Anion Inclusion

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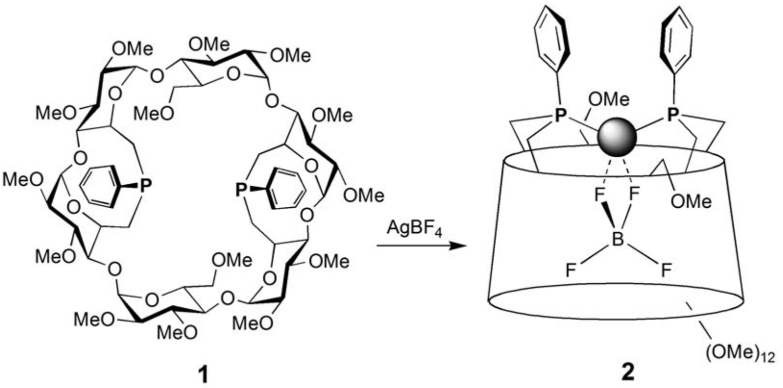
A Metallocavitand Functioning as a Container for Anions: Formation of Noncovalent Linear Assemblies Mediated by a Cyclodextrin-Entrapped NO$_3^-$ Ion**

Laurent Poorters, Dominique Armspach, Dominique Matt,* Loïc Toupet, and Peter G. Jones*

Much effort is currently invested in the design and development of metallated container molecules. Complexes of this type constitute valuable objects for studying the influence of a second coordination sphere on the properties of a metal center[1] and for achieving catalytic reactions in a confined environment.[2] An increasingly prominent field concerns the use of metallocavitands for anion complexation.[3] For example, transition-metal ions that are bound through π interactions to the outside walls of calix[*n*]arenes were shown to be capable of enhancing the receptor properties of these cone-shaped molecules towards anions.[4] A different approach consists of generating coordination cages through metal-templated self-assembly, thereby allowing anions to be retained within the cavity through weak interactions with the metal center.[5] Surprisingly, no example of anion encapsulation with dual binding to a complexed metal ion and an appended cavity has so far been reported. Moreover, the degree of guest encapsulation is rather small in the anion "inclusion" complexes reported to date. We now report the first example of a metallated cyclodextrin that is able to fully encapsulate medium-sized inorganic anions.

The present study was carried out with the cyclodextrin (CD) derivative **1**, a rigidified diphosphine in which the lone pairs of electrons on both phosphorus atoms are directed towards the CD axis.[6] Reaction of **1** in CH$_2$Cl$_2$/THF with AgBF$_4$ afforded complex **2** quantitatively [Eq. (1)]. All NMR data are consistent with a C_2-symmetric chelate complex and indicate the presence of an undistorted, circular-shaped CD torus. These features were confirmed by an X-ray diffraction study (Figure 1), which revealed the presence of two closely related molecules (a and b) in the unit cell. Diphosphine **1** was initially designed as a *trans* chelator,[6] and it is hardly surprising that its bite angle, as observed in complex **2** in the solid state, is rather large (152° on average). Remarkably, the BF$_4^-$ counterion lies deep inside the cavity with two fluorine atoms coordinated to the silver center, which adopts a pseudotetrahedral stereochemistry (Ag-F: 2.598(3) and 2.620(3) Å in a; 2.534(3) and 2.570(3) Å in b).



1

2

(1)

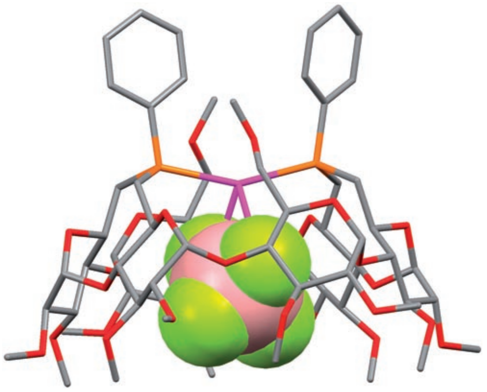


Figure 1. Molecular structure of **2** showing the encapsulated BF$_4^-$ ion. For clarity, a single molecule of the unit cell is shown.

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[*] Dr. L. Poorters, Dr. D. Armspach, Dr. D. Matt
Laboratoire de Chimie Inorganique Moléculaire
Institut de Chimie UMR 7177 CNRS
Université Louis Pasteur
67008 Strasbourg Cedex (France)
Fax: (+33) 3-9024-1749
E-mail: darmspach@chimie.u-strasbg.fr
dmatt@chimie.u-strasbg.fr

Dr. L. Toupet
Groupe Matière Condensée et Matériaux, UMR 6626 CNRS
Université de Rennes 1
35042 Rennes Cedex (France)

Prof. Dr. P. G. Jones
Institut für Anorganische and Analytische Chemie
TU Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)

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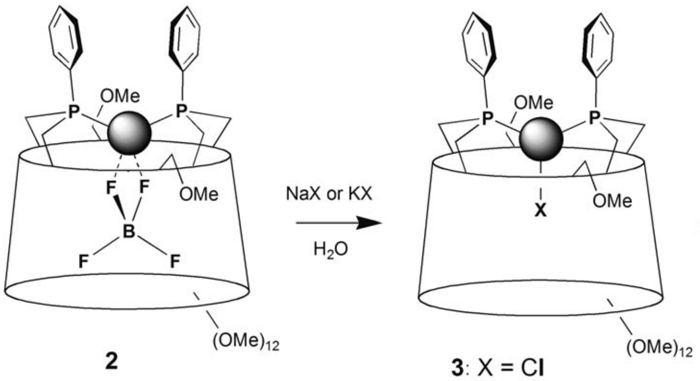
Careful examination of the structures shows that while each coordinated F atom interacts with three inwardly oriented H5 atoms, weak interactions also occur between the other F atoms and some H5 as well as H3 atoms (shortest CH$\cdots$F$_{\text{noncoord}}$ distances: 2.72, 2.80, and 2.86 Å in a; 2.77, 2.84, and 2.97 Å in b). Interestingly, structure **2** represents the first example of a BF$_4^-$ ion that behaves as an F,F-chelating ligand in a mononuclear transition-metal complex.[7] The BF$_4^-$ ion could not be displaced by acetonitrile. Note that a cyclodextrin silver(I) complex able to bind nitrile ligands inside the cavity has already been reported.[8]

To assess the ability of the [Ag(**1**)]$^+$ ion to act as a receptor towards other anions, complex **2** [Eq. (2)] was treated with a solution of NaCl in H$_2$O. This reaction led readily to the chloro complex **3**. As expected for entrapped M–Cl moieties, the ^{1}H NMR spectrum of **3** shows that two symmetrically sited H5 atoms, both belonging to a P-linked glucose unit, have undergone a significant low-field shift ($\Delta\delta = +0.69$ ppm), a good indication for the presence of noncovalent bonds between the cavity wall and the anion. In the solid state (Figure 2), the shortest Cl$\cdots$H–C separations are those involving the C(35′) and C(15′)-bonded H5 atoms (2.96 and 2.99 Å, respectively, in one of the two cocrystallizing molecules of the unit cell). Although these separations are larger than those found in other CDs with M–Cl bonds, they remain typical for weak M–Cl$\cdots$H–C interactions.[9]



(2)

2

3: X = Cl
4: X = Br
5: X = I

The coordinated chloride atom could be reversibly displaced in water with bromide or iodide anions, thereby resulting in **4** and **5**, respectively. In keeping with the presence of larger halide atoms in these complexes, the variation in the chemical shift of the H5 atoms that interact with the halide is larger than that observed for **3** ($\Delta\delta = +0.80$ and $+1.03$ ppm, respectively, versus **1**).

On extending our investigations to oxygen-containing anions we observed that [Ag(**1**)]$^+$ is also able to host a single CH$_3$CO$_2^-$ or NO$_3^-$ ion to form complexes **6**[10] and **7**, respectively. The addition of an excess of NaBF$_4$ to these complexes regenerated **2**. As for the complexes described above, in both molecules a single H5 signal (2H) in the NMR spectrum is significantly affected by the presence of the anion inside the cavity. A single-crystal X-ray diffraction study carried out on **7** revealed that the nitrate ion is fully included in the cavity, with two oxygen atoms coordinated to the tetrahedrally coordinated silver atom (Figure 3). As in **3**, additional, noncovalent binding occurs between the anion (here through the coordinated oxygen atoms) and an H5 atom of each P-substituted glucose unit ($\Delta\delta_{\text{H-5}} = +0.38$ ppm).[11] Remarkably, unlike the structures of **2** and **3** in which the CD units arrange themselves in a typical fishbone structure, the CD units of **7** are stacked on top of each other to form nitrate-containing tubes. The observed solid-state organization is clearly anion-templated and involves mainly hydrogen-bonding interactions between the protruding oxygen atom of the nitrate ligand at the secondary face and a *meta*-hydrogen atom of each PPh ring (average distance 2.77 Å). The *para*-H atom of one of the two PPh units also interacts with the NO$_3^-$ ion (CH$\cdots$O: 2.83 Å). The distance between two successive silver ions is only 11.70 Å (versus 14.16 Å in **2** and 14.10 Å in **3**).

Finally, it is worth mentioning that ^{31}P NMR spectroscopy is very effective at discriminating between the different anions mentioned in this study, thus making [Ag(**1**)]$^+$ in particular a good

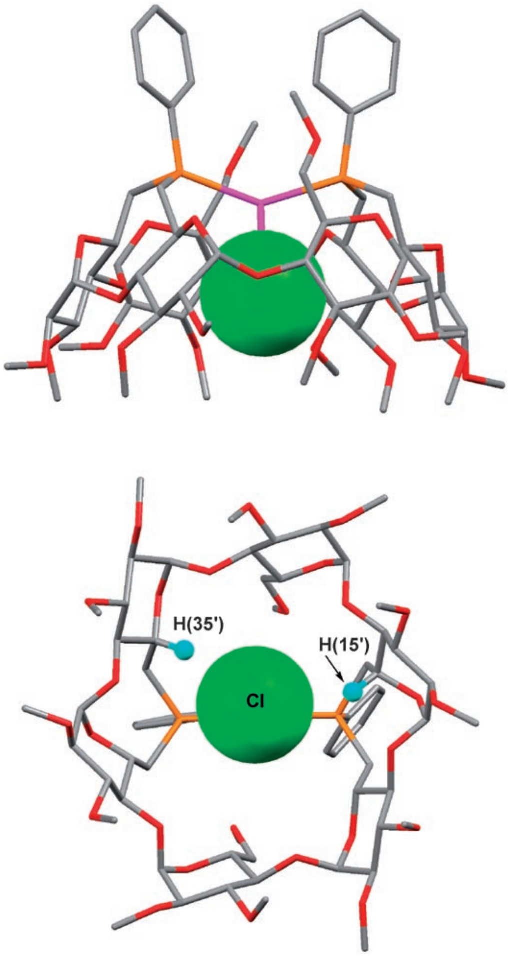


Figure 2. Molecular structure of **3**: side view (top) and view from the secondary face (bottom).

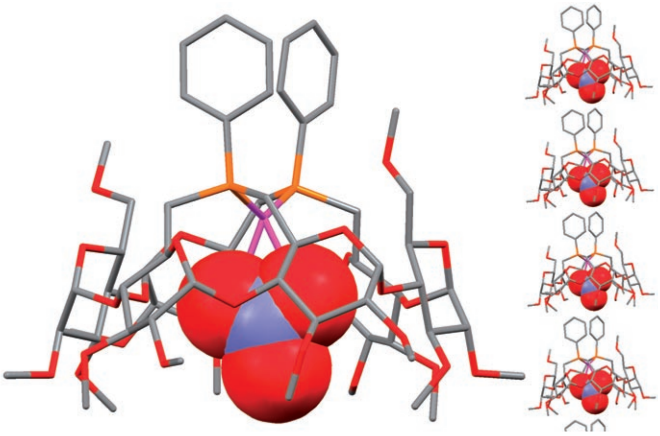


Figure 3. X-ray structure of **7** showing the encapsulated NO_3^- ion.

probe for sensing medium-sized anions present in aqueous media (Figure 4).

Overall, we have shown that the $[Ag(\mathbf{1})]^+$ metallocavitand is perfectly suited for hosting medium-sized, coordinating anions. The present study provides a rare example of anion encapsulation in a funnel-shaped complex and illustrates the fact that a number of CH−X bonds may contribute to the stabilization of encapsulated anions inside a cyclodextrin in combination with dative anion–metal and electrostatic interactions. These results also open the way to the anion-mediated construction of chiral superstructures.

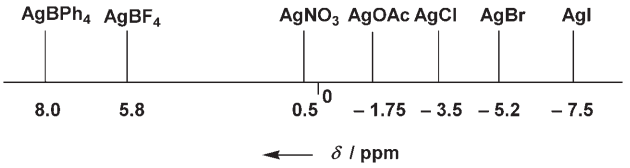


Figure 4. Chemical shifts of the complexes $[AgX(\mathbf{1})]$ in the ^{31}P NMR ($CDCl_3$) spectra.

Experimental Section

Full experimental details including X-ray structural data are given in the Supporting Information. CCDC-272302, 625926, and 601087 (**2**, **3**, and **7**, respectively) contain 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.

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[10] A spatial proximity between the Me group and the H3 protons of the P-bridged glucose units was established by a ROESY NMR experiment.

[11] This complex as well as **2** are weak electrolytes in CH_3CN (20 °C).