Gas-phase Ion Complexes of a Perfluorinated Cryptand with O_2 and F^-

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The formation and characterization of gas-phase ion complexes of a perfluorinated cryptand, perfluoro 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, with F^- and O_2 demonstrates that intrinsic host–guest chemistry may be examined in the solvent-free environment of a mass spectrometer.

Cryptands are macrobicyclic compounds[1] that form stable complexes with metal cations and may act as hosts for specific guests *via* molecular recognition.[2] Perfluorinated cryptands[3] are particularly interesting derivatives because they are physiologically compatible and may possess important biological properties, such as the ability to carry oxygen and transport ions through membranes. Recently, the unusual ability of fluorinated macrocycles to bind fluoride ion *via* four C–H hydrogen bonds in solution was reported.[4] Additionally, the complexation chemistry of molecular oxygen and fluoride

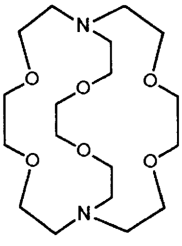


Fig. 1 Structure of perfluorocryptand

with several binuclear copper azo-cryptands[5] and azo-oxo-crown ethers[6] were examined in solution. In the light of the increasing interest in understanding fundamental aspects of host–guest interactions, we have initiated an effort to examine intrinsic host–guest chemistry in the solvent-free environment of a mass spectrometer. Our preliminary results indicate that macrocycles such as crown ethers demonstrate an interesting array of complexation chemistry in the gas phase.[7]

The adducts of interest, $(M + O_2)^{-\bullet}$ and $(M + F)^-$, were formed *via* ion–molecule reactions of perfluoro 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Fig. 1) in the source of a triple quadrupole mass spectrometer[8] or in a four sector JEOL/HX110/HX110 mass spectrometer.[†] The structures of the ion complexes were characterized *via* low or high energy collision induced dissociation (CID).[9]

The high energy CID spectrum of the molecular anion, $M^{-\bullet}$, of the perfluorocryptand, in Fig. 2(*a*), shows similar fragmentation patterns to the low energy CID spectrum. This spectrum serves as a comparison to the CID spectrum recorded for $(M + F)^-$ and $(M + O_2)^{-\bullet}$ adducts. The CID spectrum of $M^{-\bullet}$ contains fragment ions at *m/z* 346, 443, 559, 676, 792 and 908 due to cleavage of the bicyclic structure. The fragments at *m/z* 908, 792 and 676 are due to elimination of one, two or three units of C_2F_4O, respectively. These fragment ions likely retain a monocyclic structure, with the cleavages of the C_2F_4O units occurring from one branch of the cryptand. The fragment ions at *m/z* 559 and 443, are formed *via* elimination of C_4F_9N in conjunction with two or three units of C_2F_4O, respectively. These ions likely have acyclic structures because cleavage of one of the nitrogen-containing bridges disrupts the entire macrocyclic skeleton during the dissociation process.

Moderately abundant $(M + F)^-$ adducts (relative abundance is 10% compared to $M^{-\bullet}$) are formed by reaction of F^- with the cryptand molecules. The high energy CID spectrum of these adduct ions, shown in Fig. 2(*b*), is similar to the CID spectrum for $M^{-\bullet}$, with the exception that each fragment ion is shifted to a higher mass by 19 u (due to the fluorine addition). Only this series of fragment ions at $(\text{fragment} + F)^-$ is observed, indicating that the fluorine is *always* retained by the ionic portion during dissociation. The most abundant dissociation process is loss of two C_2F_4O units. The simple loss of $F\cdot$ or F_2 is not observed. This suggests a very strong cryptand–fluoride binding interaction. A possible mechanism for formation and dissociation of $(M + F)^-$ is shown in Scheme 1. Upon activation, the fluoride attacks the least nucleophilic carbon position, which promotes ring opening, resulting in a branched monocyclic structure. This could then undergo facile elimination of one or two C_2F_4O units. The initial adduct structure may be a ring-opened monocyclic structure or an anion–molecule complex with the fluoride ion stabilized through ion–dipole attractions within the cavity of the cryptand (as shown).

When O_2 is admitted to the source, the $(M + O_2)^{-\bullet}$ adduct is typically 50% of the abundance of the non-complexed molecular anion, $M^{-\bullet}$. A previous study has shown that the most likely reaction occurring to produce $(M + O_2)^{-\bullet}$ is the addition of O_2 to $M^{-\bullet}$.[7] The CID spectrum of $(M + O_2)^{-\bullet}$ reveals similarities to the CID spectrum of $M^{-\bullet}$ (see Fig. 3). The same series of fragment ions seen in the CID spectrum of $M^{-\bullet}$ is observed, in addition to a series of less abundant

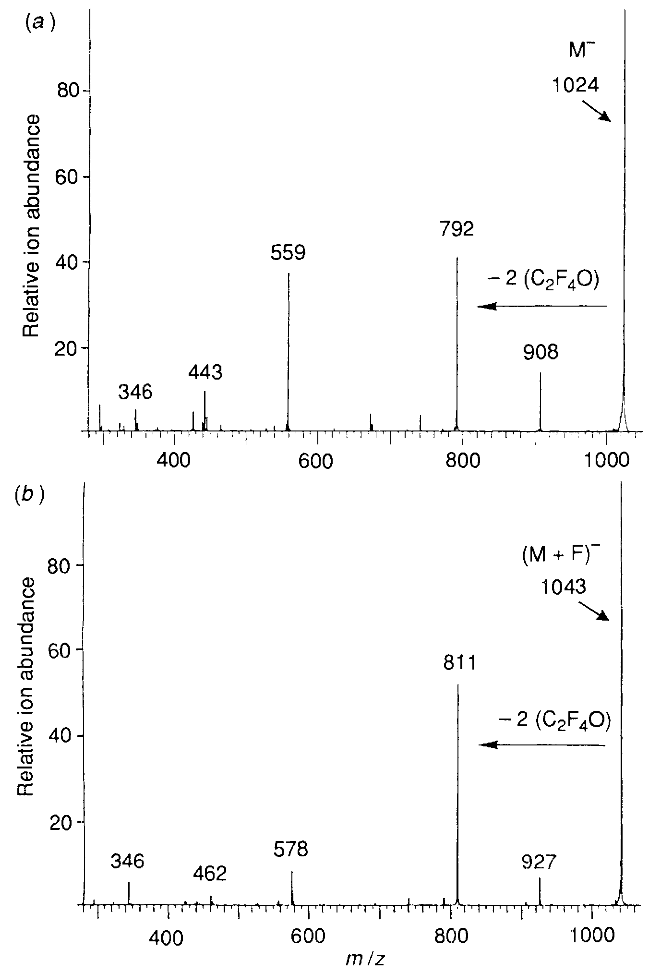


Fig. 2 (*a*) High energy CID spectrum of the molecular anion, $M^{-\bullet}$, of perfluorocryptand.[‡] (*b*) High energy CID spectrum of the $(M + F)^-$ adduct of perfluorocryptand.[‡]

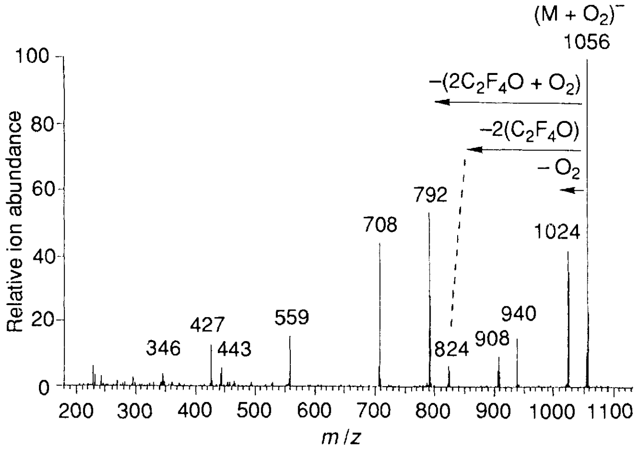
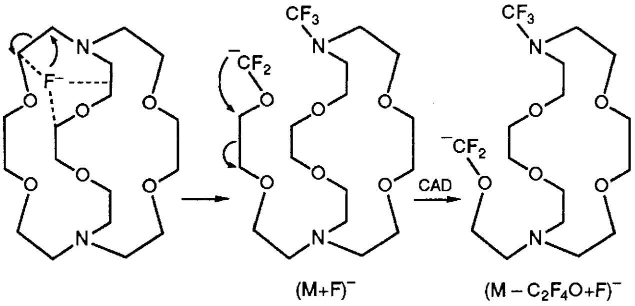


Fig. 3 Low energy CID spectrum of the $(M + O_2)^{-\bullet}$ adduct of perfluorocryptand[§]

[†] Located in the Massachusetts Institute of Technology Mass Spectrometry Facility.

[‡] For the sector experiments, fluoride adducts were generated by fast atom bombardment ionization of a mixture of NaF with the perfluorinated cryptand. CID was done by using xenon as the collision gas and a collision energy of 2 keV.

[§] For the triple quadrupole mass spectrometric experiments, the perfluoro cryptand was introduced into the gas phase *via* a solids probe. O_2 or 1,1-difluoroethylene (as a source of F^-) was admitted into the source as reagent gas, and methane was added to attain a manifold pressure of about 1×10^{-5} Torr. Methane was used to aid in the production of thermal electrons for negative ionization. Reactions occurred in the source region to produce the desired adduct ions. Collision induced dissociation of the selected adduct ion was performed by passing the adduct ion into the centre collision quadrupole at 25 eV kinetic energy. Argon, the collision gas, was admitted to 2 mTorr which corresponds to multiple collision conditions.



Scheme 1 Proposed mechanism for dissociation of $(M + F)^-$ adducts

fragments at $(\text{fragment} + O_2)^{-\bullet}$. This dual series indicates that O_2 is preferentially eliminated during the dissociation processes, but also may be retained by the ionic portion. This contrasts with the dissociation of $(M + O_2)^{-\bullet}$ adduct ions of perfluoro crown ethers. For those adducts, retention or elimination of O_2 was equally favoured. Although absolute quantitative conclusions about binding energies cannot be drawn, it appears that O_2 is bound less strongly to the cryptand than to the crown ethers. Additionally, the loss of simple O_2 occurs to a great extent, resulting in $M^{-\bullet}$ at m/z 1024. This loss was never a predominant process for the crown ether–O_2 adducts. This adds support to the proposal that the cryptand O_2 adducts are more loosely bound than the crown–O_2 complexes.

It was proposed that the gas-phase crown ether–O_2 adduct ions were perhaps inclusion complexes in which the O_2 was electrostatically bound in the cavity of the crown ether,[7] and this rationalized the strong binding interactions. The increasingly sterically hindered structure of the cryptand may disfavour formation of such a complex in the gas-phase, however, and result in the weaker complexation observed in the present study.

The support of the Welch Foundation, and an ASMS research award are gratefully acknowledged. The assistance of C.-C. Liou for some of the triple quadrupole results and J. A. Hill for the sector experiments with the array detector is acknowledged. The MIT Mass Spectrometry Facility acknowledges a grant from NIH (RR00317) awarded to Professor Klaus Biemann.

Received, 10th July 1991; Com. 1/03470G

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