Partially Fluorinated Macrocycles: Synthesis of the Tetrafluoro Analogue of the [2S.2O.2O]-Cryptand and the Crystal Structure of the Sodium Complex

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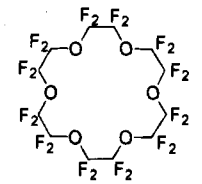
Tetrafluoro-1,2-bis(chlorosulfenyl)ethane is used for the synthesis of two fluorine containing macrocycles. The insertion of ethylene into the S−Cl bond, followed by an exchange of Cl against I gives 1,8-diiodo-3,6-dithia-4,4,5,5-tetrafluorooctane in two steps (overall yield 75%). This compound has been cyclized with 1,8-diamino-3,6-dioxaoctane to produce 1,4-dithia-7,16-diaza-10,13-dioxa-2,2,3,3-tetrafluorocyclooctadecane with a 30% yield, which on further reaction with 1,8-diiodo-3,6-dioxaoctane gives the cryptand 1,10-diaza-4,7,13,16-tetraoxa-21,-24-dithia-22,22,23,23-tetrafluorobicyclo[8.8.8]hexacosane, which is the fluorinated analogue of the [2S.2O.2O]-cryptand. The effect of the complexation of alkaline metal ions on the ^{19}F NMR shifts has been investigated. The solid state structure of the sodium complex of the fluorocryptand is reported.

Introduction

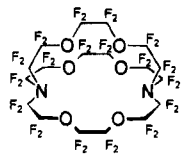
Even though the chemistry of macrocyclic hosts has experienced an explosive growth in the years since Pedersen's breakthrough work, examples of macrocycles containing fluorine are very rare.[1]

The substitution of hydrogen by fluorine has been used in organic chemistry to change electronic properties and to introduce an NMR probe, while largely retaining the same stereochemical features.[2] This is also an interesting motivation for the design of macrocyclic hosts, especially with a view to the development of novel sensor materials, which are based on the shifts of the ^{19}F NMR resonance upon complexation of a metal cation within the macrocycle.[3] Therefore it is quite surprising that only very few such structures have been described. The first compounds of this type were synthesized by Lagow et al. by controlled exposure of crown ethers to elemental fluorine.[4] However, these compounds in common with those prepared by Farnham, Dixon et al.[5] suffer from the serious drawback of not forming stable complexes with metal cations. Consequently these compounds are lacking *the* essential property of crown ethers, the reason for this being the electron withdrawing effect of the CF_2 groups, which effectively destroys the basicity of the donor atoms (Chart 1).

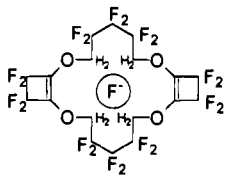
Chart 1. Fluorinated Crown Ethers



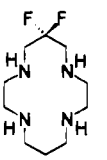
Lagow et al.



Lagow et al.



Farnham, Dixon et al.



Kimura et al.

To retain the unique ability of macrocycles to form stable complexes with the cations of alkaline and earth alkaline metals the degree of fluorination must be low. As it is extremely difficult to control the direct fluorination process without ending up in a mixture of numerous regioisomers, another concept is required.

The only succesful approach was recently demonstrated by Kimura et al., who used partially fluorinated malonic ester as a building block for the synthesis of different cyclam (1,4,8,11-tetraazacyclotetradecane) derivatives.[6] However, according to the HSAB principle nitrogen donors are not well suited for the complexation of group I metal ions.

It was of interest therefore to use other fluorine containing molecules for the construction of macrocyclic structures. Such building blocks should be closely related to the ethylene glycols which are often used for the synthesis of crown ethers and whose donor atoms are linked by a more favorable C_2-bridge. A

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molecule well suited for this purpose is tetrafluoro-1,2-dichlorosulfenylethane, **1**. The synthesis of this compound has already been desribed in the early 1960's,[7] but its chemistry remained largely unknown up to the pioneering work of Roesky et al. in the 1980's.[8]

I wish to report on the synthesis of two partially fluorinated macrocyclic ligands which are synthesized starting from tetrafluoro-1,2-bis(chlorosulfenyl)ethane as the basic building block.

Experimental Section

Only reactions involving tetrafluoro-1,2-bis(chlorosulfenyl)ethane were carried out under dry nitrogen using standard Schlenk techniques. Commercially available solvents and reagents were purified according to literature procedures. Chromatography was carried out with silica MN 60. NMR spectra were recorded at 300 K with a Bruker AC200 F (^{1}H NMR 200 MHz, ^{13}C NMR 50 MHz, ^{19}F NMR 188 MHz) or a Varian Unity 300 (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz). ^{1}H NMR referenced to residual hydrogen in the solvent and ^{13}C NMR to the solvent signals: $CDCl_3$ (7.26 ppm, 77.0 ppm) and CD_3CN (1.93 ppm, 1.30 ppm). In the ^{1}H and ^{13}C NMR spectra of the tetraphenylborate salts the resonances of the anion are not listed. ^{19}F NMR spectra referenced to internal $CFCl_3$ (0 ppm). Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. Melting points were determined with a Meltemp melting point apparatus in sealed capillaries. Starting materials were commercially available or prepared according to literature procedures: tetrafluoro-1,2-bis(chlorosulfenyl)ethane,[9] 1,8-diiodo-3,6-dioxaoctane.[10]

Safety Notes. Compounds **2** and **3** which are products of the insertion of ethylene into sulfur−chlorine bonds should be treated with utmost care and must not be brought in contact with the skin, since they are related to highly toxic mustard gas.

1-(Chlorosulfenyl)-1,1,2,2-tetrafluoro-3-thia-5-chloropentane (2). A solution of 1,2-$C_2F_4(SCl)_2$ (11.75 g, 50 mmol) in 150 mL of dry CH_2Cl_2 was heated under reflux. Ethylene was bubbled through the stirred solution until the starting material had been consumed (^{19}F NMR). The reaction mixture now contains approximately 65% of the monoinsertion product **2**. The solvent is evaporated and the product distilled under vacuo (0.1 Torr, 40 °C) over a short Vigreux column. Yield: approximately 7.9 g (60%). ^{19}F NMR ($CDCl_3$): δ = −86.22 (t, $^3J_{FF}$ = 12 Hz, $CF_2SC_2H_4Cl$), −89.96 (t, $^3J_{FF}$ = 12 Hz, CF_2SCl).

1,8-Dichloro-3,6-dithia-4,4,5,5-tetrafluorooctane (3). A solution of 1,2-$C_2F_4(SCl)_2$ (23.5 g, 100 mmol) in 250 mL of dry CH_2Cl_2 was transferred into a high pressure reactor and shaken under 50 atm of ethylene at 50 °C for 48 h. After releasing the pressure the CH_2Cl_2 was evaporated and the product distilled under vacuo (0.1 Torr/ 80 °C). Yield: 27.4 g (94%). ^{1}H NMR ($CDCl_3$): δ = 3.24 (t, J = 7.5 Hz, 4H), 3.73 (t, J = 7.5 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ = 30.65 (t, $^3J_{CF}$ = 2 Hz, SCH_2), 42.61 (s, CH_2Cl), 125.06 (t,t, $^2J_{CF}$ = 34 Hz, $^1J_{CF}$ = 288 Hz, CF_2). ^{19}F NMR ($CDCl_3$): δ = −86.62.

1,8-Diiodo-3,6-dithia-4,4,5,5-tetrafluorooctane (4). A solution of 1,8-dichloro-3,6-dithia-4,4,5,5-tetrafluorooctane (27.4 g, 94 mmol) and NaI (56.5 g, 376 mmol) in 800 mL acetone was heated under reflux for 48 h. Afterward the acetone was evaporated, the residue dissolved in CH_2Cl_2 and washed repeatedly with aqueous thiosulfate. The organic phase was separated, dried over $MgSO_4$, the volatiles were evaporated and the residue recrystallized from 250 mL of petrol ether. Yield: 35.6 g (80%), mp 45−47 °C. Anal. Calcd for $C_6H_8F_4I_2S_2$ (474.1): C, 15.20; H, 1.70. Found: C; 15.82; H 2.1. ^{1}H NMR ($CDCl_3$): 3.36 (s). ^{13}C NMR ($CDCl_3$): 1.29 (CH_2I), 31.27 (t, $^3J_{CF}$ = 2 Hz, SCH_2), 125.02 (t,t, $^1J_{CF}$ = 289 Hz, $^2J_{CF}$ = 34 Hz, CF_2). ^{19}F NMR ($CDCl_3$): −86.48.

1,4-Dithia-7,16-diaza-10,13-dioxa-2,2,3,3-tetrafluorocyclooctadecane (5). A mixture of 1,8-diiodo-3,6-dithia-4,4,5,5-tetrafluorooctane (20.0 g, 42.1 mmol), 1,8-diamino-3,6-dioxaoctane (6.24 g, 42.1 mmol), Na_2CO_3 (17.8 g, 0.168 mmol) and 5g NaI in 2000 mL CH_3CN was heated under reflux for 48 h. Afterward the reaction mixture was filtered and the CH_3CN evaporated. To the residue were added 50 mL 10% aq. NaOH and the product extracted with CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, the CH_2Cl_2 evaporated and the remaining oil distilled under high vacuum (heat gun ca. 300 °C, 1 × 10^{-4} Torr). Yield: 4.6 g (30%). Anal. Calcd for $C_{12}H_{22}F_4N_2O_2S_2$ (366.48): C, 39.33; H, 6.05. Found: C, 40.54; H 6.33. ^{1}H NMR ($CDCl_3$): δ = 2.82 (t, J = 4.9 Hz, 4 H, NCH_2), 2.94 (t, J = 5.7 Hz, 4 H, NCH_2), 3.15 (t, J = 5.6 Hz, 4 H, SCH_2), 3.61 (s, 4 H, OCH_2), 3.62 (t, J = 4.8 Hz, 4H, OCH_2). ^{13}C NMR ($CDCl_3$): δ = 29.87 (SCH_2), 47.55 (NCH_2), 48.44 (NCH_2), 70.16 (OCH_2), 70.38 (OCH_2), 125.29 (t,t, $^1J_{CF}$ = 299 Hz, $^2J_{CF}$ = 33 Hz, CF_2). ^{19}F NMR ($CDCl_3$): δ = −88.58. (CD_3CN): δ = −87.58. ^{19}F NMR shifts upon addition of 1 equiv of the respective salts, Δ is the difference of the NMR shifts of the complex and the free ligand in CD_3CN: $LiClO_4$ (−88.26, Δ = −0.68), $NaBPh_4$ (−87.58, Δ = zero), $KBPh_4$ (−87.77, Δ = −0.19).

[2S(C_2F_4).2O.2O]-Cryptand (6) (1,10-Diaza-4,7,13,16-tetraoxa-21,24-dithia-22,22,23,23-tetrafluorobicyclo[8.8.8]hexacosane). A mixture of 7,16-diaza-1,4,10,13-tetraoxacyclooctadecane (131 mg, 0.5 mmol), 1,8-diiodo-3,6-dithia-4,4,5,5-tetrafluorooctane (184 mg, 0.5 mmol), and Na_2CO_3 (250 mg) in 50 mL CH_3CN was heated under reflux for 72 h. The cooled mixture was filtered and the volatiles evaporated. To the residue was added 5 mL of water and the mixture extracted with $CHCl_3$ (three times with 25 mL). The organic layer was separated, dried with a small amount of $MgSO_4$, filtered and evaporated to dryness. Yield (determined by ^{19}F NMR): 10%.

[2S(C_2F_4).2(O).2(O)]-Cryptand (6). A mixture of 1,4-dithia-7,-16-diaza-10,13-dioxa-2,2,3,3-tetrafluorocyclooctadecane (549 mg, 1.5 mmol), 1,8-diiodo-3,6-dioxaoctane (558 mg, 1.5 mmol) (alternatively the ditosylate may be used) and Na_2CO_3 (800 mg) in 100 mL CH_3CN was heated under reflux for 21 d. The cooled mixture was filtered and the volatiles evaporated. To the residue was added 5 mL of water and the mixture extracted with $CHCl_3$ (three times with 25 mL). The organic layer was separated, dried with a small amount of $MgSO_4$ and filtered over a silica plug. The product was extracted with $CHCl_3$/CH_3OH (10:1). The volatiles were evaporated and the residue recrystallized from petrolether three times. Mp: 89 °C. Yield: 0.22 g (30%). Anal. Calcd for $C_{18}H_{32}F_4N_2O_4S_2$ (480.58): C, 44.99; H, 6.71. Found: C, 44.72; H, 7.02. ^{1}H NMR ($CDCl_3$): δ = 2.55−2.62 (m, 8H, NCH_2), 2.72 (t, 6.2 Hz, 4 H, NCH_2), 3.09 (t, 6.1 Hz, 4 H, SCH_2), 3.51−3.57 (m, 8 H, OCH_2), 3.61−3.68 (m, 4H, OCH_2), 3.83−3.90 (m, 4H, OCH_2). ^{13}C NMR ($CDCl_3$): δ = 28.37 (SCH_2), 53.64 (NCH_2), 55.55 (NCH_2), 68.91 (OCH_2), 70.77 (OCH_2), 125.60 (t,t, $^1J_{CF}$ = 318 Hz, $^2J_{CF}$ = 30 Hz, CF_2). ^{19}F NMR ($CDCl_3$): δ = −90.10. ^{1}H NMR (CD_3CN): δ = 2.53 (m, 8H, NCH_2), 2.69 (t, J = 6.2 Hz, 4H, NCH_2), 3.10 (t, J = 6.1 Hz, SCH_2), 3.48 (m, 8H, OCH_2), 3.55−3.60 (m, 4H, OC*H*H), 3.72−3.77 (m, 4 H, OCH*H*). ^{13}C NMR (CD_3CN): δ = 29.27 (SCH_2), 54.08 (NCH_2), 56.21 (NCH_2), 69.80 (OCH_2), 71.52 (OCH_2). ^{19}F NMR (CD_3CN): δ = −87.67. ^{19}F NMR shifts upon addition of 1 equiv of the respective salt, Δ is the difference of the NMR shifts in CD_3CN: $LiClO_4$ (−87.67, Δ = zero), $NaBPh_4$ (−88.73, Δ = −1.1), $KBPh_4$ (−88.81, Δ = −1.1), $RbBPh_4$ (−88.71, Δ = −1.0), $Ba(ClO_4)_2$ (−88.66, Δ = −1.0).

[2S(C_2F_4).2O.2O]-Cryptand·$NaBPh_4$. ^{1}H NMR (CD_3CN): δ = 2.57 (t, 5.0 Hz, 8 H, NCH_2), 2.66 (t, J = 5.9 Hz, 4 H, NCH_2), 3.18 (t, J = 5.9 Hz, 4 H, SCH_2), 3.44−3.64 (m, OCH_2, 8 H), 3.61 (s, OCH_2, 8 H). ^{13}C NMR (CD_3CN): δ = 28.32 (SCH_2), 53.08 (NCH_2), 53.74 (NCH_2), 68.63 (OCH_2), 70.55 (OCH_2).

[2S(C_2F_4).2O.2O]-Cryptand·$KBPh_4$. ^{1}H NMR (CD_3CN): δ = 2.45−2.70 (m, NCH_2), 2.65 (t, J = 5.5 Hz, NCH_2), 3.15 (t, J = 5.5 Hz, SCH_2), 3.48−3.55 (m, OCH_2, 8 H), 3.59 (s, OCH_2, 8 H). ^{13}C NMR (CD_3CN): δ = 29.10 (SCH_2), 52.37 (NCH_2), 56.64 (NCH_2), 68.41 (OCH_2), 71.07 (OCH_2).

[2S(C_2F_4).2O.2O]-Cryptand·$RbBPh_4$. ^{1}H NMR (CD_3CN): δ =

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Table 1. Atomic Coordinates ($\times 10^4$) for **6**·$NaClO_4$

	x	y	z
N(1)	5292(3)	2254(3)	3607(3)
C(1)	5682(5)	1433(4)	4080(5)
C(2)	5259(5)	1368(4)	4970(5)
O(1)	4087(3)	1258(2)	4946(2)
C(3)	3671(5)	1233(4)	5777(4)
C(4)	2505(5)	886(4)	5767(3)
O(2)	1794(3)	1504(2)	5293(2)
C(5)	665(5)	1228(4)	5344(4)
C(6)	−101(5)	1964(5)	4996(4)
N(2)	19(3)	2189(3)	4102(3)
C(7)	−322(5)	1418(5)	3554(5)
C(8)	72(6)	1530(6)	2653(4)
O(3)	1232(3)	1559(3)	2649(2)
C(9)	1641(7)	1720(5)	1824(4)
C(10)	2769(6)	1346(5)	1754(3)
O(4)	3506(3)	1814(2)	2347(2)
C(11)	4614(6)	1494(4)	2258(4)
C(12)	5421(5)	2146(4)	2693(4)
C(13)	5880(4)	3079(4)	3912(4)
C(14)	5210(4)	3940(4)	3726(4)
S(1)	3887(1)	3760(1)	4210(2)
C(15)	3200(5)	4805(4)	3894(4)
F(1)	3724(3)	5552(2)	4237(3)
F(2)	3195(3)	4966(3)	3001(2)
C(16)	2000(5)	4792(4)	4123(5)
F(3)	2043(4)	4781(3)	5001(2)
F(4)	1524(3)	5599(2)	3906(3)
S(2)	1329(2)	3829(2)	3626(2)
C(17)	26(5)	3886(5)	4132(6)
C(18)	−601(5)	3026(5)	3903(5)
Na(1)	2630(2)	1631(2)	3813(1)
Cl(1)	2348(1)	−786(1)	3349(1)
O(13)	3432(8)	−543(9)	3078(8)
O(11)	2066(10)	−123(6)	3914(5)
O(12)	1634(13)	−823(7)	2687(8)
O(14)	2500(5)	1634(4)	3765(4)

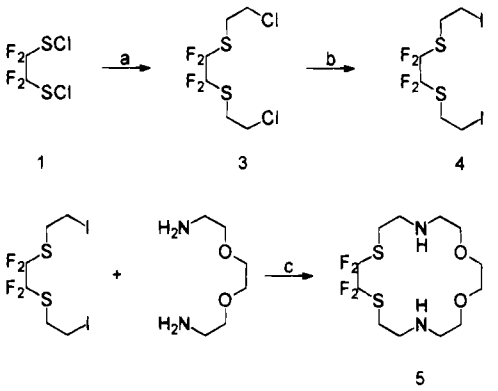
2.45−2.75 (m, NCH_2), 2.68 (t, J = 5.8 Hz, NCH_2), 3.15 (t, J = 5.8 Hz, 4 H, SCH_2), 3.53 (t, J = 4.7 Hz, 8 H, OCH_2), 3.60 (s, 8 H, OCH_2). ^{13}C NMR (CD_3CN): δ = 29.7 (SCH_2), 52.54 (NCH_2), 56.4 (NCH_2), 68.74 (OCH_2), 70.83 (OCH_2).

Crystal Structure Determination of 6·$NaClO_4$. Single crystals of **6**·$NaClO_4$ were grown by allowing ether to slowly diffuse into an acetonitrile solution. A suitable crystal was mounted on top of a glass capillary. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (71.069 pm) and a graphite monochromator. Structure Solution, Structure Refinement on F^2: SHELXS 86, SHELXL 93.[11] Crystal Dimensions: 0.8 × 0.6 × 0.5 mm^3. Theta range: 2.8−26.3°. Index range: *hkl* (−14/14) (0/18) (0/19) Formula: $C_{18}H_{32}ClF_4N_2O_8S_2$ (580.0). Space group: $P2_1/c$. Cell Dimensions: a = 11.937(2), b = 14.486(3), c = 15.641(3) Å; β = 91.67(3). Volume: 2703.5(9) $Å^3$. Z = 4. $F(000)$ = 1256. Density: 1.482 g cm^{-3}. Absorption coefficient: 0.383 mm^{-1}. Absorption correction: empirical, psi-scans. Refinement method: Full-matrix least squares on F^2. Reflections (collected, independent): 5686, 5479. Data/parameter = 4007/352. GooF = 1.10. Final R indices ($4\sigma(I)$): $R1$ = 7.65%, w$R2$ = 21.28%. Largest difference peak and hole = +0.60/−0.415 e/$Å^3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The perchlorate group is disordered 2-fold and was included in the refinement in two different orientations with s.o.f. 0.8 and 0.2, respectively. All hydrogen atoms were refined with fixed isotropic temperature coefficients (riding model). Definition of R-values: $R1 = \Sigma|F_o - F_c|/\Sigma(F_o)$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; GooF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

Results and Discussion

Synthesis of the Partially Fluorinated Macrocycles. The tetrafluorinated $N_2O_2S_2$-crown ether was synthesized according to Scheme 1. In the first step the fluorinated building block tetrafluoro-1,2-bis(chlorosulfenyl)ethane (**1**) is elongated on both ends by C_2-chains. This is accomplished by insertion of an olefin into the sulfur−chlorine bonds. The reaction of ethylene and **1** in CH_2Cl_2 at slightly elevated temperatures and 50 atm pressure of ethylene, gives an almost quantitative yield of the double insertion product 1,8-dichloro-3,6-dithia-4,4,5,5-tetrafluorooctane **3**. The insertion of ethylene occurs in a stepwise manner, therefore the reaction may be carried out in such a way that the predominant product is the monoinsertion compound 1-(chlorosulfenyl)-1,1,2,2-tetrafluoro-3-thia-5-chloropentane (**2**). Bubbling ethylene through a solution of **1** in CH_2Cl_2 held at reflux temperature leads to a mixture consisting mainly of **2**, which can be purified by destillation.

Scheme 1. Synthesis of the Fluorinated Crown Ether **5**[a]



[a] Key: a, 50 atm C_2H_4, 48 h, 50 °C; b, NaI, acetone, 48 h reflux; c, acetonitrile, Na_2CO_3, 48 h reflux.

Reactions of **3** with primary amines do not proceed in the desired way, as elimination of HCl rather than the nucleophilic substitution of chlorine is the preferred reaction channel (a typical problem in organofluorine chemistry). To introduce a better leaving group, the Finkelstein reaction with NaI in acetone was carried out. This gives an 80% yield of stable 1,8-diiodo-3,6-dithia-4,4,5,5-tetrafluorooctane (**4**), which may be stored for extended periods without decomposition. **3** and **4** belong to the class of β-halogen thioethers which contains numerous highly toxic compounds. However, it is expected that the strongly electron withdrawing effect of the C_2F_4 unit reduces the nucleophilicity of two sulfur atoms and hence the toxicity of these two halides.

A procedure modeled after the Kulstad and Malmsten[12] synthesis of diaza-18-C-6 can also be used for the synthesis of 1,4-dithia-7,16-diaza-10,13-dioxa-2,2,3,3-tetrafluorocyclooctadecane ($N_2O_2S_2(C_2F_4)$-18-C-6) (**5**). The reaction of 1,8-diamino-3,6-dioxaoctane with **4** and Na_2CO_3 gives a 30% yield of **5**. When Et_3N is used as a base instead only small amounts of **5** are formed. The rather high yield of this macrocycle (**5**) is somewhat surprising, since the soft donor atoms in **4** are not well suited for an efficient preorganization around the templating sodium cations.

To improve the cation binding ability of the partially fluorinated macrocycle **5**, the number of donor atoms was increased. The synthesis of a partially fluorinated cryptand was therefore attempted with both routes d and e (Scheme 2) leading to the desired macrobicyclic compound. The reaction of **5** and 1,8-diiodo-3,6-dioxaoctane, however, gives a much better yield (40%) of the cryptand **6**, since the reaction of the secondary amine diaza-18-C-6 with **4** mainly generates elimination products, which are also difficult to separate. The macrobicyclic

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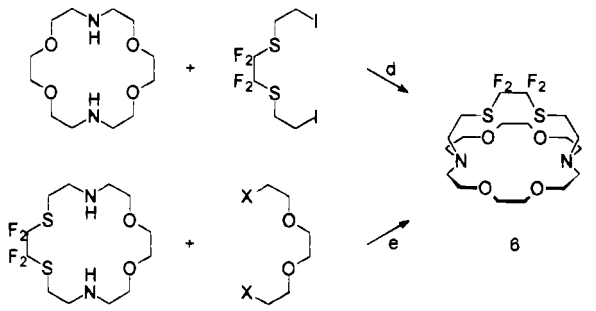
Scheme 2. Synthesis of the Fluorinated Cryptand[a]



[a] Key: d, Na_2CO_3, acetonitrile, 14 d reflux; e, Na_2CO_3, acetonitrile, 21 d reflux (X = I, OTs).

compound **6** is the tetrafluorinated analogue of 1,10-diaza-4,7,13,16-tetraoxa-21,24-dithiabicyclo[8.8.8]hexacosane ([2S.2O.2O]-cryptand), which was first described by Lehn at al.[13] Very little is known about the complexation characteristics of this compound,[14] and it was of interest to see how the tetrafluorinated relative **6** would behave upon addition of metal salts.

NMR Complexation Studies of 5 and 6. NMR spectroscopy may be used as an indicator for the ability of ligands to form metal complexes. Conformative changes in the ligand upon complexation and the electric charge of a cation change the position of NMR resonances. In **5** the mixed $N_2O_2S_2$-donor set contains too many soft donor atoms to form stable complexes with the ions of the alkaline metals. This is evidenced by the small changes in the ^1H and ^{19}F NMR spectra upon addition of the cations. Larger shifts of the ^{19}F NMR resonances are observed with softer metal ions such as Cu(I), Ag(I) and Zn(II), because of the higher affinity toward sulfur.

Stable complexes with group I metal ions are formed by the macrobicyclic ligand **6**. The corresponding metal complexes are prepared by dissolving **6** and the respective metal tetraphenylborates or perchlorates of Li^+, Na^+, K^+, Rb^+, and Ba^{2+} in CH_3CN. The solid materials are isolated by precipitation with Et_2O. Metal complexes of **6** produce signal shifts in the ^{19}F NMR spectrum of ~ -1 ppm (see Experimental Section) with respect to the free ligand. It is concluded therefore that neither an interaction of the metal ions with sulfur nor with the negatively polarized fluorine atoms occurs. The uniform shift differences with different ions may be attributed to a change in the conformation of the fluorine containing chain, which seems to have the same conformation regardless of the cation within the macrocyclic cavity. To support this hypothesis a X-ray crystal structure of a metal complex of **6** was performed.

Solid State Structure of the Sodium Complex of the Cryptand 6. Obviously the cavity of the [2S(C_2F_4).2O.2O]-cryptand (**6**) is too big to perfectly accommodate the small sodium cation, which is not located in the center of the cryptand and is only coordinated by four ring oxygen and one perchlorate oxygen in the first coordination sphere (Figure 1).

The exodentate orientation of the sulfur atoms which is so typical for crown thioethers[15] is not found in **6**·$NaClO_4$ even though it was observed for the nonfluorinated [2S.2O.2O]-cryptand.[14] In the solid state structure of this compound the sulfur atoms are oriented toward the inside of the macrocyclic cavity. Due to the peripheral position of Na^+ the distance

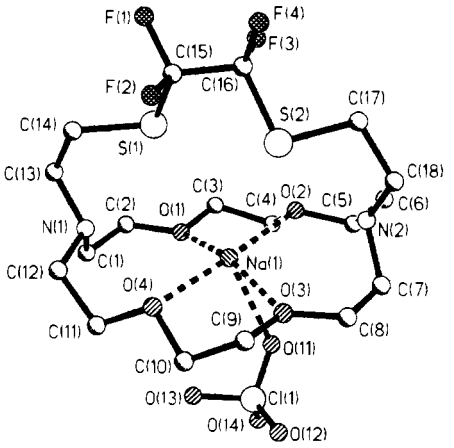


Figure 1. Solid state structure of **6**·$NaClO_4$.

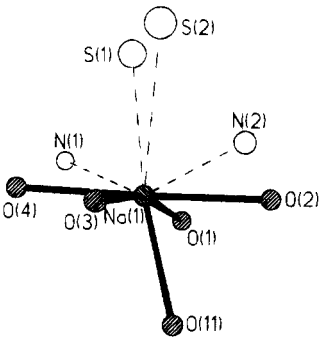


Figure 2. Coordination sphere of Na^+ and relevant bond lengths (pm) and angles (deg): Na(1)–O(1) 250.6(4), Na(1)–O(2) 255.4(4), Na(1)–O(3) 243.6(4), Na(1)–O(4) 256.1(4), Na(1)–O(11) 263.5(10), Na(1)–N(1) 332.8(6), Na(1)–N(2) 347.8(6), Na(1)–S(1) 347.8(6), Na(1)–S(2) 355.0(6); O(4)–Na(1)–O(2) 177.9(1), O(1)–Na(1)–O(3) 164.9(2).

sodium–sulfur is too large for a direct donor bond. However, an attractive interaction of the sulfur lone pairs and the sodium cation seems to be present (Figure 2), which apparently is stronger than a potentially attractive interaction of the negatively polarized fluorine and the sodium cation. This is somewhat surprising since fluorine is known to take part in metal coordination.[16] The weak participation of sulfur and nitrogen is also apparent in the square-pyramidal coordination sphere around the sodium cation seen when only the oxygen donor atoms are taken into account. The open face created by this unusual coordination geometry of sodium[17] lies on the inside of the cavity and is supplemented with electron density through weak interactions with the sulfur and nitrogen lone pairs.

The nitrogen–sodium distances (332.8, 326.4 pm) are much larger than typically observed in complexes of Na^+ with azamacrocycles.[18] Even though the cation is not in the center of the cryptand, the orientation of the chain atoms in the

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macrobicyclic compound roughly corresponds to a 3-fold symmetry (along the N1−N2 axis).

Conclusions

The synthesis of two partially fluorinated crown ethers as well as the determination of the crystal structure of **6**·$NaClO_4$ were succesfully performed. The partially fluorinated cryptand is the first macrobicyclic compound which is known to form stable complexes with alkaline metal ions. The position of the ^{19}F NMR resonances change significantly upon complexation of metal cations but does not respond selectively to a given cation.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and full bond lengths and angles for **6**·$NaClO_4$ (6 pages). Ordering information is given on any current masthead page.