

Coordination Chemistry with CF Units as σ Donors: Ag^+ Complexes of Partially Fluorinated Crown Ethers with Direct Metal–Fluorine Interactions

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The partially fluorinated cryptands **FN₂O₄** and **BenzoFN₂O₄**, which are relatives of the [2.2.1]cryptand, were synthesized in good yields from 1,3-bis(bromomethyl)-2-fluorobenzene and diaza-18-crown-6 or benzodiaza-18-crown-6, respectively. These macrobicyclic ligands form very stable complexes with Ag(I) salts, and it was shown that close fluorine–silver interactions occur in solution as well as in the solid state. Numerous experimental evidence for this is available: NMR competition experiments show that Ag^+ complexes of **FN₂O₄** are significantly more stable than those of **HN₂O₄** (the two ligands are identical except that one fluorine atom is replaced by one hydrogen atom in **HN₂O₄**); the $^1J_{\text{CF}}$ coupling

constants of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ and $\text{Ag}^+ \cdot \text{BenzoFN}_2\text{O}_4$ are reduced by 10 Hz compared to those of the respective free ligands **FN₂O₄** ($^1J_{\text{CF}} = 253 \text{ Hz}$) and **BenzoFN₂O₄** ($^1J_{\text{CF}} = 252 \text{ Hz}$). The X-ray crystal structure of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ reveals short $\text{Ag}^+ \cdots \text{F}$ distances [271.4(3) pm]; coupling of the $^{107,109}\text{Ag}^+$ and ^{19}F nuclei is observed in the ^{19}F -NMR spectra ($J = 24 \text{ Hz}$ for $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$, $J = 25 \text{ Hz}$ for $\text{Ag}^+ \cdot \text{BenzoFN}_2\text{O}_4$). The ^1H -NMR spectrum of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ is very complex and exhibits sixteen unique proton resonances, whose evaluation yielded coupling constants and NOEs, which show that the structure in solution is compatible with the results obtained by the X-ray crystal structure determination.

Covalently bound fluorine can act as an efficient σ donor for alkaline and alkaline earth metal ions in solution as well as in the solid state. This is the conclusion drawn from complexation studies of partially fluorinated crown ethers^[1] and chelating ligands of the EDTA type^[2] with group-I and group-II metal ions, which is supported by numerous experimental evidence^[3,4]: i) The complexes of group-I and -II metal ions with macrocyclic ligands containing C–F units are significantly more stable than the almost identical macrocyclic complexes which possess a C–H instead of a C–F unit. ii) The $^1J_{\text{CF}}$ coupling constant is strongly correlated with the degree of metal–fluorine interaction, i.e. the closer the interaction, the smaller the coupling constant. iii) In several X-ray crystal structures of metal complexes of alkaline and alkaline earth metal ions with fluorinated macrocycles, fluorine behaves like an oxygen atom in the coordination sphere of a metal ion. iv) Complexation of metal ions by fluorinated macrocycles results in large shifts of the ^{19}F -NMR resonances relative to those of the metal-free ligands.

It was recognized previously by Glusker et al. that close C–F-to-metal contacts in the solid state are not uncommon, and it was thus believed that the C–F bond should be capable of significant, if not prominent, interactions with both alkaline metal ions and proton donors^[5]. However, in most cases such contacts result from the packing of the metal salts in the crystal, which does not persist in solution^[6]. No attempts have previously been made to rationally design ligands, which take advantage of the donor ability of covalently bound fluorine in metal ion complexes.

A significant advantage when studying fluorine coordination in solution is the fact that the interaction with metal ions can be monitored easily by ^{19}F -NMR spectroscopy, which is very sensitive to changes in the fluorine environment. Consequently, the ^{19}F -NMR resonances of the metal complexes of the fluoro macrocycles may be shifted by up to 18.3 ppm compared with the resonances of the respective metal-free ligands. The high sensitivity, the large signal dispersion and the absence of a natural background thus make ^{19}F -NMR spectroscopy an extremely useful tool for studying the coordination chemistry of diamagnetic metal ions.

It was of interest therefore to learn whether C–F coordination is also of significance in the case of metal ions other than those of the alkaline and alkaline earth metals.

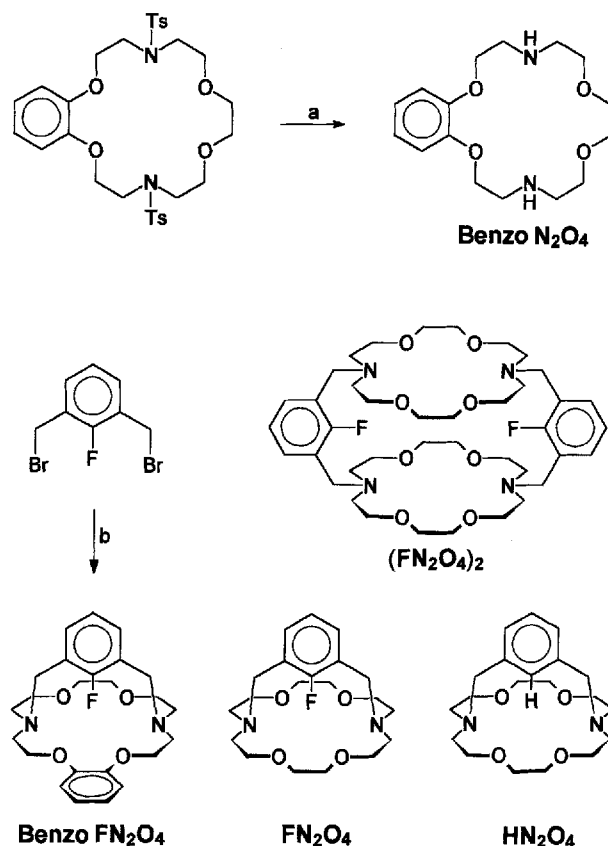
Consequently, we decided to investigate complexes of Ag(I) salts with fluorinated macrocycles, since the coordination chemistry of this metal ion is related to that of the alkaline metal ions^[7].

Results and Discussion

Synthesis of the Ligands: For an efficient complexation of the relatively large Ag^+ ion a correspondingly large macrocyclic cavity is required, and fluorinated relatives of the [2.2.1]cryptand therefore seemed to be the best choice. In previous investigations the cavity of fluoro cryptands like **FN₂O₄** had already proven well suited for the complexation of metal ions such as Na^+ and K^+ and should thus be ideal for Ag^+ since its ionic radius (115 pm, C.N. 6) is intermediate between that of Na^+ (102 pm, C.N. 6) and K^+ (138 pm, C.N. 6)^[8].

The new fluorocryptand **BenzoFN₂O₄** was synthesized in a yield of 27% utilizing the standard reaction of 1,3-bis-(bromomethyl)-2-fluorobenzene with the diazamacrocycle **BenzoN₂O₄**^[9] (Scheme 1). For the synthesis of ditosylated **BenzoN₂O₄** we followed a procedure by Jurczak et al.^[10] continuing with a standard detosylation procedure by heating at reflux a solution of the protected macrocycle in THF with a tenfold excess of LiAlH₄. However, whereas reaction times typically are shorter than 48 h, the detosylation of **BenzoN₂O₄** proved more difficult, since even after seven days at reflux some monoprotected macrocycle was still present, with the overall yield of **BenzoN₂O₄** being only modest.

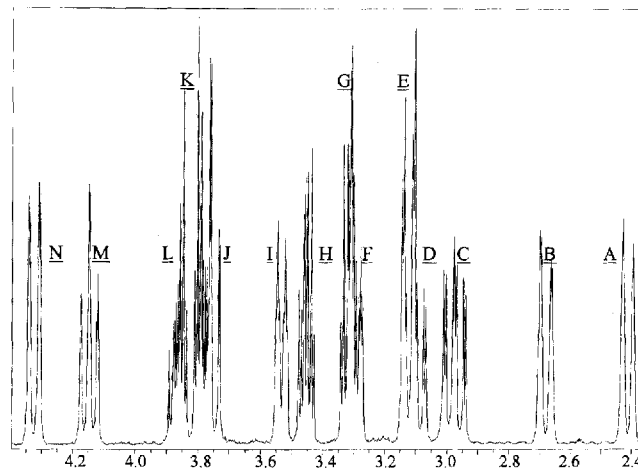
Scheme 1. Macrocycles used for the complexation of Ag⁺ and synthesis of **BenzoFN₂O₄**: Reagents and conditions: a. LiAlH₄, refluxing THF, 7 d. – b. **BenzoN₂O₄**/Na₂CO₃, refluxing CH₃CN



NMR Spectroscopical Investigations: The ¹H-NMR spectra of Ag⁺ · **FN₂O₄** and Ag⁺ · **BenzoFN₂O₄** as well as those of the ligands are characterized by very complex multiplet patterns (Figure 1). Both complexes have a mirror plane perpendicular to the plane of the fluorobenzene ring which generates an ABB'X spin system for the abundant nuclei (spin = 1/2) attached to the aromatic ring. The protons of each CH₂ group are magnetically and chemically inequivalent since the rigid oxyethylene chain is wrapped around the silver ion which leads to inside and outside orientations of the CH units. The difference in the chemical shifts of two diastereotopic protons of a CH₂ group can be as high as 1.2 ppm. One oxyethylene chain of Ag⁺ · **FN₂O₄** and Ag⁺

· **BenzoFN₂O₄** is roughly in the plane of the fluorobenzene ring, whereas the other one more or less exhibits a perpendicular orientation (Figures 2 and 4). This gives rise to complicated NMR spectra with Ag⁺ · **FN₂O₄** displaying sixteen unique ¹H-NMR signals. Each of the two symmetry-independent NC₂H₄O units represents an independent ABCD spin system, whereas the two different OC₂H₄O units display an AA'BB' pattern.

Figure 1. Aliphatic region of the ¹H-NMR spectrum (δ scale) (400 MHz, CD₃COCD₃, T = 300 K) of Ag⁺ · **FN₂O₄**. This spectrum consists of five independent spin systems. NC₂H₄O (BDIM), NC₂H₄O (ACFJ), OC₂H₄O (KL), OC₂H₄O (GH), ArCH₂ (EN)

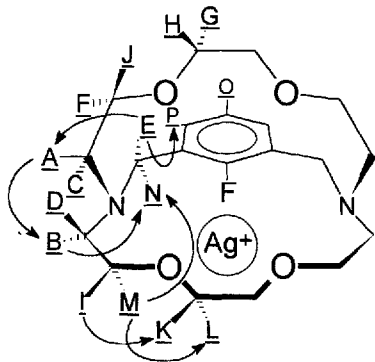


The assignment of all proton resonances and connectivities within each group of Ag⁺ · **FN₂O₄** was straightforward with the aid of (¹H, ¹H) COSY, TOCSY and (¹H, ¹³C) COSY spectra. The orientation of the different CH₂CH₂ units and the inside/outside orientation of the protons was established by NOESY spectra (Figure 2). However, the inside-outside orientation of the respective protons of the two central OCH₂CH₂O units (KL) and (GH) in Ag⁺ · **FN₂O₄** is not known with certainty, since the difference in the chemical shifts of the respective protons (KK'LL') and (GG'HH') is very small.

The inequality of the two oxyethylene chains raises the possibility of Ag⁺ · **BenzoFN₂O₄** to exist as two different isomers which differ with respect to the orientation of the two benzene rings. It seems likely that one isomer occurs in solution since the ¹³C-NMR spectrum displays only one set of resonances. On the basis of geometric considerations a coplanar orientation of the two six-membered rings appears more likely, but different NMR techniques do not give conclusive evidence for either of the two possibilities. This phenomenon makes the complete assignment of the ¹H-NMR resonances very difficult, since the (¹H, ¹H) COSY as well as the TOCSY spectra display too many crosspeaks to allow a distinction between the different chains.

Solution Structure of Ag⁺ · **FN₂O₄:** In order to obtain more stereochemical information for a better understanding of the structure of Ag⁺ · **FN₂O₄** in solution, we determined the ¹H-NMR shifts of all protons as well as all ¹H-¹H coupling constants (Table 1) by simulation of the ¹H-NMR spectrum^[11]. Additional structural information is available from

Figure 2. Stereochemical assignment of the ¹H-NMR resonances in Ag⁺ · FN₂O₄. The underlined letters symbolize the respective protons (only heteroatoms are denoted by their standard atomic symbols) with the same lettering as in Figure 1. The NOEs observed are marked by arrows between the respective protons



the NOEs which were obtained from NOESY spectra. The ¹H-NMR resonances of each NCH₂CH₂O resonances display besides the large geminal coupling two small (1.6–3.0 Hz) and one large (11.5, 11.8 Hz) vicinal ¹H-¹H coupling constant. From the Karplus equation^[12] it is evident that the small couplings corresponds to HCCH torsion angles of around 60°, whereas the large ones are a result of torsion angles close to 180°. We thus attempted to calculate the vicinal coupling constants by using the generalized Karplus equation by Haasnoot, Altona et al.^[13] with torsion angles obtained from the crystal structure determination, but we could only obtain a rough fit with our data, which is most likely due to the unusual ring system and the coordination of oxygen and nitrogen atoms to the silver ion.

Another unusual feature is the fact that the M proton in Ag⁺ · FN₂O₄ displays an additional small splitting of 0.8 Hz, which can be due to a ¹⁹F-¹H through-space coupling. This explanation is supported by the fact that the distance H(M)...F, as obtained from X-ray data, is only 273 pm.

Table 1. ¹H-NMR shifts and coupling constants of Ag⁺ · FN₂O₄ in CD₃COCD₃. Underlined letters denote the respective protons as depicted in Figures 1 and 2

	δ	<i>J</i> (gem) [Hz]	<i>J</i> (vic) [Hz]	<i>J</i> (vic) [Hz]	<i>J</i> _{HF} [Hz]	<i>v</i> _{1/2} [Hz]
<u>A</u>	2.411	(<u>AC</u>) = 13.7	(<u>AF</u>) = 2.6	(<u>AJ</u>) = 1.7		2.0
<u>B</u>	2.681	(<u>BD</u>) = 14.2	(<u>BI</u>) = 2.8 Hz	(<u>BM</u>) = 1.6		1.6
<u>C</u>	2.974	(<u>CA</u>)	(<u>CF</u>) = 3.0	(<u>CJ</u>) = 11.8		1.3
<u>D</u>	3.102	(<u>DB</u>)	(<u>DI</u>) = 2.8	(<u>DM</u>) = 11.5		1.4
<u>E</u>	3.124	(<u>EN</u>) = 12.9			2.8	1.6
<u>F</u>	3.293	(<u>FJ</u>) = 12.2	(<u>FA</u>)	(<u>FC</u>)		1.6
<u>G</u>	3.316	(<u>GH</u>) = 9.8	(<u>GG'</u>) = 2.2	(<u>GH'</u>) = 6.3		0.8
<u>H</u>	3.453	(<u>HG</u>)	(<u>HH'</u>) = 2.4	(<u>HG'</u>)		0.8
<u>I</u>	3.532	(<u>IM</u>) = 9.9	(<u>IB</u>)	(<u>ID</u>)		2.2
<u>J</u>	3.760	(<u>JF</u>)	(<u>JA</u>)	(<u>JC</u>)		1.1
<u>K</u>	3.783	(<u>KL</u>) = 11.8	(<u>KK'</u>) = 2.7	(<u>KL'</u>) = 6.5		1.2
<u>L</u>	3.862	(<u>LK</u>)	(<u>LK'</u>)	(<u>LL'</u>) = 2.4		1.2
<u>M</u>	4.145	(<u>MI</u>)	(<u>MB</u>)	(<u>MD</u>)	0.8	1.2
<u>N</u>	4.323	(<u>NE</u>)			2.2	1.7

A comparison of the structural information obtained from the X-ray crystal structure determination with the

NMR data (coupling constants, NOEs) reveals that the latter suggest a higher symmetry of the complex than found in the crystal structure. Whereas in the solid state Ag⁺ is asymmetrically bound within the cavity, in solution the metal ion is most likely oscillating between two positions within the cavity. These two locations for Ag⁺ are symmetry-related through the aforementioned mirror plane perpendicular to the fluorobenzene unit and seem to be accessible by a low-energy pathway. Hence, recording of the NMR spectra at low temperatures (200 K) did not result in the freezing of this motion. Alternatively, a static, symmetric position of Ag⁺ with respect to the donor atoms is unlikely, since then torsion angles of close to zero should have produced large ³*J* coupling constants (>10 Hz) within the OCH₂CH₂O units, which however were not observed. To obtain more information on the solution structure of Ag⁺ · FN₂O₄ the NOESY spectra were evaluated and interhydrogen distances calculated according to standard procedures^[14,15]. These distances were compared with those from the X-ray structure. The values obtained qualitatively correspond to the H...H distances as obtained from the X-ray crystal structure^[16].

NMR Evidence for Close Fluorine-Silver Contacts in Solution: NMR spectroscopy is an extremely useful tool to establish the presence of close Ag⁺–F interactions in solution, since both elements have a nuclear spin of 1/2. Strong evidence for a direct bond between Ag⁺ and F comes from the ¹⁹F-NMR spectra of the Ag⁺ complexes, where the ¹⁹F{¹H} resonances of Ag⁺ · FN₂O₄ and Ag⁺ · BenzoFN₂O₄ are split into doublets with coupling constants *J* = 24 (Ag⁺ · FN₂O₄) and 25 Hz (Ag⁺ · BenzoFN₂O₄)^[17]. It is obvious that this splitting must be due to a coupling between ^{107,109}Ag⁺ and ¹⁹F^[18]. This magnetic interaction of the nuclear spins between a covalently bound fluorine and a silver ion is quite unusual and to the best of our knowledge has not been observed before. It should also be mentioned that in the corresponding complex Ag⁺ · HN₂O₄ there seems to exist an (agostic)^[19] interaction between Ag⁺ and the aromatic hydrogen atom, since in the low-temperature NMR spectra (230 K in CD₃COCD₃) a very small coupling between ^{107,109}Ag and ¹H (*J* = 3.3 Hz) is observed^[20]. It is apparent that the reduced coupling constant *J*(Ag⁺–H) is smaller than *J*(Ag⁺–F) by almost one order of magnitude [magnetogyric ratio of ¹H (2.675) to ¹⁹F (2.517)]^[21]. However, the frequency of the ¹H-NMR resonance of this aromatic hydrogen in HN₂O₄ (δ = 8.31) is almost the same as in Ag⁺ · HN₂O₄ (δ = 8.18), whereas in the related 5-oxa-2,8-dithia[9]-*m*-cyclophane the ¹H-NMR resonance of the hydrogen atom in the 2-position of the aromatic ring is shifted by 0.5 ppm upon addition of AgBF₄^[22].

More evidence for close Ag⁺–F contacts is available by determining the ¹*J*_{CF} coupling constants. In the complexes of alkaline and alkaline earth metal ions with fluoro macrocycles this parameter was found to be correlated with the degree of metal-fluorine interaction in solution, i.e. the stronger the metal-fluorine bond, the smaller the ¹*J*_{CF} coupling constant as compared to that of the free fluoro-

cryptand^[4]. It is significant that this trend was also found in the case of the Ag^+ complexes described here. For FN_2O_4 ($^1J_{\text{CF}} = 253 \text{ Hz}$), $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ ($^1J_{\text{CF}} = 243 \text{ Hz}$), $\text{BenzoFN}_2\text{O}_4$ ($^1J_{\text{CF}} = 252 \text{ Hz}$), and $\text{Ag}^+ \cdot \text{BenzoFN}_2\text{O}_4$ ($^1J_{\text{CF}} = 242 \text{ Hz}$) the reduction amounts to 10 Hz in both cases. None of those observations for close metal-fluorine interactions were made in the case of the complex of $(\text{FN}_2\text{O}_4)_2$ with Ag^+ . Hence, upon addition of an excess of Ag^+ salt neither $^1J_{\text{CF}}$ was changed nor did we observe any spin coupling. This finding therefore suggests that the above-mentioned effects require a good preorganization of the ligating atoms, which was obviously not present in the dimer of FN_2O_4 .

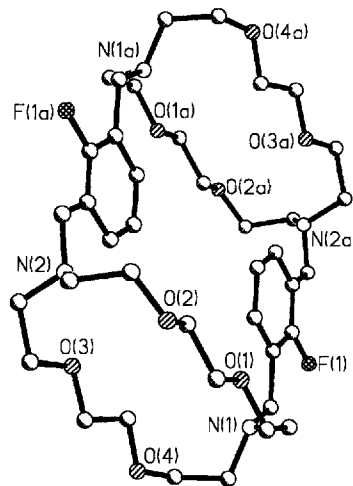
To directly probe the effect of fluorine-silver contacts on the overall stability of the complexes, we performed NMR competition experiments with FN_2O_4 and $\text{BenzoFN}_2\text{O}_4$, which are very useful when one expects only small differences in the stability constants of the metal complexes. In a typical experiment an AgCF_3SO_3 solution of known concentration in CD_3CN was added stepwise to the same solvent containing known, equimolar amounts of FN_2O_4 and HN_2O_4 . Since the complexation/decomplexation reactions proceed in the slow exchange region, their course can be followed by comparing the integrals of the ^{19}F - and ^1H -NMR resonances (complexed and uncomplexed) of the single hydrogen or fluorine atom pointing into the cavity. The higher stability of the Ag^+ complex with FN_2O_4 is most obvious, when equimolar amounts of Ag^+ , FN_2O_4 and HN_2O_4 are present in solution. At this point approximately two thirds of the Ag^+ present in solution is coordinated within the cavity of the fluorinated cryptand, whereas only one third of the HN_2O_4 contains a metal ion. This result demonstrates that the fluorine-containing ligand forms more stable complexes with Ag^+ salts, even though hydrogen is sterically less demanding than fluorine.

However, this small difference in stability must not be confused with the strength of the $\text{Ag}^+ - \text{F}$ interaction, since the observed difference of the stability constants simply reflects the overall difference in energy between the two complexes. An effective compensation for the loss of $\text{Ag}^+ - \text{F}$ interactions in $\text{Ag}^+ \cdot \text{HN}_2\text{O}_4$ by, for example, a lower conformational energy within the ligand or improved contacts of Ag^+ to solvent molecules or the counterion could very well mask the positive contribution of an $\text{Ag}^+ - \text{F}$ interaction – or vice versa! Whereas these disturbing influences cannot be totally excluded, it should be kept in mind that the alkaline metal complexes with fluoro cryptands are more stable only when metal-fluorine contacts are sterically possible. As soon as the metal ion is too large to penetrate the cavity of the fluoro macrocycle and thus cannot contact the fluorine buried inside, the fluoro macrocycles form complexes just as stable as their fluorine-free relatives.

Solid-State Structures of $(\text{FN}_2\text{O}_4)_2$ and $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$: In the solid-state structure of $(\text{FN}_2\text{O}_4)_2$ the transoidal arrangement of carbon and oxygen atoms within the 18-membered crown ether ring leads to an elongated ellipsoidal shape of the ring (Figure 3). The two benzene rings which are sym-

metry-equivalent through an inversion center are coplanar and located on the inside of the cavity. The two aromatic hydrogen atoms opposite to the respective fluorine atoms are fairly close (265.7 pm) and are located in the vicinity of the crystallographic inversion center. This endohedral orientation of the aromatic rings fills the cavity between the two crown ether units. Other bonding parameters are unspectacular, and the carbon-fluorine distance of 137.3(2) pm is in the normal range.

Figure 3. Molecular structure of $(\text{FN}_2\text{O}_4)_2$ in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [pm]: C(1)–F(1) 137.3(2), aver. C–O 141.4, aver. C–C 149.7 (within the macrocycle)

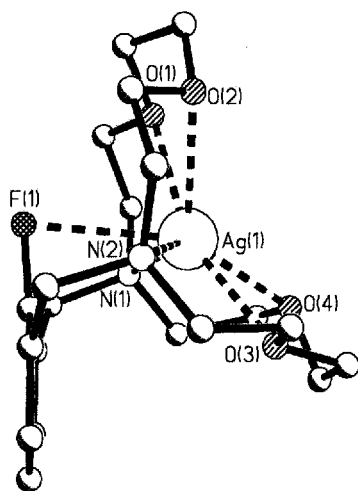


Complexes of crown ethers with Ag(I) are not very common since hard oxygen donors are not ideal for the coordination of the relatively soft Ag^+ . Consequently, these complexes are less stable than those of group-I and group-II metal ions^[23]. It is therefore hardly surprising that only few solid-state structures of Ag(I) -crown ether complexes were described, with the $\text{Ag}^+ - \text{O}$ distances in these complexes ranging between 240 and 275 pm^[24].

In the crystal structure of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ the metal ion is coordinated by four oxygen [$\text{Ag}^+ - \text{O}$ 247.8(2)–262.7(3) pm] atoms, two nitrogen [$\text{Ag}^+ - \text{N}$ 258.5(3), 269.4(3) pm] atoms and one fluorine atom [$\text{Ag}^+ - \text{F}$ 271.4(3) pm] with the triflate counterion being strictly noncoordinating (Figure 4). The donor atoms in the coordination sphere of Ag^+ are unevenly distributed since the surface of the metal ion opposite to fluorine is devoid of donor atoms. The $\text{Ag}^+ - \text{F}$ distance is rather short and only slightly longer than $\text{Ag}^+ - \text{N(2)}$ but still within the range covered by the $\text{Ag}^+ - \text{O}$ distances in other complexes^[25]. It is obvious therefore that fluorine can be an active part of the silver coordination sphere. Short $\text{Ag}^+ - \text{F}$ contacts are not common, and we are aware of only four other structures in which a CF unit displays contacts to Ag^+ which are shorter than 330 pm: two structures by Uson, Cotton et al.^[26] [$\text{CF} - \text{Ag}^+ = 260(1) - 269(1) \text{ pm}$] and one each by Girolami et al.^[27] [$\text{CF} - \text{Ag}^+ = 288.6, 292.6 \text{ pm}$] and Strähle et al.^[28] [$\text{CF} - \text{Ag}^+ = 301.8 \text{ pm}$].

Another remarkable structural feature of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ is that the silver ion is located above the CF bond

Figure 4. Molecular structure of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: $\text{Ag}-\text{F}(1)$ 271.4(3), $\text{Ag}-\text{O}(1)$ 258.6(2), $\text{Ag}-\text{O}(2)$ 262.1(3), $\text{Ag}-\text{O}(3)$ 247.8(2), $\text{Ag}-\text{O}(4)$ 262.7(3), $\text{Ag}-\text{N}(1)$ 258.5(3), $\text{Ag}-\text{N}(2)$ 269.4(3); $\text{F}(1)-\text{Ag}(1)-\text{N}(1)$ 71.9(8), $\text{F}(1)-\text{Ag}(1)-\text{N}(2)$ 70.9(8), $\text{F}(1)-\text{Ag}(1)-\text{O}(1)$ 75.0(8), $\text{F}(1)-\text{Ag}(1)-\text{O}(2)$ 85.3(8), $\text{F}(1)-\text{Ag}(1)-\text{O}(3)$ 125.5(9), $\text{F}(1)-\text{Ag}(1)-\text{O}(4)$ 140.0(9).



[C(1)–F(1)–Ag(1) = 80.9°]. Consequently, the Ag⁺–C distance is fairly short [Ag⁺–C(1) 283.7(4) pm]. However, neither this η² shift of the silver ion, which was also observed for Ba²⁺ in its complex with a related fluoro crown ether^[3], nor the short metal fluorine contacts lead to any significant lengthening of the C(1)–F(1) bond [136.5(4) pm], which also parallels the behavior displayed by the complexes of alkaline metal ions with fluoro macrocycles.

Conclusions

We have shown that close interactions of covalently bound fluorine with Ag^+ occur in the complexes of $\text{Ag}(\text{I})$ salts with fluorocryptands both in solution and in the solid state. Experimental evidences for the significance of these contacts are:

i) The complex $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ is more stable than $\text{Ag}^+ \cdot \text{HN}_2\text{O}_4$. – ii) Coupling of the nuclear spins of $^{107,109}\text{Ag}$ and ^{19}F was observed in the solution-NMR spectra. – iii) In the case of the $\text{Ag}(\text{I})$ complexes of FN_2O_4 and $\text{BenzoFN}_2\text{O}_4$ the $^1J_{\text{CF}}$ value is reduced by 10 Hz compared to that of the free ligands. – iv) In the solid-state structure of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ short contacts between Ag^+ and F [271.4(3) pm] were detected. The same phenomena, though more pronounced, were observed with the complexes of alkaline and alkaline earth metal ions with fluoro macrocycles. Hence, the conclusion drawn from the results presented here is that covalently bound fluorine can act as a (weak) σ donor towards Ag^+ ions.

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Experimental

Commercially available solvents and reagents were purified according to literature procedures. — Chromatography was carried out with silica MN 60. — NMR: recorded at 300 K (unless noted otherwise), Bruker AC200 F (^1H 200, ^{13}C 50.3, ^{19}F 188.2 MHz), Varian Unity 300 (^1H 300, ^{13}C 75 MHz), or Bruker AM 400 (^1H 400 MHz). ^1H -NMR spectra were referenced to residual H atoms of the solvent. ^{13}C -NMR shift values are given with respect to solvent signals: CDCl_3 ($\delta = 7.26, 77.0$), CD_3CN ($\delta = 1.93, 1.30$), and CD_3COCD_3 ($\delta = 2.04$). 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 -NMR spectra were referenced to internal CFCl_3 ($\delta = 0$). NOESY spectra were recorded in strictly oxygen-free anhydrous solutions. — Elemental analyses: Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. — Melting points: Meltemp melting point apparatus in sealed capillaries. — Starting materials were available commercially or prepared according to literature procedures: 2-fluoro-1,3-dimethylbenzene^[29], 1,3-bis(bromomethyl)-2-fluorobenzene^[30], diaza-18-crown-6^[31], ditosylated 2,3-benzo-7,16-diaza-1,4,10,13-tetraoxacyclooctadecane^[10], FN_2O_4 ^[4], $(\text{FN}_2\text{O}_4)_2$ ^[4], HN_2O_4 ^[4].

Synthesis of $\text{FN}_2\text{O}_4 \cdot \text{Ag}^+$: Et_2O was allowed to slowly diffuse into a solution of FN_2O_4 (191 mg, 0.5 mmol) and AgCF_3SO_3 (128 mg, 0.5 mmol) in CH_3CN (5 ml). After 24 h crystals of $\text{Ag}^+ \cdot \text{FN}_2\text{O}_4$ deposited on the walls of the glass vessel. — ^1H NMR (CD_3CN): δ = 2.30 (d, J = 13.6 Hz, 1H), 2.56 (d, J = 14.1 Hz, 1H), 2.82 (dd, J = 11.5, 3.1 Hz, 1H), 2.92–3.06 (m, 2H), 3.16–3.24 (m, 2H), 3.34–3.47 (m, 2H), 3.64 (t, d, J = 10.6, 1.5 Hz, 1H), 3.72 (s, 2H), 4.03 (t, J = 12 Hz, 1H), (dd, J = 12.9, J_{HF} = 1.9 Hz, 1H), 7.10–7.18 (m, 1H), 7.31–7.39 (m, 2H). — ^{13}C NMR: δ = 55.04 (AC, BD), 55.33 (ENJ), 67.20 (FJ), 67.65 (IM), 69.59 (KL), 70.38 (GH), 124.55 (d, J_{CF} = 4.5 Hz), 130.70 (d, J_{CF} = 11 Hz), 131.82 (d, J_{CF} = 4 Hz), 161.14 (d, J_{CF} = 243 Hz). — ^{19}F NMR: δ = –116.45 [d, $J(^{107,109}\text{Ag}-^{19}\text{F})$ = 24.0 Hz].

Solutions of $(\text{FN}_2\text{O}_4)_2 \cdot 2 \text{Ag}^+$ or $\text{HN}_2\text{O}_4 \cdot \text{Ag}^+$ for the NMR experiments were prepared by dissolving AgCF_3SO_3 (0.1 mmol) and the respective ligand $(\text{FN}_2\text{O}_4)_2$ (0.05 mmol) or HN_2O_4 (0.1 mmol) in CD_3CN .

(**FN₂O₄**)₂ · 2 Ag⁺: ¹H NMR (CD₃CN): δ = 2.9 (v br., 16H), 3.72 (br., 12H), 3.85 (br., 16H), 6.72–6.79 (m, ArH, 2H), 7.50–7.58 (m, ArH, 4H). – ¹³C NMR (CD₃CN): δ = 53.18, 56.4 (br.), 65.49, 69.77, 124.72 (d, *J*_{CF} = 15 Hz), 125.13 (d, *J*_{CF} = 4 Hz), 131.53 (d, *J*_{CF} = 4 Hz), 160.75 (d, *J*_{CF} = 246 Hz).

HN₂O₄ · Ag⁺: ¹H NMR (CD₃CN): δ = 2.63 (t, *J* = 4.0 Hz, NCH₂, 8H), 3.40–3.63 (m, NCH₂, OCH₂, 20H), 7.23–7.27 (m, ArH, 3H), 8.18 (br., ArH, 1H). — ¹H NMR (CD₃COCD₃, 210 K, ArH only): δ = 7.15–7.25 (m), 7.35 (s), 8.37 [d, *J*(^{107,109}Ag–¹H) = 3.3 Hz].

2,3-Benzo-7,16-diaza-1,4,10,13-tetraoxacyclooctadecane (Benzo-N₂O₄): Ditosylated benzodiazia-18-C-6 (4.56 g, 7.9 mmol) and LiAlH₄ (6.08 g, 160 mmol) in THF (250 ml) were heated at reflux for 7 d. Afterwards, excess LiAlH₄ was destroyed by *carefully* adding water to the ice-cooled reaction mixture. The solids were filtered off, extracted with CHCl₃ (3 × 25 ml) and the combined filtrates evaporated to dryness. The residue was purified by chromatography (cyclohexane/Et₂NH, 5:1, product eluted with CHCl₃/Et₂NH, 100:1) and recrystallized from petroleum ether. Yield: 0.5 g (20%), colorless oil. — ¹H NMR (CD₃CN): δ = 2.75 (t, *J* = 4.7 Hz, 4H, NCH₂), 2.92 (t, *J* = 4.7 Hz, 4H, NCH₂), 3.45–3.56 (m, 12H, OCH₂), 4.02–4.07 (m, 4H, OCH₂), 6.88–6.91 (m, 4H, ArH).

Synthesis of BenzoFN₂O₄: A mixture of 2,3-benzo-7,16-diaza-1,4,10,13-tetraoxacyclooctadecane (220 mg, 0.71 mmol), 1,3 bis-(bromomethyl)-2-fluorobenzene (340 mg, 0.71 mmol), KBr (340 mg), and K₂CO₃ (400 mg) in acetonitrile (70 ml) was refluxed for 18 h. The mixture was filtered, washed with acetonitrile (15 ml) and the solvent evaporated in vacuo. The residue was recrystallized from CHCl₃/diethyl ether resulting in the formation of colorless crystals of m.p. 242 °C, which proved to be the KBr adduct of **BenzoFN₂O₄**. A solution of **BenzoFN₂O₄** · KBr in CHCl₃ was extracted with water to remove KBr from the organic layer. The CHCl₃ solution was separated, dried with MgSO₄, filtered and evaporated to dryness. After evaporation of the volatile components in vacuo pure **BenzoFN₂O₄** was available. Yield: 83 mg (27%). – ¹H NMR (CD₃CN, 320 K): δ = 2.55–2.78 (m, 6H), 2.85–2.98 (m, 2H), 3.06–3.14 (m, 2H), 3.29 (d, *J* = 13.0 Hz, 2H, ArCH₂), 3.35–3.43 (m, 2H), 3.57–3.92 (m, 10H), 6.72–6.76 (m, 4H, OAr). – ¹³C NMR (CD₃CN, 320 K): δ = 54.22, 55.79, 57.79, 66.76, 70.17 (d, *J*_{CF} = 3.5 Hz), 112.95, 120.96, 122.94 (d, *J*_{CF} = 4 Hz), 129.49 (d, *J*_{CF} = 13.5 Hz), 130.83 (d, *J*_{CF} = 5 Hz), 149.92, 162.98 (d, *J*_{CF} = 252 Hz). – ¹⁹F NMR (CD₃CN): δ = –113.45 (s). – C₂₄H₃₁FN₂O₄ (430.5): calcd. C 67.00, H 7.26, N 6.50; found C 67.31, H 7.45, N 6.33.

BenzoFN₂O₄ · KBr: ¹H NMR (CDCl₃): δ = 2.67 (d, *J* = 14.2 Hz, 2H), 2.75–2.82 (m, 2H), 2.97 (d, *J* = 13.9 Hz, 2H), 3.11–3.21 (m, 4H), 3.45 (t, *J* = 2.2 Hz, 1H), 3.48 (t, *J* = 2.4 Hz, 1H), 3.63–3.69 (m, 2H), 3.94–4.13 (m, 10H), 6.35 (t, *J* = 7.3 Hz, 1H, ArH), 6.50–6.54 (m, 2H, ArH), 6.69–6.78 (m, 4H, OArH). – ¹⁹F NMR (CD₃CN): δ = –119.85 (s).

BenzoFN₂O₄ · Ag⁺: Et₂O was allowed to slowly diffuse into a solution of **BenzoFN₂O₄** (108 mg, 0.25 mmol) and AgCF₃SO₃ (64 mg, 0.25 mmol) in CH₃CN (3 ml). After 24 h crystals of **BenzoFN₂O₄ · Ag⁺** deposited on the walls of the glass vessel. – ¹H NMR (CD₃CN): δ = 2.63 (d, m, *J* = 14.0 Hz, 4H), 2.96–3.12 (m, 6H), 3.46 (dm, *J* = 10.1 Hz, 2H), 3.66 (m, AA'BB', 4H), 3.82–4.16 (m, 6H), 4.29 (dd, *J* = 12.8, 2.0 Hz), 6.20–6.33 (m, 4H, ArH), 7.10 (t, *J* = 7.5 Hz, 1H, ArH), 7.36 (t, 2H, *J* = 7.5 Hz). – ¹³C

NMR (CD₃CN): δ = 54.83, 55.27, 55.52, 63.81, 67.24, 69.34, 112.07, 122.15, 124.68 (d, *J*_{CF} = 5 Hz), 130.56 (d, *J*_{CF} = 12 Hz), 147.28, 161.09 (d, *J*_{CF} = 242 Hz). – ¹⁹F NMR (CD₃CN): δ = –116.42 [d, *J*(^{107,109}Ag–¹⁹F) = 25.2 Hz]. – ¹H NMR (CD₃COCD₃): δ = 2.77 (m, 4H, NCH₂), 3.17–3.25 (m, 2H + 4H, ArCH₂ + NCH₂), 3.57 (dm, *J* = 9.9 Hz, 2H, OCH₂), 3.64–3.70 (m, AA', 2H, OC₂H₄O), 3.81–3.87 (m, BB', 2H, OC₂H₄O), 4.08 (dm, *J* = 11.8 Hz, 2H, OCH₂), 4.14 (dd, *J* = 11.7, 1.3 Hz, 2H, OCH₂), 4.21 (d, m, *J* = 11.0 Hz, 2H, OCH₂), 4.44 (dd, *J* = 12.7, ⁴*J*_{HF} = 2.0 Hz, 2H, ArCH₂), 6.87–6.93 (m, AA'BB', 4H, ArH), 7.21 (t, *J* = 7.8 Hz, 1H, ArH), 7.52 (t, *J* = 7.5 Hz, 2H, ArH).

X-Ray Crystal Structure Determinations (Table 2): Suitable crystals were mounted on top of a glass fiber. X-ray data were collected with an Enraf-Nonius CAD4 diffractometer by using Mo-*K*_α radiation (71.069 pm) and a graphite monochromator. All structures were solved (SHELXS-86)^[32] and refined (SHELXL-93)^[33] against *F*². In the structures described all non-hydrogen atoms were refined by using anisotropic temperature coefficients. Hydrogen atoms were refined with fixed isotropic temperature coefficients (riding model). An empirical absorption correction (psi scans) was applied in both cases^[34].

Table 2. Compilation of X-ray crystal structure data

Compound	(FN ₂ O ₄) ₂	Ag ⁺ ·FN ₂ O ₄
Empirical formula	C ₄₀ H ₅₂ F ₂ N ₄ O ₈	C ₂₄ H ₃₁ AgF ₄ N ₂ O ₇ S
Formula mass [g mol ^{–1}]	764.94	639.41
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n
Unit cell dimensions [pm or °]		
<i>a</i> =	9.409(1)	13.024(3)
<i>b</i> =	11.691(1)	13.797(3)
<i>c</i> =	19.315(1)	14.306(3)
α =	90	90
β =	97.65(1)	94.61(3)
γ =	90	90
Volume [Å ³]	2105.8(3)	2562.2(10)
<i>Z</i>	2	4
Density [g cm ^{–3}]	1.206	1.658
Absorption [mm ^{–1}]	0.089	0.941
<i>F</i> (000)	824	1304
Crystal size [mm]	0.8 × 0.6 × 0.5	0.6 × 0.5 × 0.4
Theta range [°]	2.9–26.0	2.5–26.3
Index range (<i>hkl</i>)	–11/11, –14/0, 0/23	–16/16, 0/17, –17/0
Reflections collected/independent	4268, 4141	5403, 5194
Data/parameters	4130/244	4720/391
Goof	1.084	1.075
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> ₁ , <i>wR</i> ₂	0.0385, 0.0904	0.0363, 0.0933
Final <i>R</i> indices (all data)		
<i>R</i> ₁ , <i>wR</i> ₂	0.0750, 0.1147	0.0536, 0.1076
Largest peak and hole [e Å ^{–3}]	+0.14, –0.16	+0.53, –0.95

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