previous conclusions that homoaromaticity does not exist in neutral molecules[10b] and that monohomoaromaticity is not an important effect in anions,[10c] this work suggests that homoaromaticity may be restricted to cationic systems which can distort to increase the overlap of the interacting orbitals.

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Na^+ Complexes with Acyclic Polyethers. Stabilities, Enthalpies, and Entropies of Reaction in Acetonitrile and Pyridine. A Sodium-23 NMR Study

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Abstract: Multinuclear NMR (^1H, ^{13}C, and ^{23}Na) is applied to complex formation between Na^+ and a series of linear polyethers. The most interesting finding is the considerable difference in complexation enthalpies and entropies: while $\Delta H = -18 \pm 3$ kJ·mol^{-1} and $\Delta S = -11 \pm 3$ J·K^{-1}·mol^{-1} for the sodium complex of 1,20-bis(*o*-(methylamido)phenoxy)-3,6,9,12,15,18-hexaoxaeicosane (**2**·Na), the homologous ligand 1,11-bis(*o*-(methylamido)phenoxy)-3,6,9-trioxaundecane (**1**·Na) has $\Delta H = -66 \pm 10$ kJ·mol^{-1} and $\Delta S = -185 \pm 45$ J·K^{-1}·mol^{-1}. This difference reflects pyridine solvent participation in **1**·Na (but not in **2**·Na) complex formation. When the weaker electron-donor solvent acetonitrile is used, solvent coordination to the cation is no longer significant for the **1**·Na complex.

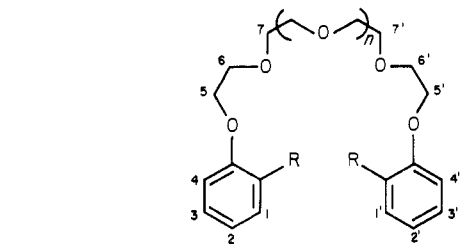
Introduction

The preparation by Pedersen[2] of cyclic polyethers which form strong complexes with metallic ions has ushered in a new era in chemistry. Crown ethers[3] and cryptands[4] are now routinely used in many industrial and chemical processes, for enhancing the solubility of salts in organic solvents and also for their cation-binding selectivity.[5] Crown ethers are synthetic analogues of natural macrocycles such as those present in many antibiotic ionophores, which are known for their efficiency and selectivity in binding ions. Examples of *acyclic* ionophore antibiotics include monensin, nigericin, grisorixin, X-537 A (lasalocid), alborixin, and emericid.[6] These biomolecules wrap themselves around the cation, in a manner very similar to the cyclic species.[6] Acyclic synthetic analogues should behave likewise and thus should be useful additions to the available crown ethers and cryptands. Furthermore, acyclic oligoethers, called podands,[5,6] are obtained simply and cheaply; there is no need for high-dilution techniques or for template effects in their preparation.[8] Vögtle's group has synthesized numerous such open-chain ligands.[6]

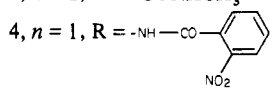
We have already shown the potential utility of ^{23}Na nuclear magnetic resonance for studying cation binding by organic and biological ionophores.[9] In a preliminary communication the complexing properties of ligand **1** toward the Na^+ cation were described.[10] We report here results obtained also with the podands listed in Chart I.

We have selected these ligands, from a row of polyethers synthesized in the laboratory of Professor Vögtle in Bonn, because they include pentaethers (compounds **1**, **3**, and **4**), having also two nitrogen heteroatoms available for coordination to the cation.

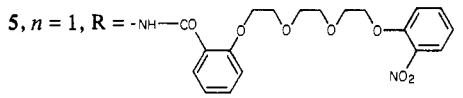
Chart I



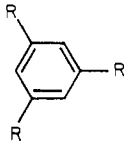
1, $n = 1$, R = -NHCOCH$_3$
2, $n = 3$, R = -NHCOCH$_3$
3, $n = 1$, R = -CONHCH$_3$

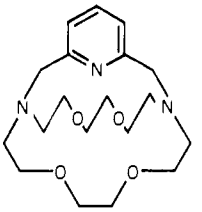


4, $n = 1$, R = -NH—CO—

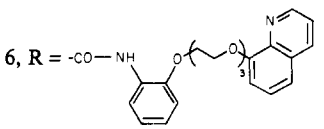


5, $n = 1$, R = -NH—CO—





7



6, R = -CO—NH—

1, 1,11-bis(*o*-(methylamido)phenoxy)-3,6,9-trioxaundecane; 2, 1,20-bis(*o*-(methylamido)phenoxy)-3,6,9,12,15,18-hexaoxaeicosane; 3, 1,11-bis(*o*(methylamido)phenoxy)-3,6,9-trioxaundecane; 4, 1,11-bis[*o*-((*o*-nitrophenyl)amido)phenoxy]-3,6,9-trioxaundecane; 5, 1,11-bis[*o*-[[*o*-(10-(*o*-nitrophenyl)-1,4,7,10-tetraoxadecyl)phenyl]amido]phenoxy]-3,6,9-trioxaundecane; 6, 1,3,5-tris[[*o*-(9-(8-quinolyloxy)-1,4,7-trioxanonyl)phenyl]amido]benzene; 7, pyridinophane cryptand ((2.2.1)py)[13]

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The topology leads to helical wrapping of the ligand around the cation, in certain cases leaving room for additional coordination from the counterion[11,12] or from a solvent molecule. We wanted to test for the latter possibility. The influence of chain length and the number of oxygen atoms, structural features such as ortho substituents, and the nature of the solvent on the binding properties of podands was investigated by using multinuclear NMR. Combined use of ^{23}Na, ^1H, and ^{13}C NMR provided information on the structure and microdynamics of the complexes in order to monitor the mutual perturbation of the cation and the ligand upon complexation.

Experimental and Data Analysis

The ligands were supplied by Professor F. Vögtle of the University of Bonn. Compounds **1**–**7** were prepared following the procedure described elsewhere.[13] All the solutions were prepared under a dry argon atmosphere. Sodium perchlorate (Merck P.A.) was dried under vacuum at 110 °C for several hours. Pyridine (Baker P.A.) and acetonitrile (Aldrich gold label) were dried by refluxing over potassium hydroxide or calcium hydride, respectively, and distilled under argon. The samples were sealed in NMR tubes under vacuum. Viscosities were measured[9] by using a Desreux-Bischoff viscosimeter and calibrated by using pyridine.

^{23}Na and ^{13}C spectra were obtained on a Bruker WP-80 spectrometer at 21.16 and 20.12 MHz, respectively. ^{23}Na-free induction decays (FIDs) were accumulated by using single-phase crystal filter detection, a spectral width of 6024 Hz, and 8K data. The FIDs were exponentially multiplied (2-Hz apodization), zero filled to 8K data points, and Fourier transformed. ^{13}C spectra were obtained by using a spectral width of 6024 Hz and 8K data points; the 3-Hz exponential line broadening was applied before Fourier transformation of the FIDs. ^1H spectra were obtained on a Bruker HFX-90 instrument operating at 90 MHz in the FT mode by using 1200-Hz spectral width and 8K data points.

Proton chemical shifts are given for the centers of the multiplet resonances for positions 1,1′, 2,2′, 3,3′, 4,4′, and 5,5′. Assignment of the various peaks was performed by using model aromatic compounds and by comparison of the spectra of the free ligands in deuteriochloroform and pyridine-d_5 solutions. Carbon-13 NMR spectra of ligands **1**–**3** show two well-resolved peaks for the methylenic carbons, which can be assigned to the methylene oxy or to the 5,5′ and 6,6′ carbons from their relative intensities. Upon Na^+ complexation, these carbons give rise to three closely spaced resonances. Longitudinal relaxation times, T_1, were measured by using the $(180°-\tau-90°-T)_n$ sequence, with a delay $T = 5T_1$ between acquisitions. T_1s was calculated by using a non-linear least-squares analysis with 7 τ values. ^{23}Na line widths were reduced to unit viscosity by using measured bulk viscosities.

The resulting reduced line widths $\Delta\nu_{1/2}^*$ were adjusted to the set of equations

$$\Delta\nu_{1/2}^* = p_F(\Delta\nu_{1/2}^*)_F + p_B(\Delta\nu_{1/2}^*)_B \quad (1)$$

where the subscripts F and B refer to the free and the bound states, respectively and p is a mole fraction

$$p_F = [Na^+]_F/[Na^+]_t$$

$$p_B = ([Na^+]_t - [Na^+]_F)/[Na^+]_t$$

From these equations together with the definition of the stability constant K for a 1:1 complex, the *free* cation concentration is given by eq 2, where

$$[Na^+]_F = \frac{1}{2K}\{-K[L]_t + K[Na^+]_t - 1 + (-(K[L]_t - K[Na^+]_t + 1)^2 + 4K[Na^+]_t)\}^{1/2} \quad (2)$$

$[L]_t$ is the total ligand concentration. Starting with trial values of K and $(\Delta\nu_{1/2}^*)_B$, eq 1 and 2 yield calculated values of $\Delta\nu_{1/2}^*$ for each of the values of the $[Na^+]_t/[L]_t$ molar ratio; 7–10 data points were used for each of the ligands studied. The procedure was repeated, iterating on the two parameters K and $(\Delta\nu_{1/2}^*)_B$ until self-consistency was achieved, i.e., a difference of less than 5% between experimental and calculated $\Delta\nu_{1/2}^*$ values was obtained for all data points. As an example, we show in Figure 1 the experimental points and the calculated curves for 1:1 complex formation between Na^+ and **3** in pyridine solution, at five different temperatures.

Table I. Formation Constants and Limiting Line Widths of the Sodium Complexes in Pyridine at Different Temperatures

ligand	T, K	K, M^{-1}	$\Delta\nu_{1/2}^B$, Hz/cP
1	279	548 ± 55	270 ± 13
	290	247 ± 25	220 ± 11
	305	86 ± 15	181 ± 9
	321	12 ± 3	190 ± 10
2	273	769 ± 80	380 ± 19
	283	576 ± 60	310 ± 15
	294	403 ± 40	270 ± 13
	306	349 ± 35	245 ± 12
	316	256 ± 30	210 ± 11
3	273	609 ± 60	400 ± 20
	283	186 ± 20	375 ± 18
	294	71 ± 12	345 ± 17
	306	54 ± 10	315 ± 15
	316	39 ± 8	270 ± 13
6	303	1980 ± 200	790 ± 40
	317	1323 ± 150	720 ± 35
	330	281 ± 30	600 ± 35
	345	77.5 ± 8	650 ± 35
	360	37.8 ± 6	550 ± 30

Table II. Thermodynamic Parameters for the Complexation of Na^+ by Cyclic Polyethers in Pyridine Solution

ligand	$\Delta H°$, kJ·mol^{-1}	$\Delta S°$, J·K^{-1}·mol^{-1}
1	−66 ± 10	−185 ± 45
2	−18 ± 3	−11 ± 3
3	−45 ± 7	−115 ± 25
6	−62 ± 15	−142 ± 35

Two separate resonances for free and bound sodium ions were observed in only one system, that of **7**, at molar ratios $[L]/[Na^+]_t$ below unity. The "bound" resonance occurs at 11.3-ppm downfield from the signal for "free" Na^+ in pyridine. At molar ratios greater than unity, only the low-field peak is observed. We did not perform accurate measurement of the line widths for this system. However, the high-field signal is systematically narrower by a few hertz than its low-field counterpart. The "free" resonance has a line width of ca. 40 Hz at 314 K, which is as expected for a 0.05 M $NaClO_4$ solution in pyridine at this temperature. Increasing the temperature, in pyridine or in acetonitrile solution, did not change the chemical shift difference. This observation sets a lower limit on the lifetime of the (**7**·Na^+) complex at $\sim 7 \times 10^{-4}$ s.

For all the other ligands, at all molar ratios and temperatures, fast-exchange conditions prevailed; increasing the temperature led to line narrowing, which indicates a negligible contribution to the observed transverse relaxation rate from the residence time in the bound state (τ_B). Changes in chemical shifts are very small (within the experimental uncertainty) and do not make substantial contribution to the observed line broadenings. Hence, the observed enhancements in the transverse relaxation rate $R_2 = \pi\Delta\nu_{1/2}$ are due solely, or almost exclusively, to the increased relaxation rate in the bound state. Curves such as those of Figure 1 point to the predominant formation of complexes with 1:1 stoichiometry. In no case, could the agreement betwen experimental and calculated values be improved by the recourse to different stoichiometries such as 1:2 and 2:1. The formation constants K in eq 2 are true formation constants at the low ionic strength ($I < 0.08$) of our solutions.[15]

Results and Discussion

Formation constants for 1:1 complexes between Na^+ ions and podands **1**, **2**, **3**, and **6**, in pyridine solutions are listed in Table I. The corresponding ΔH and ΔS variations are shown in Table II. These results are noteworthy because apparently small changes in the structure of the ligands, between **1** and **2** or between **2** and **3**, lead to drastic differences in the enthalpy and entropy terms.

We intended to confirm these measurements from an independent calorimetric determination of the heat of complex for-

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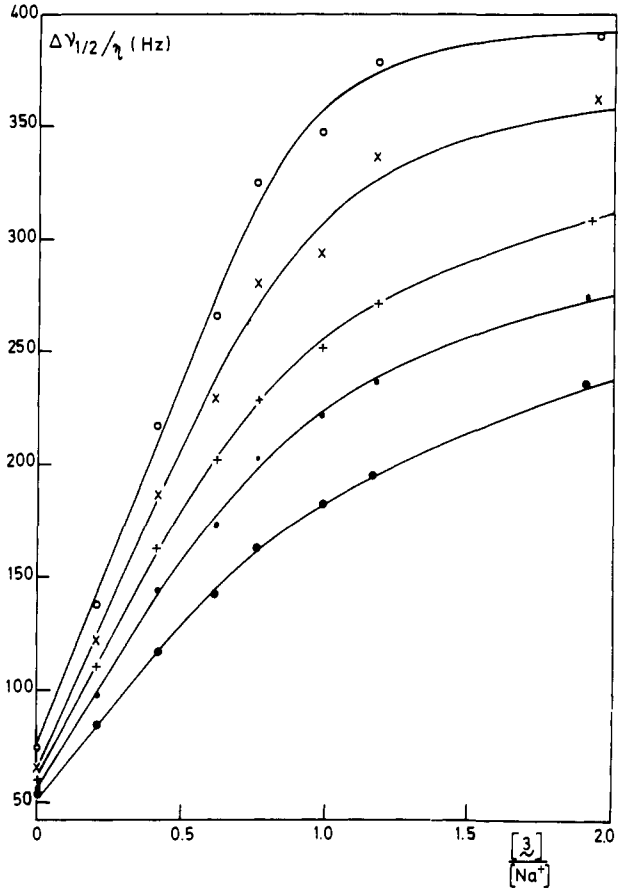

Figure 1. Plots of the line widths at half-height, reduced to unit viscosity, against the [3]/[Na^+] molar ratio at different temperatures. Experimental points: o, 273 K; ×, 283 K; +, 294 K; •, 306 K; ●, 316 K. The curves drawn are the calculated curves (see text).

Table III. ^{1}H Complexation Shifts (±0.1 ppm) in Pyridine-d_5

	1 → 1·Na	2 → 2·Na	3 → 3·Na
NH(2)	+0.50	+0.59	+0.50
1,1′	−0.98	−1.04	−0.51
2,2′, 3,3′, 4,4′	−0.07	0.00	0.00
5,5′	−0.04	−0.05	+0.06
-OCH_2-	−0.01	−0.05	−0.05
	−0.3[a]	−0.7[a]	−1.6[a]
-CH_3	−0.07	−0.04	−0.16
	−0.5[a]	−0.2[a]	−1.2[a]
>C=O	+1.7[a]	+0.8[a]	+3.1[a]

[a] The ^{13}C complexation shifts, ±0.4 ppm, are also given.

mation for 1·Na and 2·Na: however, the calorimeter used did not allow us to work with evacuated samples, and at the low concentration of our experiments, ca. 10 mM, the hygroscopy of the pyridine solvent is such as to preclude simple determination of the heat of mixing between pyridine solutions of **1** (or **2**) and $NaClO_4$, respectively. Hence, in order to gain more information about the conformation and the conformational mobility of the polyether chains in the bound state, we determined the ^{1}H and ^{13}C NMR chemical shift parameters for the free and complexed ligands (Table III). In the ^{1}H NMR spectra (Table III), the only resonances significantly affected are those of the NH protons, which are shifted downfield upon cation binding, consistent with nitrogen coordination to the univalent ion; and those for the 1,1′ protons, which are shifted *upfield*. The shift of the 1,1′ protons is perhaps due to a helical conformation of the complex with partial stacking of the aromatic rings, as found in the solid state for closely related complexes.[11,12,16] From the complexation shifts in the ^{1}H

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Table IV. Longitudinal Relaxation Times T_1 (±10%) and Their Ratios ρ for Free and Complexed Podands 1 and 2

	1	1·Na	ρ	2	2·Na	ρ
Ar–*H*	1.26	0.77	1.63 ± 0.3	1.77	0.79	2.24 ± 0.4
-O-C*H*$_2$-	0.50	0.22	2.26 ± 0.4	0.66	0.13	5.07 ± 1
-C*H*$_3$	0.60	0.38	1.58 ± 0.3	1.01	0.32	3.16 ± 0.6

NMR spectra (Table III), ligands **1** and **2** form complexes with similar structures; and the differences between the values corresponding to ligands **2** and **3** can be ascribed to the -NH—CO- unit being reversed in the structure of these two ligands. The ^{13}C chemical shifts (Table III) likewise do not differ significantly between these three ligands, **1**, **2**, and **3**.

The change in conformational mobility of the podands **1** and **2**, or **2** and **3**, between the free state and their Na^+ complex could differentiate between them and be responsible, at least in part, for the observed differences in the complexation entropies (Table II). Because of limited solubility, we could not approach the microdynamics from measurement of ^{13}C longitudinal relaxation rates. Thus, we have resorted to determining ^{1}H relaxation rates, under conditions in which they are dominated by intramolecular factors, by using a deuterated solvent, at low ligand concentration, and on carefully degassed samples.[17] The T_1 values are shown for ligands **1** and **2**, and their Na^+ complexes, in Table IV. Only the average values are indicated for the aromatic and the methylenic protons; however, we have verified that no significant differences exist between the relaxation rates of protons having distinct resonance frequencies in each of these groups. These data are insufficient for a full quantitative analysis, to provide the individual diffusion constants. However, its qualitative interpretation is straightforward; a decrease in T_1 upon sodium complexation reflects a general decrease in conformational mobility all along the polyether chain (Table IV). Similar results have been obtained in the complexation of cations by cyclic[18,19] or acyclic[20] polyethers. The ratio T_1(complex)/T_1(free ligand) is an index to the restriction in local mobility; it is with acyclic ligands that the smaller values are observed.[20] From the ρ value in Table IV, there is a somewhat greater restriction of internal rotations in **2**, as compared to **1**. However, it cannot account either in magnitude *or in sign* for the considerable difference in the complexation entropies for these two systems (Table II).

In a preliminary communication,[10] we had ascribed the strongly negative complexation entropy of **1** to the loss of internal rotations upon coordination to Na^+. On the basis of the new data presented here, this is no longer an acceptable proposition. As seen with a ligand such as **2**, at least in pyridine solution, the entropy loss due to the restriction of the ligand around the cation, together with the entropy loss from formation of a single complex from its two freely diffusing components (**2** and Na^+), is almost fully compensated for by the gain in translational entropy upon desolvation of each of the two partners. It is a different matter when one (or more) solvent molecule(s) remains attached to the cation in the complex; this is the *predominant* cause for the strongly negative entropy in the formation of **1**·Na and of **3**·Na.

Such a conclusion is consistent with the difference in the complexation entropies: the gain in translational entropy from liberation of *one* pyridine solvent molecule is estimated to be 105–165 J·K^{-1}·mol^{-1},[21] which compares rather well with the differences between the complexation entropies of **2** and **1**, or **2** and **3**, viz. 175 and 106 J·K^{-1}·mol^{-1}, respectively.

The reason for the solvation difference, Na^+ having no pyridine solvent molecule in its complex with podand **2** while its complex with lower homologues **1** and **3** retain one (or two) pyridine solvent molecule(s), is simple. Podand **2**, with 8 oxygen and 2 nitrogen

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Table V. Formation Constants and Limiting Line Widths for the Sodium Complexes in Acetonitrile

ligand	T, K	K, M^{-1}	$\Delta\nu_{1/2}^{B}$, Hz/cP
1	273	34.3 ± 7.7	370 ± 15
	286	30.1 ± 8.1	300 ± 15
	297	29.5 ± 5.3	265 ± 10
	307	27.3 ± 4.1	247 ± 7
	324	28.9 ± 7.7	201 ± 10
4	286	27.0 ± 5.3	302 ± 14
	297	29.3 ± 7.0	263 ± 15
	307	30.0 ± 3.7	228 ± 8
	324	34.6 ± 4.8	180 ± 8
5	274	11.7 ± 2.5	1400 ± 100
	285	17.7 ± 3.0	970 ± 80
	296	26.2 ± 4.5	770 ± 70
	306	19.5 ± 3.5	700 ± 70
	320	20.3 ± 3.5	600 ± 65

heteroatoms capable of coordination to the cation, wraps itself helically around the positive ion, which it shelters within a spherical cavity. Such a closed structure has been found by X-ray for the Rb^+ complex of a podand having 8 oxygens and 2 nitrogens coordinated to the cation.[16] By contrast, ligands **1** and **3** with their shorter polyether chain cannot engulf the cation completely, even if they do wrap themselves around the cation in a helical manner. Therefore, there is room for coordination of an additional pyridine solvent molecule to Na^+, further stabilizing the complex. Likewise, the X-ray structure of the Na^+ complex of a podand having 6 oxygens coordinated to the ion shows a helical conformation of the ligand allowing for additional coordination by the SCN^- counterion,[22] and the crystal structure of a Rb^+ complex with another oligoether having a total of 7 heteroatoms (5 oxygens + 2 nitrogens, just as in ligands **1** and **3**) shows additional coordination to an iodide counterion.[11]

Our results, in short, are consistent with the proposition that the complex formed between Na^+ and **2** in pyridine solution is fully desolvated, while complexes formed in this solvent by **1** or by **3** retain at least one solvation molecule.

The test we devised for this idea is to examine complex formation in a solvent of much weaker donicity than that of pyridine yet with a high enough dielectric constant that the perchlorate counterion does not interact strongly with the Na^+ cation. Acetonitrile with a high dielectric constant (ϵ = 37.5) and a Guttmann donicity[23] significantly lower than that of pyridine (14.1 vs. 33.1) is such a solvent. The Na^+ complexes of ligands such as **1** or **3** are predicted to be much less solvated in acetonitrile than in pyridine. Comparison of the results for ligand **1** in pyridine (Table I) and in acetonitrile (Table V) is striking: in the latter solvent, the complexation entropy is close to zero and the acetonitrile molecule is too weak an electron donor to coordinate to the Na^+ cation. In other words, the lower enthalpy which would result from coordination of one acetonitrile is insufficient to offset the attendant loss in translational entropy. Podands **4** and **5**, with differing terminal groups, exhibit similar behavior (Table V).

It thus appears that podands display binding constants toward Na^+ which do not vary markedly with temperature if one of the following two conditions is fulfilled: (i) enough heteroatoms (at least 8) are built into the structure for full wrapping of the cation into a quasi-spherical cavity; (ii) use of a weak donor solvent such as acetonitrile.

The limiting ^{23}Na line widths of Na^+ in the bound state ($\Delta\nu_{1/2}^{B}$) are considerably greater for **5**·Na than for **1**·Na (Table V); this is as expected, since the reorientational correlation time is also expected to be greater for the bulkier ligand **5**, and the quadrupolar coupling constant should remain approximately the same for the three ligands **1**, **2**, and **5**.

Conclusion

From the results of this study, the complexes formed between Na^+ and acyclic polyethers appear to have similar conformations in the liquid phase as in the solid state. The ligands wrap themselves around the cation in a helical manner. With enough heteroatoms available for coordination, a spherical cavity is provided for the cation, as in the **2**·Na complex. When such a spherical wrapping is precluded by an insufficient chain length, additional coordination sites remain, as in the **1**·Na and **3**·Na complexes. Solvent molecules can enter these sites and further stabilize the complex, given they have enough electron-donor potential, for the resulting enthalpy gain to offset the corresponding loss in translational entropy. Pyridine is such a coordinating solvent (to the **1**·Na or **3**·Na complex). Acetonitrile is too weak an electron donor to play such a role.

Future use of acyclic polyethers and their cyclic analogues, the crown ethers, will benefit from use of high donicity solvents such as pyridine or hexamethylphosphortriamide acting in synergism with heteroatoms from the ligand, for increased cation complexation.

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