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

Herbert Plenio* and **Ralph Diodone**

Institut für Anorganische und Analytische Chemie, Universität Freiburg,
Albertstraße 21, D-79104 Freiburg, Germany
E-mail: plenio@ruf.uni-freiburg.de

Received April 4, 1996

Key Words: Silver / Macrocycles / Cryptands / Fluorine

The partially fluorinated cryptands $\mathbf{FN_2O_4}$ and $\mathbf{BenzoFN_2O_4}$, 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 $\mathbf{FN_2O_4}$ are significantly more stable than those of $\mathbf{HN_2O_4}$ (the two ligands are identical except that one fluorine atom is replaced by one hydrogen atom in $\mathbf{HN_2O_4}$); the $^1J_{CF}$ coupling constants of $Ag^+ \cdot \mathbf{FN_2O_4}$ and $Ag^+ \cdot \mathbf{BenzoFN_2O_4}$ are reduced by 10 Hz compared to those of the respective free ligands $\mathbf{FN_2O_4}$ ($^1J_{CF} = 253$ Hz) and $\mathbf{BenzoFN_2O_4}$. ($^1J_{CF} = 252$ Hz). The X-ray crystal structure of $Ag^+ \cdot \mathbf{FN_2O_4}$ reveals short $Ag^+{-}F$ distances [271.4(3) pm]; coupling of the $^{107,109}Ag^+$ and ^{19}F nuclei is observed in the ^{19}F-NMR spectra ($J = 24$ Hz for $Ag^+ \cdot \mathbf{FN_2O_4}$, $J = 25$ Hz for $Ag^+ \cdot \mathbf{BenzoFN_2O_4}$). The ^1H-NMR spectrum of $Ag^+ \cdot \mathbf{FN_2O_4}$ 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 posses a C−H instead of a C−F unit. ii) The $^1J_{CF}$ 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].

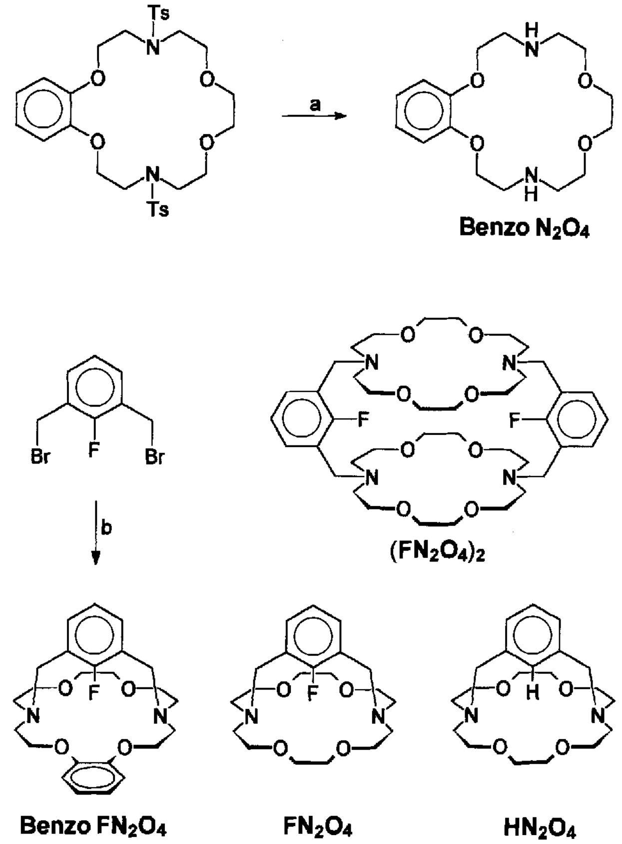
Results and Discussion

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 $\mathbf{FN_2O_4}$ 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].

0009−2940/96/1010−1211 $ 15.00+.25/0

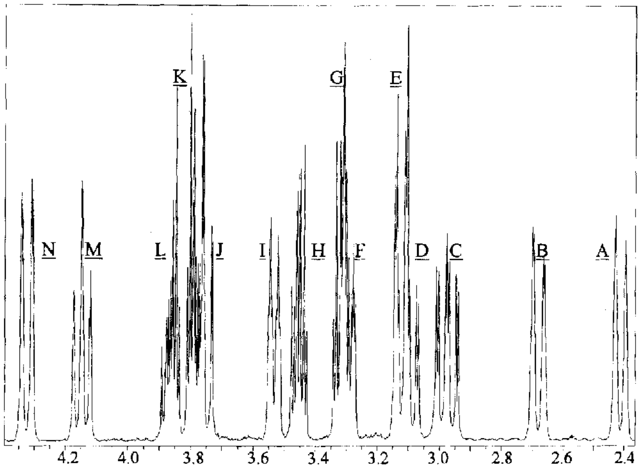
The new fluorocryptand **BenzoFN$_2$O$_4$** was synthesized in a yield of 27% utilizing the standard reaction of 1,3-bis(bromomethyl)-2-fluorobenzene with the diazamacrocycle **BenzoN$_2$O$_4$**[9] (Scheme 1). For the synthesis of ditosylated **BenzoN$_2$O$_4$** we followed a procedure by Jurczak et 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 $LiAlH_4$. However, whereas reaction times typically are shorter than 48 h, the detosylation of **BenzoN$_2$O$_4$** proved more difficult, since even after seven days at reflux some monoprotected macrocycle was still present, with the overall yield of **BenzoN$_2$O$_4$** being only modest.

Scheme 1. Macrocycles used for the complexation of Ag^+ and synthesis of **BenzoFN$_2$O$_4$**: Reagents and conditions:
a. $LiAlH_4$, refluxing THF, 7 d. – b. **BenzoN$_2$O$_4$**/Na_2CO_3, refluxing CH_3CN



NMR Spectroscopical Investigations: The ^{1}H-NMR spectra of Ag^+ · **FN$_2$O$_4$** and Ag^+ · **BenzoFN$_2$O$_4$** 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 CH_2 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 CH_2 group can be as high as 1.2 ppm. One oxyethylene chain of Ag^+ · **FN$_2$O$_4$** and Ag^+ · **BenzoFN$_2$O$_4$** 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^+ · **FN$_2$O$_4$** displaying sixteen unique ^{1}H-NMR signals. Each of the two symmetry-independent NC_2H_4O units represents an independent ABCD spin system, whereas the two different OC_2H_4O units display an AA'BB' pattern.

Figure 1. Aliphatic region of the ^{1}H-NMR spectrum (δ scale) (400 MHz, CD_3COCD_3, T = 300 K) of Ag^+ · **FN$_2$O$_4$**. This spectrum consists of five independent spin systems. NC_2H_4O (BDIM), NC_2H_4O (ACFJ), OC_2H_4O (KL), OC_2H_4O (GH), $ArCH_2$ (EN)



The assignment of all proton resonances and connectivities within each group of Ag^+ · **FN$_2$O$_4$** was straightforward with the aid of (^{1}H,^{1}H) COSY, TOCSY and (^{1}H,^{13}C) COSY spectra. The orientation of the different CH_2CH_2 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 OCH_2CH_2O units (KL) and (GH) in Ag^+ · **FN$_2$O$_4$** 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 possiblity of Ag^+ · **BenzoFN$_2$O$_4$** 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 ^{13}C-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 possiblities. This phenomenon makes the complete assignment of the ^{1}H-NMR resonances very difficult, since the (^{1}H,^{1}H) COSY as well as the TOCSY spectra display too many crosspeaks to allow a distinction between the different chains.

Solution Structure of Ag^+ · **FN$_2$O$_4$**: In order to obtain more stereochemical information for a better understanding of the structure of Ag^+ · **FN$_2$O$_4$** in solution, we determined the ^{1}H-NMR shifts of all protons as well as all ^{1}H-^{1}H coupling constants (Table 1) by simulation of the ^{1}H-NMR spectrum[11]. Additional structural information is available from

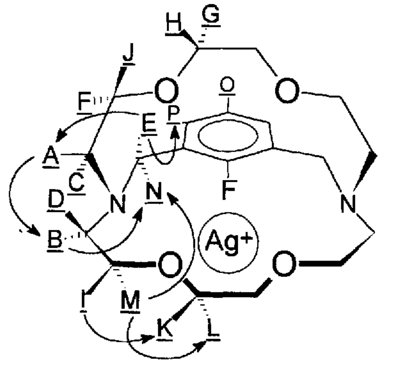


Figure 2. Stereochemical assignment of the ^{1}H-NMR resonances in $Ag^+ \cdot$ **FN_2O_4**. The underlined letters symbolize the respective protons (only heteroatoms are denoted by their standard atomic symbols) with the same lettering as in Figure 1. The NOEs observed are marked by arrows between the respective protons

the NOEs which were obtained from NOESY spectra. The ^{1}H-NMR resonances of each NCH_2CH_2O resonances display besides the large geminal coupling two small (1.6–3.0 Hz) and one large (11.5, 11.8 Hz) vicinal ^{1}H-^{1}H 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 Haasnot, 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 $Ag^+ \cdot$ **FN_2O_4** displays an additional small splitting of 0.8 Hz, which can be due to a ^{19}F-^{1}H 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. ^{1}H-NMR shifts and coupling constants of **$Ag^+ \cdot FN_2O_4$** in CD_3COCD_3. Underlined letters denote the respective protons as depicted in Figures 1 and 2

	δ	J (gem) [Hz]	J (vic) [Hz]	J (vic) [Hz]	J_{HF} [Hz]	$\nu_{1/2}$ [Hz]
A	2.411	(AC)= 13.7	(AF)= 2.6	(AJ)= 1.7		2.0
B	2.681	(BD)= 14.2	(BI)= 2.8 Hz	(BM)= 1.6		1.6
C	2.974	(CA)	(CF)= 3.0	(CJ)= 11.8		1.3
D	3.102	(DB)	(DI)= 2.8	(DM)= 11.5		1.4
E	3.124	(EN)= 12.9			2.8	1.6
F	3.293	(FJ)= 12.2	(FA)	(FC)		1.6
G	3.316	(GH)= 9.8	(GG')= 2.2	(GH')= 6.3		0.8
H	3.453	(HG)	(HH')= 2.4	(HG')		0.8
I	3.532	(IM)= 9.9	(IB)	(ID)		2.2
J	3.760	(JF)	(JA)	(JC)		1.1
K	3.783	(KL)= 11.8	(KK')= 2.7	(KL')= 6.5		1.2
L	3.862	(LK)	(LK')	(LL')= 2.4		1.2
M	4.145	(MI)	(MB)	(MD)	0.8	1.2
N	4.323	(NE)			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 ^3J coupling constants (>10 Hz) within the OCH_2CH_2O units, which however were not observed. To obtain more information on the solution structure of $Ag^+ \cdot$ **FN_2O_4** 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 ^{19}F-NMR spectra of the Ag^+ complexes, where the ^{19}F{H} resonances of $Ag^+ \cdot$ **FN_2O_4** and $Ag^+ \cdot$ **$BenzoFN_2O_4$** are split into doublets with coupling constants $J = 24$ ($Ag^+ \cdot$ **FN_2O_4**) and 25 Hz ($Ag^+ \cdot$ **$BenzoFN_2O_4$**)[17]. It is obvious that this splitting must be due to a coupling between $^{107,109}Ag^+$ and ^{19}F[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 $Ag^+ \cdot$ **HN_2O_4** 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 CD_3COCD_3) a very small coupling between ^{107,109}Ag and ^{1}H ($J = 3.3$ 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 ^{1}H (2.675) to ^{19}F (2.517)][21]. However, the frequency of the ^{1}H-NMR resonance of this aromatic hydrogen in **HN_2O_4** (δ = 8.31) is almost the same as in $Ag^+ \cdot$ **HN_2O_4** (δ = 8.18), whereas in the related 5-oxa-2,8-dithia[9]-*m*-cyclophane the ^{1}H-NMR resonance of the hydrogen atom in the 2-position of the aromatic ring is shifted by 0.5 ppm upon addition of $AgBF_4$[22].

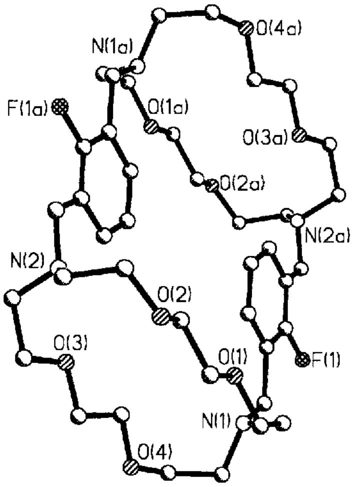
More evidence for close Ag^+–F contacts is available by determining the $^1J_{CF}$ coupling constants. In the complexes of alkaline and alkaline earth metal ions with fluoro macrocycles this parameter was found to be correlated with the degree of metal-fluorine interaction in solution, i.e. the stronger the metal-fluorine bond, the smaller the $^1J_{CF}$ coupling constant as compared to that of the free fluorocryptand[4]. It is significant that this trend was also found in the case of the Ag^+ complexes described here. For **FN_2O_4** ($^1J_{CF}$ = 253 Hz), Ag^+ · **FN_2O_4** ($^1J_{CF}$ = 243 Hz), **Benzo-FN_2O_4** ($^1J_{CF}$ = 252 Hz), and Ag^+ · **BenzoFN_2O_4** ($^1J_{CF}$ = 242 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 **$(FN_2O_4)_2$** with Ag^+. Hence, upon addition of an excess of Ag^+ salt neither $^1J_{CF}$ 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 **BenzoFN_2O_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 Ag^+-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 Ag^+-F interactions in Ag^+ · **HN_2O_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 Ag^+-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 **$(FN_2O_4)_2$** *and* Ag^+ · **FN_2O_4**: In the solid-state structure of **$(FN_2O_4)_2$** 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 symmetry-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 **$(FN_2O_4)_2$** 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)

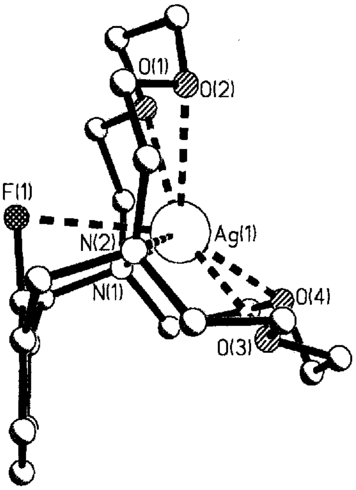


Complexes of crown ethers with Ag(I) are not very common since hard oxygen donors are not ideal for the coordination of the relatively soft Ag^+. Consequently, these complexes are less stable than those of group-I and group-II metal ions[23]. It is therefore hardly surprising that only few solid-state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

In the crystal structure of Ag^+ · **FN_2O_4** the metal ion is coordinated by four oxygen [Ag^+-O 247.8(2)–262.7(3) pm] atoms, two nitrogen [Ag^+-N 258.5(3), 269.4(3) pm] atoms and one fluorine atom [Ag^+-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 Ag^+-F distance is rather short and only slightly longer than $Ag^+-N(2)$ but still within the range covered by the Ag^+-O distances in other complexes[25]. It is obvious therefore that fluorine can be an active part of the silver coordination sphere. Short Ag^+-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] [$CF-Ag^+$ = 260(1)–269(1) pm] and one each by Girolami et al.[27] [$CF-Ag^+$ = 288.6, 292.6 pm] and Strähle et al.[28] [$CF-Ag^+$ = 301.8 pm].

Another remarkable structural feature of Ag^+ · **FN_2O_4** is that the silver ion is located above the CF bond

Figure 4. Molecular structure of Ag$^+$ · **FN$_2$O$_4$** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Ag−F(1) 271.4(3), Ag−O(1) 258.6(2), Ag−O(2) 262.1(3), Ag−O(3) 247.8(2), Ag−O(4) 262.7(3), Ag−N(1) 258.5(3), Ag−N(2) 269.4(3); F(1)−Ag(1)−N(1) 71.9(8), F(1)−Ag(1)−N(2) 70.9(8), F(1)−Ag(1)−O(1) 75.0(8), F(1)−Ag(1)−O(2) 85.3(8), F(1)−Ag(1)−O(3) 125.5(9), F(1)−Ag(1)−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 η^2 shift of the silver ion, which was also observed for Ba^{2+} 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 Ag(I) salts with fluorocryptands both in solution and in the solid state. Experimental evidences for the significance of these contacts are:

i) The complex Ag$^+$ · **FN$_2$O$_4$** is more stable than Ag$^+$ · **HN$_2$O$_4$**. − ii) Coupling of the nuclear spins of ^{107,109}Ag and ^{19}F was observed in the solution-NMR spectra. − iii) In the case of the Ag(I) complexes of **FN$_2$O$_4$** and **BenzoFN$_2$O$_4$** the $^1J_{CF}$ value is reduced by 10 Hz compared to that of the free ligands. − iv) In the solid-state structure of Ag$^+$ · **FN$_2$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.

This work was supported by the *Fonds der Chemischen Industrie*, the *Deutsche Forschungsgemeinschaft*, and the *Freiburger Wissenschaftliche Gesellschaft*. We thank Dr. *W. Deck* and Dipl.-Chem. *M. Ruf* for collecting the X-ray data sets, *V. Brecht* for recording several 2D-NMR spectra, and Prof. Dr. *H. Vahrenkamp* for his support.

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 (^{1}H 200, ^{13}C 50.3, ^{19}F 188.2 MHz), Varian Unity 300 (^{1}H 300, ^{13}C 75 MHz), or Bruker AM 400 (^{1}H 400 MHz). ^{1}H-NMR spectra were referenced to residual H atoms of the solvent. ^{13}C-NMR shift values are given with respect to solvent signals: CDCl$_3$ (δ = 7.26, 77.0), CD$_3$CN (δ = 1.93, 1.30), and CD$_3$COCD$_3$ (δ = 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$_3$ (δ = 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$_2$O$_4$**[4], **(FN$_2$O$_4$)$_2$**[4], **HN$_2$O$_4$**[4].

Synthesis of **FN$_2$O$_4$** · Ag$^+$: Et$_2$O was allowed to slowly diffuse into a solution of **FN$_2$O$_4$** (191 mg, 0.5 mmol) and AgCF$_3$SO$_3$ (128 mg, 0.5 mmol) in CH$_3$CN (5 ml). After 24 h crystals of Ag$^+$ · **FN$_2$O$_4$** deposited on the walls of the glas vessel. − ^{1}H NMR (CD$_3$CN): 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, $^4J_{HF}$ = 1.9 Hz, 1H), 7.10−7.18 (m, 1H), 7.31−7.39 (m, 2H). − ^{13}C NMR: δ = 55.04 ($\underline{\mathrm{AC}}$, $\underline{\mathrm{BD}}$), 55.33 ($\underline{\mathrm{EN}}$]), 67.20 ($\underline{\mathrm{FJ}}$], 67.65 ($\underline{\mathrm{IM}}$), 69.59 ($\underline{\mathrm{KL}}$), 70.38 ($\underline{\mathrm{GH}}$), 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, $^1J_{CF}$ = 243 Hz). − ^{19}F NMR: δ = −116.45 [d, $J(^{107,109}\mathrm{Ag}\text{-}^{19}\mathrm{F})$ = 24.0 Hz].

Solutions of **(FN$_2$O$_4$)$_2$** · 2 Ag$^+$ or **HN$_2$O$_4$** · Ag$^+$ for the NMR experiments were prepared by dissolving AgCF$_3$SO$_3$ (0.1 mmol) and the respective ligand **(FN$_2$O$_4$)$_2$** (0.05 mmol) or **HN$_2$O$_4$** (0.1 mmol) in CD$_3$CN.

(FN$_2$O$_4$)$_2$ · 2 Ag$^+$: ^{1}H NMR (CD$_3$CN): 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). − ^{13}C NMR (CD$_3$CN): 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, $^1J_{CF}$ = 246 Hz).

HN$_2$O$_4$ · Ag$^+$: ^{1}H NMR (CD$_3$CN): δ = 2.63 (t, J = 4.0 Hz, NCH$_2$, 8H), 3.40−3.63 (m, NCH$_2$, OCH$_2$, 20H), 7.23−7.27 (m, ArH, 3H), 8.18 (br., ArH, 1H). − ^{1}H NMR (CD$_3$COCD$_3$, 210 K, ArH only): δ = 7.15−7.25 (m), 7.35 (s), 8.37 [d, $J(^{107,109}\mathrm{Ag}\text{-}^1\mathrm{H})$ = 3.3 Hz].

2,3-Benzo-7,16-diaza-1,4,10,13-tetraoxacyclooctadecane (**BenzoN$_2$O$_4$**): Ditosylated benzodiaza-18-C-6 (4.56 g, 7.9 mmol) and LiAlH$_4$ (6.08 g, 160 mmol) in THF (250 ml) were heated at reflux for 7 d. Afterwards, excess LiAlH$_4$ was destroyed by *carefully* adding water to the ice-cooled reaction mixture. The solids were filtered off, extracted with CHCl$_3$ (3 × 25 ml) and the combined filtrates evaporated to dryness. The residue was purified by chromatography (cyclohexane/Et$_2$NH, 5:1, product eluted with CHCl$_3$/Et$_2$NH, 100:1) and recrystallized from petroleum ether. Yield: 0.5 g (20%), colorless oil. − ^{1}H NMR (CD$_3$CN): δ = 2.75 (t, J = 4.7 Hz, 4H, NCH$_2$), 2.92 (t, J = 4.7 Hz, 4H, NCH$_2$), 3.45−3.56 (m, 12H, OCH$_2$), 4.02−4.07 (m, 4H, OCH$_2$), 6.88−6.91 (m, 4H, ArH).

Synthesis of **BenzoFN$_2$O$_4$**: 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 K_2CO_3 (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 $CHCl_3$/diethyl ether resulting in the formation of colorless crystals of m.p. 242°C, which proved to be the KBr adduct of **BenzoFN$_2$O$_4$**. A solution of **BenzoFN$_2$O$_4$** · KBr in $CHCl_3$ was extracted with water to remove KBr from the organic layer. The $CHCl_3$ solution was separated, dried with $MgSO_4$, filtered and evaporated to dryness. After evaporation of the volatile components in vacuo pure **BenzoFN$_2$O$_4$** was available. Yield: 83 mg (27%). – ^1H NMR (CD_3CN, 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, $ArCH_2$), 3.35–3.43 (m, 2H), 3.57–3.92 (m, 10H), 6.72–6.76 (m, 4H, OAr). – ^{13}C NMR (CD_3CN, 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). – ^{19}F NMR (CD_3CN): δ = –113.45 (s). – $C_{24}H_{31}FN_2O_4$ (430.5): calcd. C 67.00, H 7.26, N 6.50; found C 67.31, H 7.45, N 6.33.

BenzoFN$_2$O$_4$ · KBr: ^1H NMR ($CDCl_3$): 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). – ^{19}F NMR (CD_3CN): δ = –119.85 (s).

BenzoFN$_2$O$_4$ · Ag^+: Et_2O was allowed to slowly diffuse into a solution of **BenzoFN$_2$O$_4$** (108 mg, 0.25 mmol) and $AgCF_3SO_3$ (64 mg, 0.25 mmol) in CH_3CN (3 ml). After 24 h crystals of **BenzoFN$_2$O$_4$** · Ag^+ deposited on the walls of the glas vessel. – ^1H NMR (CD_3CN): 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_c, 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). – ^{13}C NMR (CD_3CN): 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, $^1J_{CF}$ = 242 Hz). – ^{19}F NMR (CD_3CN): δ = –116.42 [d, $J(^{107,109}Ag\text{-}^{19}F)$ = 25.2 Hz]. – ^1H NMR (CD_3COCD_3): δ = 2.77 (m, 4H, NCH_2), 3.17–3.25 (m, 2H + 4H, $ArCH_2$ + NCH_2), 3.57 (dm, J = 9.9 Hz, 2H, OCH_2), 3.64–3.70 (m, AA', 2H, OC_2H_4O), 3.81–3.87 (m, BB', 2H, OC_2H_4O), 4.08 (dm, J = 11.8 Hz, 2H, OCH_2), 4.14 (dd, J = 11.7, 1.3 Hz, 2H, OCH_2), 4.21 (d, m, J = 11.0 Hz, 2H, OCH_2), 4.44 (dd, J = 12.7, $^4J_{HF}$ = 2.0 Hz, 2H, $ArCH_2$), 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).

Table 2. Compilation of X-ray crystal structure data

Compound	$(FN_2O_4)_2$	$Ag^+ \cdot FN_2O_4$
Empirical formula	$C_{40}H_{62}F_2N_4O_8$	$C_{21}H_{31}AgF_4N_2O_7S$
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 °]		
a =	9.409(1)	13.024(3)
b =	11.691(1)	13.797(3)
c =	19.315(1)	14.306(3)
α =	90	90
β =	97.65(1)	94.61(3)
γ =	90	90
Volume [Å]	2105.8(3)	2562.2(10)
Z	2	4
Density [gcm^{-3}]	1.206	1.658
Absorption [mm^{-1}]	0.089	0.941
F(000)	824	1304
Crystal size [mm]	0.8 x 0.6 x 0.5	0.6 x 0.5 x 0.4
Theta range [°]	2.9 – 26.0	2.5 – 26.3
Index range (*hkl*)	–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 R indices [$I>2\sigma(I)$] $R1$, $wR2$	0.0385, 0.0904	0.0363, 0.0933
Final R indices (all data) $R1$, $wR2$	0.0750, 0.1147	0.0536, 0.1076
Largest peak and hole [eÅ^{-3}]	+0.14, –0.16	+0.53, –0.95

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].

---

[1] H. Plenio, *Inorg. Chem.* **1994**, *33*, 6123.

[2] H. Plenio, D. Burth, *J. Chem. Soc., Chem. Commun.* **1994**, 2297.

[3] H. Plenio, R. Diodone, *Angew. Chem.* **1994**, *106*, 2267; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2175.

[4] H. Plenio, R. Diodone, *J. Am. Chem. Soc.* **1996**, *118*, 356, and references therein.

[5] P. Murray-Rust, W. C. Stalling, C. T. Monti, R. K. Preston, J. P. Glusker, *J. Am. Chem. Soc.* **1983**, *105*, 3206.

[6] [6a] R. J. Kulawiec, R. H. Crabtree, *Coord. Chem. Rev.* **1990**, *99*, 89. – [6b] J. L. Kipplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373.

[7] G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Pergamon Press, London, **1987**.

[8] R. D. Shannon, *Acta Crystallogr., Sect.A*, **1976**, *32*, 751.

[9] [9a] K. R. A. S. Sandanayake, I. O. Sutherland, *Tetrahedron Lett.* **1993**, *19*, 3165. – [9b] J. Jurczak, T. Stankiewicz, P. Salanski, S. Kasprzyk, P. Lipkowksi, *Tetrahedron* **1993**, *49*, 1478.

[10] R. Ostaszewski, U. Jacobsson, J. Jurczak, *Bull. Pol. Acad. Sci. Chem.* **1988**, *36*, 221.

[11] WIN-DAISY, Version 1.12.1995, Bruker-Franzen Analytik GmbH.

[12] M. J. Minch, *Concepts Magn. Reson.* **1994**, *6*, 41.

[13] C. A. Hasnoot, F. A. A. M. DeLeeuw, C. Altona, *Tetrahedron* **1980**, *36*, 2783.

[14] H. Kessler, M. Gehrke, C. Griesinger, *Angew. Chem.* **1988**, *100*, 507; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 490.

[15] W. R. Croasmun, R. M. Carlson (Eds.), *Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, **1994**.

[16] The CH distances obtained from the solid-state structure (riding model) were not used directly, but were normalized to 109 pm.

[17] S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, G. Thieme Verlag, Stuttgart, **1994**.

[18] The difference in coupling between ^{19}F and ^{107}Ag (51.8%), ^{109}Ag (48.2%) could not be resolved due to the similar magnetogyric ratios of the Ag isotopes (1.083–1.245) and the rather broad ^{19}F-NMR signals ($\nu_{1/2}$ = 3 Hz).

[19] R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

[20] A. Albinati, H. Lehner, L. M. Venanzi, M. Wolfer, *Inorg. Chem.* **1987**, *26*, 3933.

[21] R. K. Harris, B. E. Mann, *NMR and the Periodic Table*, Academic Press, **1978**.

[22] J. Casabo, T. Flor, M. N. S. Hill, H. A. Jenkins, J. C. Lockhart, S. J. Loeb, I. Romero, F. Teixidor, *Inorg. Chem.* **1995**, *34*, 5410.

[23] [23a] T. Burchard, B. G. Cox, P. Firman, H. Schneider, *Ber. Bunsenges. Phys. Chem.* **1994**, *98*, 1526. – [23b] T. Burchard, P. Firman, H. Schneider, B. G. Cox, *Ber. Bunsenges. Phys. Chem.* **1994**, *98*, 1534.

[24] [24a] R. Wiest, R. Weiss, *J. Chem. Soc., Chem. Commun.* **1973**, 678. – [24b] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L.

Atwood, B. C. Lynn, A. E. Kaifer, G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583. – [24c] J. S. Bradshaw, J. S. McDaniel, B. D. Skidmore, R. B. Nielsen, B. E. Wilson, N. K. Dalley, R. M. Izatt, *J. Heterocycl. Chem.* **1987**, *24*, 1085. – [24d] P. G. Jones, T. Gries, H. Grützmacher, H. W. Roesky, J. Schimkowiak, G. M. Sheldrick, *Angew. Chem.* **1984**, *96*, 357; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 376. – [24e] H. W. Roesky, E. Peymann, J. Schimkowiak, M. Noltemeyer, W. Pinkert, G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* **1983**, 981.

[25] [25a] J. W. Silbert, S. J. Lange, D. J. Williams, A. G. M. Barrett, B. M. Hoffman, *Inorg. Chem.* **1995**, *34*, 2300. – [25b] H. Andrianatoandro, Y. Barrans, P. Marsau, J. P. Desvergne, F. Fages, H. Bouas-Laurent, *Acta Crystallogr., Sect. B*, **1995**, *51*, 293.

[26] [26a] R. Uson, J. Fornies, M. Tomas, J. Casas, F. A. Cotton, L. R. Falvello, R. Llusar, *Organometallics* **1988**, *7*, 2279. – [26b] R. Uson, J. Fornies, M. Tomas, F. A. Cotton, L. R. Falvello, *J. Am. Chem. Soc.* **1984**, *106*, 2482. – [26c] R. Uson, J. Fornies, *Inorg. Chim. Acta* **1982**, *198–200*, 165.

[27] P. M. Jeffries, S. R. Wilson, G. S. Girolami, *J. Organomet. Chem.* **1993**, *203*, 449.

[28] E. Hartmann, J. Strähle, *Z. Anorg. Allg. Chem.* **1990**, *583*, 31.

[29] H. Plenio, R. Diodone, *Z. Naturforsch., Part B*, **1995**, *50*, 1075.

[30] M. S. Nasir, B. J. Cohen, K. D. Karlin, *J. Am. Chem. Soc.* **1992**, *114*, 2482.

[31] [31a] S. Kulstad, L. A. Malmsten, *Acta Chem. Scand., Ser. B*, **1979**, *33*, 469. – [31b] S. Kulstad, L. A. Malmsten, *Tetrahedron Lett.* **1980**, *21*, 643.

[32] G. M. Sheldrick, *SHELXS-86, A Program for the Solution of X-Ray Crystal Structures*, Universität Göttingen, **1986**.

[33] G. M. Sheldrick, *SHELXL-93, A Program for the Refinement of X-Ray Crystal Structures*, Universität Göttingen, **1993**.

[34] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404012 and CSD-404013, the names of the authors and the journal citation.

[96069]