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Synthesis and Complex-Forming Properties of N-Substituted Diazacrown Ethers

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Abstract — N-Substituted mono- and diazacrown ether with ethoxycarbonylmethyl, 7-phenyl-3,6-dioxaheptyl, *p*-methoxy, and *p*-nitrobenzyl groups in the side chain have been synthesized. Their reactions with alkali and alkaline-earth metals have been studied. Substituents affect the complex-forming ability of the "base" macrocycle by changing the basicity of the nitrogen atoms and coordinating with the complexing ion.

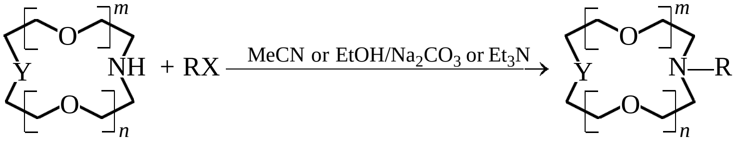
Complex formation of mono- and divalent cations with lariate crown ethers has been intensively studied from the very discovery of the latter [1]. The complex-forming capacity of the latter depends both on the macrocyclic ligand and on the side chains that can additionally coordinate with the cation [1–8]. In general, side chains much affect most properties of the "base" macroring, such as conformation, electronic properties of binding centers and their steric accessibility, etc.. On the other hand, flexible side chains containing heteroatoms can embrace cations, thus forming cryptand-like 3D structures [2, 6–8]. As a result, unusual complex-forming properites arise, which are not directly related to the concept of size compatibility of cation and macroring cavity but strongly depend of the nature of the side chains.

Comprehensive assessment of the effect of side chains is quite an intricate problem, and molecular design of lariate crown ethers has so far remained empirical.

At present lariate crown ethers are rather well studied. At the same time, limited information is available on their complex formation with alkali and alkaline-earth cations, which prevents substantiated conclusions as to the electronic and structural effects of substituents on the complex-formation reaction.

The main purposes of the present work were to synthesize a series of N-substituted aza- and diazacrown ethers and to study their complex-forming properties and the effect of the substituents on them.

The target azacrown ethers were prepared by alkylation of mono- and diazacrown ethers with benzyl chlorides (compounds **VII**–**XII** and **XVII**–**XIX**) or (7-phenyl-3,6-dioxaheptyl) toluenesulfonate (compounds **XV** and **XVI**), or ethyl chloroacetate (compounds **XIII**, **XIV**, **XX**, and **XXI**). The alkylations were performed in the presence of sodium carbonate or triethylamine in boiling acetonitrile or ethanol over the course of 12–16 h. The yields of pure target products were 73–96%. Azacrown ethers **VII** and **XIV**–**XX** we obtained for the first time. The composition and structure of the synthesized compounds were proved by elemental analysis, ^{1}H NMR spectroscopy, and mass spectrometry.



I–**VI** **VII**–**XXI**

Y = O (**I–III, VII–XVI**), NH (**IV–VI**), NR (**XVII–XXI**); *n* = *m* = 1 (**I, IV, VII, X, XVII, XX**); *n* = 1, *m* = 2 (**II, V, VIII, XI, XIII, XV, XVIII**); *n* = *m* = 2 (**III, VI, IX, XII, XIV, XVI, XIX, XXI**); R = $4\text{-}O_2NC_6H_4CH_2$ (**VII–IX**), $4\text{-}MeOC_6H_4 \cdot CH_2$ (**X–XII**, **XVII–XIX**), $EtOCOCH_2$ (**XIII**, **XIV**, **XX**, **XXI**), $PhCH_2OCH_2CH_2OCH_2CH_2$ (**XV**, **XVI**).

The protonation and complex-formation constants were determined by pH-metric titration in methanol at 25°C. The resulting data are summarized in Table 1. Lariate diazacrown ether **VII**–**XXI** almost all, irrespective of the ring size, exhibit K^+-selectivity in the series of alkali metals and Sr^{2+}- or Ba^{2+}-selectivity in the series of alkaline-earth metals. Exceptions are *N*-(ethoxycarbonylmethyl)aza-15-crown-5 (**XIII**) and

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Table 1. Protonation and stability constants of complexes (log *K*; *K*, dm^3/mol) of N-substituted mono- and diazacrown ethers **VII**–**XXI** with alkali and alkaline-earth metals in methanol at 25°C

Comp. no.	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
VII	8.30±0.01[a]	<1.5	<1.5	2.05±0.06	<1.5	1.8±0.2	<1.5	2.20±0.08	2.01±0.08
VIII	7.93±0.01[a]	<1.5	2.0±0.2	2.47±0.03	2.02±0.09	2.05±0.07	2.2±0.2	2.50±0.06	2.56±0.02
IX	8.04±0.01[a]	1.5±0.1	3.00±0.03	4.52±0.01	3.70±0.02	3.60±0.02	2.8±0.1	5.04±0.02	5.10±0.03
X	10.06±0.01[a]	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
XI	9.95±0.01[a]	<1.5	2.80±0.04	2.70±0.03	<1.5	<1.5	2.28±0.09	2.96±0.04	3.25±0.05
XII	9.80±0.02[a]	1.9±0.1	3.40±0.02	4.68±0.02	3.84±0.02	3.70±0.04	3.25±0.04	5.87±0.02	5.90±0.01
XIII	7.80±0.02[a]	2.1±0.1	4.01±0.05	3.77±0.03	3.19±0.03	2.85±0.01	4.27±0.01	5.29±0.07	5.18±0.03
XIV	8.11±0.02[a]	1.80±0.02	4.31±0.04	5.36±0.04	4.43±0.03	3.69±0.05	5.60±0.03	7.41±0.04	7.50±0.03
XV	10.01±0.02[a]	1.5±0.3	4.13±0.03	4.34±0.02	3.61±0.04	3.11±0.02	3.52±0.02	5.16±0.03	5.10±0.01
XVI	10.11±0.04[a]	1.8±0.2	4.26±0.02	5.76±0.02	5.04±0.01	4.47±0.06	4.2±0.02	6.58±0.06	7.32±0.01
XVII	10.29±0.01[a] 7.11±0.03[b]	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
XVIII	10.21±0.01[a] 7.57±0.02[b]	1.90±0.10	2.85±0.03	3.29±0.07	<1.5	<1.5	2.83±0.01	3.30±0.04	3.20±0.04
XIX	9.79±0.01[a] 8.09±0.02[b]	1.88±0.01	2.85±0.03	3.35±0.02	2.35±0.04	2.51±0.07	2.92±0.07	5.21±0.04	4.88±0.03
XX	9.08±0.01[a] 4.74±0.02[b]	<1.5	4.63±0.07	3.74±0.01	1.9±0.1	<1.5	6.79±0.01	6.83±0.01	6.52±0.01
XXI	7.85±0.01[a] 5.81±0.03[b]	2.2±0.1	5.02±0.01	5.34±0.01	3.96±0.02	3.08±0.04	7.70±0.02 4.48±0.03[c]	9.15±0.04 5.49±0.05[c]	8.78±0.03 5.06±0.05[c]

[a] Logarithms of the protonation constants corresponding to the equilibrium L + H+ = LH+. [b] Logarithms of the protonation constants corresponding to the equilibrium $LH^+ + H^+ = LH_2^{2+}$. [c] Logarithms of the stability constants corresponding to the equilibrium $LH^+ + M^{n+} = LHM^{(n+1)+}$.

N,*N*'-bis(ethoxycarbonylmethyl)diaza-12-crown-4 (**XX**), which selectively react with Na^+ ions.

The stability of the complexes is determined by the macroring size and the nature of the side groups. At the same side groups, the stability of the complexes increases with the ring size of the N-substituted azacrown ether, from 12- to 15- and further to 18-membered (Table 1).

Substituents appreciably affect the basicity of the nitrogen atoms, which suggests change in the complex-forming properties of the macroring. On the other hand, side chains containing donor atoms can react with the complexing cation. Molecular modeling of the complexes shows that in crown ethers with *p*-nitrobenzyl and *p*-methoxybenzyl side groups such intramolecular reactions are impossible.

However, more flexible groups, such as ethoxycarbonylmethyl and 7-phenyl-3,6-dioxaheptyl, are readily available for cooperative interaction with the macroring.

To trace the effect of the basicity of the nitrogen atoms on the complex-forming properties of N-substituted azacrown ethers, we can use the example of compounds **VIII**, **IX** and **XI**, **XII**, whose side groups are incapable of additional coordination with the complexing cation (Table 2).

Increasing basicity of nitrogen increases the relative stability both of alkali and of alkaline-earth cation complexes. The strongest effect is observed with Na^+, Sr^{2+} and Ba^{2+}, which enhances the Sr^{2+}/Ca^{2+}- and Ba^{2+}/Ca^{2+}-selectivities and attenuates the K^+/Na^+-selectivity.

The effect of side groups on the stability of complexes of crown ethers **VII**–**XVI** is more intricate. At the same ring size and almost equal basicity, as in compounds **XIII**–**XVI**, side chains capable of additionally coordinating with the complexing cation enhance stability of both alkali and alkaline-metal cation complexes (Table 1). Therewith, the strongest effect in the former complexes is produced by ether side groups (crown ethers **XV** and **XVI**), whereas in the latter complexes, by ester side groups (compounds **XIII** and **XIV**). This phenomenon is probably explained by the fact that cations with a high charge

Table 2. Effect of the basicity of the nitrogen atom in N-substituted monoazacrown ethers **VIII, IX, XI**, and **XII** on the relative stability of their complexes (Δlog *K*)

Δlog *K*	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log K_{\mathbf{XI}} - \log K_{\mathbf{VIII}}$	2.02	0	0.80	0.23	>–0.5	>–0.6	0.08	0.46	0.69
$\log K_{\mathbf{XII}} - \log K_{\mathbf{IX}}$	1.76	>0.4	0.40	0.16	0.14	0.10	0.45	0.83	0.80

Table 3. Effect of the nature of side chains in N-substituted monoazacrown ethers **VIII, IX**, and **XI–XVI** on the relative stability of their complexes (Δlog *K*)

Δlog *K*	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log K_{\mathbf{XIII}} - \log K_{\mathbf{VIII}}$	–0.13	>0.6	2.01	1.3	1.2	0.8	2.07	2.79	2.62
$\log K_{\mathbf{XIV}} - \log K_{\mathbf{IX}}$	0.07	0.3	1.31	0.84	0.7	0.1	2.8	2.37	2.4
$\log K_{\mathbf{XV}} - \log K_{\mathbf{XI}}$	0.06	0	1.33	1.64	>2.1	>1.6	1.24	2.2	1.85
$\log K_{\mathbf{XVI}} - \log K_{\mathbf{XII}}$	0.31	–0.1	0.86	1.08	1.2	0.8	0.95	0.71	1.42

Table 4. Relative stability of complexes (Δlog *K*) of mono- and diazacrown ethers **XI, XII, XIV, XVIII, XIX**, and **XXI** with the same side groups

Δlog *K*	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log K_{\mathbf{XVIII}} - \log K_{\mathbf{XI}}$	0.40	0.05	0.59	0.00	0.00	0.55	0.34	–0.05
$\log K_{\mathbf{XIX}} - \log K_{\mathbf{XII}}$	–0.02	–0.55	–1.33	–1.49	–1.19	–0.33	–0.66	–1.02
$\log K_{\mathbf{XXI}} - \log K_{\mathbf{XIV}}$	0.40	0.71	–0.02	–0.47	–0.61	2.10	1.74	1.28

density prefer to interact with the carbonyl group of the side chain (Table 3).

Comparison of the stabilities of complexes of mono- and diazacrown ethers with the same ring size and substituents (Table 4) shows that replacement of one oxygen atom in 15-membered crown ether **XI** by nitrogen (diazacrown ether **XVIII**) results in a slight stability enhancement of complexes with all the ions studied. By contrast, 18-membered diazacrown ether **XIX** forms less stable complexes than monoazacrown ether **XII**. Complexes of diazacrown ethers **XVIII** and **XIX** get less stable compared with complexes of monoazacrown ethers **XI** and **XII** as the size of the cation increases along the series of both alkali and alkaline-earth metals. An exception are potassium complexes of crown ethers **XI** and **XVIII**. As concerns 18-membered crown ethers **XIV** and **XXI** which contain in the side chain ethoxycarbonyl groups capable of additionally coordinating with the complexing ion, diazacrown ether **XXI** forms more stable complexes with all the alkaline-earth metal cations, as well as with Li^+ and Na^+. Probably, both side groups are involved in complex formation with these ions.

EXPERIMENTAL

The melting points were measured in open capillaries and were not corrected. The ^1H NMR spectra were run on Bruker AM-200 (200 MHz) and Bruker AM-250 (250 MHz) spectrometers in $CDCl_3$, internal reference TMS. The mass spectra were obtained on Varian MAT-112 and MX-1331 instruments with direct inlet at ionizing energies of 70 and 12 eV. Thin-layer chromatography was performed on Silufol-254 plates (Chemapol).

All commercial reagents were used as received, unless otherwise stated. Azacrown ethers **I**–**III** and diazacrown ethers **IV**–**VI** were prepared as described in [9–11]. 7-Phenyl-3,6-dioxaheptyl *p*-toluenesulfonate was prepared from diethylene glycol monobenzyl ether [12] according to [13].

***N*-(4-Nirobenzyl)azacrown ethers VII–IX, *N*-(4-methoxybenzyl)azacrown ethers X–XII, and *N*,*N*'-bis(4-methoxybenzyl)diazacrown ethers XVII–XIX** *(general procedure).* A mixture of 20 mmol of monoazacrown ether or 10 mmol of diazacrown ether, 22 mmol of corresponding benzyl chloride, 45 mmol of powdered sodium carbonate, and

70 ml of dry acetonitrile was refluxed with stirring for 14 h. After cooling, the precipitate was filtered off, and the solvent was removed by rotary evaporation. The residue was dissolved in 100 ml of chloroform, and the resulting solution was treated with 5% HCl (3×20 ml). The combined acidic extracts were made alkaline (pH 10) with concentrated NaOH and then treated with chloroform (3×50 ml). The extracts were dried with $MgSO_4$, and the solvent was removed at reduced pressure. Solid residues were recrystallized from ethanol. Oily residues were treated with hot hexane (3×40 ml), the solvent was removed, and the procedure was repeated.

***N*-(4-Nitrobenzyl)aza-12-crown-4 (VII).** Colorless crystals. Yield 90%, mp 54–56°C. ^1H NMR spectrum, δ, ppm: 2.73 t (4H, NCH_2), 3.67 m (14H, OCH_2, $ArCH_2$), 7.56 d (2H, H_{arom}), 8.12 d (2H, H_{arom}). Found, %: C 58.17; H 7.03; N 9.14. $C_{15}H_{22}N_2O_5$. Calculated, %: C 58.05; H 7.15; N 9.03.

***N*-(4-Nitrobenzyl)aza-15-crown-5 (VIII).** Oil. Yield 89%. ^1H NMR spectrum, δ, ppm: 2.76 t (4H, NCH_2), 3.68 m (16H, OCH_2), 3.84 s (2H, $ArCH_2$), 7.59 d (2H, H_{arom}), 8.15 d (2H, H_{arom}). Found, %: C 58.51; H 7.23; N 8.02. $C_{17}H_{26}N_2O_6$. Calculated, %: C 57.61; H 7.39; N 7.90.

***N*-(4-Nitrobenzyl)aza-18-crown-6 (IX).** Oil. Yield 88%. ^1H NMR spectrum, δ, ppm: 2.84 t (4H, NCH_2), 3.69 m (20H, OCH_2), 3.85 s (2H, $ArCH_2$), 7.60 d (2H, H_{arom}), 8.19 d (2H, H_{arom}). Found, %: C 57.18; H 7.68; N 7.21. $C_{19}H_{30}N_2O_7$. Calculated, %: C 57.27; H 7.59; N 7.03.

***N*-(4-Methoxybenzyl)aza-12-crown-4 (X).** Oil. Yield 86%. ^1H NMR spectrum, δ, ppm: 2.69 t (4H, NCH_2), 3.65 m and 3.78 s (17H, OCH_2, $ArCH_2$, and OCH_3), 6.80 d (2H, H_{arom}), 7.21 d (2H, H_{arom}). Found, %: C 65.21; H 8.41; N 4.89. $C_{16}H_{25}NO_4$. Calculated, %: C 65.06; H 8.53; N 4.74.

***N*-(4-Methoxybenzyl)aza-15-crown-5 (XI).** Oil. Yield 89 %. ^1H NMR spectrum, δ, ppm: 2.70 t (4H, NCH_2), 3.67 m and 3.76 s (21H, OCH_2, $ArCH_2$, and OCH_3), 6.80 d (2H, H_{arom}), 7.21 d (2H, H_{arom}). Found, %: C 63.21; H 8.55; N 4.25. $C_{18}H_{29}NO_5$. Calculated, %: C 63.69; H 8.61; N 4.13.

***N*-(4-Methoxybenzyl)aza-18-crown-6 (XII).** Oil. Yield 92 %. ^1H NMR spectrum, δ, ppm: 2.74 t (4H, NCH_2), 3.62 m, 3.66 m and 3.76 s (25H, OCH_2, $ArCH_2$, and OCH_3), 6.81 d (2H, H_{arom}), 7.23 d (2H, H_{arom}). Found, %: C 62.80; H 8.81; N 3.52. $C_{20}H_{33} \cdot NO_6$. Calculated, %: C 62.64; H 8.67; N 3.65.

***N,N*'-Bis(4-methoxybenzyl)-4,10-diaza-12-crown-4 (XVII).** Oil. Yield 91%. ^1H NMR spectrum, δ, ppm: 2.78 t (8H, NCH_2), 3.59 m and 3.76 m (18H, OCH_2, $ArCH_2$, and OCH_3), 6.81 d (4H, H_{arom}), 7.22 d (4H, H_{arom}). Found, %: C 69.41; H 8.43; N 6.83. $C_{24}H_{34}N_2O_4$. Calculated, %: C 69.54; H 8.27; N 6.76.

***N,N*'-Bis(4-methoxybenzyl)-4,10-diaza-15-crown-5 (XVIII).** Oil. Yield 87%. ^1H NMR spectrum, δ, ppm: 2.78 t (8H, NCH_2), 3.61 m and 3.79 m (22H, OCH_2, $ArCH_2$, and OCH_3), 6.81 d (4H, H_{arom}), 7.24 d (4H, H_{arom}). Found, %: C 68.39; H 8.52; N 6.72. $C_{26}H_{38}N_2O_5$. Calculated, %: C 68.10; H 8.35; N 6.11.

***N,N*'-Bis(4-methoxybenzyl)-4,13-diaza-18-crown-6 (XIX).** Colorless crystals. Yield 86 %, mp 45–47°C. ^1H NMR spectrum, δ, ppm: 2.78 t (8H, NCH_2), 3.59 m and 3.77 m (26H, OCH_2, $ArCH_2$, and OCH_3), 6.81 d (4H, H_{arom}), 7.22 d (4H, H_{arom}). Found, %: C 67.03; H 8.59; N 5.72. $C_{28}H_{42}N_2O_6$. Calculated, %: C 66.91; H 8.42; N 5.57.

***N*-(4-Ethoxycarbonylmethyl)azacrown ethers XIII and XIV and *N,N*'-bis(4-ethoxycarbonylmethyl)diazacrown ethers XX and XXI** *(general procedure).* A mixture of 20 mmol of monoazacrown ether or 10 mmol of diazacrown ether, 22 mmol of ethyl chloroacetate, and 40 mmol of triethylamine in 50 ml of ethanol was heated under reflux with stirring for 16 h, cooled, and poured into 200 ml of water. The resulting solution was treated with chloroform (6×20 ml). The combined chloroform extracts were dried with $MgSO_4$, and the solvent was removed at reduced pressure. The residue was treated with boiling hexane (3×25 ml), the solvent was removed at reduced pressure, and the residue was distilled in a vacuum.

***N*-(Ethoxycarbonylmethyl)aza-15-crown-5 (XIII).** Oil. Yield 81%, bp 148–151°C (0.05 mm). ^1H NMR spectrum, δ, ppm: 1.23 t (3H, CH_3), 2.90 t (6H, NCH_2), 3.46 s and 3.55 m (16H, OCH_2), 4.14 d (2H, $COCH_2$). Found, %: C 55.20; H 9.03; N 4.43. $C_{14}H_{27}NO_6$. Calculated, %: C 55.07; H 8.91; N 4.59.

***N*-(Ethoxycarbonylmethyl)aza-18-crown-6 (XIV).** Oil. Yield 77%, bp 172–175°C (0.05 mm). ^1H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3), 2.92 t (6H, NCH_2), 3.47 s and 3.56 m (20H, OCH_2), 4.15 d (2H, $COCH_2$). Found, %: C 54.83; H 9.08; N 3.92. $C_{16}H_{31}NO_7$. Calculated, %: C 55.00; H 8.94; N 4.01.

***N,N*'-Bis(ethoxycarbonylmethyl)-4,10-diaza-12-crown-4 (XX).** Oil. Yield 73%, bp 184–187°C (0.05 mm). ^1H NMR spectrum, δ, ppm: 1.23 t (6H, CH_3), 2.90 t (12H, NCH_2), 3.46 s and 3.55 m (8H, OCH_2), 4.14 d (4H, $COCH_2$). Found, %: C 55.33; H 8.64; N 8.01. $C_{16}H_{30}N_2O_6$. Calculated, %: C 55.47; H 8.73; N 8.09.

***N*,*N*'-Bis(ethoxycarbonylmethyl)-4,13-diaza-18-crown-6 (XXI).** Oil. Yield 86%, bp 202–205°C (0.05 mm). ^{1}H NMR spectrum, δ, ppm: 1.24 t (6H, CH_3), 2.92 t (12H, NCH_2), 3.47 s and 3.56 m (16H, OCH_2), 4.16 d (4H, $COCH_2$). Found, %: C 55.40; H 8.92; N 6.38. $C_{20}H_{38}N_2O_8$. Calculated, %: C 55.28; H 8.81; N 6.45.

***N*-(7-Phenyl-3,6-dioxaheptyl)azacrown ethers XV and XVI** *(general procedure).* A mixture of 20 mmol of monoazacrown ether, 22 mmol of 7-phenyl-3,6-dioxaheptyl *p*-toluenesulfonate, and 45 mmol of powdered sodium carbonate in 80 ml of dry acetonitrile was heated under reflux with stirring for 12 h. The mixture was cooled, the precipitate was filtered off, and the solvent was removed at reduced pressure. The residue was dissolved in 100 ml of chloroform and washed with 30 ml of water, saturated NaCl solution (2 × 30 ml), and dried with $MgSO_4$. The solvent was removed at reduced pressure, and the residue was dissolved in 50 ml of 5% HCl. The resulting solution was treated with chloroform (2 × 20 ml), made alkaline (pH 10) with concentrated NaOH, and treated again with chloroform (3 × 50 ml). The extract was dried with $MgSO_4$, and the solvent was removed at reduced pressure. The residue was treated with boiling hexane (3 × 25 ml). The solvent was removed in a vacuum to leave pure products as thick oils.

***N*-(7-Phenyl-3,6-dioxaheptyl)aza-15-crown-5 (XV).** Oil. Yield 79%. ^{1}H NMR spectrum, δ, ppm: 2.81 m (6H, NCH_2), 3.66 m (24H, OCH_2, $ArCH_2$), 7.36 m (5H, H_{arom}). Found, %: C 63.31; H 8.69; N 3.45. $C_{21}H_{35}NO_6$. Calculated, %: C 63.45; H 8.87; N 3.52.

***N*-(7-Phenyl-3,6-dioxaheptyl)aza-18-crown-6 (XVI).** Oil. Yield 75%. ^{1}H NMR spectrum, δ, ppm: 2.78 t and 2.83 t (6H, NCH_2), 3.63 m (28H, OCH_2, $ArCH_2$), 7.30 m (5H, H_{arom}). Found, %: C 62.68; H 9.08; N 3.09. $C_{23}H_{39}NO_7$. Calculation, %: C 62.56; H 8.90; N 3.17.

Determination of the protonation and complex-formation constants of azacrown ethers VII–XXI. The solvent, methanol (Carlo Erba, water content <0.01 %) was used as received. Solutions of ligands were obtained by dissolving weighed samples in methanol. The ionic strengths of the solutions were maintained constant (10^{-2} M) by adding tetraethylammonium perchlorate recrystallized from methanol. The titrant was a solution of tetraethylammonium hydroxide obtained by dilution of a commercial solution (25% in MeOH, Fluka) and standardized against potassium hydrogen phthalate.

The stability constants of complexes were determined potentiometrically by the proton competition technique. A combined glass electrode (Ingold) coupled with an automated titrator (Titrino DMS-716), at 25°C. The standard internal solution of the reference electrode (saturated aqueous KCl) of the combined glass electrode was replaced by a 0.01 M solution of Et_4NCl in MeOH, saturated with AgCl. Parameters (pH_0 and S) of the electrode function $pH_{obs} = pH_0 + S\log[H^+]$ were determined from the titration curve of a 0.001 M solution of $HClO_4$ in MeOH [obtained by dilution of concentrated (11.6 M) perchloric acid] with a 0.01 M solution of Et_4NOH in the presence of 0.01 M Et_4NClO_4. For methanol pK_{MeOH} –16.7 was used. The protonation constants and the complex-formation constants b_{xyz} relating to the overall complex-formation equilibrium ($xMn^+ + yL + zH^+ = (M_xL_yH_z^{(nx+z)+})$) were determined from the pH-metric data obtained in the course of neutralization of the acidic solution of ligand with a 0.01 M solution of Et_4NOH in MeOH under argon in the presence or in the absence of metal salts. Data treatment was performed using the SIRKO program [14] which allows simultaneous calculation of b_{xyz}, electrode parameters, and component concentrations. The overall titration curve in the range pH 3–12 was used in calculations. The electrode parameters and the stability (b_{xyz}) and protonation (b_{0yz}) constants obtained by titration of ligands in the absence of metals were set constant at preliminarily calculated values.

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