The Coordination Chemistry of Fluorocarbons: Group-I and Group-II Metal Ion Complexes of Fluoro Macrocycles

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Two new fluoro macrocycles **BenzoFN$_2$O$_3$** and **F(N$_2$O$_2$)$_2$C$_2$H$_4$** were synthesized in the reactions of 1,3-bis(bromomethyl)-2-fluorobenzene with benzo-diaza-15-crown-5 and 1,2-bis(diaza-12-crown-4)ethane, respectively, in 30% yield each. Close CF···metal ion interactions in the respective alkaline metal complexes in solution are evidenced by characteristic shifts of the ^{19}F-NMR resonances of up to $\delta = 18.7$ relative to the free ligand and by a decrease of the ^1J(CF) coupling constant of up to 20 Hz, which is most pronounced in **BenzoFN$_2$O$_3$** · Li$^+$ and **F(N$_2$O$_2$)$_2$C$_2$H$_4$** · K$^+$. In **BenzoFN$_2$O$_3$** · Li$^+$ a ^1J(^{19}F-^{7}Li) of 15.5 Hz was observed, which is indicative of very close CF···Li$^+$ interactions in solution. In the X-ray crystal structures of **BenzoFN$_2$O$_3$** · Na$^+$ [CF···Na$^+$ 246.8(2) pm], 26-fluoro-4,7,13,16-tetraoxa-1,10-diazatricyclo[8.8.7.1^{20,24}]-hexacosa-20,22,24(26)triene · Na$^+$ {CF···Na$^+$ 267.1(2) pm} and 21-fluoro-3,6,9,12,15,18-hexaoxabicyclo[18.3.1^{1,20}]heneicosa-1(24),20,22-triene · Ba^{2+} [CF···Ba^{2+} 299.0(3) pm] short CF···metal interactions were found. Such close CF···metal ion interactions do not result in a lengthening of the C–F bonds, which is not a sign of weak CF···metal ion interactions, since a Cambridge Structural Database search revealed that a shortening of the C–O bond length is also not observed in crown ether complexes of alkaline metals.

The coordination chemistry of alkaline and alkaline earth metal ions is dominated by oxygen donor centers which are available in ligands like ethers, alcohols, esters, amides, and water[1]. According to the HSAB principle such hard donors are best suited for the complexation of equally hard metal ions[2]. These basic considerations have raised the idea of regarding fluorocarbons as ligands well suited for the complexation of the above mentioned class of metal ions. Glusker et al. were the first to adress this problem by performing a Cambridge Structural Data base search for unusual short CF···metal ion contacts in the solid state and were succesful in locating a few crystal structures of group-I and group-II metal ions, with such interactions[3]. Since the early 1980's the enormous increase in the number of crystal structure determinations has also led to the discovery of a number of new complexes with short CF···metal ion contacts[4]. However, until very recently such contacts easily could have been dismissed as secondary effects resulting from packing forces of molecules in the crystals or as the result of the formation of close ion pairs, rather than being due to an inherently stabilizing CF···metal ion interaction. These arguments could not be refuted as long as the proof of the existence of such contacts in solution had not been made.

In order to provide unequivocal evidence for CF···metal ion contacts in solution and to firmly establish the coordination chemistry of fluorocarbons, we have recently synthesized several fluorine-containing macrocycles of the coronand and the cryptand type[5,6]. Due to the fact that these ligands contain a preorganized array of donor atoms they can form very stable complexes with alkaline and alkaline earth metal ions and it was shown by various NMR techniques and by X-ray crystal structure analysis that close CF···metal ion contacts in such complexes occur in solution as well as in the solid state. Moreover the determination of the stability constants of complexes with the fluoro macrocycles has shown that the presence of CF donor units exerts a stabilizing effect on the complexes of alkaline metal ions[7,8] and also allows stabilizing CF···Ag$^+$ interactions[9].

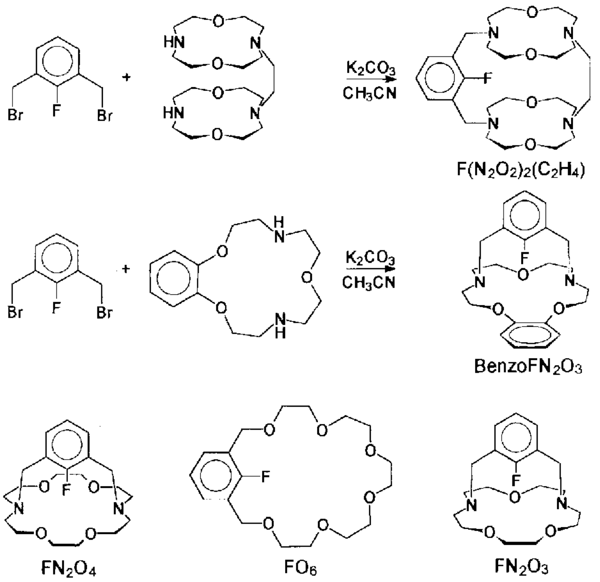
In order to better understand the coordination chemistry of CF units we have prepared new complexes of fluoro macrocycles with alkaline and alkaline earth metal ions. Several X-ray crystal structures of complexes of fluoro macrocycles with Na$^+$ and Ba^{2+} salts have been determined to gain more information on CF···metal ion distances in the solid state and the investigation of such complexes by NMR spectroscopy has provided clear evidence for the existence of CF···metal contacts, which will be the subject of this paper.

Results and Discussion

Synthesis of the Fluoro Cryptands

The standard building block for all fluoro macrocycles described here is 1,3-bis(bromomethyl)-2-fluorobenzene, which was allowed to react with different diaza-crown ethers [1,2-bis(diaza-12-crown-4)ethane, benzodiaza-15-crown-5, diaza-18-crown-6] in refluxing acetonitrile in the

Scheme 1. Synthesis of the new fluoro macrocycles **BenzoFN$_2$O$_3$** and **F(N$_2$O$_2$)$_2$C$_2$H$_4$** as well as drawings of previously synthesized fluoro macrocycles relevant for this paper



presence of an excess of a templating base (Scheme 1). The synthesis of **BenzoFN$_2$O$_3$** was straightforward in the presence of K$_2$CO$_3$ and yielded the fluoro cryptand in a 30% yield after chromatographic workup. The reaction of 1,2-bis(diaza-12-crown-4)ethane with 1,3-bis(bromomethyl)-2-fluorobenzene and K$_2$CO$_3$ as a base results in the formation of the cylindrical macrocycle **F(N$_2$O$_2$)$_2$C$_2$H$_4$** in a 30% yield. The fluoro macrocycles **FO$_6$** and **FN$_2$O$_4$** were described previously[7].

NMR Spectroscopy

The ^{1}H-NMR spectra of the small cryptand **BenzoFN$_2$O$_3$** and it's metal complexes are characterized by fairly complex multiplets since the NCH$_2$CH$_2$O groups display ABCD spin systems, while the OCH$_2$CH$_2$O unit has an AA'BB' spin system. This NMR behavior is the consequence of the rigid orientation of the CH$_2$ groups which results in diastereotopic CH$_2$ units. In the ^{13}C-NMR spectra the coordination of the metal ion induces additional shielding of the ^{13}C-NMR signals (Table 1), and not as one might have expected a deshielding due to the positive charge of the metal ions.

^{19}F-NMR spectroscopy is an extremely useful tool for the investigation of complexes of fluoro macrocycles since coordination of the metal ion within fluoro cryptands or fluoro crown ethers gives rise to characteristic changes in the chemical shift of the ^{19}F-NMR resonances[10]. In the complexes of **BenzoFN$_2$O$_3$** and **F(N$_2$O$_2$)$_2$C$_2$H$_4$** with Li$^+$, Na$^+$, K$^+$, and Rb$^+$ each metal complex displays a characteristic ^{19}F-NMR resonance, which is listed in Table 1. Most notable is the 18.4-ppm shift of the ^{19}F-NMR signal of **BenzoFN$_2$O$_3$** upon complexation of lithium; coordination of all other metal ions invokes much smaller shifts of the ^{19}F-NMR resonance. Strong interactions between the lithium ion and the CF unit in solution are also evidenced by the observation of a coupling constant of 15.5 Hz between ^{7}Li-^{19}F. Coupling constants between ^{7}Li-^{19}F are rarely observed and the requirements for their occurrence seem to be quite stringent, since even in the Li$^+$ complex of **FN$_2$O$_4$** (whose cavity is enlarged by only one OC$_2$H$_4$ unit with respect to that of **BenzoFN$_2$O$_3$**) coupling was absent. Apart from the complex Li$^+$ · **FN$_2$O$_3$** [$J(^7\text{Li-}^{19}\text{F})$ = 19 Hz] only very few other examples of $^{6/7}$Li-^{19}F couplings are known[11]. In compounds with Si−**F−Li**−N[12] and P−**F−Li**−N[13] four-membered rings, which display large ^1J(CF), the Li···F interactions may be viewed as those of a performed LiF trapped in the course of iminosilane or iminophosphane formation.

Table 1. Selected ^{13}C- and ^{19}F-NMR data of the ligands **BenzoFN$_2$O$_3$** (top) and **F(N$_2$O$_2$)$_2$C$_2$H$_4$** (bottom) and their complexes with the respective metal triflates[a]

	$\delta(^{19}F)$ [ppm]	^1J(CF) [Hz]	$\delta(^{13}C)$ [ppm]
BenzoFN$_2$O$_3$			
Ligand	−106.40	259	164.86
+ Li$^+$	−125.12	239	162.62
+ Na$^+$	−113.82	248	162.44
+ K$^+$	−104.72	257	163.42
F(N$_2$O$_2$)$_2$C$_2$H$_4$			
Ligand	−118.70	252	162.49
+ Li$^+$	−120.28	250	161.55
+ Na$^+$	−122.34	249	162.42
+ K$^+$	−124.72	243	161.02
+ Rb$^+$	−121.91	245	160.42

[a] $\delta(^{19}F)$ is the NMR shift of the fluorine coordinated to the metal ion in CD$_3$CN solution vs. CFCl$_3$ standard; ^1J(CF) is the coupling constant ^{13}C-^{19}F in the ligand; $\delta(^{13}C)$ is the NMR shift of the phenyl carbon atom bonded to the fluorine atom

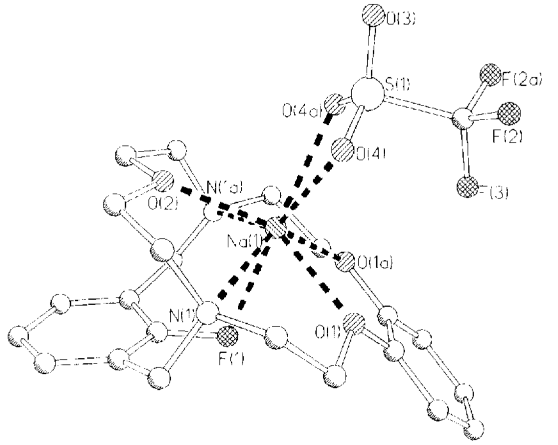
It may seem surprising that the complexation of a metal cation by a fluoro macrocycle leads to an additional shielding of the ^{19}F-NMR resonances of the ligand, but this seems to be a general trend in such complexes. High level ab initio calculations on C$_6$H$_5$F · (HF)$_x$ aggregates also suggest that the approach of a positive charge to C$_6$H$_5$F leads to an additional shielding of the ^{19}F-NMR resonances[14]; preliminary calculations on the complexes of metal ions by fluoro crown ethers seem to point into the same direction[15].

Whereas it has proven difficult to correlate the shifts of the ^{19}F-NMR resonance upon complexation of a metal ion by a fluoro macrocycle with the degree of CF···metal ion interaction, a reliable tool is available with the ^1J(CF) coupling constants. To explain this one has to realize that in the metal complexes of the fluoro cryptands the metal ions coordinated within the macrocyclic cavity, compete with the phenyl ring for fluorine lone pair electron density. The metal ion will be succesful in this game when it is efficiently coordinated by a CF unit within the macrocyclic cavity, since this leads to a withdrawal of lone pair electron density from the CF bond, which is consequently accompagnied by a decrease of the ^1J(CF) coupling constant. A closely related phenomenon has long been known from organic derivatives of fluorobenzene in which electron-withdrawing or -donating substituents at the ring, change the electron density in the CF bond and consequently the ^1J(CF) coupling constant[16]. The data listed in Table 1 show that the small macrocyclic cavity of **BenzoFN_2O_3** is best suited for the complexation of the small lithium ion, whereas complexation of the same metal by the much larger cavity of the cylindrical macrocycle **F$(N_2O_2)_2C_2H_4$** only evokes a small reduction of ^1J(CF). The smallest coupling constant of a complex of the latter ligand is observed with potassium salts indicating the best fit for this cation.

X-ray Crystal Structures

The solid-state structures of three fluoro macrocycles with sodium and barium salts were determined in order to gain more information on CF···metal ion contacts in the solid state.

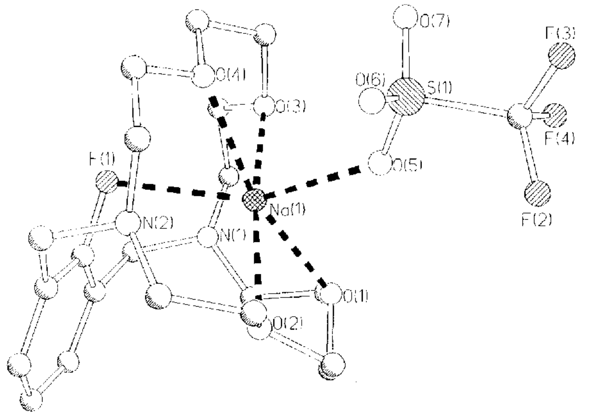
Figure 1. Molecular Structure of **BenzoFN_2O_3** · $NaCF_3SO_3$[a]



[a] Selected bond lengths [pm] and angles [°]: Na–F1 246.8(2), Na–O2 230.1(2), Na–O1 234.6(2), Na–O4 260.0(2), Na–N1 262.6(2), C4–F1 136.5(3), Na1–F1–C4 108.3(2).

BenzoFN_2O_3 · $NaCF_3SO_3$ (Figure 1): In the crystal the sodium ion has a coordination number of eight with all donor atoms of the fluoro cryptand participating in the bonding of Na^+ – including the triflate counter ion, which acts as a bidentate ligand via two oxygen atoms. A summary of selected bond lengths is given in the legend of Figure 1, which depicts **BenzoFN_2O_3** · $NaCF_3SO_3$. The atoms F(1), Na(1), and S(1) define a crystallographic mirror plane within the molecule. The oxygen and the nitrogen atoms of the macrocyclic unit are roughly located in a plane, above which – in the direction of the triflate counter ion – the sodium ion is placed. In spite of this the Na(1)–F(1) distance is the third shortest bond in the coordination sphere of sodium and is still 13.2 pm shorter than the Na(1)–O(4) distance to the triflate oxygen atom. The sodium–nitrogen distance constitute the longest bond in the coordination sphere of the metal ion being only slightly longer (2.6 pm) than the distances to the oxygen atom of $CF_3SO_3^-$. The crystal structure of **BenzoFN_2O_3** · $NaCF_3SO_3$ can be compared to that of **FN_2O_3** · $NaClO_4$[7] and in both structures the metal ion is slightly too big for the macrocyclic cavity. It therefore seems appropriate to compare the coordination behavior of **FN_2O_3** and **BenzoFN_2O_3** to that of the [2.1.1]-cryptand, since in the sodium complex of the latter ligand the metal ion is also slightly too big for the cavity of the ligand and forms can exclusive cryptate[17].

Figure 2. Molecular Structure of **FN_2O_4** · $NaCF_3SO_3$[a]

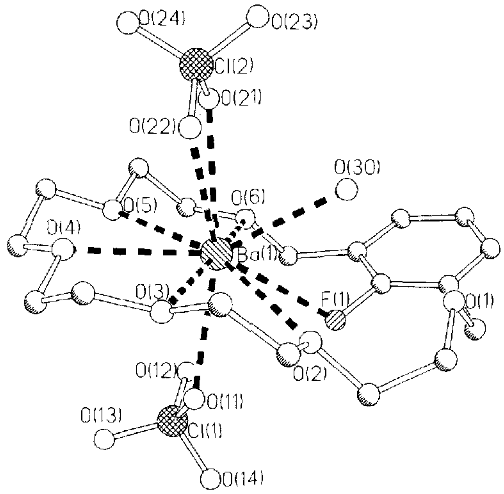


[a] Selected bond lengths [pm] and angles [°]: Na1–F1 267.1(2), Na1–O3 242.6(2), Na1–O4 243.9(2), Na1–O1 246.2(2), Na1–O2 247.61(14), Na1–O5 248.6(2), F1–C8 137.1(2), Na1–F1–C8 100.73(9).

FN_2O_4 · $NaCF_3SO_3$ (Figure 2): In the crystal the metal ion has a coordination number of six, since the sodium–nitrogen distances are too long [Na(1)–N(1) 299.3(2), Na(1)–N(2) 300.3(2) pm] to account for a reasonably strong interaction, hence only four oxygen atoms and the single fluorine atom of the fluoro cryptand, as well as one oxygen atom of the triflate counter ion are coordinated to the metal ion. A summary of selected bond lengths is given in the legend of Figure 2, which depicts **FN_2O_4** · $NaCF_3SO_3$. The oxygen atoms O(1), O(2), O(3), and O(4) of the fluoro cryptand as well as the sodium ion are located in a plane (mean deviation 12 pm). F(1) and O(5) are found above and below this plane, respectively, spanning an angle F(1)–Na(1)–O(5) of 152°. In the complex of **FN_2O_4** · $NaCF_3SO_3$ the CF···Na distances [267.1(2) pm] are quite large compared to the sodium–oxygen distances in this complex. A comparison with sodium complexes of other fluoro macrocycles reveals that this sodium–fluorine distance is larger than related distances observed in other crystal structures [**FN_2O_3** · $NaClO_4$ 257.5(2) pm and **FO_5** · $NaClO_4$ 237.4(5) pm][7]. Such large variation of bond lengths in the coordination sphere are not unusual in complexes of group-1 metal ions and simply reflect the shallow energy potential for metal–ligand bonds. This was shown by Hay et al.[18] for oxygen coordination, but most likely also holds true for metal–fluorine bonds.

FO_6 · $Ba(ClO_4)_2$ · H_2O: In the solid state the barium ion displays its typical coordination number of ten, which can be seen in Figure 3 together with a summary of selected bond lengths and angles in the legend. One fluorine atom and only five out of six oxygen atoms from the macrocyclic ligand **FO_6** contribute to the coordination sphere of the metal ion. Two perchlorate ions provide three additional oxygen donors and with the coordination of one water mol-

Figure 3. Molecular Structure of $\mathbf{FO_6} \cdot Ba(ClO_4)_2 \cdot H_2O$[a]



[a] Selected bond lengths [pm] and angles [°]: Ba1−F1 299.0(3), Ba1−O30 271.6(4), Ba1−O11 275.7(7), Ba1−O5 280.0(3), Ba1−O3 284.1(3), Ba1−O21 288.0(4), Ba1−O4 288.2(3), Ba1−O2 294.4(3), Ba1−O22 298.6(4), Ba1−O6 303.5(3), F1−C18 137.6(6), C18−F1−Ba1 123.4(3).

ecule O(30), the barium coordination sphere is completed. It is obvious that the cavity of the crown ether is too large for the barium ion and this seems to be the reason why one of the benzylic oxygen atoms is not at all bonded to the metal ion. It should, however, be taken into account that the benzylic oxygen O(1) and O(6) are not well suited for the simultaneous bonding to the metal ion since the rigid *m*-xylyl spacer disfavors a BaO_2 chelate. The CF···Ba^{2+} distance amounts to 299.0(3) pm which is fairly long compared to the Ba^{2+}−O distances and about 20 pm longer than in the complex of the related fluoro crown ether $\mathbf{FO_5}$ (whose cavity is smaller by one C_2H_4O unit)[5]. As stated before the large variations in the bond length are a typical feature of group-I and group-II metal complexes.

The general belief in the literature seems to be that upon coordination of alkaline and alkaline earth metal ions by a crown ether, the carbon−oxygen bond has to experience a lengthening. We have therefore been interested whether such an effect is visible in group-I and group-II metal ion complexes of fluoro macrocycles and collected the following C−F distances from our fluoro macrocycles [pm]: 136.5(4)[7] and 137.3(2)[9] and 136.6(4), 136.9(4), 135.3(2), 135.3(2), 135.8(2), 135.6(2)[19]. In the metal complexes the following C−F distances were found [pm]: $\mathbf{FN_2O_3} \cdot Li^+$ 137.9(3)[7] and $\mathbf{FN_2O_3} \cdot Na^+$ 136.4(3)[7] and $\mathbf{BenzoFN_2O_3} \cdot Na^+$ 136.5(3) and $\mathbf{FN_2O_4} \cdot Na^+$ 137.1(2) and $\mathbf{FO_5} \cdot Na^+$ 137.1(7)[7] and $\mathbf{FO_6} \cdot Ba^{2+}$ 137.6(6) and c-$\mathbf{F_4N_4O_4} \cdot Cs^+$ 135.5(5), 136.9(6), 135.9(5), 135.9(4)[8a]. The average C−F bond lengths in the free ligands of 136.2 pm and in the metal complexes of 136.6 pm were calculated from the above data and found to be virtually identical. This result was disappointing at first glance since it seemed to indicate that the CF···metal ion interactions are very weak. However, the results obtained in our previous studies had shown without any doubt that the strength of the CF···metal ion bond is far from negligible.

We therefore considered it well worth asking whether the claim for a lengthening of the C−F or C−O bonds upon coordination to alkaline metal ions was supported by X-ray data. Some doubts about this view arose after we studied a recent publication by Glendening et al.[20] who had proposed that for the bonding of alkaline metal ions in crown ethers, the electrostatic component is much more important than the bond-energy contribution originating from covalent interactions. We were thus interested to find data which answer our question and performed a Cambridge Structural Data base analysis[21] of C−O bonds in crown ethers of the 18-crown-6 type and their alkaline metal complexes. Consequently, 1390 C−O distances were found with an average C−O bond length of 142.0 pm, while in the alkaline metal ion complexes of such ligands 1250 C−O distances were found with an average C−O distance of 141.6 pm[22]. It is obvious from these results that the claim for a lengthening of the C−O bonds in these complexes is not supported by the CSD data and it is thus concluded that the absence of a lengthening of the C−F bonds in the complexes of the fluoro macrocycles is not indicative of weak CF···metal ion interactions.

Summary and Conclusion

Two new fluoro macrocycles $\mathbf{BenzoFN_2O_3}$ and $\mathbf{F(N_2O_2)_2C_2H_4}$ and their alkaline metal ion complexes have been synthesized. Metal ion complexation by these ligands results in characteristic shifts of the ^{19}F-NMR resonances of up to 18.6 ppm relative to those the free ligand. Some of the complexes display close CF···metal interactions in solution as evidenced by the variation of the ^1J(CF) coupling constant, which shows the lowest values for $\mathbf{BenzoFN_2O_3} \cdot Li^+$ and $\mathbf{F(N_2O_2)_2C_2H_4} \cdot K^+$. Short CF···metal ion interactions also occur in the solid state as evidenced by the solid-state structures of $\mathbf{BenzoFN_2O_3} \cdot Na^+$, $\mathbf{FN_2O_4} \cdot Na^+$, and $\mathbf{FO_6} \cdot Ba^{2+}$. In these complexes the C−F bonds are not significantly lenghtened with respect to the C−F bonds in the free ligands. To understand whether this was due to an inherent weakness of the CF···metal ion interaction or if it respresents a typical attribute of crown ether complexes of alkaline metals, we have performed a CSD search and compared the C−O bond lengths in 18-crown-6 derivatives with those in their respective metal complexes. As a result it was found that the C−O bond lengths in the ligand and in the respective metal complexes are virtually the same.

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Experimental Section

General: Commercially available solvents and reagents were purified according to literature procedures. − Chromatography was carried out with silica gel MN 60. − NMR spectra were recorded at 300 K (unless otherwise noted) with a Bruker AC200 F (^{1}H: 200 MHz; ^{13}C: 50.3 MHz; ^{19}F: 188.2 MHz) or a Varian Unity 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz). ^{1}H was referenced to residual H impurities of the deuterated solvent; ^{13}C to the respective solvent signals: $CDCl_3$ (δ = 7.26, 77.0), CD_3CN (δ = 1.93, 1.30). The ^{13}C-NMR spectra were accumulated in 32 k data files both in the time and frequency domain with a digital resolution of 0.7 Hz/data point. ^{19}F was referenced to internal $CFCl_3$ (δ = 0). – Starting materials were available commercially or prepared according to literature procedures: 1,3-dimethyl-2-fluorobenzene[23], 1,3-bis(bromomethyl)-2-fluorobenzene[24], diaza-18-crown-6[25], benzodiaza-15-crown-5[26], **FN_2O_4**[7], **FN_2O_3**[7], **FO_6**[7], 1,2-bis(diaza-12-crown-4)ethane[27].

27-Fluoro-6,13,24-trioxa-3,16-diazatetracyclo[16.5^{3,16}.3.1.0^{7,12}]-heptaeicosa-1(27),7,9,11,18,20-hexene (**$BenzoFN_2O_3$**): A mixture of 2,3-benzo-1,4,10-trioxa-7,13-diazacyclopentadecane (1.0 g, 3.75 mmol), 1,3-bis(bromomethyl)-2-fluorobenzene (1.06 g, 3.75 mmol), KBr (1.79 g, 15 mmol), and K_2CO_3 (2.7 g, 15 mmol) in acetonitrile (500 ml) was heated at 70°C for 22 h. The mixture was filtered, washed with acetonitrile (50 ml) and the solvent evaporated in vacuo. The residue was subjected to silica-gel column chromatography with cyclohexane/diethylamine (5:1) yielding **$BenzoFN_2O_3$** as a colorless solid. Yield: 440 mg (1.14 mmol, 30%); m.p. 106°C. – ^1H NMR (CD_3CN): δ = 2.31–2.35 (4H, m), 2.79–2.97 (6H, m), 3.14–3.27 (4H, m, CH_2 + $ArCH_2$), 3.92–4.00 (4H, m, CH_2 + $ArCH_2$), 4.16–4.26 (2H, m), 6.68–7.00 (7H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 53.56, 56.09, 56.17, 66.23, 72.28, 113.57 (Ar), 120.87 (Ar), 121.54 (d, J_{CF} = 0.6 Hz, Ar), 129.85 (d, J_{CF} = 5.1 Hz, Ar), 130.32 (d, J_{CF} = 12.0 Hz, Ar), 149.91 (Ar), 164.86 (d, $^1J_{CF}$ = 258.6 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = 106.40.

The metal complexes were prepared by mixing stoichiometric amounts of the respective metal triflate and **$BenzoFN_2O_3$** in CH_3CN. Evaporation of these solutions gave the pure complexes.

$BenzoFN_2O_3$ · $LiCF_3SO_3$: ^1H NMR (CD_3CN): δ = 2.26–2.69 (6H, m), 3.09–3.16 (4H, m), 3.25–3.35 (4H, m), 4.29–4.41 (6H, m), 7.05–7.39 (7H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 52.89, 55.25, 55.88, 66.25, 68.28, 113.70 (Ar), 123.50 (Ar), 126.22 (d, J_{CF} = 3.5 Hz, Ar), 130.35 (d, J_{CF} = 12.1 Hz, Ar), 131.20 (d, J_{CF} = 5.5 Hz, Ar), 146.78 (Ar), 162.62 (d, $^1J_{CF}$ = 239 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –125.12 [q, $^1J(^7Li^{19}F)$ = 15.5 Hz].

$BenzoFN_2O_3$ · $NaCF_3SO_3$: ^1H NMR (CD_3CN): δ = 1.96–2.10 (2H, m), 2.72–2.80 (2H, m), 3.05–3.16 (10H, m), 4.16 (2H, dt, J = 4.0 Hz, J = 10.5 Hz), 4.32–4.53 (4H, m), 6.98–7.30 (7H, m). – ^{13}C NMR (CD_3CN, 325 K): δ = 54.71, 58.49, 60.80, 68.45, 69.70, 115.52 (Ar), 123.46 (Ar), 124.50 (Ar), 130.33 (d, J_{CF} = 5.4 Hz, Ar), 148.79 (Ar), 162.54 (d, $^1J_{CF}$ = 248.0 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –113.82.

$BenzoFN_2O_3$ · KCF_3SO_3: ^1H NMR (CD_3CN): δ = 2.25 (2H, dt, J = 4.2 Hz, J = 11.2 Hz), 2.55–2.62 (2H, m), 2.72–3.09 (10H, m), 4.16–4.30 (6H, m), 6.85–7.14 (7H, m). – ^{13}C NMR (CD_3CN): δ = 55.10, 57.20, 58.48, 115.04 (Ar), 122.41 (Ar), 122.71 (d, J_{CF} = 4.0 Hz, Ar), 129.39 (d, J_{CF} = 5.6 Hz, Ar), 130.24 (d, J_{CF} = 12.0 Hz), 149.56 (Ar), 163.42 (d, $^1J_{CF}$ = 257.0 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –104.72.

34-Fluoro-6,15,26,31-tetroxa-3,9,12,18-tetraazatetracyclo-[18.5^{3,9}.5^{12,18}.3.1]tetratriaconta-1(34),20,22-triene, **$F(N_2O_2)_2C_2H_4$**: A mixture of 1,2-ethanediylbis(1,7-dioxa-4,10-diazacyclododecane) (250 mg, 670 µmol), 1,3-bis(bromomethyl)-2-fluorobenzene (189 mg, 670 µmol), and K_2CO_3 (370 mg, 2.7 mmol) in acetonitrile (40 ml) was refluxed for 16 h. The mixture was filtered, washed with acetonitrile (200 ml) and the solvent evaporated in vacuo. Water (10 ml) was added to the residue and the suspension extracted with CH_2Cl_2 three times. The residue was subjected to column chromatography with cyclohexane/diethylamine (5:1) to give **$F(N_2O_2)_2C_2H_4$** as a colorless solid (R_f = 0.24). Yield: 100 mg (0.2 mmol, 30%); m.p. 63°C. – ^1H NMR(CD_3CN): δ = 2.40–2.72 (20H, m, NCH_2 + NCH_2CH_2N), 3.40–3.65 (20H, m, OCH_2 + $ArCH_2$), 6.95–7.02 (1H, m, ArH), 7.10–7.17 (2H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 56.46, 56.97, 57.06, 57.63, 70.07, 70.34, 123.41 (d, J_{CF} = 4 Hz, Ar), 128.46 (d, J_{CF} = 15 Hz, Ar), 131.94 (d, J_{CF} = 5 Hz, Ar), 162.49 (d, $^1J_{CF}$ = 252 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –118.70.

The metal complexes were prepared by mixing stoichiometric amounts of the respective metal triflate and **$F(N_2O_2)_2C_2H_4$** in CH_3CN. Evaporation of this solution gave the pure complexes.

$F(N_2O_2)C_2H_4$ · $LiCF_3SO_3$: ^1H NMR (CD_3CN): δ = 2.55–2.82 (20H, m, NCH_2 + NCH_2CH_2N), 3.37–3.65 (20H, m, OCH_2 + $ArCH_2$), 7.07–7.14 (1H, m, ArH), 7.23–7.30 (2H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 54.17, 55.59, 55.91, 55.96, 57.29, 68.99, 124.30 (d, J_{CF} = 4 Hz, Ar), 126.23 (d, J_{CF} = 15.2 Hz, Ar), 133.94 (d, J_{CF} = 4 Hz, Ar), 161.55 (d, $^1J_{CF}$ = 249.6 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –120.28.

$F(N_2O_2)_2C_2H_4$ · $NaCF_3SO_3$: ^1H NMR (CD_3CN): δ = 2.51–2.64 (16H, m), 2.83–2.95 (4H, m), 3.37–3.66 (20H, m), 7.06–7.10 (1H, m, ArH), 7.20–7.27 (2H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 52.73, 52.78, 53.02, 55.54, 56.72, 68.23, 71.30, 124.43 (d, J_{CF} = 4.7 Hz, Ar), 128.43 (d, J_{CF} = 12.8 Hz, Ar), 131.30 (d, J_{CF} = 5 Hz, Ar), 162.42 (d, $^1J_{CF}$ = 249.0 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –122.34.

$F(N_2O_2)_2C_2H_4$ · KCF_3SO_3: ^1H NMR (CD_3CN): δ = 2.43–2.80 (20H, m, NCH_2 + NCH_2CH_2N), 3.43–3.55 (20H, m, OCH_2 + $ArCH_2$), 7.08–7.15 (1H, m, ArH), 7.21–7.29 (2H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 53.49, 53.97, 55.85, 56.23, 56.26, 68.28, 68.67, 124.99 (d, J_{CF} = 4.0 Hz, Ar), 128.03 (d, J_{CF} = 13.6 Hz, Ar), 132.56 (d, J_{CF} = 4.8 Hz, Ar), 161.02 (d, $^1J_{CF}$ = 243.3 Hz, Ar). – ^{19}F NMR (CD_3CN): δ = –124.72.

$F(N_2O_2)_2C_2H_4$ · $RbCF_3SO_3$: ^1H NMR (CD_3CN): δ = 2.52 (20H, s br, NCH_2 + NCH_2CH_2N), 3.42–3.56 (20H, br, OCH_2 + $ArCH_2$), 7.10–7.17 (1H, m, ArH), 7.23–7.36 (2H, m, ArH). – ^{13}C NMR (CD_3CN): δ = 52.90 (s, br), 56.20, 56.25, 57.12, 68.20 (s, br), 124.96 (d, J_{CF} = 4.0 Hz, Ar), 127.65 (d, J_{CF} = 14.4 Hz,

Table 2. Crystallographic data for **$BenzoFN_2O_3$** · $NaCF_3SO_3$, **FN_2O_4** · $NaCF_3SO_3$, and **FO_6** · $Ba(ClO_4)_2$ · H_2O

Compound	**$BenzoFN_2O_3$**·$NaCF_3SO_3$	**FN_2O_4**·$NaCF_3SO_3$	**FO_6**·$Ba(ClO_4)_2$
Empirical formula	$C_{23}H_{27}F_4N_2NaO_6S$	$C_{21}H_{31}F_4N_2NaO_7S$	$C_{18}H_{27}BaCl_2FO_{15}$
Formula weight [$gmol^{-1}$]	558.52	554.53	710.64
T [K]	223(2)	120(2)	150(2)
Crystal system	orthorhombic	triclinic	triclinic
Space group	*Pnnm*	*P*–1	*P*1
Unit cell dimensions [pm or °]			
a	13.222(3)	10.626(2)	9.400(2)
b	15.815(3)	10.768(2)	11.370(2)
c	11.608(2)	12.079(2)	13.653(3)
α	90	64.40(3)	70.30(3)
β	90	83.29(3)	75.64(3)
γ	90	89.36(3)	77.28(3)
V [$Å^3$]	2427.3(8)	1236.7(4)	1315.9(5)
Z	4	2	2
ρ [gcm^{-3}]	1.528	1.489	1.79
μ [mm^{-1}]	0.226	0.223	1.789
F(000)	1160	580	708
Crystal size [mm]	0.6 × 0.3 × 0.2	0.7 × 0.6 × 0.5	1.8 × 1.5 × 1.5
θ range [°]	3.5–22.6	3.7–22.6	3.6–22.6
Index range (*hkl*)	–14/14, –17/17, –12/12	–11/11, –10/11, –10/13	–9/5, –11/12, 0/14
Reflections collected/independent	4739/1692	3615/3151	3632/2584
Data/parameters	1625/181	3151/325	2581/334
GooF	1.054	1.091	1.116
Final *R* indices [$I > 2\sigma(I)$]			
*R*1, *wR*2	0.0347, 0.0808	0.0281, 0.0701	0.0277, 0.0715
Largest peak and hole [$eÅ^{-3}$]	+0.22, –0.37	+0.26, –0.32	+0.56, –0.46

Ar), 133.27 (d, J_{CF} = 4.8 Hz, Ar), 160.42 (d, $^1J_{CF}$ = 244.8 Hz, Ar). – ^{19}F NMR (CD_3CN): $\delta = -121.91$.

X-ray Crystal-Structure Determinations (Table 2): Suitable crystals were mounted on top of a glass fiber. X-ray data were collected on an Siemens AED diffractometer using Mo-K_α radiation (λ = 71.069 pm) and a graphite monochromator. All structures were solved (SHELXS-86)[28] and refined (SHELXL-93)[29] against F^2. In the structures described all non-hydrogen atoms were refined using anisotropic temperature coefficients. Hydrogen atoms were refined with fixed isotropic temperature coefficients (riding model). An empirical absorption correction (ψ scans) was applied in the barium complex[30]

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[30] Crystallographic data (exluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100119. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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