The Coordination Chemistry of the CF Group of Fluorocarbons: Thermodynamic Data and Ab Initio Calculations on CF – Metal Ion Interactions

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Abstract: Metal complexes ($M = Li^+$, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+) of the two closely related pairs of macrocycles **FN_2O_4** and **HN_2O_4** (26-fluoro-4,7,13,16-tetraoxa-1,10-diaza-tricyclo[8.8.7.1,20,24]hexacosa-20,22,24(26)-triene and 4,7,13,16-tetraoxa-1,10-diaza-tricyclo[8.8.7.1,20,24]hexacosa-20,22,24-(26)-triene, respectively) and **FN_2O_3** and **HN_2O_3** (23-fluoro-4,7,20-trioxa-1,10-diazatricyclo[8.7.5.1,12,16]tricosa-12,14,16-(23)-triene and 4,7,20-trioxa-1,10-diaza-tricyclo[8.7.5.1,12,16]tricosa-12,14,16(23)-triene, respectively) [optimized synthesis yields for **FN_2O_3** of 73 % and for **FN_2O_4** of 70 %] were investigated by potentiometry and calorimetric titrations. A comparison of the complexes of the fluoro cryptands **FN_2O_4** and **FN_2O_3** with those of the closely related macrocycles **HN_2O_3** and **HN_2O_4** provides information on the stabilizing effect of CF – M interactions, since the two types of ligand differ only in the substitution of the fluorine atom by hydrogen in the latter compounds. In most cases the fluoro cryptands form more stable complexes (up to 3.5 log$K$ units) with the metal ions. This phenomenon is most pronounced when the radius of the metal ion and the size of the macrocyclic cavity are complementary. Mismatched metal complexes of, for example, Cs^+ with **FN_2O_4** or **HN_2O_4** are of equal stability, since the metal ion is too large to be coordinated by the CF group within the macrocyclic cavity. The X-ray crystal structure of the most stable complex **FN_2O_4**-$Ba(ClO_4)_2$ was determined, and its short $F{-}Ba^{2+}$ distance of 284.2(2) pm indicates significant stabilization due to $F{-}Ba^{2+}$ interactions. Ab initio calculations on the model reactions $Li^+(OMe_2)_3(C_6H_5F) \rightarrow Li^+(OMe_2)_3 + C_6H_5F$ and $Li^+(C_6H_5F) \rightarrow C_6H_5F$ gave $Li^+{-}F$ interaction energies of 43.7 and 78.7 kJ mol^{-1}, respectively (counterpoise-corrected MP2 energies on DFT(BP86)-optimized structures). These values amount to about 64 and 51 %, respectively, of the corresponding calculated $Li^+(OMe_2)_3 - OMe_2$ and $Li^+ - OMe_2$ binding energies.

Keywords: ab initio calculations · calorimetry · coordination chemistry · cryptands · fluorocarbons

Introduction

The coordination chemistry of fluorocarbons is now well established.[1] The first systematic investigations of fluorocarbon – metal coordination were performed in the early 1980s by Glusker, Murray-Rust et al., who found unusually short CF – metal ion contacts in some X-ray crystal structures.[2] In the following years further complexes displaying these features, mainly with the hard metal ions of Groups 1 and 2, were structurally characterized,[3, 4] but as late as the early 1990s evidence for such interactions in solution remained scarce.[5] This changed when Plenio et al. synthesized partially fluorinated crown ethers and cryptands, which allowed the first systematic studies of CF – metal ion coordination.[6] Apart from X-ray crystal structure determinations, NMR spectroscopy and picrate extraction were used to investigate the nature of CF – metal ion interactions.[7] Erker et al.,[8] Marks et al.,[9] and others[10] discovered that the CF groups of fluorinated phenylborate ligands can allow hemilabile coordination of cationic zirconocenes. Erker et al. suggested that such weak contacts might be used to reversibly control the catalysis of Ziegler – Natta-type olefin transformations.

While numerous X-ray crystal structures and NMR-spectroscopic studies have produced a fairly clear picture of the coordination behavior of fluorocarbons towards hard metal ions in the solid state and in solution, quantitative data on the coordinating ability of the CF group have remained scarce. Apart from two dynamic NMR studies by Siedle et al.[11] and

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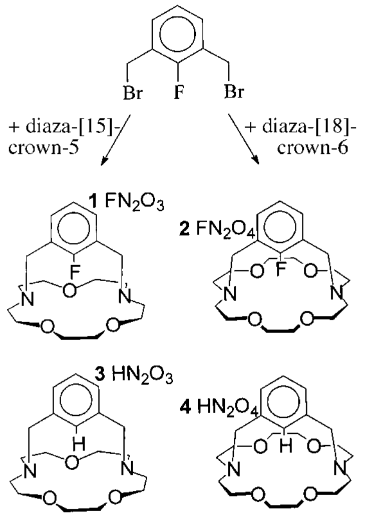
Erker et al.,[12] little is known about the energetics of CF–metal interactions.

To close this gap, we determined the stability constants and enthalphic/entropic effects in complexes of two fluoro cryptands **FN_2O_4** and **FN_2O_3** and—to gauge the effect of the CF group—their fluorine-free counterparts **HN_2O_4** and **HN_2O_3** by potentiometry and calorimetric titrations. Ab initio calculations were carried out on the simplified systems $Li^+(OMe_2)_3(C_6H_5F)$ and $Li^+(OMe_2)_4$ to obtain information on the bonding energetics in the gas phase.

Results and Discussion

Synthesis of the fluoro cryptands: Recently we described the preparation of the fluoro cryptands **FN_2O_3** and **FN_2O_4** by simply mixing the starting materials in acetonitrile and heating the reaction mixture to reflux in the presence of a templating base. This resulted in acceptable yields of 51 and 35%, respectively (Scheme 1). However, especially in the synthesis of the larger cryptand, most of the starting material is converted to the undesired [2+2] addition product. Since we we required larger amounts of these compounds for this study, we optimized our synthesis. This was done by carrying out the reaction at high dilution by simultaneously pumping solutions of the reactants in acetonitrile into a suspension of the templating base in the same solvent. This modified procedure increases the yields to 73 (**FN_2O_3**) and 70% (**FN_2O_4**) and simplifies workup.



Scheme 1. Synthesis of the fluoro cryptands and the structural diagrams of fluorine-free cryptands.

Crystal structure of FN_2O_4-$Ba(ClO_4)_2$: The crystal structure of this complex was of special interest since **FN_2O_4**-$Ba(ClO_4)_2$ has the highest stability constant of all complexes described here (see Tables 1 and 2). Furthermore the Ba^{2+} complex of the **FN_2O_4** ligand is significantly stabilized (+1.7 log*K* units) with respect to the Ba^{2+} complex of **HN_2O_4**.

In the solid state, the barium cation has a coordination number of eleven with short contacts to eight oxygen atoms (274.9(2)–295.2(2) pm; four O atoms of the macrocycle and two bidendate perchlorate anions), two nitrogen atoms (305.2(2)–308.3(2) pm) and one fluorine atom 284.16(17) pm (Figure 1). The fairly short F–Ba^{2+} distance is noteworthy and comparable to those of other Ba^{2+} complexes with related fluoro crown ethers (F–Ba^{2+} 279.9 pm,[6c] 299.0 pm[6e])[1] and provides clear evidence that fluorine is an important donor in the coordination sphere of Ba^{2+}. The remaining Ba^{2+}–O distances are in the normal range; the Ba^{2+}–N contacts are fairly long but not unusually so.

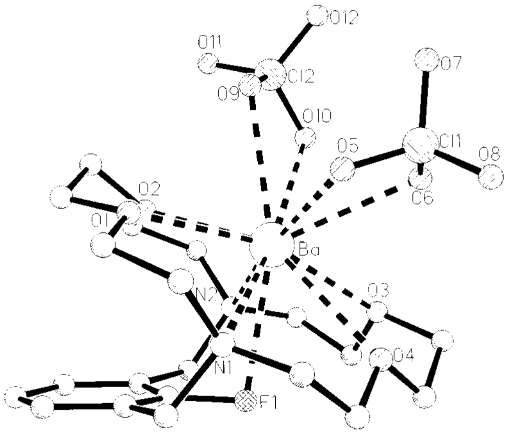


Figure 1. Crystal structure of **FN_2O_4**-$Ba(ClO_4)_2$ (hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ba–O2 274.9(2), Ba–O3 282.7(2), Ba–O1 283.5(2), Ba–F1 284.16(17), Ba–O6 286.3(2), Ba–O5 287.7(2), Ba–O9 288.92, Ba–O4 292.5(2), Ba–O10 295.9(2), Ba–N1 305.2(2), Ba–N2 308.3(2); Ba-C1-F1 96.87(13).

Thermodynamics of the complexation reactions: To evaluate more precisely the role of the CF group in the binding of metal ions in the fluoro cryptands, we determined thermodynamic parameters such as the stability constants and ΔH and $T\Delta S$ values of complexation reactions of **FN_2O_3** and **FN_2O_4** with metal ions from Groups 1 and 2 by means of potentiometric and calorimetric titrations. Since the values derived from such measurements have little meaning on their own,[13] the same techniques were also applied to complexation reactions of the fluorine-free macrocycles **HN_2O_3** and **HN_2O_4** with the same metal ions. These two sets of ligands only differ in that the fluorine atoms of one group are replaced by hydrogen atoms in the other (see Scheme 1). Consequently, to a first approximation any difference in behavior towards metal ions should be due to the presence or absence of CF groups.

It is instructive to follow the stability trends within the series of metal complexes with **FN_2O_4** and **HN_2O_4** (Table 1), which regarding the size of their cavity should be comparable to [2.2.1]cryptand, even though complexes with the latter ligand are more stable (e.g., log*K* ([2.2.1]-Na^+) = 9.3, log*K* ([2.2.1]-K^+) = 8.5)[14, 15] than those of **FN_2O_4**. The most significant result of the titration experiments (see Tables 1 and 2) is that in most cases the complexes of the fluoro cryptands are much more stable than those of the fluorine-free macrocycles **HN_2O_3** and **HN_2O_4**.[16] The most impressive examples are the Li^+ complexes of **FN_2O_3** (log*K* = 4.34) and **HN_2O_3** (log*K* = 0.81), which can be understood by examining the X-ray crystal structures of the two Li^+ complexes.[7] The

Table 1. Stability constants K and thermodynamic values ΔH and $T\Delta S$ for the complexation of metal ions of Groups 1 and 2 with **HN_2O_4** and **FN_2O_4** in methanol at 298.15 K. $\Delta(\log K)$ is the difference between $\log K_F$ and $\log K_H$.

Ion	$\log K_H$ (**HN_2O_4**)	$\log K_F$(**FN_2O_4**)	$\Delta(\log K)$	$-\Delta H$(**HN_2O_4**) [kJ mol^{-1}]	$-\Delta H$(**FN_2O_4**) [kJ mol^{-1}]	$T\Delta S$(**HN_2O_4**) [kJ mol^{-1}]	$T\Delta S$(**FN_2O_4**) [kJ mol^{-1}]
Na^+	4.90	7.02	+2.1	26.7	36.2	1.1	3.7
K^+	5.56	6.71	+1.1	41.5	39.6	−9.9	−1.5
Rb^+	4.68[a]	4.99[a]	+0.3	44.3	45.1	−17.7	−16.8
Cs^+	4.76[a]	4.70[a]	0	44.2	43.7	−17.2	−17.0
Ca^{2+}	2.15	4.36	+2.2	−3.7	2.2	15.9	22.6
Sr^{2+}	4.44	6.55	+2.1	4.6	8.2	20.6	29.0
Ba^{2+}	5.94	7.63	+1.7	28.6	25.3	5.2	18.1
Ag^+	10.39	10.69	+0.3	62.5	54.8	−3.5	5.9

[a] Calorimetric data.

fluoro cryptand offers a stable tetrahedral FO_3 coordination environment for the metal ion, in contrast to **HN_2O_3**-$Li^+(H_2O)$, in which the metal ion is coordinated at the periphery of the cavity in an unusual trigonal-pyramidal O_4 environment with an apical water molecule.

In general, **FN_2O_4** forms more stable complexes with metal ions of Groups 1 and 2 than the fluorine-free macrocycle; the only exception is Cs^+. The largest $\Delta(\log K)$ is observed for the smaller ions Na^+, Ca^{2+}, and Sr^{2+}, and with increasing size of the metal cation, this difference decreases and finally disappears in the Cs^+ complexes. From these data we conclude that only the smaller cations can be located within the cavity and hence profit from being coordinated to the CF group. In other words, the larger the cation, the less closely can it approach the CF group located in the cavity. Consequently, the absence of complementarity between metal ion and ligand cavity leads to a complete loss of relative stabilization, as is the case for **FN_2O_4** with Cs^+.[17]

The structural rigidity of **HN_2O_4**, which may be better viewed as an *m*-xylenediyl-bridged derivative of diaza-[18]crown-6, increases the stability constants for Na^+ and K^+ complexation by roughly three to four orders of magnitude with respect to the monocyclic ligand.[14]

Roughly the same trends as for the larger macrocycles, although less pronounced, are discernible in the complexes of **HN_2O_3** and **FN_2O_3** (Table 2), which in general are less stable due to the smaller number of donor atoms in the ligand. Again the smaller ions Li^+ and Na^+, whose size better suits the macrocyclic cavity, form more stable complexes with the fluoro cryptand, while all other metal complexes are relatively weakly bound and appear to lack significant stabilization by the CF group.

Examining the ΔH and $T\Delta S$ values with respect to CF–metal coordination yields roughly the same conclusions as the analysis of the $\log K$ values: metal ions which are small enough (equal to or smaller than K^+/Ba^{2+} for **FN_2O_4** and equal to or smaller than Na^+ for **FN_2O_3**) to contact the CF donor inside the macrocyclic cavity typically display more negative values of ΔH and $T\Delta S$ than complexes of their fluorine-free relatives. Consequently, all metal ions which are too large have the same $\log K$ and almost equal ΔH and $T\Delta S$ values.

The alkali and alkaline earth metal ions behave quite differently with respect to ΔH and $T\Delta S$. Complexes of Group 1 metal ions are primarily stabilized by high negative reaction enthalpies, while the main stabilizing force for complexes of Group 2 metal ions are entropy effects. Two significant exceptions are **FN_2O_3**-Li^+ and **FN_2O_4**-Na^+, in which a combination of strong enthalphic and entropic terms occurs. These complexes, however, are special cases since the two metal ion radii appear to match perfectly with the cavities of their respective hosts, as judged from the respective crystal structures.[6c, 7] By disregarding entropy losses within the ligands, the enthalpy/entropy phenomenon can be attributed to the higher number of solvent molecules in the first coordination shell of the doubly charged metal ions (this applies to a lesser extent also to Li^+ and Na^+) and is thus typical for cryptand complexes of metal ion.[18]

So far we have evaluated the effect of the CF group by comparing the respective fluorine-containing and fluorine-free macrocycles. This approach appears reasonable, but we also wish to discuss possible limitations. The two sets of ligands **FN_2O_3/FN_2O_4** and **HN_2O_3/HN_2O_4** are very similar but not identical. First, the cavities of the fluorinated cryptands should be somewhat smaller than those of their fluorine-free counterparts, since the fluorine atom is larger than the hydrogen atom. This subtle difference should have some influence on the respective stability constants; nonetheless, we do not expect this to be a significant problem for the evaluation of the data. However, another more important aspect must be considered here: the absence of one donor

Table 2. Stability constants K and thermodynamic values ΔH and $T\Delta S$ for the complexation of metal ions of Groups 1 and 2 with **HN_2O_3** and **FN_2O_3** in methanol at 298.15 K. $\Delta(\log K)$ is the difference between $\log K_F$ and $\log K_H$.

Ion	$\log K_H$ (**HN_2O_3**)	$\log K_F$(**FN_2O_3**)	$\Delta(\log K)$	$-\Delta H$(**HN_2O_3**) [kJ mol^{-1}]	$-\Delta H$(**FN_2O_3**) [kJ mol^{-1}]	$T\Delta S$(**HN_2O_3**) [kJ mol^{-1}]	$T\Delta S$(**FN_2O_3**) [kJ mol^{-1}]
Li^+	0.81	4.34	+3.6	2.1	5.5	2.5	19.2
Na^+	2.86	4.70	+1.8	23.6	24.8	−7.4	1.9
K^+	2.50[a]	2.52[a]	0	24.5	3.3	−10.3	11.0
Ca^{2+}		2.21			0.4		12.2
Sr^{2+}		2.30			1.6		11.5
Ba^{2+}		2.55[a]			1.0		13.5
Ag^+	5.82	6.39	+0.6	37.7	38.5	−4.6	−2.2

[a] Calorimetric data.

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atom in the fluorine-free macrocycles could result in different coordination environments for the fluorinated and fluorine-free metal complexes, and this must influence the differences in the stability constants. This problem appears to be more serious, as the stabilizing effect of a CF group is certainly weaker than that of an oxygen atom. Hence the replacement of a CF donor unit by a solvent molecule might partially compensate for the stabilizing effect of the CF group, which is difficult to quantify. However, for the qualitative interpretation of the data, none of the above effects leads to an overestimation of the CF donor properties, and a relative stabilization of metal complexes with the fluoro cryptands can still be observed and rationalized.

These considerations suggest that it is not straightforward to experimentally determine the contribution of a CF group to the stability of metal complexes. It would be advantageous to exclude the solvation of metal ions, and it seemed that FT ion cyclotron resonance mass spectrometry (FT-ICR MS) could be useful in this respect. However, preliminary experiments showed that the volatility of the fluoro cryptands was too low for quantitative FT-ICR MS measurements.[19]

Ab initio calculations: Computational techniques are a valuable tool for understanding the nature of metal–ligand interactions and for designing highly selective ligands for particular metal ions, which could find applications in the purification of nuclear waste[20] or the construction of sensors for metal ions.[21]

We were interested in calculating the energetic contribution of the CF–metal ion interactions in complexes of the fluoro cryptands. The fluoro cryptands were simplified by modeling the oxygen donor centers with dimethyl ether, and the CF moiety with fluorobenzene. We examined the smallest alkali metal ion, Li^+. The energetics of the four dissociation reactions listed in Table 3 were calculated. Closely related computational experiments were recently performed by More et al., who investigated the binding energy of $Li^+(OMe_2)_n$ complexes by a combined approach of experimental (collision-induced dissociation) and computational techniques,[22] and more recently by Hill et al., who presented detailed studies on Li^+–dimethyl ether[23] and Li^+–dimethoxyethane[24] complexes of various compositions. The calculations by Hill et al. used similar methods and gave similar results to our calculations. Therefore, for a more detailed discussion of the $Li^+(OMe_2)_n$ complexes, see ref. [23].

Several theoretical[25, 26] and experimental studies[27] describe related complexes $M^+(H_2O)_n$ (M = alkali metal). Despite its smaller dipole moment, OMe_2 binds more strongly to Li^+ than water, a fact that was attributed to the much higher polarizability of the ether oxygen atom.

To give a preliminary indication of the energetics involved, the coordination energies of FC_6H_5 and OMe_2 to bare Li^+ ions were compared. The DFT-optimized structures of these two model complexes have Li^+–F and Li^+–O distances of 178.6 and 186.9 pm, respectively (the Li^+–O distance is slightly larger than the HF and MP2 values given in reference [23], but the C-O-C angle of 111.4° compares well with the MP2 data). The calculated C–F distance of 143.8 pm in $Li^+(FC_6H_5)$ is 7.2 pm longer than that of free C_6H_5F, and the F-C-C angle of 116.9° is 2.1° smaller. These structural changes in the ligand upon coordination are somewhat more pronounced than those calculated for $Li^+(OMe_2)$.[22]

The calculated counterpoise-corrected binding energies are listed in Table 3. The HF result for $Li^+(FC_6H_5)$ appears to be somewhat high, whereas the DFT value is somewhat lower than the MP2 value. Taking the counterpoise-corrected MP2 results to give the best, most conservative estimate, the binding energy in $Li^+(FC_6H_5)$ is roughly half (51 %) of that in $Li^+(OMe_2)$. This may be taken as an intrinsic value for a bare Li^+ ion, against which we may judge the more realistic model calculations below. Our result for $Li^+(OMe_2)$ is about 8 kJ mol^{-1} below that calculated at the MP2/6-31 + G*//HF/6-31 + G* level by More et al.[22] (and ca. 5 kJ mol^{-1} below their value on extrapolation to the basis set limit). This is due to our slightly larger DFT-optimized bond lengths (see above).

A more realistic model of the bonding of the metal ions in their cryptand complexes, however, would have to take account of the complete coordination sphere of the metal ion. This was done by coordinating three additional molecules of dimethyl ether. The optimized structure of the resulting complex $Li^+(FC_6H_5)(OMe_2)_3$ is shown in Figure 2. The optimization did not employ symmetry, but the converged structure is close to C_s symmetry, and the phenyl ring bisects the O2-Li-O3 and the C-O1-C angles. The two nonequivalent sets of OMe_2 ligands (O1/O2, O3) differ slightly in their dimensions, likely due to the electronic (π bonding) and steric requirements of the FC_6H_5 ligand. The average Li–O distance is slightly shorter than those calculated at the same level for $Li^+(OMe_2)_4$ (199.7 pm, optimized in S_4 symmetry), consistent with fluorobenzene being a weaker ligand than OMe_2. The lengthening of the Li^+–F distance on inclusion of the three additional OMe_2 ligands is almost 20 pm relative to $Li^+(FC_6H_5)$.

The calculated dissociation energies of the $Li^+(L)(OMe_2)_3$ complexes (Table 3) are lower than those of the $Li^+(L)$ minimal models. The dependence on electron correlation and on the computational method employed is also larger. The DFT values are lower than the HF results, which in turn lie below the MP2 binding energies. The MP2 results for

Table 3. Calculated[a] binding energies [kJ mol^{-1}].

Reaction	BP86	HF	MP2
$Li^+(Me_2O) \rightarrow Li^+\ Me_2O$	150.2 (151.5)	162.5 (164.0)	155.9 (159.0)
$Li^+(C_6H_5F) \rightarrow Li^+\ C_6H_5F$	80.1 (108.7)	101.6 (119.4)	78.7 (112.2)
$Li^+(Me_2O)_4 \rightarrow Li^+(Me_2O)_3 + Me_2O$	44.9 (54.3)	54.8 (63.8)	68.8 (91.2)
$Li^+(Me_2O)_3(C_6H_5F) \rightarrow Li^+(Me_2O)_3 + C_6H_5F$	28.0 (32.5)	34.7 (40.0)	43.7 (60.3)

[a] On DFT(BP86)-optimized structures. Results with counterpoise correction for BSSE (uncorrected results in parentheses).

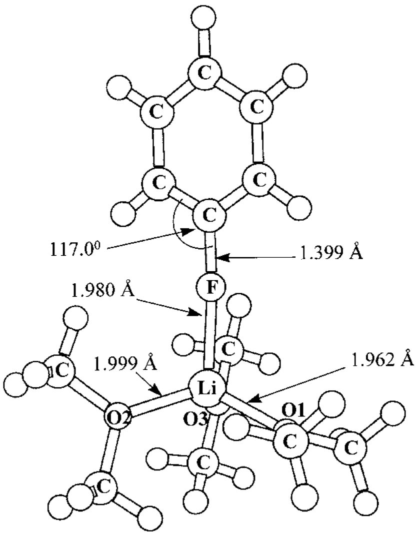

Figure 2. DFT(BP86)-optimized structure of $Li^+(Me_2O)_3(C_6H_5F)$. Selected bond angles [°]: Li^+-F-C 175.5, F-Li^+-O1 110.6, F-Li^+-O2, F-Li^+-O3 104.6.

$Li^+(OMe_2)_4$ are within about 1 kJ mol^{-1} of the MP2/6-31 + G*//HF/6-31 + G* calculations of More et al.[22] It seems possible that the DFT calculations ignore some dispersion contributions related to ligand–ligand repulsion, and the MP2 calculations may overestimate the binding energies. Nevertheless, we regard the larger MP2 values as being more reliable in the present case. The dissociation energy of $(OMe_2)_3Li^+(FC_6H_5)$ is about 62–64 % of that of the $(OMe_2)_3$-Li^+OMe_2 and is almost independent of the level of theory. This is a larger fraction than for the simpler models discussed above and suggests that the steric requirement of the fluorobenzene ligand may be less than that of dimethyl ether, as one would expect from the structures of these two ligands. The steric requirements in crown ether or cryptand complexes will depend on the binding mode. Hence, the present calculations give only an order-of-magnitude estimate for the actual binding abilities of CF groups. Nevertheless, they show that fluorobenzene should be viewed as a normal type of ligand for metal cations.

In crown ether and cryptand complexes containing a CF group, the binding of the metal cation is usually not along the C–F axis but at C-F-Li angles smaller than 180°, typically around 100°. We have investigated the loss in binding energy due to bending by reducing the C-F-Li angle in the $Li^+(FC_6H_5)$ model complex from 180° to 100° in steps of 20°. Figure 3 shows the energy curves obtained when all other degrees of freedom were reoptimized for each C-F-Li angle with bending in or out of the phenyl plane. While the energy loss becomes significant for small angles of in-plane bending, the curve for out-of-plane bending is relatively shallow. Even at 100°, the energy loss is only about 10 kJ mol^{-1}. Of course the energy dependence in the real systems is also influenced by steric requirements of the ligands, which in the case of the fluoro cryptands favors a C-F-M angle close to 100°.[1] However, the shortest F–M distances are observed when this angle is close to 180°. An instructive example are the different F–Cs^+ distances in the X-ray crystal structure of a cesium cation embedded in a soccer-ball-like fluoro ligand.[6b]

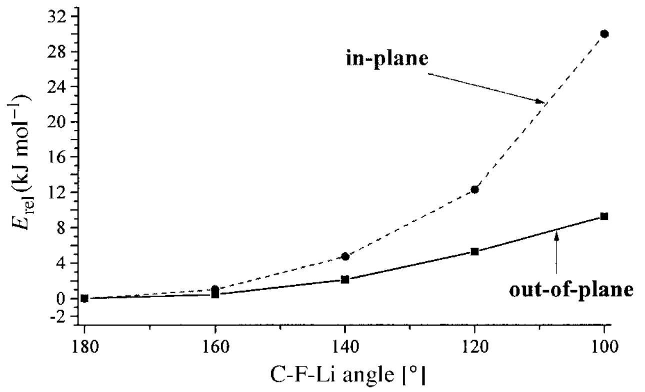

Figure 3. Dependence of the DFT (BP86) energy of $Li^+(FC_6H_5)$ on the C-F-Li angle. For each C-F-Li angle, all other degrees of freedom were optimized.

Summary and Conclusions

A potentiometric and calorimetric study of the coordination behavior of the two fluoro cryptands $\mathbf{FN_2O_4}$ and $\mathbf{FN_2O_3}$ and their fluorine-free analogues $\mathbf{HN_2O_4}$ and $\mathbf{HN_2O_3}$ towards metal ions of Groups 1 and 2 was carried out. The experimental values of log*K*, Δ*H*, and *T*Δ*S* of the complexation reactions provide unequivocal evidence for the stabilizing effect of CF coordination in such complexes, which is most pronounced when the metal ion is complementary in size to the macrocyclic cavity. The crystal structure of the most stable complex $\mathbf{FN_2O_4}$-$Ba(ClO_4)_2$ was determined and is also indicative of strong F–Ba^{2+} interactions. Since complicated solvation effects make the thermodynamic data unsuitable for deriving quantitative data on the energy of interaction between a CF group and a metal ion, ab initio calculations were performed on simple Li^+ complexes. The MP2 F–Li^+ interaction energy for the model system $Li^+(FC_6H_5)(OMe_2)_3$ was calculated to be about 64 % of the corresponding O–Li^+ interaction in $Li^+(OMe_2)_4$.

The data presented here leave no doubt about the ability of fluorine atoms in fluorocarbons to act as efficient donor atoms in complexes with alkali and alkaline earth metal ions. For the first time quantitative data on such complexation reactions have been described. Both the experimentally derived log*K* values and the ab initio calculated binding energies provide strong support that fluorine in fluorocarbons should be viewed as a normal donor towards hard metal cations.

Experimental Section

General: The salts of the highest purity commercially available were used and dried prior to use: $LiClO_4$ (Ventron), $NaNO_3$ (Merck), KI (Merck), $RbNO_3$ (Merck), CsF (Ventron), $Ca(NO_3)_2$ (BDH), $SrBr_2$ (Ventron), $Ba(ClO_4)_2$ (Merck), $AgNO_3$ (Merck) and tetraethylammonium perchlorate (TEAP, Fluka). The fluorine-free cryptands $\mathbf{HN_2O_3}$ and $\mathbf{HN_2O_4}$ were synthesized according to the literature procedure.[7] The heptafluorobutyrates of the alkaline earth cations were prepared by the addition of solid alkaline earth metal hydroxides to a concentrated aqueous solution of heptafluorobutyric acid (Aldrich) until no more dissolution of the hydroxide could be observed. The reaction mixture was filtered, and the

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volatile substances evaporated. The residue was washed with CH_2Cl_2 and dried in vacuo.

Potentiometry: For the potentiometric titrations, dry methanol (max. 0.01 % H_2O, Merck) was used as solvent. The ionic strength was kept constant at $I = 0.05\,\mathrm{mol\,L^{-1}}$ by using TEAP as an inert electrolyte. The experimental setup is described in detail elsewhere.[28] A silver electrode (Methrom EA 282) was used to determine the activity of the uncomplexed cation according to the Nernst equation. For the determination of the Ag^+ stability constant, a solution of the ligand ($0.01\,\mathrm{mol\,L^{-1}}$) was added to a solution of $AgNO_3$ ($1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$). The stability constant of the complex formed was calculated from the potential measured at ligand concentrations higher than the salt concentration. Competitive potentiometric titrations were performed to measure the stability constants of other cations. A solution of the ligand ($0.01\,\mathrm{mol\,L^{-1}}$) and of the salt ($0.02\,\mathrm{mol\,L^{-1}}$) was titrated into a solution containing $AgNO_3$ ($1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$). Consequently, the ratio of the stability constants of the silver complex and the complexes of the metal ions M^{n+} of Group 1 or 2 determines the position of the following equilibrium and hence the concentration of free silver cations: $LM^{n+} + Ag^+ \rightleftharpoons LAg^+ + M^{n+}$. The measured potential was used to calculate the activity of the uncomplexed silver ion, which leads to the ratio of the competing equilibrium constants. By using the previously determined silver complexation constant, the stability constant of M^{n+} can be calculated.

Calorimetric titrations: All calorimetric titrations were performed with a Tronac Model 458 calorimeter. A solution of the ligand (0.06–0.08 $\mathrm{mol\,L^{-1}}$) was added continuously to a solution of the salt ($(3-5) \times 10^{-3}\,\mathrm{mol\,L^{-1}}$). After corrections for all chemical heat effects (e.g., stirring of the solution), the measured heat Q is related to the number of moles Δn of the complex formed at any time during the titration and the reaction enthalpy ΔH: $Q = \Delta n \times \Delta H$.

The number of moles of complex formed depends on the stability constant. By least-squares analysis, the unknown stability constant and reaction enthalpy can be fitted to the experimental data.[29, 30] Since the ionic strength changes during titration the activities of the ions were calculated with the Debye–Hückel equation. When only the reaction enthalpy was measured, the ligand solution (0.06–0.08 $\mathrm{mol\,L^{-1}}$) was added to the salt solution ($0.01\,\mathrm{mol\,L^{-1}}$). Under these conditions only 1:1 complexes between ligands and cations are formed.[31] The accuracy of the experimental methods was demonstrated elsewhere.[32]

Methods of calculation: Structure optimizations for the model systems $Li^+(OMe_2)$, $Li^+(OMe_2)_3$, $Li^+(OMe_2)_4$, $Li^+(C_6H_5F)$, and $Li^+(OMe_2)_3(C_6H_5F)$, and for the free ligands, were carried out at the DFT level with the Gaussian 94 program package[33] and with Becke's exchange functional [34] and Perdew's correlation functional[35] (a combination frequently denoted as BP86). For consistency with related calculations on systems incorporating heavier atoms, effective-core potentials (ECPs) and (4s4p1d)/[2s2p1d] valence basis sets were used for C, O, and F.[36] An ECP was also used for Li, with a (4s4p)/[2s2p] valence basis.[37] A (5s)/[2s] basis set was used for hydrogen.[38] All six cartesian components of the d functions were retained. No symmetry was used in the calculations on $Li^+(OMe_2)_3(C_6H_5F)$. Calculations on OMe_2, $Li^+(OMe_2)$, C_6H_5F, and $Li^+(C_6H_5F)$ were performed in C_{2v} symmetry, that on $Li^+(OMe_2)_3$ in D_3, and that on $Li^+(OMe_2)_4$ in S_4.[23] Subsequent binding energy calculations on the optimized structures were performed at the DFT(BP86), HF, and MP2 levels of theory. In these calculations, a diffuse sp set was added to the O and F basis sets (with exponents of 0.068 and 0.090, respectively) to reduce basis-set superposition errors (BSSE). The energies were then corrected for BSSE by using the counterpoise procedure.[39]

Improved synthesis of the fluoro cryptands $\mathbf{FN_2O_3}$ and $\mathbf{FN_2O_4}$: The content of two syringes filled with solutions of the respective diazacrown ether (diaza-[15]crown-5 or diaza-[18]crown-6, 5 mmol in 50 mL solvent) and 1,3-bisbromomethyl-2-fluorobenzene (1.41 g, 5 mmol in 50 mL solvent) in acetonitrile was pumped over about 12 h into acetonitrile (300 mL) containing M_2CO_3 (2 g, $M = Na^+$ for $\mathbf{FN_2O_3}$, $M = K^+$ for $\mathbf{FN_2O_4}$) held at reflux. After complete mixing of the starting materials, refluxing was continued for another 6 h. Finally the cold reaction mixture was filtered and evaporated to dryness. Water (10 mL) was added to the residue, and the product extracted with $CHCl_3$ (3×50 mL). The combined organic solutions were dried over $MgSO_4$, filtered, and evaporated to dryness. The products were purified by flash chromatography (cyclohexane/diethylamine 5/1). $\mathbf{FN_2O_3}$ yield = 73 %. Only minute quantities of the [2+2] addition product are formed (yield < 5 %). $\mathbf{FN_2O_4}$ yield = 70 %. The [2+2] addition product is formed in small amounts (yield ca. 10 %) and can be separated by chromatography. Physical properties as described previously.[7]

Crystal structure determination. Single crystals of $\mathbf{FN_2O_4}$-$Ba(ClO_4)_2$ were prepared by allowing diethyl ether to slowly diffuse into a solution of the complex in acetonitrile. Suitable crystals were mounted on a glass fiber. X-ray data of $\mathbf{FN_2O_4}$-$Ba(ClO_4)_2$ were collected on an Enraf-Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 71.069$ pm) and a graphite monochromator. All structure calculations were performed with SHELX-97[40] and refined against F^2. All non-hydrogen atoms were refined with anisotropic temperature coefficients. Hydrogen atoms were refined with fixed isotropic temperature coefficients and fixed site occupation factors, but the coordinates were free to refine. An empirical absorption correction based on ψ-scans was applied.[41]

Crystal data: $C_{20}H_{31}BaCl_2FN_2O_{12}$, $M_r = 718.71$; $T = 213(2)$ K; $\lambda = 0.71069$ Å; monoclinic, $P2_1/c$; $a = 10.051(2)$, $b = 16.305(3)$, $c = 16.929(3)$ Å, $\beta = 106.25(3)$; $V = 2663.5(9)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.792\,\mathrm{g\,cm^{-3}}$; $\mu = 1.762\,\mathrm{mm^{-1}}$; $F(000) = 1440$; crystal dimensions $0.3 \times 0.3 \times 0.2$ mm; θ range 2.9–26.0°; index ranges: h 0–12, k 0–20, l −20–20; reflections collected/unique reflections: 5518/5213; $R(\mathrm{int}) = 0.0198$; completeness to $2\theta(26.0)$: 96.1; refinement method: full-matrix least-squares on F^2; data/parameters: 5213/436; GOF on F^2: 1.065; final R indices $[I > 2\sigma(I)]$: $R1(2\sigma I) = 2.60$, $wR2 = 6.63$; R indices (all data): $R1 = 3.15$, $wR2 = 6.80$; largest difference peak and hole: $+1.01/-1.15$ e Å^3 around Ba^{2+}.

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