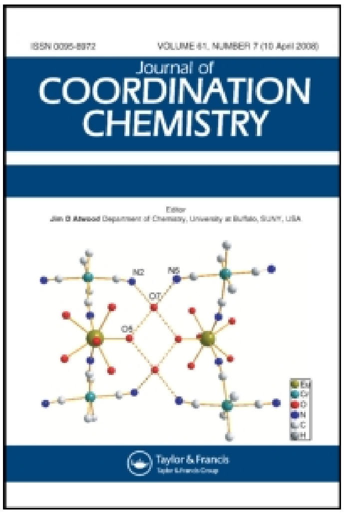

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Luis Echegoyen[a]; Dennisse Parra[a]; Libero J. Bartolotti[a]; Christopher Hanlon[a]; George W. Gokel[a]
[a] Department of Chemistry, University of Miami Coral Gables, Florida, U.S.A.

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INCREASED RIGIDITY IN COMPLEXES FORMED FROM NEGATIVELY CHARGED LARIAT ETHERS AND ALKALI METAL CATIONS

LUIS ECHEGOYEN,* DENNISSE PARRA, LIBERO J. BARTOLOTTI,
CHRISTOPHER HANLON, AND GEORGE W. GOKEL*
Department of Chemistry, University of Miami
Coral Gables, Florida 33124 U.S.A.

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Abstract C-13 NMR longitudinal relaxation times have been measured for lariat ether complexes in which a negative charge is present in the ligand but the system is diamagnetic. A $-CH_2COO^-$ group connected to the nitrogen of aza-15-crown-5 results in drastically increased T_1's in the presence of Li^+ compared to the values for the free carboxylic acid and for the acid in the presence of $LiClO_4$. Longer relaxation times upon complexation show the "cryptand-like" behavior of the complexes, resulting from overall molecular reorientation rates due to compression. These conclusions are supported by molecular mechanics calculations described herein.

Keywords: Lariat ethers, relaxation, rigidity

INTRODUCTION

Since the first report of lariat ethers in 1980,[1] these compounds have proved to be interesting and versatile cation complexing agents. One of the especially valuable applications of these structures has been as electrochemically-switched cation binders and transporting agents.[2] The first observation of electrochemically-switched lariat ethers[3] proved unusual in that two redox waves were observed when Li^+, Na^+, or K^+ was added to the solution. This was remarkable since all previous observations of ion-pairing phenomena resulted in a shift of the redox wave rather than the observation of a separate, new wave. As the studies evolved, it became apparent that not only were the cation binding constants considerably increased upon reduction, the complexes became much more rigid. As such, a cavity-size relationship appeared to play an important role that complemented the Coulombic or charge-density induced selectivity.

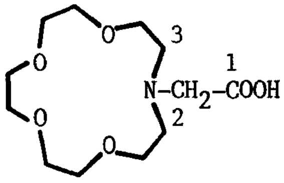
Simple monocyclic crown ethers such as 12-crown-4, 15-crown-5, 18-crown-6, etc. and non-charged lariat ethers have been shown generally to select cations based upon the cation's charge density. Thus, weakly solvated K^+ is favored by simple mono-macrocycles over either Li^+ or Na^+ irrespective of ring size.[4] The same appears generally to be true for the non-charged lariat ethers. Of course, the more rigid, three-dimensional cryptands are well-known to exhibit a cavity size relationship.

There has been considerable discussion in the literature[5] to the effect that making the sidearm of a lariat ether charged enhances the cation binding strength.[6] In addition, much has been said of the correlation between macroring hole size and cation size in these structures. In our own EPR studies of N-(2-nitrobenzyl)aza-15-crown-5 and -18-crown-6, we noted a selectivity of the smaller ring for Na^+ and the larger ring for K^+.[7] We conclude from these results along with numerous other indications that not only does charge increase cation binding strength, it increases complex rigidity. Thus the cavity-size argument is applicable in these cases whereas it is inappropriate in the absence of charge. Therefore the charge effect on cation binding has been recognized both by us and by others[8] but its importance in cation binding selectivity[9] has been grossly neglected.

We present below C-13 NMR longitudinal relaxation time data determined as previously described[10] in conjunction with molecular mechanics calculations that support the combined effect of charge and rigidity to confer upon lariat ethers a hole- or cavity-size selectivity profile.

RESULTS AND DISCUSSION

N-(Carboxymethyl)aza-15-crown-5 (**1**) was prepared[11] by alkylation of aza-15-crown-5 with ethyl bromoacetate followed by hydrolysis. Its structure and the numbering system are shown below. C-13 NMR relaxation time measurements for **1** can be found in Table I.



Compound **1**

TABLE I C-13 NMR Relaxation times for compound **1**[a]

Carbon number	Relaxation time in seconds[b]				
	Free	NaClO$_4$	NaH	LiClO$_4$	LiH
1	6.54	4.71	9.97	6.82	13.52
2	0.25	0.72	0.69	0.26	1.26
3	0.41	0.35	0.53	0.26	1.56
Ring	0.45	0.57	0.38	0.69	1.80

[a] Values determined in CH$_3$CN at ambient temperature (ca. 25 °C) in 0.5M solutions. [b] One equivalent each of the additive.

C-13 NMR longitudinal relaxation time measurements are a useful indication of mobility because their magnitudes diminish with increasing rigidity. This is true only if the nucleus in question has a mechanism available to it (such as a directly bonded proton) for dipole-dipole relaxation. The carboxyl carbon atom in **1** does not have such a relaxation mechanism available to it and the data for position 1, above, are ambiguous and will therefore not be discussed further.

The typical behavior of C-13 T$_1$ values differs quite remarkably for cryptands in which the cryptate complexes undergo both compression and desolvation and therefore exhibit increased relaxation times. Although a reduction in segmental mobility surely occurs, this effect is overwhelmed by the large increase in overall molecular (complex) reorientational motion. Thus a complex that mimics cryptate behavior will show an increase in relaxation times rather than a decrease. Such behavior is uncommon and remarkable and previously reported only by our group[12] and later confirmed by Popov and coworkers.[13] In compound **1**, complexation of either Na^+ or Li^+ at neutral pH is expected to lead to some, if small, reductions in relaxation times. When **1** reacts with LiH or NaH, both deprotonation and complexation occur so that a neutral ion-pair is formed. Because the charge density of Li^+ is considerably greater than that of Na^+, the complex is expected to be quite rigid and quite cryptand-like. Thus, $Li^+\cdot\mathbf{1}^-$ should show an increase in T_1 values whereas the behavior of $Na^+\cdot\mathbf{1}^-$ may be less remarkable. Indeed, the values shown in Table I confirm these expectations.

Molecular Mechanics

The conformational energies of the lariat ethers and their complexes were minimized using the All Atom Force Field of the AMBER[14] program. The non-bonded parameters that were added to the program are contained in Table II. A complete MNDO calculation was initially performed for the free acid and for the deprotonated species using the MOPAC[15] package, followed by an INDO calculation. Since AMBER is known to be very sensitive to atomic charges, we utilized the charge values obtained from the INDO results. Starting conformations were drawn on an IBM PC using Macromodel.[16] The initial conformations had the sidearm atoms placed directly over the macroring with the cation in the center. Finally, a conjugated gradient method was performed on each conformation followed by a final steepest descent minimization. The energy convergence criterion was 1x10^{-7} kcal/mole. All calculations were performed on a VAX 8650 computer and the final drawings were obtained using the graphics from the NAMOD perspective drawing program.

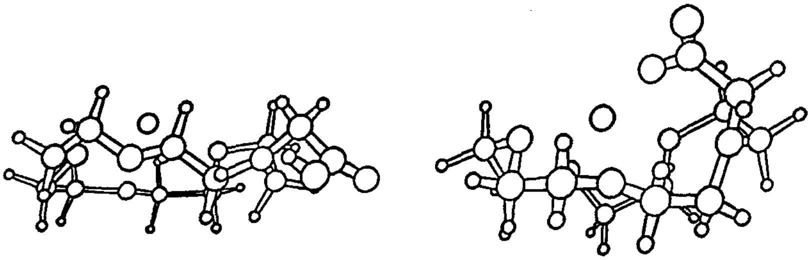


Figure 1. Computer-drawn images of $Li^{+}\cdot\mathbf{1}$ and $Li^{+}\cdot\mathbf{1}^{-}$

TABLE II Energy parameters for non-bonded interactions

Atom	Alpha[a]	N_{eff}[b]	Ionic radius[c]
H[d]	0.42	0.9	1.20
Li^{+}[e]	0.20	3.0	1.00
C[f]	1.77	7.0	1.90
N[d]	0.87	6.1	1.55
O[f]	0.64	7.0	1.60
Na^{+}[f]	0.24	10.0	1.60

[a]Polarizability. [b]Effective atomic number. [c]R_i^o. [d]See reference 17. [e]See Reference 18. [f]See reference 19.

The computed total energies for the free carboxylic acid and its deprotonated (carboxylate) form along with those for their corresponding Li^{+} and Na^{+} complexes are as follows: **1**, 39.084; $\mathbf{1}^{-}$, 42.319; $Li^{+}\cdot\mathbf{1}$, -30.884; $Li^{+}\cdot\mathbf{1}^{-}$, -58.540; $Na^{+}\cdot\mathbf{1}$, -23.910; and

$Na^{+}\cdot 1^{-}$, -30.620 kcal/mole. As expected, the lowest energy (most stable) system is the complex that forms between the carboxylate form of **1** and Li^{+}. The computer-drawn images that describe the Li^{+} complexes are shown in Figure 1, above. Note that both macroring and sidearm participate in the carboxylate complex, but not in the neutral acid complex. The same is true for the Na^{+} complexes (not shown). Note that a crystal structure reported by Lipscomb and coworkers[20] are in accord with these calculations.

CONCLUSION

We have shown by a combination of direct experimental observation and calculations that a flexible lariat ether forms a highly rigid complex when the sidearm is deprotonated. This, in turn, leads to the expected cavity size selectivity and rigidity characteristic of cryptate complexes.

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