do not change considerably upon cooling the solution to 223 K. Thus, the O–H···O and O–H···X^- hydrogen bonds present in the crystalline state cannot be distinguished. In general, however, the structure in

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solution is in agreement with the cavitand-like structure found in the crystal, and represents a rare example of the binding of four anions[9] by a single receptor molecule.[10]

Addition of $Et_3NH^+Cl^-$ to the solution of $\mathbf{1c}^{4+}\cdot 4Br^-$ in $CDCl_3$ at 303 K results in fast anion exchange and broad average NH and OH signals (Figure 2c). At 223 K the exchange becomes slow and the OH resonance splits into two singlets corresponding to the hydroxyl groups hydrogen bonded to Cl^- and Br^- ions (Figure 2d). The ratio between these signals is close to 1:4, which is in accord with the Cl:Br ratio.[11] The signal of the NH protons splits into three broadened peaks presumably because of the formation of heterocomplexes in which both anions are bound to the same tetracation. Anion exchange between $\mathbf{1c}^{4+}\cdot 4Cl^-$ and $\mathbf{1c}^{4+}\cdot 4Br^-$ is slow on the NMR timescale, even at 303 K (Figure 2e). This result reflects the high stability of the hydrogen-bonded array in $\mathbf{1c}^{4+}\cdot 4X^-$ which must be broken twice to exchange one anion. Although the chemical shifts of the OH signals are the same as in pure $\mathbf{1c}^{4+}\cdot 4Cl^-$ and $\mathbf{1c}^{4+}\cdot 4Br^-$, the four broadened resonances of the NH_2^+ protons suggest that the equilibrium involves heterocomplexes. Essentially the same ^{1}H NMR spectroscopic results were obtained for $\mathbf{1a}^{4+}\cdot 4X^-$ and $\mathbf{1b}^{4+}\cdot 4X^-$.

The ^{1}H NMR spectroscopic studies of $\mathbf{1a}^{4+}\cdot 4Cl^-$ in combination with the crystal structure strongly suggest that the complexes $\mathbf{1}^{4+}\cdot 4X^-$ ($X^- = Cl^-$, Br^-) keep a firm cavitand-like structure in $CDCl_3$ in which each anion is hydrogen bonded to two ammonium ions and two neighboring hydroxyl groups of the resorcinol rings. Therefore, we expected that small molecules fitting into the resorcarene cavity and capable of hydrogen bonding with halogen ions and/or NH_2^+ groups could be included by $\mathbf{1}^{4+}\cdot 4X^-$ in apolar solvents.

Indeed, $\mathbf{1}^{4+}\cdot 4Cl^-$ binds several aliphatic alcohols in $CDCl_3$. The guest exchange, for example, in the system $\mathbf{1c}^{4+}\cdot 4Cl^-$/*n*BuOH, is slow on the NMR time scale at 223 K (500 MHz). The ^{1}H NMR spectrum contains three broadened signals for the complexed butanol molecule at $\delta = 0.36$ (CH_2) -0.89 (CH_2), and -2.29 (CH_3, $\Delta\delta = -3.1$), which is clearly a result of its inclusion into the π-basic resorcarene cavity (Figure 3a).

The OH and NH signals of $\mathbf{1c}^{4+}\cdot 4Cl^-$ shift to higher and lower field, respectively, upon complexation (Figure 3b). This effect can be explained by the formation of hydrogen bonds between the OH group of *n*-butanol and the polar wide rim of $\mathbf{1c}^{4+}\cdot 4Cl^-$.[12] In principle, this could include both O–H$\cdots$Cl and HO$\cdots H_2N^+$ interactions, however, definite conclusions cannot be drawn from the NMR data.

The signals of the complex grow with increasing amounts of *n*BuOH, and at a ratio of [*n*BuOH]:[$\mathbf{1c}^{4+}\cdot 4Cl^-$] = 10:1 no free $\mathbf{1c}^{4+}\cdot 4Cl^-$ is detected (Figure 3b). Integration of appropriate signals shows that the inclusion complex has a 1:1 stoichiometry and leads to stability constants of $47 \pm 5\,M^{-1}$ at 213 K and $29 \pm 5\,M^{-1}$ at 223 K.

A similar complexation was also observed with *n*-propanol, 2-butanol, 2-methyl-2-propanol (*t*BuOH), and cyclopentanol. In the presence of a 1:1 mixture of *n*BuOH and *t*BuOH both complexes are formed in a 1:1 ratio, which shows there is no selectivity for their inclusion into the cavity of $\mathbf{1}^{4+}\cdot 4Cl^-$. For ethanol, 2-propanol, *n*-pentanol, *n*-hexanol, and cyclohexanol only the characteristic changes of the NH and OH signals were detected, while no strong upfield shifts could be observed for the CH protons of the guests. These results can be explained by an imperfect fit of the alkyl groups into the cavity of $\mathbf{1c}^{4+}\cdot 4Cl^-$; while the Et and *i*Pr groups are too small, the *n*-pentyl, *n*-hexyl, and cyclohexyl units are too big to be efficiently included.

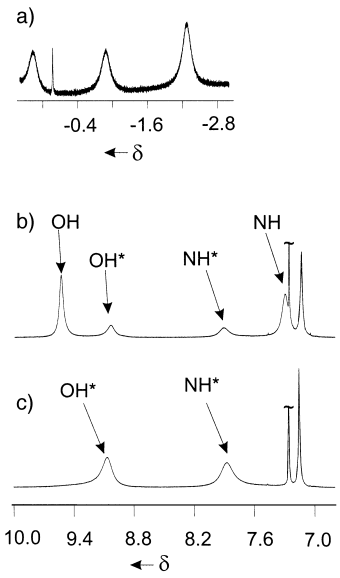

Figure 3. Sections of the ^{1}H NMR spectrum of $\mathbf{1c}^{4+}\cdot 4Cl^-$ in $CDCl_3$ in the presence of *n*BuOH at 223 K ([$\mathbf{1c}^{4+}\cdot 4Cl^-$] = 10^{-2} M, $CDCl_3$, 500 MHz): a) the signals of the shielded butyl chain; b) the aromatic region when [*n*BuOH]:[$\mathbf{1c}^{4+}\cdot 4Cl^-$] = 1:1; c) the aromatic region when [*n*BuOH]:[$\mathbf{1c}^{4+}\cdot 4Cl^-$] = 10:1. The NH and OH signals of the complex with *n*BuOH are marked with an asterisk. The assignment of the signals is based on ^{1}H-^{15}N GHSQC experiments.

The complexation of alcohols is anion dependent and no interaction occurs between $\mathbf{1c}^{4+}\cdot 4Br^-$ and ROH in $CDCl_3$. This result could be a consequence of the weaker O–H$\cdots X^-$ hydrogen bonds and/or to a smaller size of the intramolecular cavity produced through blocking by bulky bromide ions.

In conclusion, the attachment of four ammonium groups to the wide rim of resorcarenes leads to an effective complexation of four anions within a remarkably stable hydrogen-bonded cyclic array. The complexes $\mathbf{1}^{4+}\cdot 4X^-$ can be considered as hydrogen-bonded analogues of cavitands[13] which are capable of anion-dependent complexation of certain alcohols in $CDCl_3$. The almost unlimited structural diversity, the possible chirality,[5] and the simple synthesis of $\mathbf{1}^{4+}\cdot 4X^-$ make these systems a promising new family of self-assembled receptors.

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[12] This result is also in accordance with the fact that no interaction occurs between the acetonitrile molecule and **1c**$^{4+} \cdot 4\,Cl^-$ in $CDCl_3$.

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Synthesis of the Square-Planar Gallium Species $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (Trip = C_6H_2-2,4,6-*i*Pr$_3$): The Role of Aryl – Alkali Metal Ion Interactions in the Structure of Gallium Clusters**

Brendan Twamley and Philip P. Power*

Electron-precise one- or two-dimensional, molecular gallium clusters can in principle be reduced to afford species which may contain Ga–Ga multiple bonds. For example, reduction of tetraorganodigallanes yields the radical anions $[R_2GaGaR_2]^{-\bullet}$ **1**[1] and **2**.[2]

$[R_2GaGaR_2]^{-\bullet}$

1: R = Trip **2**: R = $CH(SiMe_3)_2$

The Ga–Ga distances in **1** and **2** are 0.14 – 0.17 Å shorter than those in the neutral R_2GaGaR_2 precursors, and EPR data show that the unpaired electron resides in a π orbital to give a formal Ga–Ga bond order of 1.5. However, the attempted addition of a second electron to **1** results in rearrangement to the tetrametallic trigallylgallane salt **3**, which has shorter Ga–Ga bonds (av 2.39 Å) than the unreduced species **4** (Ga–Ga, av 2.47 Å) consistent with a formal Ga–Ga bond order of 1.33.[3]

$Na_2[Ga(GaTrip_2)_3]$ **3** $Ga(GaTrip_2)_3$ **4**

An important aspect of the structure of **3** is that the shortest of the three Ga–Ga bonds corresponds to the complexation of the two Na^+ ions between the Trip substituents spanning the bond. Parallel work involving direct reduction of terphenylgallium dihalides has afforded the unprecedented cyclic trigallyl compounds **5**[4a] and **6**[4b] (Mes = C_6H_2-2,4,6-Me_3), or the dimeric **7**[5] which also involve similar interactions between the alkali metal the aryl group across the Ga–Ga bond(s). However, the description of **7** as a "gallyne" on the basis of its short Ga–Ga bond (2.319(3) Å) has generated controversy,[6] since the Na^+ – aryl interactions could also have caused the shortened Ga–Ga distance.[7] Density functional theory (DFT) calculations[8] on the model compounds for **7** – **9**, $Na_2[(GaC_6H_3\text{-}2,6\text{-}Ph_2)_2]$ (**8**), and $Na_2[(GaPh)_2]$ (**9**), suggest that such effects are structurally important since the Ga–Ga distance in **8** (2.362 Å), which has Na^+ – aryl interactions, is about 0.1 Å shorter than that in **9** (2.461 Å) which has no Na^+ – aryl contacts.

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