Lariat ethers with fluoroaryl side-arms: a study of $CF \cdots$ metal cation interaction in the complexes of N-(o-fluoroaryl)azacrown ethers[†]

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New lariat ethers, *N*-(*o*-fluorophenyl)aza-15-crown-5 (F-A15C5) and N,N'-bis(*o*-fluorophenyl)diaza-18-crown-6 (F_2 - A_2 18C6), were prepared by the *N*-arylation of the corresponding azacrown ethers. The interaction of the ligands with metal cations was studied in solution by ¹H and ¹⁹F NMR (in acetone-d₆) and UV spectroscopy (MeOH) confirming the formation of complexes of F_2 - A_2 18C6 with K⁺, Na⁺, Ag⁺, Ba²⁺, Pb²⁺ and of F-A15C5 with Na⁺ and giving evidence of CF ··· metal cation interaction. Cation binding constants (β , evaluated by UV titration method), demonstrate that F-A15C5 and F₂- A_2 18C6 form more stable complexes than their fluorine-free analogs. The effect depends on the nature of the metal cation and is at a maximum for hard, singly charged cations (up to 3 log β units for K⁺ complex of F₂- A_2 18C6). The X-ray structures of complexes [Pb(F₂- A_2 18C6)-(H₂O)](ClO₄)₂ (1) and [Ba(F₂- A_2 18C6)(ClO₄)₂] (2) reveal short Pb–F (2.805 Å) and Ba–F (2.965 Å) contacts. Complex 2 is centrosymmetric (C₁), while complex 1 has C₂ symmetry with one-side coordination of *o*-fluorophenyl groups to Pb²⁺. This "one-side" coordination mode of Pb²⁺ is indicative of a partial localization of the Pb²⁺ lone pair.

Introduction

The importance of cation coordination with C-F units of fluorocarbons and even the very fact of the existence of C- $F \cdots M^{n+}$ interactions have only been recognized in relatively recent times. It was only in the early 1980s that Glusker and Murray-Rust et al. pointed to a widespread occurrence of short CF-Mⁿ⁺ contacts in crystal structures and concluded that "...C-F bond is capable of significant, if not prominent, interactions with both alkaline metal cations and proton donors".1 However, the coordination chemistry of fluorocarbons is now a well established field, primarily due to the works of the Plenio²⁻⁶ and Takemura^{7,8} groups on fluorocryptands and fluorine-containing cage compounds. Understanding of the importance of Zr ··· F-C interactions in zirconocenium based Ziegler-Natta olefin polymerization catalysts gave another stimulus to the development of this field.^{3,9} The incorporation of fluorine donor centres into macrocyclic organic ligands enable the use of ¹⁹F NMR for the detection of complexation phenomena, thanks to the high sensitivity, comparable with protons, and large signal dispersion of ¹⁹F NMR. Another, less explored, aspect concerns the effect of fluorine, as the hardest possible donor centre, on the coordination properties of the ligand, such as its selectivity.

Existing fluorine-containing ligands utilize the endocyclic fluorophenyl groups bonded though CH_2 -bridges as fluorine donor centres, organized in a polycyclic cage framework. Thus, the effect of $C-F\cdots$ M coordination is achieved through a very high degree of ligand preorganization. A lariat ether with fluorine-containing side-arms would be a simpler and readily available model for the study of $C-F\cdots$ M interaction. However, ligands with *o*-fluorobenzyl side arms (CH_2 -bridges) are known to show only weak⁵ or no signs of $C-F\cdots$ M⁺ interactions.⁸

If the *o*-fluorophenyl group is bound directly to the nitrogen atom of the azacrown ring it will be more conformationally rigid. At the same time the basicity of fluorine will be enhanced due to the direct conjugation between nitrogen and fluorine centres. In the present paper we have synthesized N-(*o*-fluorophenyl)aza-15-crown-5 and N,N'-bis(*o*-fluorophenyl)diaza-18-crown-6 ethers and studied their interaction with metal cations, both in solution and in solid state.

It emerged that fluorine in these ligands can effectively participate in the coordination of the metal cations increasing the stability of the complexes. Moreover, the incorporation of fluorine produces a marked effect on the selectivity of *N*-arylazacrown ethers.

Results and discussion

Synthesis of ligands

Conventional methods for the preparation of *N*-aryl azacrown ethers use rather tedious multistep cyclizations starting from the corresponding anilines. Progress in Pd-catalyzed amination reactions allowed the development of a more straightforward approach based upon the direct arylation of the free azacrown ether with the corresponding aryl halide. We used this direct method to

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prepare the *N*-*o*-fluorophenyl derivative of aza-15-crown-5 by its reaction with *o*-bromofluorobenzene (Scheme 1) utilizing 2dimethylamino-2'-dicyclohexylphosphinobiphenyl as a ligand for palladium. This ligand showed the best performance in palladiumcatalyzed arylation of bulky secondary amines and azacrown ethers in particular.¹⁰ The reaction gave the desired product (F-A15C5), but only in meagre yield (20%) and was accompanied by hydrodebromination of the substrate giving fluorobenzene. Using other phosphine ligands (P(*t*Bu)₃, *rac*-BINAP, *rac*-1-[2-(diphenylphosphino)ferocenyl]ethylmethyl ether) or lowering the reaction temperature (from 100 °C to 70 °C) only worsened the yields.

The direct arylation of diaza-18-crown-6 ether under the conditions in Scheme 1 gave the monoarylated product in low yield. Therefore, we had to resort to a three-step procedure beginning with nucleophilic aromatic substitution on activated 1,2-difluoro-4-nitrobenzene for the synthesis of bis-*o*-fluorophenylated diaza-18-crown-6 ether (Scheme 2). The nitro group was then reduced to an amino group with H₂ and 10% Pd/C at atmospheric pressure and the amino group was removed by a standard hydrodediazonation procedure utilizing H₃PO₂. The target *bis*(*o*fluorophenyl)diaza-18-crown-6 ether (F₂-A₂18C6) was obtained in 50% overall yield in three steps.

Metal cation binding to F-A15C5 and F₂-A₂18C6 in solution

We examined the effect of the addition of metal salts on the ¹H and ¹⁹F NMR spectra of F-A15C5 and F_2 -A₂18C6. As can be seen from the data presented in Table 1 both hard (I and II group)

and soft (Ag⁺ and Pb²⁺), singly and doubly charged cations cause significant changes in the ¹H NMR spectrum of F₂-A₂18C6. Some of the signals of the CH₂-groups of the crown ring (OCH₂CH₂O) are shifted downfield, but the signals of the NCH₂ groups are shifted upfield. The upfield shift upon complexation may seem unusual, but actually it is characteristic for NCH₂ groups in Naryl azacrown ethers and can be attributed to the shielding effect of the aromatic ring current brought about by the perpendicular orientation of the aromatic ring to the ring of the macrocycle in the complex.^{11,12} The cation field effect acts in the opposite direction, resulting in smaller upfield shifts for doubly charged cations. A downfield shift is observed for all four aromatic protons. It indicates that both nitrogen and fluorine centres are involved in metal coordination since in N-aryl azacrown ethers without additional ortho-donor centres only protons ortho- to nitrogen exhibit a strong downfield shift upon complexation.¹²

Similar trends (upfield shift of the NCH₂ group signal and downfield shift of the aromatic protons) are found in the effect of the Na⁺ cation on the ¹H NMR spectrum of F-A15C5.

The shifting of the ¹⁹F NMR signals to higher field upon the addition of group I cations (Table 1) is another indication of cation–fluorine interaction in the complexes of F-A15C5 and F_2 -A₂18C6. Interaction with the cation through the nitrogen centre only would have resulted in a downfield shift of the fluorine resonance. The upfield shift of ¹⁹F signals is characteristic of cation–fluorine coordination according to the literature data,^{4,9,13} and it is also predicted by *ab initio* calculations.^{13,14} In conformationally relaxed macrocycles, the ¹⁹F resonances are shifted upfield upon binding of singly charged cations, but with doubly charged cations



Scheme 1 Synthesis of F-A15C5 by Pd-catalyzed arylation of aza-15-crown-5 ether.



Scheme 2 Synthesis of F_2 - A_2 18C6.

Table 1	The metal cation	induced chang	e in ¹ H	and ¹⁹ F	NMR	chemical	shifts ($\Delta\delta$, ppm) ^a	of N	V-(o-fluorophen	yl)aza-15-crowr	15 (F	-A15C5) and
N, N'-bis	(o-fluorophenyl)dia	aza-18-crown-6	ether (F	$_{2}-A_{2}18C0$	5) ^b								

			F-A15C5 n= F₂-A₂18C6 r	H∜ H ⁵ 1 Z=O h=2 Z=NC ₆ H₄- <i>o</i> -F	H ³ F H ⁶ O	Yo Zn O			
		NCH_2	NCCH ₂ O	OCH ₂ CH ₂ O	H ³	H^4	H^{5}	H^6	¹⁹ F
Ligand	\mathbf{M}^+	δ /ppm (mi	ultiplicity)						
F-A15C5 F ₂ -A ₂ 18C6		3.47 (t) 3.54 (t)	3.67 (t) 3.64 (t)	3.60 (s) 3.56 (s)	6.98 (m) 7.01 (m)	6.81(m) 6.84 (m)	7.03 (m) 7.05 (m)	7.10 (t) 7.12 (t)	-122.9 -122.5
$\Delta \delta / \text{ppm}^a$ F-A15C5 F ₂ -A ₂ 18C6 F ₂ -A ₂ 18C6 F ₂ -A ₂ 18C6 F ₂ -A ₂ 18C6 F ₂ -A ₂ 18C6	$\begin{array}{c} Na^{*} \\ K^{*} \\ Na^{*} \\ Ag^{*} \\ Ba^{2*} \\ Pb^{2*} \end{array}$	-0.13 -0.23 -0.12 -0.06 -0.09 -0.02	$-0.08 \\ -0.19 \\ -0.01 \\ 0.10 \\ 0.08 \\ 0.34$	0.19 0.01 0.11 0.16 0.23 0.39	0.28 0.29 0.10 0.10 0.36 0.36	0.41 0.42 0.34 0.44 0.50 0.49	0.23 0.25 0.18 0.07 0.32 0.32	0.45 0.41 0.34 0.41 0.54 0.54	-1.7 -1.2 -3.5 4.2 2.5 3.5

 $^{a}\Delta\delta = \delta$ (complex) – δ (crown ether). b Solvent acetone-d₆, 20 °C, $c \approx 5 \times 10^{-3}$ mol L⁻¹, 3 equivalents of metal salt, counterion – [SCN]⁻ for K⁺, I⁻ for Na⁺ and [ClO₄]⁻ for Ag⁺, Ba²⁺ and Pb²⁺. Signal assignment is based on NMR simulation (aromatic region) and 2D NOESY correlations (Fig. S1–S3 of the ESI⁺).

the opposite downfield shift was observed.⁵ In F_2 - A_2 18C6 the effect of cations on the ¹⁹F signal shift (except for Ag⁺) follows the same trend (Table 1).

No changes in the ¹H and ¹⁹F NMR spectra of F-A15C5 and F_2 -A₂18C6 were observed upon the addition of $Y(NO_3)_3$ ·6H₂O to F-A15C5 and La(NO₃)₃·6H₂O or La(ClO₄)₃·6H₂O to F₂-A₂18C6, indicating the absence of any complexation between these ligands and the rare earth metal salts.

Next, the effect of fluorine on the stability of the complexes was estimated by measuring the cation binding constants for F-A15C5 and F₂-A₂18C6 and comparing them with the literature data for the corresponding fluorine-free ligands *N*-phenylaza-15crown-5 (H-A15C5)¹⁵ and *N*,*N'*-diphenyldiaza-18-crown-6 (H₂-A₂18C6).¹⁶ Binding constants (β) determined from the results of UV spectrophotometric titrations are given in Table 2. The ligands F-A15C5 and F₂-A₂18C6 have identical UV spectra consisting of a strong band at $\lambda_{max} = 252$ nm with a weaker shoulder at 275–295 nm. Upon the addition of metal salts the absorbance of both bands gradually decreases (Fig. S4 and S5 of the ESI \dagger).

As can be seen from the data given in Table 2, one ortho-fluorine centre in F-A15C5 makes the Na⁺ complex forty-fold more stable compared to H-A15C5, while two ortho-fluorines in F2-A218C6 increase the binding constant with K⁺ by 3 orders of magnitude. As a result, F_2 - A_2 18C6, in contrast to H_2 - A_2 18C6, forms quite a stable complex with K⁺. The magnitude of complex stabilization caused by the ortho-fluorine donor centres depends on the nature of the metal cation. For the softer Pb2+ cation the increase of the binding constant in F₂-A₂18C6 compared to H₂-A₂18C6 is much smaller than for hard K⁺. It means that incorporation of fluorine changes the selectivity of the ligand. Interestingly, F₂-A₂18C6 forms a more stable complex with a singly charged alkaline metal cation (K^+) than with a doubly charged alkaline earth cation (Ba²⁺) of a similar ionic radii, an opposite trend to the increase of the charge density of the cation and rather unusual for a crown ether. Stronger solvation of a highly charged cation, which is not

Table 2 The cation binding constants ($M+L \xrightarrow{\beta} ML$) for *N*-(*o*-fluorophenyl)aza-15-crown 5 (F-A15C5) and *N*,*N'*-bis(*o*-fluorophenyl)diaza-18-crown-6 (F₂-A₂18C6) ethers in comparison with the literature data for *N*-phenylaza-15-crown-5 (H-A15C5), *N*,*N'*-diphenyldiaza-18-crown-6 (H₂-A₂18C6) and *N*,*N'*-bis(*o*-methoxyphenyl)diaza-18-crown-6 [(MeO)₂-A₂18C6] ethers in MeOH, 22 °C

	$\log\!\beta$								
Crown ether	$\overline{\mathbf{K}^{+}}$	Na ⁺	Ba ²⁺	Mg^{2+}	Pb ²⁺				
F-A15C5	_	$2.5 (\pm 0.1)$	_	_	_				
F_2-A_218C6 $H_2-A_218C6^d$	4.0 (± 0.1) 1.1	$(\pm 0.1)^c$	2.9 (± 0.1) <1	1.2 (± 0.1)	4.0 (± 0.1) 2.7 ^e				
$(MeO)_2 - A_2 18C6^{f}$	3.9	4.0		<1					

^{*a*} Counterion – I⁻ for K⁺, Br⁻ for Na⁺ and [ClO₄]⁻ for Mg²⁺, Ba²⁺ and Pb²⁺, ^{*b*} Data from ref. 15. ^{*c*} When NaClO₄ was used instead of NaBr log β = 2.45(±0.1) was obtained. ^{*d*} Data from ref. 16 ^{*e*} Data from ref. 18. ^{*f*} Data from ref. 17, 50 : 50 MeOH–H₂O mixture.

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compensated by the interaction with weak and weakly polarizable fluorine donor centres, seems a natural explanation.

It is worth noting that F_2 -A₂18C6 and F-A15C5 are the first examples of monocyclic ligands where fluorine exerts such a marked effect on the complex stability, approaching the maximum values reported for fluorocryptands.^{3,4,6}

It is also instructive to compare the cation selectivity of F_2 - A_218C6 with that of its *ortho*-methoxy analog (N,N'-bis(*o*-methoxyphenyl)diaza-18-crown-6, $((MeO)_2$ - A_218C6).¹⁷ $(MeO)_2$ - A_218C6 has the same binding constant for K⁺ as F_2 - A_218C6 (Table 2), though in a more polar medium, but it has no K/Na selectivity, while F_2 - A_218C6 has a fifty-fold preference for binding K⁺ over Na⁺.

X-Ray structure of F_2 -A₂18C6 complexes with Pb(ClO₄)₂ and Ba(ClO₄)₂

The composition of crystals formed by the reaction of $Pb(ClO_4)_2$ and F_2 - A_218C6 corresponds to a monohydrated complex with the formula $[Pb(F_2-A_218C6)(H_2O)](ClO_4)_2$ (1). Reaction with $Ba(ClO_4)_2$ gave an anhydrous complex $[Ba(F_2-A_218C6)(ClO_4)_2]$ (2).

The structure of **1** consists of complex cations $[Pb(F_2-A_218C6)(H_2O)]^{2+}$ and ClO_4^- anions. In the cation, the metal atom lies on the two-fold axis (Fig. 1). The metal centre is bonded to four oxygen atoms of the F₂-A₂18C6 macrocycle with approximately equal Pb–O distances (2.626(7) and 2.639 (9) Å) and to the water atom O(3) (d(Pb-O) = 2.429(14) Å). The coordination number (CN) of the lead atom is increased to nine by more distant nitrogen atoms of the macrocycle and two *ortho*-fluorine atoms (d(Pb-N) = 2.843(9), d(Pb-F) = 2.805(10) Å). Selected bond lengths and angles are listed in Table 3.



CIG

F(1A

Taking into account the first coordination sphere of the metal atom only, the coordination polyhedron (CP) of lead may be considered as a highly distorted tetragonal pyramid (TP) with

Pb(1)-O(3)	2.431(14)	O(3)Pb(1)O(1A)	71.4(5)
Pb(1)-O(1)	2.626(7)	O(3)Pb(1)O(1)	74.1(5)
Pb(1)-O(2)	2.639(9)	O(1A)Pb(1)O(1)	145.2(4)
Pb(1)-N(1)	2.843(9)	O(3)Pb(1)O(2A)	89.1(4)
Pb(1)-F(1)	2.805(10)	O(1)Pb(1)O(2A)	113.4(3)
F(1)-C(12)	1.334(9)	O(3)Pb(1)O(2)	76.2(4)
O(2A)Pb(1)O(2)	165.3(5)	O(1)Pb(1)O(2)	61.7(3)
" Symmetry transfor	rmation A: $-x + 1$.	$v_{z} - z + 1/2$.	

the atoms O(1), O(1A), O(2) and O(2A) occupying equatorial positions and the water atom O(3) lying in an axial position. The metal atom is displaced from the equatorial plane of TP by 0.562 Å in the direction opposite to the axial atom O(3).

It is of interest to compare the structure of complex 1 with the previously reported dihydrated perchlorate complex of Pb with N,N'-bis(tetrafluoropyridin-4-yl)diaza-18-crown-6 (L'), $[Pb(L')(H_2O)_2](ClO_4)_2$ (3).¹⁸

The change of the tetrafluoropyridyl substituent on the crown ether nitrogen atom in 3 to an o-fluorophenyl moiety in 1 leads to a change of complex stoichiometry (the loss of one coordinated water molecule and the decrease of the CN of lead from 10 to 9). The latter resulted in the noticeable ordering of the CP of lead. Contrary to 1, in the structure of 3 the bond distances formed by Pb and crown oxygen atoms are significantly different (2.558(6)-2.727(6) Å). The Pb-O(H₂O) distances also differ seriously (2.450(8) and 2.704(8) Å). The Pb-N(1) and Pb-F(1) bond lengths in the structure of 1 are shorter than in 3 (d(Pb-N)-2.978(8) and 3.108(8); d(Pb-F)-2.890(10) and 3.123(9) Å, correspondingly). The latter indicates a stronger bonding interaction of nitrogen and fluorine atoms with the metal centre in 1 and is in accordance with the greater stability of compound 1 in solutions. In the structure of 1, the Pb-F(1) distance is slightly longer than the shortest known $Pb \cdots F$ contacts (organic molecule) (2.761(2), 2.784(8) Å).^{3,20}

The main structural feature of complexes 1 and 3 is the trend to "one-side" coordination of lead atom. For 1, in the irregular ninevertex polyhedron five oxygen atoms O(1), O(1A), O(2), O(2A) and O(3) lie on one side of metal atom at relatively short distances (2.429(14)–2.639(9) Å), while the other four atoms (2 N + 2F) occupy opposite side at longer distances. Similar to 1, the tenvertex polyhedron PbO₆N₂F₂ in 3 comprises from three oxygen atoms lying at one side (d(Pb-O)–2.450(8)–2.608(6) Å) and other seven ligands (3O + 2 N + 2F) occupying the opposite side.

The Pb(II) atom represents the *p*-element in low-valent state. In general, the CP geometry of these elements depends on the stereochemical behavior of the lone electron pair (LEP).¹⁹ The observed "one-side" coordination of Pb atom in **1** and **3** confirms the partial stereochemical activity (localization) of LEP. In both compounds the LEP is localized at the side occupied by more distant ligands (2 N + 2F for **1** and 3O + 2 N + 2F for **3**).

The crystals of **2** comprise neutral centrosymmetrical molecules $[Ba(F_2-A_218C6)(ClO_4)_2]$ (Fig. 2). Selected bond lengths and angles are listed in Table 4. As for the lead atom in **1**, the Ba atom in **2** is coordinated by four oxygen atoms at slightly different distances (av. 2.804 Å) and by the nitrogen and fluorine atoms of ligand L (d(Ba-N) = 2.991(4), d(Ba-F) = 2.965(3) Å). The CP of the Ba atom is supplemented with four oxygen atoms of unsymmetrically

C(4)

CG

C(12)

C(8

C(9)

C(10



Fig. 2 Molecular structure of $[Ba(F_2-A_218C6)(ClO_4)_2]$. All hydrogen atoms have been omitted for clarity.

Table 4	Selected	bonds	distances	(Å)	and	angles	(°)	for	2
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Ba(1)–O(2)	2.785(3)	O(3)Ba(1)N(1)	70.14(11)
Ba(1) - O(1)	2.822(3)	F(1)Ba(1)N(1)	54.93(10)
Ba(1) - O(3)	2.916(4)	O(2)Ba(1)O(4)	65.40(10)
Ba(1) - F(1)	2.965(3)	O(1)Ba(1)O(4)	65.06(10)
Ba(1)-N(1)	2.991(4)	O(3)Ba(1)O(4)	44.20(10)
Ba(1)–O(4)	3.196(5)	F(1)Ba(1)O(4)	123.48(9)
F(1) - C(12)	1.368(6)	N(1)Ba(1)O(4)	102.73(10)
O(1)Ba(1)F(1)	58.89(9)	O(2)Ba(1)O(1)	59.85(10)
O(3)Ba(1)F(1)	119.17(9)	O(2)Ba(1)O(3)	106.80(11)
O(2)Ba(1)N(1)	117.83(11)	O(1)Ba(1)O(3)	73.26(11)
O(1)Ba(1)N(1)	60.35(10)	O(2)Ba(1)F(1)	80.64(9)

bonded perchlorate anions (d(Ba–O) = 2.916(4)–3.196(5) Å). In **2** the CN of the Ba atom is equal to 12. High coordination numbers are not unusual for Ba atoms, but, in most cases the CNs of Ba atoms are not greater than $11.^{20}$ The increased CN (for **2**) may be attributed to the bidentate behavior of perchlorate anions and to the presence of fluorine donor centres in the side chains of the ligands.

Many examples of short Ba ··· F contacts have been reported previously (2.76–3.287 Å). However, the majority of these contacts were found in the complexes of hexafluoroacetylacetone (Hfa) and hexafluoro-*tert*-butylate.^{3,20} Two complexes of barium perchlorate with fluoro-containing crown ethers were investigated, namely 1,3-(2-fluorobenzo)-18-crown-5 (FO₅)² and 1,3-(2-fluorobenzo)-21-crown-6 (FO₆).¹³ In **2** the Ba ··· F distance is comparable with that found for Ba(FO₆)(ClO₄)₂ – 2.990(3) Å. However, it is 0.186 Å longer than the value reported for Ba(FO₅)(ClO₄)₂ – 2.799(8) Å. In the last case, the surprisingly short contact may be attributed to the small size of the cavity in the FO₅ ligand.

The coordination mode of the F_2 - A_2 18C6 ligand is similar in structures 1 and 2. However, the symmetry of these complexes is different (C_2 for 1 and C_i for 2). In 1 the fluorophenyl substituents lie on one side of the macrocyclic plane, while in 2 one lies to each

Table 5Selected torsion angles ($^{\circ}$) for 1 and 2

	1	2
C(6A)N(1)C(1)C(2)	168.7	165.0
N(1)C(1)C(2)O(1)	60.3	63.0
C(1)C(2)O(1)C(3)	176.1	178.5
C(2)O(1)C(3)C(4)	172.6	171.6
O(1)C(3)C(4)O(2)	55.7	59.4
C(3)C(4)O(2)C(5)	169.5	172.2
C(4)O(2)C(5)C(6)	171.5	177.4
O(2)C(5)C(6)N(1A)	57.8	68.6
C(5)C(6)N(1A)C(1A)	73.9	169.6

side. In 1 the lead atom is displaced from the mean plane of the macrocyclic oxygen atoms ([4O], $\Delta = 0.224$ Å) by 0.557 Å, while in 2 the barium atom is sited in the plane [4O]. In 2 the aromatic rings are approximately perpendicular to the mean plane of the macrocycle (torsion angle is 96.2°), while in 1 that angle is equal to 64°.‡

Compounds 1 and 2 differ in the F_2 - A_2 18C6 ligand conformations around the C–N bonds. Selected torsion angles for 1 and 2 are listed in Table 5. In both complexes, all eight C–O bonds adopt a more stable *trans*-conformation, all six C–C bonds have a *gauche*conformation. However, in 1, two C–N bonds adopt a *trans*conformation, and the other two have a *gauche*-conformation. In 2 all four C–N bonds adopt a *trans*-conformation. Obviously, these differences are the result of different arrangements of fluorophenyl ligands around the plane of the macrocycle. Thus, the conformational formulae of the macrocycles are as follows (starting from the N(1)–C(1) bond):

1- T_N GT TGT TGG_N T_N GT TGT TGG_N **2**- T_N GT TGT TGT TGT_N T_N GT TGT TGT_N (G = gauche, T = trans)

‡ The mean displacements of N and O atoms from the plane of the macrocyclic ligand (Δ) are 0.425 Å for **1** and 0.247 Å for **2**.

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The average geometrical parameters of the F_2 - A_2 18C6 cycles in **1** and **2** are listed below: bond lengths C–O - 1.419(16) *vs* 1.430(6); C(sp3)–N - 1.505(19) *vs*. 1.475(6); C(sp2)–N - 1.453(13) *vs*. 1.440(6); C–F - 1.334(9) *vs*. 1.368(6); C–C - 1.50(2) *vs*. 1.499(7) Å; bond angles CCO - 110.6(15) *vs*. 109.3(4); COC - 114.9(11) *vs*. 111.6(4); CNC - 108.4(12) *vs*. 109.0(4); NCC - 116.0(15) *vs*. 114.0(5)°.

In both 1 and 2 the geometry of the nitrogen atoms indicates that their LEPs are involved in metal atom coordination. In both cases the nitrogen atoms adopt pyramidal configuration (the displacements of the N atom from the plane of substituents are 0.488 and 0.443 Å, the sum of the valence angles at N(1) are 329.3 and 333.7°, bond lengths N(1)–C(7) are equal 1.453(13) and 1.440(6) Å in 1 and 2, respectively).

It is worth mentioning that the structures of complexes of Ba(ClO₄)₂ with F_2 -A₂18C6 (**2**) and Ba(ClO₄)₂ with N,N'bis(4-dimethylaminophenyl)diaza-18-crown-6 ether (**4**) are very similar.¹² They do not differ significantly in either Ba–O distances (av. 2.779 ± 0.009 Å in **4**) or Ba–N distances (3.004 Å in **4**). In both **2** and **4**, the macrocycles adopt centrosymmetric (C_i) conformation and adopt a roughly perpendicular arrangement of aromatic rings around the macrocyclic planes (105° for **4**). This similarity shows that aryl side arms in N,N'-diaryldiaza-18-crown-6 complexes adopt a conformation favourable for metal cation binding by the donor centres in the *ortho*-positions of the aryl groups.

In the structure of **1**, the complex cation $[Pb(F_2-A_218C6)(H_2O)]^{2+}$ is linked with two symmetrically related ClO₄⁻ anions by weak hydrogen bonds O(3)–H(1)···O(12) (x, -y, z + 1/2) (O(3)–H(1) - 0.85, H(1)···O(12) - 1.85, O(3)···O(12) - 2.69(2) Å, O(3)H(1)O(12) - 169°) and O(3)–H(2)···O(12)' (-x + 1, -y, -z) (O(3)–H(2) - 0.85, H(2)···O(12)' - 1.86, O(3)···O(12)' - 2.70(2) Å, O(3)H(2)O(12)' - 170°). The latter results in neutral aggregates [Pb(F₂-A₂18C6)(H₂O)](ClO₄)₂ combined in the crystal by van der Waals interactions only.

In the structure of **2** the stacks of complex molecules $[Ba(F_2-A_218C6)(CIO_4)_2]$ form a base-cantered motif and are linked by van der Waals interactions only.

Conclusion

New azacrown lariat ethers, F-A15C5 and F₂-A₂18C6, bearing florophenyl side arms, were prepared and their interaction with metal cations was examined. Both the NMR data (1H and 19 F) obtained in solution and the X-ray analysis of F₂-A₂18C6 complexes with Ba and Pb perchlorates show that fluorine in these ligands is coordinated to the metal cation. Relatively short metal \cdots F–C contacts are found in both the Ba²⁺ (2.965 Å) and the Pb^{2+} (2.805 Å) complexes, but the structural motifs of Ba(ClO₄)₂ (C_i) and $Pb(ClO_4)_2(C_2)$ complexes are different. The observed onesided coordination of Pb²⁺ with fluorophenyl side arms reflects the tendency of Pb2+ to localize its lone pair. The cation-fluorine interaction results in a significant stabilization of F-A15C5 and F_2 -A₂18C6 complexes as shown by the measurement of cation binding constants (Table 2). Fluorine also modifies the selectivity of the ligands, increasing their affinity towards hard singly charged alkaline metal cations, which should be attributed to the hardness of fluorine as donor centre.

Experimental

NMR spectra were recorded using Bruker Avance spectrometer operating at 400.13 (¹H), 100.62 (¹³C) and 376.46 (¹⁹F) MHz, respectively, with TMS as a reference for ¹H and ¹³C and C₆F₆ ($\delta = -162.9$ ppm) as a reference for ¹⁹F. MALDI MS spectra were obtained on Bruker Daltonics Autoflex II spectrometer equipped with N₂ laser (337 nm), accelerating voltage 19 kV, in positive ion mode using dithranol as a matrix. UV-spectrophotometric titrations were carried out on a Hewlett-Packard 8452 UV-Visible spectrophotometer.

13-(2-Fluorophenyl)-1,4,7,10-dioxa-13-azacyclopentadecane (F-A15C5)

Aza-15-crown-5 (110 mg, 0.50 mmol), o-bromofluorobenzene (108 mg, 0.62 mmol), t-BuONa (72 mg, 0.75 mmol), Pd₂dba₃·CHCl₃ (8.6 mg, 0.0083 mmol) and 2-dimethylamino-2'dicyclohexylphosphinobiphenyl (7.8 mg, 0.02 mmol) were placed into a Schlenk reactor. After cooling in liquid N₂ and evacuating (10^{-2} torr) , toluene (1.5 ml) was vacuum-transferred into the reactor. The reactor was filled with argon and the mixture was stirred at 100 °C for 24 h. Reaction progress was monitored by GLS. After cooling the reaction mixture was diluted with CH₂Cl₂ (5 ml), filtered through a Celite pad and the solvent was removed under reduced pressure. F-A15C5 was isolated as a colorless oil (30 mg, 19% yield) by column chromatography on silica gel (Merck 40-63) using CH_2Cl_2 -PE-MeOH (8 : 8 : 1) as eluent. ¹H and ¹⁹F NMR data are given in Table 1. $\delta_{\rm C}$ (CDCl₃) 53.53, 70.02, 70.34, 70.42, 71.03, 116.46 (d, $J_{C-F} = 22$ Hz), 119.07, 119.94 (d, $J_{C-F} = 8$ Hz), 124.21.§

7,16-Bis(2-fluoro-4-nitrophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

Diaza-18-crown-6 (393 mg, 1.5 mmol), 1,2-difluoro-4nitrobenzene (626 mg, 3.9 mmol), triethylamine (0.500 ml, 3.5 mmol) and DMF (2 ml) were stirred in a closed vessel for 2 h at 100 °C. After cooling the reaction mixture was diluted with MeOH (5 ml), the precipitated product (yellow solid, 615 mg, 76%) was collected, washed with MeOH and acetone (5 ml) and dried *in vacuo*. $\delta_{\rm H}$ (CDCl₃) 3.63 (s, 8H), 3.77 (m, 16H), 7.09 (t, J = 9 Hz, 2H), 7.85 (dd, J = 15, 2.5 Hz, 2H), 7.92 (dd, J = 9, 2.5 Hz, 2H). MS (MALDI) *m*/*z*. Expected: 539.20 [*M*-H]. Found: 538.8.

7,16-Bis(2-fluorophenyl)-1,4,10,13-tetraoxa-7,16diazacyclooctadecane (F₂-A₂18C6)

A suspension of 7,16-bis(2-fluoro-4-nitrophenyl)-1,4,10,13tetraoxa-7,16-diazacyclooctadecane (575 mg, 1.06 mmol) and Pd/C (10%, 133.4 mg) in EtOH (50 ml) was purged with argon and refluxed for 2.5 h with a slow flow of H₂ bubbled through the reaction mixture until the solution turned colorless. After purging with argon (**Caution!** Hydrogen may explode on contact with air in the presence of Pd/C) the reaction mixture was passed through a short pad of alumina to separate it from Pd/C, the pad was washed with EtOH (3 × 5 ml) and the combined filtrate was evaporated

[§] The weaker signals of quaternary carbons were not observed.

to dryness. The solid residue was dissolved in H₃PO₂ (50%, 8 ml) which required stirring for 30 min at r.t. The resulting solution was cooled to -10 °C and NaNO₂ solution (170 mg, 2.5 mmol) in H₂O (1 ml) was added dropwise under stirring (15 min). The reaction solution was allowed to warm to r.t. in 4 h, neutralized with NaOH and extracted with CH₂Cl₂ (3 × 20 ml), the extract dried over Na₂SO₄. F₂-A₂18C6 was isolated as a pale solid (308 mg, 65% yield) by column chromatography on silica gel (Merck 40–63) using CH₂Cl₂–MeOH (10 : 1) as eluent. ¹H and ¹⁹F NMR data are given in Table 1. MS (MALDI) *m/z*: Expected: 451.2 [*M* + H], 473.2 [*M* + Na], 489.2 [*M* + K]. Found: 451.1, 473.0, 489.0. EA: Calc. for C₂₄H₃₂F₂N₂O₄: C 63.98, H 7.16, N 6.22. Found: C 63.74, H 7.20, N 6.41%.

Preparation of the complexes

Crystals of the complexes suitable for X-ray diffraction were obtained by diffusion crystallization. The acetone solution (~ 0.15 M, ~ 0.2 ml) of M(ClO₄)₂·3H₂O (M = Ba, Pb) was carefully placed into a tube (~ 4 mm internal diameter) containing the solution of F₂-A₂18C6 (~ 0.15 M, ~ 0.2 ml) in CH₂Cl₂ (avoiding the mixing of the two layers) and left overnight. Pale-coloured crystals formed and were separated from the mother liquor and dried in the open air. Solution ¹H and ¹⁹F NMR data of the complexes are given in Table 1.

[Pb(F₂-A₂18C6)(H₂O)](ClO₄)₂ (1). MS (MALDI) m/z: Expected: 757.2 [M-H₂O,-ClO₄]. Found: 756.9. EA: Calc. for C₂₄H₃₄Cl₂F₂N₂O₁₃Pb: C 32.96, H 3.92, N 3.20. Found: C 33.77, H 3.84, N 3.43%.

[Ba(F₂-A₂18C6)(ClO₄)₂] (2). MS (MALDI) m/z: Expected: 687.0 [*M*-ClO₄]. Found: 686.8. EA: Calc. for C₂₄H₃₂Cl₂F₂N₂O₁₂Ba: C 36.64, H 4.10, N 3.56. Found: C 36.38, H 4.20, N 3.80%.

Cation binding constants

Working solutions were prepared in MeOH ($\leq 0.5\%$ H₂O) in a 10 ml measuring flask by mixing weighed amounts of the solutions of the ligand and the corresponding metal salt(*s*) (KI, NaBr, Mg(ClO₄)₂, M(ClO₄)₂·3H₂O, M= Ba, Pb). Total concentration of the ligand (~5 × 10⁻⁵ mol L⁻¹) was kept constant in a series while the total concentration of the metal salt was variable (5×10^{-5} -10⁻¹ mol L⁻¹). UV-spectra were recorded at 22 °C in a 1 cm quartz cell and the obtained absorbance values (A_i , in 250–290 nm range) were fitted to equation (1) to give the concentrational metal binding constant (β , Table 2) and the absorbance of the complex (A_{∞}) as objective variables. Good fits ($r^2 > 0.99$) were obtained in all cases confirming the complex formation model (metal : ligand = 1 : 1).

$$A_{L} - A_{i} = \frac{\beta[M]_{i}A_{\infty}}{\beta[M]_{i} + 1}$$
(1)

where A_L is the absorbance of the starting ligand solution and $[M]_i$ is the molar concentration of the metal salt.

X-Ray crystallography

The main crystallographic data for compounds 1 and 2 are given in Table 6. The experimental intensities for the needle-shaped lightbrown crystals of 1 were collected on a Bruker SMART APEX II diffractometer, and for the irregular-shaped light-violet crystals of 2 on an Enraf-Nonius CAD4 machine at ambient temperature (MoK α radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scanning). An absorption correction based on measurements of equivalent reflections was applied for 1²¹; ψ -scanning was used for 2.²² The low ratio of observed/unique reflections for 2 and the low C–C bond precision in 1 are caused by poor crystal quality. Both structures were solved by direct methods (SHELXS-86),²³ refined by full matrix least-squares on F^2 (SHELXL-97)²⁴

Table 6Crystal data, data collection and refinement parameters for complexes 1 and 2

Compound	1	2
Empirical formula	$C_{24}H_{34}Cl_2F_2N_2O_{13}Pb$	$C_{24}H_{32}BaCl_2 F_2N_2O_{12}$
M	874.62	786.76
Crystal size/mm ³	$0.40 \times 0.03 \times 0.02$	$0.17 \times 0.17 \times 0.11$
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
a/Å	19.423(5)	8.178(3)
b/Å	12.719(3)	12.054(3)
c/Å	13.109(3)	15.072(4)
$\beta/^{\circ}$	94.711(3)	99.02(2)
$V/Å^3$	3227.4(14)	1467.3(2)
Z	4	2
$D_c/\mathrm{Mg}~\mathrm{m}^{-3}$	1.800	1.781
μ/mm^{-1}	5.468	1.613
F(000)	1720	788
T/K	303(2)	293(2)
θ Range/°	3.12-26.00	2.17-29.97
Reflections collected	12378	6568
Independent reflections	$3154 [R_{int} = 0.0674]$	$4269 [R_{int} = 0.0824]$
Data/restraints/parameters	3154/10/181	4269/0/196
R indices $[I > 2\hat{\sigma}(I)]$	$R_1 = 0.0679$	$R_1 = 0.0442$
	$wR_2 = 0.1773$	$wR_2 = 0.0694$
R indices (all data)	$R_1 = 0.0893$	$R_1 = 0.2164$
	$wR_2 = 0.1967$	$wR_2 = 0.0992$
Gof on F^2	1.009	0.949
Largest diff. peak, hole/eA ⁻³	2.977, -1.006	0.786, -1.585

anisotropically for all statistically ordered non-hydrogen atoms. In the structure of **1** the water molecule was disordered around the crystallographic two-fold axis (0.5/0.5). High values of isotropic thermal parameters of perchlorate oxygen atoms, especially for the atoms O(11) and O(13), indicate possible disorder. The ClO₄ anion was refined with the same Cl–O bond distances and isotropic thermal parameters for O(11) and O(13) atoms. The large thermal ellipsoid for fluorine atoms and the short C(5)–C(6) distance in **1** point to possible disorder of these atoms; however, all attempts to resolve distinct positions for these atoms failed. The phenyl ring in **1** was refined as a rigid body.

For both structures, all hydrogen atoms were placed in calculated positions and refined using a riding model. CCDC numbers 681114 (1) and 681113 (2).[†]

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