Research Article

N-Methylbenzoazacrown ethers with the nitrogen atom conjugated with the benzene ring: the improved synthesis and the reasons for the high stability of complexes with metal and ammonium cations

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An improved method for the synthesis of formyl derivatives of N-methylbenzoazacrown ethers is proposed. They are prepared in up to 68% yields over fewer steps and with a much shorter time required for the last step. The stability constants of complexes formed by N-methylbenzoazacrown ethers and their structural analogs with alkali metal, alkaline-earth metal and ammonium cations were determined by ^1H NMR titration in CD_3CN. High stability of complexes of N-methyl derivatives of benzoazacrown ethers is demonstrated, comparable with or even exceeding the stability of benzocrown-ether complexes and markedly exceeding the stability of complexes of phenylazacrown ethers with the same macrocycle size. The structures of azacrown ethers and their complexes with $Ba(ClO_4)_2$ were studied by X-ray diffraction. A high degree of pre-organization of N-methylbenzoazacrown ethers toward the formation of complexes with metal and ammonium cations was noted, which is due to the clear-cut pyramidal geometry of the nitrogen atom and the orientation of the lone electron pairs (LEPs) of most heteroatoms towards the centre of the macroheterocycle. Copyright © 2009 John Wiley & Sons, Ltd.

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Keywords: benzoazacrown ethers; complex formation; metal and ammonium cations; stability

INTRODUCTION

An important feature of crown compounds is the ability to form stable complexes with metal ions, organic cations and neutral polar molecules. This ability underlies the use of crown compounds as selective ligands for metal cations, in particular, for extraction,[1,2] in ion-selective electrodes[3] and in photosensitive systems.[4–9] Of particular interest from the standpoint of using crown fragments in photosensitive ligands are those crown compounds in which the nitrogen atom occurs in conjugation with the chromophore. These azacrown compounds absorb at markedly longer wavelengths than crown-ether derivatives; this is especially important for the photometric and fluorescence analysis, for photocontrolled extraction and ion transport through membranes and for the design of photosensitive molecular devices. Currently, phenylazacrown-ether derivatives are used most widely for these purposes; however, they suffer from a substantial drawback, in particular, their complexation constants with metal ions are relatively low. In this respect, benzoannelated derivatives of azacrown ethers can have substantial advantages. The chemistry of 1-aza-2,3-benzocrown ethers has been poorly developed until recently due to the difficulty of the synthesis of these compounds by condensation

of two fragments and inaccessibility of podands for intramolecular cyclization.[10–12] The new strategy we develop[13–15] for the synthesis of functional derivatives of azacrown ethers in which nitrogen is conjugated with the benzene ring by stepwise transformation of readily available benzocrown ethers is a promising alternative to the existing methods of synthesis of

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1-aza-2,3-benzocrown ethers. As regards the use in the synthesis of photosensitive compounds, of most interest are benzoazacrown ethers **1a–c**, which contain formyl substituent in the benzene fragment in the *para*-position to nitrogen (Scheme 1).

This communication presents an improved synthesis of formyl derivatives of *N*-methylbenzoazacrown ethers **1a–c** with 12-, 15- and 18-membered macrocycles. Comparative study of structures **1** and related compounds and their complexes with metal and ammonium cations by ^{1}H NMR and X-ray diffraction analysis were carried out. The stability constants of the complexes of benzoazacrown ethers **1b,c** and their structural analogs were determined in order to demonstrate the scope of using compounds **1** as efficient macrocyclic ligands.

RESULTS AND DISCUSSION

Synthesis

Previously, we showed[16] that heating of formylbenzocrown ethers **2a–c** with an ethanol solution of MeNH$_2$ and MeNH$_3^+$Cl$^-$ affords nitrogen-containing podands **3a–c** in 66–80% yields. To cyclize podands **3** to benzoazacrown ethers **1**, the hydroxy groups of **3a–c** were replaced by chlorine and iodine,[14] i.e. by easily leaving groups. This gave chloro **4a–c** and iodo derivatives **5a–c** of podands in yields of up to 97%. We studied cyclization of the resulting iodo derivatives **5a–c** in the absence of bases and in the presence of weak bases, such as alkali metal carbonates.[14] Under the action of weak bases, this gave mixtures of azacrown compounds **1** and **6** with markedly pre-dominating *N*-methyl derivatives **1a–c** (Scheme 2). In the absence of bases, *N*-demethylated benzoazacrown ethers **6a–c** were formed as the major or even the only products. Despite the rather high yields of the target compounds **1**, this method has substantial drawbacks, in particular, the formation of product mixtures and long cyclization time (150 h). In addition, the reaction does not go to completion.

In order to optimize the synthesis of the formyl derivatives of *N*-methylbenzoazacrown ethers **1a–c** (to reduce the cyclization time and the number of synthetic steps), we studied the reactivity of chloro and iodo derivatives of azapodands **4a–c** and **5a–c** under the action of a stronger base than alkali metal carbonates, specifically, sodium hydride; this gave *N*-methylbenzoazacrown ethers **1a–c** in high yields and over short periods of time (Scheme 3, Table 1).

It was found that on heating with NaH in dry THF, chlorides **4b,c** cyclize to give *N*-methylbenzoazacrown ethers **1b** and **1c** over periods of 5.5 and 17 h in 59 and 27% yields, respectively. The
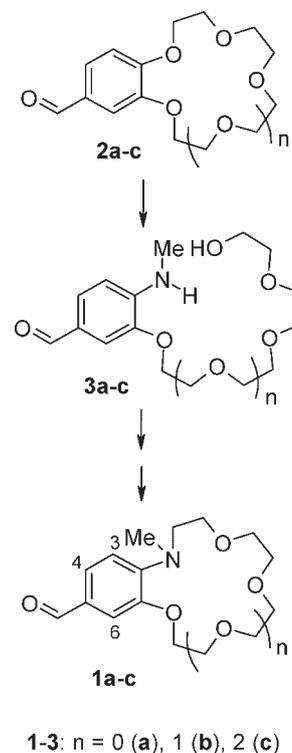
Scheme 1. General approach to the synthesis of formyl derivatives of *N*-methylbenzoazacrown ethers **1a–c**

1-3: n = 0 (**a**), 1 (**b**), 2 (**c**)

cyclization of chloride **4a** barely proceeds under these conditions. The cyclization of iodides **5a–c** to **1a–c** induced by NaH in THF with heating proceeds even faster (for 30 min) than that of chlorides **4a–c**, giving products in equally good yields, irrespective of the macrocycle size (57–68%). The cyclization of iodides **5a–c** occurs also at room temperature but over a longer period. In this case, the yields of **1** somewhat decrease. The obtained data suggest that NaH-induced cyclization of chloro and iodo azapodands proceeds through the formation of the reactive arylamide anion **7** (Scheme 3). This is indicated, first of all, by the substantial shortening of the cyclization time compared to that in the presence of alkali metal carbonates in acetonitrile. In the latter case, the cyclization is due to the intramolecular *N*-alkylation giving rise to the macrocyclic ammonium salt.[14]

Advantages of conducting the cyclization of halides under the action of NaH in THF include good yields of the target products **1**, short reaction time and the possibility of preparing individual

5a-c → **1a-c** (53-67%) + **6a-c** (11-18%)

M = Li, Na, K, Rb, Cs

1, 5, 6: n = 0 (**a**), 1 (**b**), 2 (**c**)
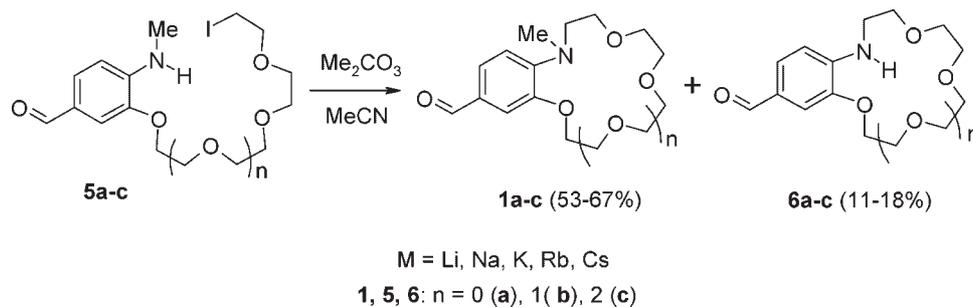
Scheme 2. Synthesis of benzoazacrown ethers **1a–c** and **6a–c** under the action of metal carbonates

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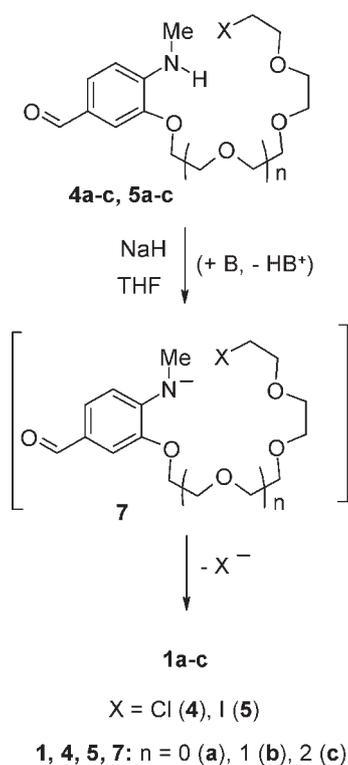
Scheme 3. Synthesis of benzoazacrown ethers **1a–c** under the action of strong base

Scheme 4. Synthesis of *N*-methylbenzoazacrown ether **1c** from benzoazacrown ether **6c** The structures of all the obtained compounds were proved by ^{1}H NMR spectroscopy

iodide under the action of NaH in THF (Scheme 4). The reaction was fast and gave **1c** in 58% yield. This reaction demonstrates the possibility of preparing, if necessary, *N*-alkyl derivatives of benzoazacrown ethers.

compounds and reducing the total number of steps in the case of synthesis of benzoazacrown ether **1b**.

Previously, we demonstrated[14] that refluxing of *N*-methyl derivative **1c** with dilute acetic acid gives rise to *N*-demethylated product **6c**. In this study, we carried out methylation of compound **6c** at the macrocycle nitrogen atom with methyl

Table 1. Cyclization of halides **4a–c** and **5a–c** into benzoazacrown ethers **1a–c** under the action of NaH in THF[a]

Initial halide	Reaction time (h)	Benzoazacrown ether	Yield of **1** (%)
4a	100	**1a**	5[c]
4b	5.5	**1b**	59
4c	17	**1c**	27
5a	0.5	**1a**	68
	72[b]		61
5b	0.5	**1b**	63
	24[b]		61
5c	0.5	**1c**	57
	19[b]		51

[a] 64 °C.
[b] Ambient temperature.
[c] The yield of **1a** was found from the ^{1}H NMR spectrum of the reaction mixture which contained **1a** and **4a** (9%). The yield of **1a** was calculated with respect to converted **4a**.

Stability of complexes

Previously, we showed[14] that benzoazacrown ethers **1a–c** and **6a–c** form 'host-guest' complexes with Ca^{2+} ions in acetonitrile. The complexation induces pronounced changes in the positions of the ^{1}H, ^{13}C and ^{15}N NMR signals, which indicates that the calcium cation resides in the macrocycle cavity. It was of interest to determine, under comparable conditions, the quantitative characteristics for the stability of complexes of compounds **1** with Group I and II metal ions and ammonium ions, to elucidate the structural features of the complexes formed and the selectivity with respect to various ions and to compare the complexation capacities of benzoazacrown ethers and related compounds.

The ability of benzoazacrown ethers **1b,c** to form complexes with metal and ammonium perchlorates was estimated quantitatively by ^{1}H NMR titration in CD$_3$CN. In most cases, the procedure of direct titration was used, which consists in adding M^{m+}(ClO$_4^-$)$_m$ [M^{m+} is the metal or ammonium cation ($m = 1, 2$)] in portions to the studied ligand.

In those cases where the magnitude of the constant exceeded the upper limit of applicability of the direct titration ($K > 10^5$ M^{-1}), the competitive ^{1}H NMR titration was used. In this case, an appropriate competing ligand was added in portions to a complex of the studied ligand. The stability constant of the complex formed by the competing ligand had been preliminarily measured and the proton NMR signals of this ligand did not overlap significantly with the signals of the ligand to be studied.

A representative example of the changes of proton signal positions, which were observed in the system **1c**/NH$_4$ClO$_4$, is shown in Fig. 1. During this direct titration, all of ^{1}H signals of the ligand demonstrated monotonic changes with increasing salt/**1c**

Figure 1. Values of $\Delta\delta_H = \delta_H(\mathbf{1c}/NH_4ClO_4 \text{ mixture}) - \delta_H(\text{free } \mathbf{1c})$ for some protons of **1c** in CD_3CN as a function of the NH_4ClO_4/**1c** concentration ratio

Table 2.

concentration ratio, indicating complex formation. The presence of ammonium ion in the crown-ether cavity entails downfield shifts of the signals of most protons (by $\Delta\delta_H = 0.08{-}0.14$ ppm). An especially great downfield shift ($\Delta\delta_H$ upto 0.33 ppm) is found for the signal of the CH(3) proton located in the *ortho*-position relative to the nitrogen atom (as shown atom numbering in Scheme 1). Apparently, this reflects switching of lone electron pair (LEP) of the nitrogen atom from conjugation with the benzene ring to hydrogen bond formation with the NH_4^+ ion. Conversely, the proton signals of the MeN and CH_2N groups shift upfield upon complexation ($\Delta\delta_H$ upto -0.22 ppm). This might be due to the overall effect of the change in the macrocycle conformation on binding to the cation and to the increase in the contribution of the sp^3 hybridization for the nitrogen atom (as shown below X-ray diffraction). These features are characteristic of all the studied azacrown compounds on complexation with all metal and ammonium cations, being more pronounced for doubly charged cations than for monovalent ones. Complex formation of model benzocrown ethers **2b,c** and **8** induced downfield shifts for all of their proton signals, excluding the cases of complexes having $2(L):1(M^{m+})$ stoichiometry (as shown below), where L is the crown compound.

The curves for the variation of the proton chemical shifts of the ligand *vs.* the amount of the salt added (or the amount of the competing ligand added) were used to calculate the stability constants of the complexes by the HYPNMR program;[17] the results fit well into the scheme of formation of $1(L):1(M^{m+})$ complexes:

$$L + M^{m+} \underset{}{\overset{K_1}{\rightleftharpoons}} (L \cdot M)^{m+} \qquad (1)$$

where K_1 (M^{-1}) is the stability constant for 1:1 complexes. In the case of metal cations with a large ionic radius, the possibility of formation of $2(L):1(M^{m+})$ sandwich complexes was also taken into account:

$$(L \cdot M)^{m+} + L \underset{}{\overset{K_1}{\rightleftharpoons}} (L_2 \cdot M)^{m+} \qquad (2)$$
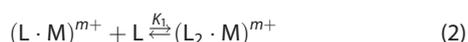
where K_2 (M^{-1}) is the stability constant of the 2:1 complex. For comparison, the ability to form complexes with these salts was studied for a number of closely related structural analogs of benzoazacrown ethers, namely, benzocrown ethers **2b,c**, **8** and *N*-phenylazacrown ethers **9a,b**. The results are summarized in
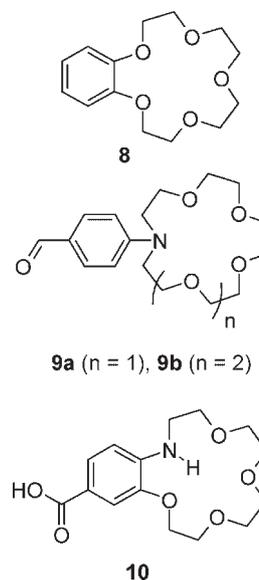
The presence of the formyl group in the crown compounds results in lower stability constants of the complexes due to the electron-withdrawing nature of the substituent.[18] Comparison of the data for benzo-15-crown-5 ether (**8**) and its formyl derivative **2b** shows an up to 20-fold decrease in the stability of complexes with any of the cations. In addition, the complexation capacity of the crown compounds studied depends on the

Table 2. Stability constants of the complexes formed by crown ethers **1b,c**, **2b,c**, **6c**, **8**, **9a,b** with metal, ammonium and ethylammonium perchlorates[a]

Ligand	$\log K_1$ ($\log K_2$)					
	Na^+	K^+	Ca^{2+}	Ba^{2+}	NH_4^+	$EtNH_3^+$
8	~5 4.8[b]	3.2 (1.9)	5.6[b]	5.4 (5.1)[b]	2.1	2.4
2b	3.5	2.9 (2.5)	4.3	4.4 (4.2)	2.0	2.2
1b	3.2	2.2	≥5 5.3[b]	4.6 (2.5)	2.0	1.7
9a	1.6	0.6	2.4	1.9	0.7	0.6
2c	>5 5.2[c]	3.7	8.4[e]	7.0[d]	4.3	3.8
1c	4.8	4.3	≥5 8.0[e]	6.8[d]	4.1	3.7
6c	3.3	2.8	4.7[b]	4.9	2.5	2.0
9b	3.4	2.3	4.8[b]	~5 4.9[b]	1.9	1.6

[a] ^{1}H NMR titration in CD_3CN, 30 °C. The total measurement errors of the stability constants were ~20% for the direct titrations and ~30% for competitive ones.
[b] From competitive ^{1}H NMR titration with compound **2b**.
[c] From competitive ^{1}H NMR titration with compound **1c**.
[d] From competitive ^{1}H NMR titration with compound **9b**.
[e] From competitive ^{1}H NMR titration with compound **8**.

nature, the size and the charge of the cation, the macrocycle size and the degree of conjugation of nitrogen with the benzene ring.

Representatives of 15-crown-5 and 18-crown-6 compounds form more stable complexes with smaller-size cations (both for the alkali metals and for alkaline-earth metals studied) and more stable complexes with NH_4^+ ions than with $EtNH_3^+$. For doubly charged cations, the stability constants of the complexes are substantially (10^2–10^4 times) higher than similar values for monovalent cations. Evidently, the higher charge density on smaller metal cations or on doubly charged cations compared to singly charged cations and the absence of electron-donating substituents in NH_4^+ promote stronger ion-dipole interactions between the macrocycle heteroatoms and the cation located in its cavity. The much higher stability of complexes of all 15-crown-5 compounds with Na^+ ions compared with the complexes with K^+ ions confirms also the classical view on the necessity of size correspondence between the crown-ether cavity and the metal ion for stronger binding of the ligand and the substrate. It is noteworthy, however, that this view proved inapplicable to all the 18-crown-6 compounds for which a better correspondence between the macrocycle and cation geometric sizes would be expected for potassium ions.

It was found that Ba^{2+} ions also form sandwich complexes 2(L):1(Ba^{2+}) with benzo-15-crown-5 compounds **1b**, **2b** and **8** owing to large size of the metal cation. However, the structures of the sandwich complexes are different. In the case of crown ethers **2b** and **8**, ligands are preferably arranged in such a way that two $RC_6H_3(OCH_2)_2$ fragments (R = H, CHO) are located closely to each other and their ^1H NMR signals are shifted upfield with respect to those in free ligands owing to mutual shielding. For benzoaza-crown ether **1b**, all types of proton signals of both the sandwich and 1:1 complexes shift in the same direction. Apparently, the methyl substituent at the nitrogen atom in **1b** creates steric
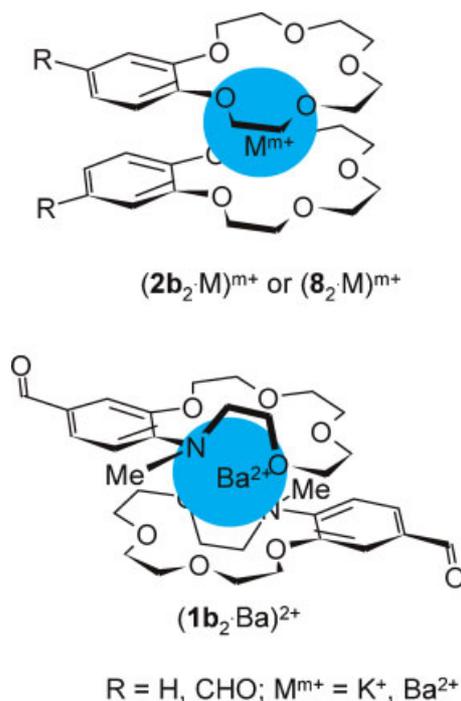
hindrance preventing the two aromatic fragments from approaching each other; therefore, in complex 2(**1b**):1(Ba^{2+}), they point most likely to opposite directions, as shown in Fig. 2.

The conclusion concerning the less favourable arrangement of the ligands in the sandwich complex 2(**1b**):1(Ba^{2+}) is also supported by the K_2 value being two orders of magnitude lower than K_1, which was not observed for the sandwich complexes of **2b** and **8**. With potassium ion, the last two compounds also form sandwich complexes similar in structure to complex 2(**1b**):1(Ba^{2+}) but markedly less stable. The stability constants of the possible sandwich complexes of **1b** with the K^+ ion and **9a** with the K^+ and Ba^{2+} ions are apparently so low ($logK_2 < 0.5$) that the complexes cannot be detected by ^1H NMR.

The stability constants of the complexes of 18-crown-6 compounds are 1.5–4 order of magnitude higher than those of analogous 15-crown-5 compounds, which is attributable to the larger number of donor heteroatoms in 18-membered crown compounds than in 15-membered compounds.

The remarkable feature of new *N*-methyl derivatives of benzoazacrown ethers **1b,c** is the formation of substantially more stable complexes with any of the cations studied compared with their closest structural analogs, phenylazacrown ethers **9a,b** (Table 2). This feature is due to the specific properties of the tertiary nitrogen atom in **1b,c**, in which the LEP is essentially eliminated from the conjugation with the benzene ring and, therefore, it can be efficiently donated for the formation of the coordination bond with the metal or ammonium cation. Conversely, as shown by our X-ray diffraction studies (as shown below), the geometric characteristics of nitrogen in **9a,b** imply a high degree of its conjugation with the benzene ring. Together with the higher flexibility of the macrocycles of phenylazacrown ethers, this feature makes these compounds less efficient ligands.[19,20] A similar effect was observed[14] for benzoaza-18-crown-6 ether **6c** whose secondary nitrogen atom is efficiently conjugated with the benzene ring. The effect of the more rigid structure of the macrocycle in **6c** compared to **9b** is, apparently, leveled by the hydrogen atom of the NH group pointing toward the macro-heterocycle centre;[14] therefore, compounds **6c** and **9b** demonstrated almost equal abilities to bind metal and ammonium cations (Table 2). One more notable fact deserves attention, namely, the complexing capacity of **1b,c** is comparable with and, in some cases, is even higher than the ability of the analogs with only oxygen atoms, namely, benzocrown ethers **2b,c** to bind the same cations.

Thus, the quantitative measurements we carried out clearly revealed the high complexation efficiency for the *N*-methyl derivatives of benzoazacrown ethers **1** with respect to various metal cations and ammonium ions, which is comparable to that of benzocrown ethers and substantially exceeds that of phenylazacrown ethers.

X-ray diffraction study

To understand the reasons for the higher complexing ability of *N*-methylbenzoazacrown compounds compared to *N*-phenylazacrown ethers we carried out X-ray diffraction studies for some of the compounds and their metal complexes. Figure 3 shows a general view and atom labelling scheme of molecule **1b**. Selected bond lengths and angles for **1b** are given in Table 1S (refer to Supplementary Material (SM) to this article).

In **1b**, some angular distortions at the C(7) atom bearing the O(1) oxygen atom are found. Two O(1)—C_{Ar}—C_{Ar} angles are

Figure 2. Proposed structures of sandwich complexes of benzocrown ethers **1b**, **2b** and **8**. This figure is available in colour online at www.interscience.wiley.com/journal/poc
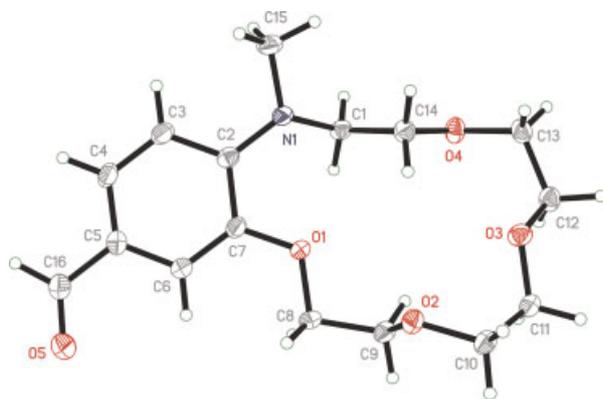
Figure 3. Structure of **1b**. Here and in Figs 5–9, all non-hydrogen atoms are shown at 50% probability of their thermal anisotropic displacement parameters. This figure is available in colour online at www.interscience. wiley.com/journal/poc

Figure 4. Orientation of the LEP of the heteroatoms in the crown ether moiety of **1b**; lone pairs are depicted as full lines and denoted as E. The lone pair of the O(1) on the 2*p* orbital involved in conjugation with the π-system of the benzene ring and the hydrogen atoms are omitted for clarity. This figure is available in colour online at www.interscience. wiley.com/journal/poc

different, the internal one, O(1)—C(7)—C(2), being reduced to 116.0(1)° compared to the other bond angle O(1)—C(7)—C(6), equal to 123.3(1)°. The O(1) atom has an *sp²* hybridization state, which is evident from the C(7)—O(1)—C(8) bond angle [117.4(1)°], which is greater than the bond angles at the other crown-ether oxygens [113.5(1)–114.1(1)°] having an *sp³* hybridization state. It should be noted that this kind of angular distortion is opposite to that possibly resulting from a steric repulsion between the O(1) and N(1) atoms. We believe that the reason for the geometric feature of molecule **1b** to be discussed is conjugation between the benzene ring and the O(1) atom. Actually, the C(8)—O(1)—C(7)—C(6) torsion angle (1.1°) is appropriate for the conjugation of a LEP of the oxygen atom occupying the 2*p* orbital. This conjugation is accomplished in spite of an essential steric hindrance between the alkyl atom C(8) and the nearest C(6)—H fragment of the benzene ring; the C(6)...C(8) distance is rather short, 2.80 Å compared to the double van der Waals radius ∼3.6 Å. This short contact could be avoided by increasing the corresponding torsion angles in the flexible crown ether.

The nitrogen atom in **1b** has a pyramidally distorted configuration of bonds. The bond angles vary within 112.4(1)–121.5(1)°, the sum of these bond angles being equal to 351.4(1)°. The N(1)—C(2) bond length is equal to 1.389(2) Å and the C(1)—N(1)—C(2)—C(7) torsion angle is equal to 45.0°. This value is a consequence of steric hindrance between the methylene substituent at the nitrogen atom and the *ortho*-AlkO substituent in the benzene ring. The methyl substituent lies almost in the benzene ring plane, the contact C(3)...C(15) (2.81 Å) being significantly shorter than the double van der Waals radius. This geometry about the nitrogen atom in **1b** is identical to that found[14] in smaller-size **1a** and, apparently, indicates some conformational rigidity of the crown-ether fragment in the vicinity of the nitrogen atom and the benzene ring. This geometry does not provide optimal conditions for involving the nitrogen LEP into the efficient conjugation with the benzene ring π-system. However, with this geometry the nitrogen LEP is oriented toward the metal cation approaching the macrocycle. Figure 4 shows the orientation of LEPs of all heteroatoms of the macrocycle **1b**. It can be seen that the LEPs of most of heteroatoms are oriented toward the centre of the macrocycle, favourably for co-operative chelating effect. The O(4) oxygen atom might change its

orientation in the flexible crown ether upon coordination to a metal cation.

In order to compare the geometry of *N*-methylbenzoazacrown ethers with that of *N*-demethylated azacrown ethers, we discuss here the X-ray structure of benzoaza-15-crown-5 ether **10**. This compound was found upon repeated crystallization of azacrown ether **6b** and appeared to be a carboxyl rather than a formyl derivative. Apparently, the carboxyl group in **10** has resulted from air oxidation of the formyl group in **6b**. Most likely, formyl and carboxyl groups have nearly the same influence on the electron density distribution in the benzene ring and the macroheterocycle conformation. For this reason, we included the data on structure **10** in our discussion and comparison.

Compound **10** contains a solvation molecule of dichloromethane; the molecular structure is shown in Fig. 5. Selected bond lengths and angles for **10** are given in Table 2S (SM). In **10**, the O(1) oxygen atom located most closely to the benzene ring has the *sp²* hybridization; the bond angle at this oxygen is 118.3(2)°. The angular distortions similar to those observed for **1b** are also characteristic of **10**: the O(1)—C_{Ar}—C_{Ar} angles are 113.1(2) and 126.1(2)°. The torsion angle C(8)—O(1)—C(7)—C(6) (−0.1°) is nearly ideal for the conjugation of the oxygen LEP with the benzene ring.

However, the geometry about the nitrogen atom in **10** differs from that in **1b**. The nitrogen atom in **10** is involved in efficient conjugation with the benzene ring. The N(1)—C(2) bond length [1.369(3) Å] is significantly shorter than the corresponding value in **1b** [1.389(2) Å] and the torsion angle C(1)—N(1)—C(2)—C(3) (−11.4°) is suitable for conjugation. The involvement of the LEP of nitrogen in the conjugation should suppress its interaction with a metal cation upon complex formation. It should be noted that the N(1)—C_{Ar}—C_{Ar} angles [117.2(2) and 123.9(2)°] show a distortion similar to that observed for the O(1)—C_{Ar}—C_{Ar} angles in **10** and **1b**.

In **10**, the hydrogen atom of the NH group points to the centre of the macrocycle and forms a hydrogen bond with at least one oxygen atom of the crown ether; the H(1N)...O(1) distance (2.16 Å) and the N(1)—H(1N)...O(1) angle (110.7°) correspond to a weak interaction. Similar structural features were observed[14] for the *N*-demethylated benzoazacrown compound **6c**. This hydrogen bond restricting the flexibility of the crown ether, together with the aforementioned nitrogen atom–benzene ring conjugation should reduce the chelating properties of this
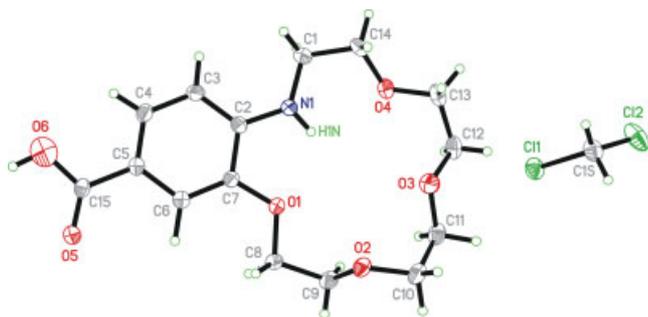
Figure 5. Structure of **10** · CH$_2$Cl$_2$

Figure 7. Structure of **9b**

macroheterocycle. Indeed, we observed a pronounced decrease in the stability constants for the complexes of compounds **6** with metal cations as compared with those for compounds **1** (Table 2).

For comparison, we also performed an X-ray structural study of *N*-(4-formylphenyl)aza-15(18)-crown-5(6) ethers **9a** and **9b**. Their molecular structures are shown in Figs 6 and 7. Two crystallographically independent molecules were found in structure **9a**. This fact demonstrates once again a high flexibility of the crown ethers. The formyl substituent is disordered over two positions in both molecules of **9a**. Tables 3S and 4S (SM) list selected geometric parameters in **9a** and **9b**.

The molecules of both compounds **9a,b** have a geometry about the nitrogen atom similar to that found in compound **10** and in the phenylaza-15-crown-5-ether chromophoric compounds studied earlier.[19,20] The nitrogen atom has a nearly planar geometry; the sums of bond angles in two independent molecules **9a** are equal to 359.3(2) and 360.0(2)° and that in molecule **9b** is 359.9(1)°. These planes are virtually coplanar to the benzene rings; the corresponding dihedral angles are 5.4 and 2.2° in **9a** and 1.0° in **9b**. The N—C$_{Ar}$ bond length is 1.366(2) Å in both molecules of **9a** and 1.377(2) Å in **9b**, which is comparable with the corresponding value in **10** [1.369(3) Å] and is shorter
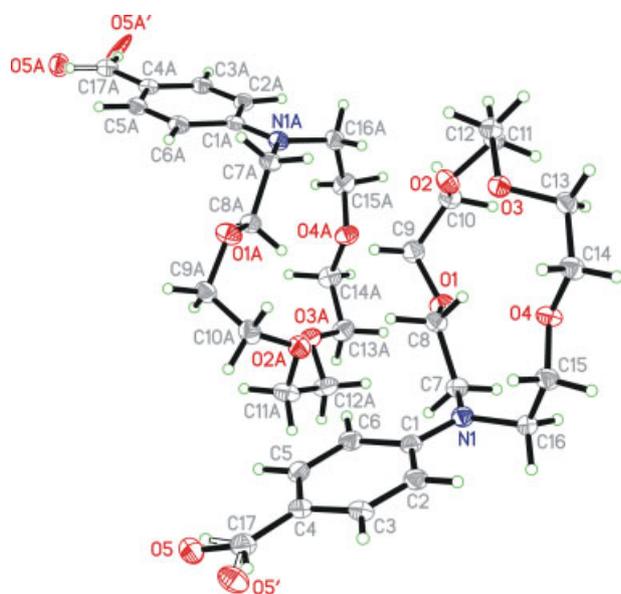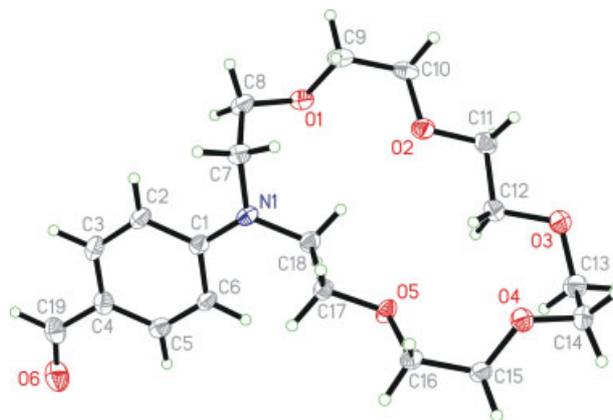
than that in **1b** [1.389(2) Å]. Thus, the LEP of the nitrogen atom in **9a,b** is involved in the conjugation with the benzene ring resulting in pronounced *para*-quinoid pattern of its bond length distribution [Tables 3S and 4S (SM)]. Evidently, a relatively low stability of the complexes formed by **9a,b** and all of the cations studied (Table 2) is a consequence of this conjugation. Most of oxygen LEPs are directed to different sides of the macrocycles of **9a** and **9b**, which is unfavourable for co-operative chelating effect.

In most of structures investigated here, the crown-ether fragment is non-symmetrical. However, in solution, it can adopt different conformations due to its flexibility, including symmetrical crown-like one favourable for the coordination with a metal cation. This is actually demonstrated by X-ray structural investigations of two crystalline Ba(ClO$_4$)$_2$ complexes with *N*-methylbenzoazacrown ethers **1b** and **1c**.

A fragment of the structure of **1b** · Ba(ClO$_4$)$_2$ is shown in Fig. 8 and selected geometric parameters are given in Table 5S (SM). The compound represents a centrosymmetrically doubled two-dimensional coordination polymer running along the *a*- and *c*-translations. The independent cell of the polymer includes two formula units, with ten-fold coordinated Ba^{2+} ions. Both barium cations are bound to four oxygen and one nitrogen atoms of the crown ether and two oxygen atoms of the bidentate perchlorate anions [Cl(2)O$_4$ and Cl(3)O$_4$]. The other two perchlorate anions [Cl(1)O$_4$ and Cl(4)O$_4$] perform a bidentate bridging function to bind a pair of centrosymmetrically related formula units each (through two different symmetry centres). The coordination sphere of Ba(1) is supplemented to ten by the formyl oxygen O(5′) atom belonging to the second formula unit [coordinated to Ba(2)] in the independent cell of the polymer, whereas the coordination of Ba(2) is supplemented by the formyl oxygen O(5A). This atom is related to the O(5) atom of the first formula unit [coordinated to Ba(1)] by the *a*-translation.

The geometry of the crown-ether coordination to the Ba^{2+} ions is nearly identical [Fig. 1S (SM)]. The barium cations are situated above the mean-square planes through the corresponding macrocycle heteroatoms, at a distance of ~1.74 Å. It is obvious that such a geometry of the 1:1 complex in solution allows an expedite approach of the second ligand molecule to form the 2(**1b**):1(Ba^{2+}) complex, as it was established in the NMR study (as shown above). A comparison of **1b** · Ba(ClO$_4$)$_2$ with free **1b** indicates that the macrocycle undergoes an insignificant

Figure 6. Two independent molecules in structure **9a**. Formyl groups are disordered over two positions
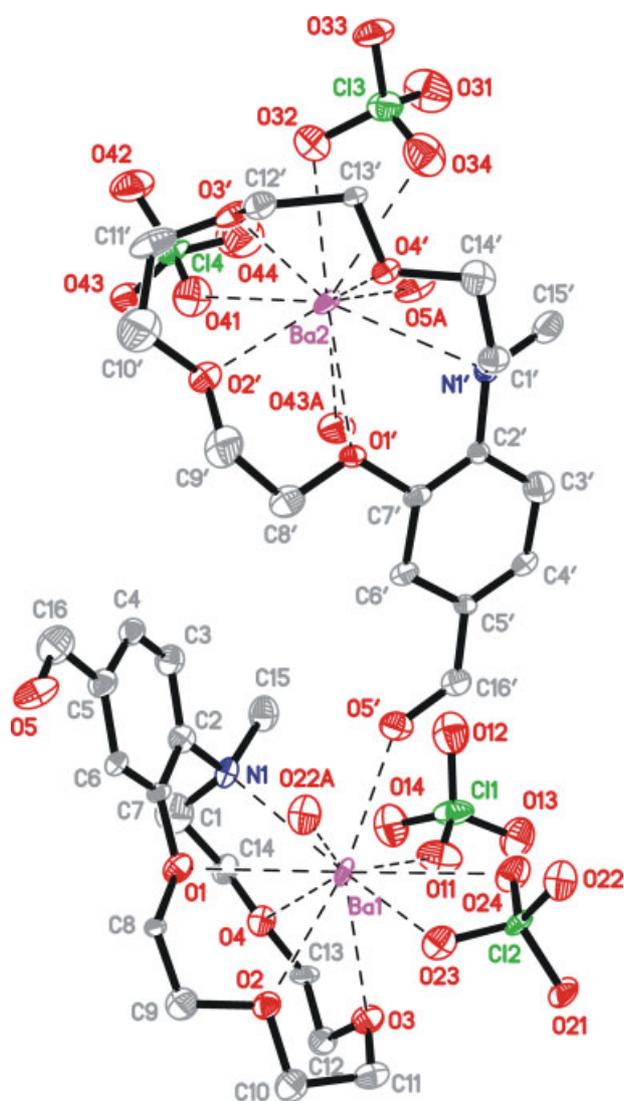
Figure 8. Structure of **1b** · Ba(ClO₄)₂. Here and in Fig. 9, all hydrogen atoms are omitted for clarity; coordination bonds are depicted as dashed lines; the additional letter 'A' indicates that atoms belong to symmetrically related units

Figure 9. Structure of **1c** · Ba(ClO₄)₂

conformational change upon coordination to the metal cation. The Ba—O—C angles vary within 106.8(17)–122.3(17)° and the Ba—N—C angles range within 103.5(16)–115(2)°. The C—N—C angles at the nitrogen atoms vary within 107(3)–114(2)°, the sums of these bond angles being 326(3) and 340(2)° for the independent complexes. These data show that the corresponding LEPs of all crown-ether heteroatoms are oriented towards the Ba²⁺ ions in the complexes and the sp^3 hybridization state of the nitrogen atoms becomes more pronounced as compared with free **1b**, indicating weakening of the conjugation of the nitrogen atom LEP with the benzene ring.

Compound **1c** · Ba(ClO₄)₂ represents a binuclear centrosymmetric complex with a ten-fold coordination of Ba²⁺ ions. Two barium cations are linked via a couple of tridentate chelating bridging perchlorate anions (Fig. 9). Each of the cations is coordinated by one more monodentate perchlorate anion and all heteroatoms of the crown ether. The formyl oxygen does not participate here in the coordination with the Ba²⁺ ion. Selected geometric parameters are given in Table 6S (SM).

In **1c** · Ba(ClO₄)₂, the cation is situated above the mean-square plane through the macrocycle heteroatoms, at a distance of only 0.63 Å [Fig. 2S (SM)], i.e. the cation is much more dipped into the crown-ether cavity in this complex than in the previous one. In this case, the corresponding LEPs of all heteroatoms are oriented towards the metal cation too. Actually, the Ba—O—C angles vary within 110.2(4)–118.7(5)° and the Ba—N—C angles, within 104.7(5)–112.5(5)°. The C—N—C angles at the nitrogen atom range within 108.0(7)–113.7(7)°. The sum of these bond angles amounts to 330.7(7)°, being indicative of a pronounced pyramidal geometry similar to that for the perfect sp^3 state of the nitrogen atom.

CONCLUSIONS

Thus, we proposed an improved method for the synthesis of formyl derivatives of *N*-methylbenzoazacrown ethers in which the nitrogen atom is conjugated with the benzene ring. The method is suitable for preparing individual benzoazacrown ethers in high yields over fewer steps and with a substantial shortening of the reaction time at the key stage, i.e. intramolecular cyclization of the podand halogen derivative.

The high efficiency of complexation of the *N*-methyl derivatives of benzoazacrown ethers with metal and ammonium cations, caused by the pyramidal geometry of the tertiary nitrogen in the macrocycle and by the pre-organization of the macrocycle conformation, is demonstrated. The stability of the resulting complexes of *N*-methyl derivatives of benzoazacrown ethers is comparable with or even higher than the stability of complexes of benzocrown ethers and is much higher than the stability of complexes formed by phenylazacrown ethers with the same macrocycle size. This feature and the arrangement of the nitrogen atom in the *para*-position of the formyl group in the benzene ring imply that benzoazacrown compounds having this structure and their derivatives formed upon modification of the formyl group may have promising characteristics as ligands for

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Group I, II metal cations and ammonium ions and allow one to predict their use in effective optical molecular sensors.

EXPERIMENTAL

General information

4′-Formylbenzo-12(15,18)-crown-4(5,6) ethers (**2a–c**)[21,22] and *N*-(4-formylphenyl)aza-15(18)-crown-5(6) ethers (**9a,b**)[23] were obtained by known methods. CD$_3$CN (water < 0.05%), NaH (60% in paraffin), THF (water < 0.005%) were used as received (Merck, Aldrich, or Fluka). NaClO$_4$, KClO$_4$, Ca(ClO$_4$)$_2$ and Ba(ClO$_4$)$_2$ (Aldrich) were dried *in vacuo* at 200 °C, NH$_4$ClO$_4$ and EtNH$_3$ClO$_4$ were dried at 70 °C.

The melting points measured with a MEL-Temp II apparatus in a capillary are uncorrected. The ^{1}H NMR spectra were recorded on a Bruker DRX500 (500.13 MHz) instrument in DMSO-d$_6$ and CD$_3$CN solutions using the solvent as an internal reference (2.50 and 1.96 ppm, respectively). The course of the reactions was monitored by TLC on DC-Alufolien Kieselgel 60 F$_{254}$ plates (Merck). Column chromatography was performed with silica gel (Kieselgel 60, 0.063–0.100 mm, Merck) and aluminium oxide (Aluminiumoxid 90, aktiv neutral, 0.063–0.200 mm, Merck). Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds in Moscow, Russia.

Preparation

*Synthesis of benzoazacrown ethers **1a–c** (general procedures).*

Method A
A mixture of iodide **5a–c** (0.1 mmol), anhydrous THF (7 ml) and 40 mg (1 mmol) of 60% NaH in paraffin was refluxed with stirring for 30 min. After cooling, the reaction mixture was diluted with water and extracted with benzene. The extracts were washed with water and concentrated *in vacuo*, and the residue was purified by column chromatography on SiO$_2$, using successively a 1: 1 benzene–EtOAc mixture and EtOAc as the eluents to give **1a–c** as light yellow oils, from which **1a** and **1b** crystallized on standing. The yields of **1a–c** are presented in Table 1.

Method B
A mixture of iodide **5a–c** (0.1 mmol), anhydrous THF (7 ml) and 60% NaH (40 mg, 1 mmol) in paraffin was stirred at room temperature until the initial iodide disappeared (TLC monitoring). The mixture was worked-up as in *Method A*. The reaction time and the yields of **1a–c** are presented in Table 1.

Method C
A mixture of chloride **4b,c** (0.1 mmol), anhydrous THF (7 ml) and 60% NaH in paraffin (40 mg, 1 mmol) was refluxed with stirring until the initial chloride disappeared (TLC monitoring). The workup was similar to that in *Method A*. The reaction time and the yields of **1b,c** are presented in Table 1.

Methylation of benzoazacrown ether 6c. A mixture of azacrown ether **6c** (15 mg, 44 μmol), 60% NaH (35 mg, 0.88 mmol) in paraffin, MeI (27 μl, 0.44 mmol) and anhydrous THF (4 ml) was refluxed for 30 min. The reaction mixture was diluted with water and extracted with benzene. The extracts were washed with water and concentrated *in vacuo* and the residue was passed

through a thin Al$_2$O$_3$ layer using benzene and then EtOAc as the eluents. The yield of **1c** was 9 mg (58%).

10-Methyl-2,3,5,6,9,10-hexahydro-8H-1,4,7,10-benzotrioxazacyclododecine-13-carbaldehyde (1a). Mp 71–72 °C (hexane), mp 71–72 °C.[14] ^{1}H NMR (DMSO-d$_6$, 30 °C) δ: 2.85 (s, 3H, MeN), 3.48 (t, J = 7.3, 2H, CH$_2$N), 3.59 (m, 2H, CH$_2$O), 3.67 (m, 2H, CH$_2$O), 3.82 (t, J = 7.3, 2H, C*H*$_2$CH$_2$N), 3.84 (m, 2H, C*H*$_2$CH$_2$OAr), 4.15 (m, 2H, C*H*$_2$OAr), 6.89 (d, J = 8.3, 1H, H(11)), 7.29 (d, J = 1.8, 1H, H(14)), 7.42 (dd, J = 8.3, J = 1.8, 1H, H(12)), 9.72 (s, 1H, CH = O).

13-Methyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13-benzotetraoxazacyclopentadecine-16-carbaldehyde (1b). Mp 49–51 °C (hexane), mp 50–51 °C.[14] ^{1}H NMR (DMSO-d$_6$, 30 °C) δ: 2.87 (s, 3H, MeN), 3.30 (t, J = 7.5, 2H, CH$_2$N), 3.57 (s, 4H, 2CH$_2$O), 3.60 (m, 4H, 2CH$_2$O), 3.82 (m, 2H, C*H*$_2$CH$_2$OAr), 3.86 (t, J = 7.5, 2H, C*H*$_2$CH$_2$N), 4.14 (m, 2H, C*H*$_2$OAr), 6.92 (d, J = 8.3, 1H, H(14)), 7.29 (d, J = 1.5, 1H, H(17)), 7.42 (dd, J = 8.3, J = 1.5, 1H, H(15)), 9.73 (s, 1H, CH = O).

16-Methyl-2,3,5,6,8,9,11,12,15,16-decahydro-14H-1,4,7,10,13,16-benzopentaoxazacyclooctadecine-19-carbaldehyde (1c). Yellowish oil.[14] ^{1}H NMR (DMSO-d$_6$, 30 °C) δ: 2.95 (s, 3H, MeN), 3.50 (t, J = 5.9, 2H, CH$_2$N), 3.52 (m, 4H, 2CH$_2$O), 3.54 (s, 4H, 2CH$_2$O), 3.60 (s, 4H, 2CH$_2$O), 3.72 (t, J = 5.9, 2H, C*H*$_2$CH$_2$N), 3.80 (m, 2H, C*H*$_2$CH$_2$OAr), 4.14 (m, 2H, C*H*$_2$OAr), 6.89 (d, J = 8.2, 1H, H(17)), 7.29 (d, J = 1.4, 1H, H(20)), 7.42 (dd, J = 8.2, J = 1.4, 1H, H(18)), 9.73 (s, 1H, CH = O).

Synthesis of complexes of crown ethers 1b,c with Ba(ClO$_4$)$_2$ (general procedure). A solution of **1b,c** (30 μmol) and Ba(ClO$_4$)$_2$ (10 mg, 30 μmol) in acetonitrile (3 ml) was slowly saturated with benzene by vapour diffusion methods (for 2–3 weeks). The single crystals formed were collected by decantation and dried in air at room temperature. The crystals were characterized by elemental analysis and used for X-ray structural study.

Complex 1b · Ba(ClO$_4$)$_2$. Obtained as colourless blocks in 89% yield; mp > 330 °C (decomp.). Anal. calcld for C$_{16}$H$_{23}$BaCl$_2$NO$_{13}$: C, 29.77; H, 3.59; N, 2.17; found: C, 29.84; H, 3.54; N, 2.19%.

Complex 1c · Ba(ClO$_4$)$_2$. Obtained as colourless blocks in 65% yield; mp 302–305 °C (decomp.). Anal. calcld for C$_{18}$H$_{27}$BaCl$_2$NO$_{14}$: C, 31.35; H, 3.95; N, 2.03; found: C, 31.26; H, 3.84; N, 2.04%.

^{1}H NMR titration

The titration experiments were performed in CD$_3$CN solutions at 30 ± 1 °C. A solution of crown ether (L) (0.5 ml, C_L = 5 × 10^{-3} M) and NaClO$_4$, Ca(ClO$_4$)$_2$, Ba(ClO$_4$)$_2$, or EtNH$_3$ClO$_4$ (C_M = 0.03 M) were added in portions to a solution of L in CD$_3$CN (0.5 ml, C_L = 5 × 10^{-3} M). In the case of NH$_4$ClO$_4$ and KClO$_4$, C_L = 2 × 10^{-3} M and C_M = 0.012 M were used for titration due to the low solubility of the salts in CD$_3$CN. In the case of competitive titration, a solution (0.5 ml) containing a mixture of L, metal perchlorate and the competing ligand (L′) (C_L = 5 × 10^{-3} M, C_M = 6 × 10^{-3} M, $C_{L'}$ = 0.2 M) was added in portions to a solution of a mixture of L and metal perchlorate in CD$_3$CN (0.5 ml, C_L = 5 × 10^{-3} M, C_M = 6 × 10^{-3} M). The proton chemical shifts were measured as a function of the M/L or L′/L ratio and the complex formation constants were then calculated using the HYPNMR program.[17]

X-ray experiments

Crystals of compounds **1b**, **9a,b** and **10** · CH$_2$Cl$_2$ were obtained by slow evaporation of the CH$_2$Cl$_2$–hexane solutions. Crystals of

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complexes **1b** and **1c** with Ba(ClO$_4$)$_2$ were grown as described above. Single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART–CCD diffractometer (graphite monochromatized Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å, ω scan mode) under a stream of cold nitrogen ($T = 120.0(2)$ K).

All structures were solved by direct methods and refined by full-matrix least-squires on F^2 in anisotropic approximation for non-hydrogen atoms. A disorder of the formyl groups of two independent molecules **9a** over two positions with a ratio of site occupation factors equal to 0.77:0.23 and 0.95:0.05 was observed. It was found that the substituent in the benzoazacrown ether **10** · CH$_2$Cl$_2$ is carboxyl rather than formyl. This observation was supported by bond lengths and the presence of a hydrogen atom at one of carboxyl oxygens.

The positions of hydrogen atoms were calculated geometrically and then refined isotropically [for **1b**, **9a,b** and **10** · CH$_2$Cl$_2$ (except for the hydrogen atom of the carboxyl group of **10** · CH$_2$Cl$_2$ and the hydrogen atoms of the disordered formyl groups in two independent molecules of **9a** which were refined using a riding model)] or using a riding model [for **1b** · Ba(ClO$_4$)$_2$ and **1c** · Ba(ClO$_4$)$_2$].

A low quality of single crystals **1b** · Ba(ClO$_4$)$_2$ and **1c** · Ba(ClO$_4$)$_2$ did not allow us to achieve accurate structures. We obtained high values of R_1 and wR_2 and residuals. However, all peaks of residual electron density are located in the vicinity of heavy atoms. In spite of low accuracy, we believe that the obtained structural motifs are correct enough to discuss the conformation features, as well as the change in the conformation of free **1b** upon its coordination to the metal cation.

Crystal data for **1b**: C$_{16}$H$_{23}$NO$_5$, $M = 309.35$, triclinic, $a = 8.1791(5)$, $b = 10.0518(6)$, $c = 10.6693(6)$ Å, $\alpha = 103.293(3)$, $\beta = 100.998(3)$, $\gamma = 104.598(3)°$, $V = 796.78(8)$ Å^3, space group $P\,1$ (no. 2), $Z = 2$, μ(Mo-K$_\alpha$) $= 0.095$ mm^{-1}, 8179 reflections measured, 4158 unique ($R_{int} = 0.0398$) which were used in all calculations. The final R_1 and wR_2 were 0.0436 and 0.1066 for 3128 reflections with $I > 2\sigma(I)$, 0.0640 and 0.1150 for all data.

Crystal data for **9a**: C$_{17}$H$_{25}$NO$_5$, $M = 323.38$, monoclinic, $a = 24.2125(7)$, $b = 15.3431(4)$, $c = 8.8104(3)$ Å, $\beta = 92.6370(10)°$, $V = 3269.55(17)$ Å^3, space group $P2_1/c$ (no. 14), $Z = 8$, μ(Mo-K$_\alpha$) $= 0.096$ mm^{-1}, 27753 reflections measured, 8656 unique ($R_{int} = 0.0570$) which were used in all calculations. The final R_1 and wR_2 were 0.0540 and 0.1196 for 5463 reflections with $I > 2\sigma(I)$, 0.0972 and 0.1312 for all data.

Crystal data for **9b**: C$_{19}$H$_{29}$NO$_6$, $M = 367.43$, monoclinic, $a = 21.6266(6)$, $b = 10.3060(3)$, $c = 8.4947(2)$ Å, $\beta = 98.747(2)°$, $V = 1871.31(9)$ Å^3, space group $P2_1/c$ (no. 14), $Z = 4$, μ(Mo-K$_\alpha$) $= 0.096$ mm^{-1}, 12397 reflections measured, 4813 unique ($R_{int} = 0.0439$) which were used in all calculations. The final R_1 and wR_2 were 0.0564 and 0.1044 for 3280 reflections with $I > 2\sigma(I)$, 0.0939 and 0.1133 for all data.

Crystal data for **10** · CH$_2$Cl$_2$: C$_{16}$H$_{23}$Cl$_2$NO$_6$, $M = 396.25$, triclinic, $a = 8.3696(7)$, $b = 11.1611(10)$, $c = 11.7965(10)$ Å, $\alpha = 106.926(2)$, $\beta = 109.505(2)$, $\gamma = 104.921(2)°$, $V = 913.63(14)$ Å^3, space group $P\,1$ (no. 2), $Z = 2$, μ(Mo-K$_\alpha$) $= 1.440$ mm^{-1}, 5104 reflections measured, 4184 unique ($R_{int} = 0.0170$) which were used in all calculations. The final R_1 and wR_2 were 0.0543 and 0.1480 for 3151 reflections with $I > 2\sigma(I)$, 0.0750 and 0.1575 for all data.

Crystal data for **1b** · Ba(ClO$_4$)$_2$: C$_{16}$H$_{23}$BaCl$_2$NO$_{13}$, $M = 645.59$, triclinic, $a = 10.7252(19)$, $b = 12.955(2)$, $c = 16.522(3)$ Å, $\alpha = 100.747(3)$, $\beta = 91.160(4)$, $\gamma = 90.423(4)°$, $V = 2254.8(7)$ Å^3,

space group $P\,1$ (no. 2), $Z = 4$, μ(Mo-K$_\alpha$) $= 2.066$ mm^{-1}, 8473 reflections measured, 5216 unique ($R_{int} = 0.0335$) which were used in all calculations. The final R_1 and wR_2 were 0.1521 and 0.3558 for 4807 reflections with $I > 2\sigma(I)$, 0.1562 and 0.3573 for all data. SADABS absorption correction was applied.

Crystal data for **1c** · Ba(ClO$_4$)$_2$: C$_{18}$H$_{27}$BaCl$_2$NO$_{14}$, $M = 689.65$, monoclinic, $a = 8.9885(5)$, $b = 26.7470(14)$, $c = 10.7487(6)$ Å, $\beta = 107.870(2)°$, $V = 2459.5(2)$ Å^3, space group $P2_1/n$ (no. 14), $Z = 4$, μ(Mo-K$_\alpha$) $= 1.904$ mm^{-1}, 26650 reflections measured, 5898 unique ($R_{int} = 0.0315$) which were used in all calculations. The final R_1 and wR_2 were 0.0655 and 0.1658 for 5408 reflections with $I > 2\sigma(I)$, 0.0703 and 0.1675 for all data. SADABS absorption correction was applied.

The crystallographic parameters, data collection and structure solution details, and the refinement parameters for **1b**, **9a**, **9b**, **10** · CH$_2$Cl$_2$, **1b** · Ba(ClO$_4$)$_2$, and **1c** · Ba(ClO$_4$)$_2$ are given also in Tables 7S-9S (SM).

All the calculations were performed using SHELXTL-Plus software.[24] Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC 694336 (**1b**), 694338 (**9a**), 694339 (**9b**), 694340 (**10** · CH$_2$Cl$_2$), 694335 (**1b** · Ba(ClO$_4$)$_2$), 694337 (**1c** · Ba(ClO$_4$)$_2$). A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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