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^{13}C-NMR RELAXATION STUDIES OF ALKALI METAL CRYPTATE COMPLEXES

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Summary: The ^{13}C spin-lattice relaxation times (T_1's) of cryptands [2.1.1], [2.2.1] and [2.2.2] as well as those of the corresponding cryptate complexes with Li^+, Na^+, and K^+ in $CDCl_3$ and $CH_3OH:D_2O$ (90:10) were measured and the results are interpreted in terms of molecular compression and desolvation effects.

There is considerable interest in the properties, structures, and dynamics of macrocyclic and macrobicyclic ligand complexes.[1-5] Surprisingly, the use of NMR relaxation times as a probe to study the dynamics and structures of these molecules has been very limited.[6,7] The results presented here demonstrate the potential utility of ^{13}C relaxation times to probe both the dynamics and structure of macrocyclic complexes in solution.

All cryptands were used directly as received without further purification. Samples were prepared under vacuum (10^{-3} mm) after careful degassing. All samples were prepared with equimolar amounts of the ligand and the perchlorate salt (0.3 M). Concentration variations (0.08-0.80 M) did not appreciably affect the measured T_1 values. Relaxation time experiments were performed using either the standard inversion recovery (IR) or the modified fast inversion recovery (FIR) technique.[8] Three samples were studied by both techniques and showed excellent agreement of at least three independent measurements. All T_1 values reported here have a standard deviation of no more than ±8%.

Relaxation time data are summarized in Tables 1 and 2. For each free ligand and for each complex, the relaxation times of the individual carbons are practically identical, indicating that molecular motion is essentially isotropic in all cases, see Tables 1 and 2. NOE factors measured by standard gated decoupling techniques show that the relaxation mechanism of the free ligands as well as of their complexes is predominantly dipolar. The measured factors fluctuated between 2.82 and 3.00 for all samples.

Upon complexation with Li^+, the T_1 values of [2.1.1] seem to remain essentially constant. Based on available data,[7] complexation should lead to reduced mobility of the carbon skeleton of the ligand and thus to a decrease in the relaxation times. This is clearly not the case for ([2.1.1] $\cdot$ Li^+), perhaps a reflection of the fact that free [2.1.1] already exists in a fairly rigid conformation.

Surprisingly, formation of the Li^+ complex of [2.2.1] leads to a dramatic increase of the individual carbon T_1's: see Tables 1 and 2. To our knowledge, the only such complexation-induced increase in T_1 values hitherto reported was for the [2.2.2] Na^+ system. "These small modifications of correlation times" were noted in passing by Popov and his coworkers in an ^{17}O-NMR study of cryptand interactions.[8] Our values for the complexes agree well with these and with those reported by Lehn. Interestingly, ([2.2.1] $\cdot$ Na^+) also has larger T_1 values than free [2.2.2], but lower than those observed for ([2.2.1] $\cdot$ Li^+). On the other hand, sodium complexation of [2.1.1] leads to decreased T_1 values compared to the free ligand, with the average T_1 values being essentially identical with both cations, while with [2.1.1] no appreciable amount of complex was formed, as judged by the large amount of undissolved salt that remained upon sample preparation.

In those cases where the cation does not "fit" the ligand cavity precisely, the anion and the solvent remain in contact with the partially complexed cation,[9,10] thus causing an increase of the correlation time and shorter T_1's. Conversely, for those cases where the cation "fits" the ligand cavity, anion and solvent participation in the complex should be minimal. Thus, the T_1's should remain unaltered. The fact that some complexes exhibit increased T_1 values can be rationalized if molecular compression and desolvation upon complexation are considered. This is probably best illustrated by the behavior of the [2.2.1] complexes. The relative T_1 increase caused by lithium complexation is larger than the corresponding increase with sodium. Lithium, being smaller than sodium, can result in a higher degree of ligand compression and desolvation. At the extreme, potassium does not "fit" into the cavity so it results in ion pair formation with a consequent decrease in T_1.

In order to test for solvent dependence, [2.2.1] and its complexes were studied in MeOH:D_2O. Results are given in Table 1. Note that the T_1 values for the free [2.2.1] ligand are similar to those observed in $CDCl_3$. In contrast, the corresponding values for the complexes are very different from those in $CDCl_3$, with larger T_1's observed in MeOH:D_2O for all cases. Even ([2.2.1] $\cdot$ K^+) has longer T_1's than the free ligand. Other cryptate complexes were not studied in MeOH:D_2O due to their extremely low solubility.

As opposed to free [2.2.1], for which the relaxation times observed in $CDCl_3$ and in MeOH:D_2O were essentially identical, free [2.1.1] showed shorter T_1's in the latter solvent. This is probably the result of stronger ligand-solvent interactions in MeOH:D_2O.

Solvent penetration into the complex cavity has been suggested to occur by Popov et al. for ([2.2.2] $\cdot$ Na^+).[10] This could explain the decreased T_1 values observed for ([2.2.2] $\cdot$ Li^+), see Table 2.

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REFERENCES AND NOTES

1. Popov. A.I., Pure Appl. Chem., **1979**, 51, 101.
2. Schneider, H., Rauh, S. and Petrucci, S., J. Phys. Chem., **1981**, 85, 2287.
3. Mei, E., Liu, L., Dye, J.L., Popov, A.I., J. Solution Chem., **1977**, 6, 771.
4. Laszlo, P., Angew. Chem. Int. Ed. Engl., **1978**, 17, 254.
5. Kaifer, A., Durst, H.D., Echegoyen, L., Dishong, D.M., Schultz, R.A., and Gokel, G.W., J. Org. Chem., **1982**, 47, 3195.
6. Lehn, J.M. and Kintzinger, J.P., J. Am. Chem. Soc., **1974**, 96, 3313.
7. Fedarko, M.C., J. Magn. Resonance, **1973**, 12, 30.
8. Popov, A.I., Smetana, A.J., Kintzinger, J.-P., Nguyen, T.T.-T., Helv. Chim. Acta, **1980**, 63, 668.
9. Canet, D., Levy, G.G. and Peat, I.R., J. Magn. Resonance, **1975**, 18, 199.
10. Lin, J.D. and Popov, A.I., J. Am. Chem. Soc., **1981**, 103, 3773.

Table 1: ^{13}C-Relaxation Times of Some Cryptands and Their Alkali MetalComplexes in MeOH:D_2O, 90:10 (v/v), at 36.0 ± 1.0°C

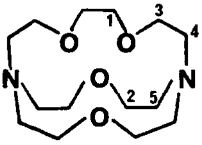
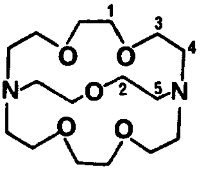
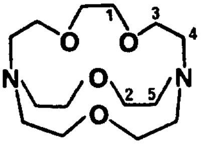
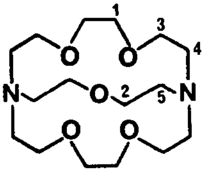
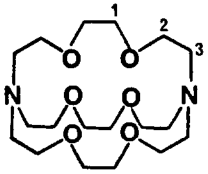
Cryptand	Position	Free	Li^+	Na^+	K^+
 [2.1.1]	1	0.69	-	1.19	-
	2	0.66	-	0.96	-
	3	0.66	-	1.10	-
	4	0.64	-	1.00	-
	5	0.62	-	1.20	-
 [2.2.1]	1	0.77	2.22	1.15	1.11
	2	0.82	2.01	1.11	1.00
	3	0.76	1.96	0.99	1.02
	4	0.74	2.06	1.17	1.07
	5	0.71	1.94	1.17	-

Table 2: ^{13}C-NMR Relaxation Times for the Cryptands and Their Alkali Metal Complexes in $CDCl_3$ Solutions at 36.0° ± 1.0°C

Cryptand	Position	Free	Li^+	Na^+	K^+
 [2.1.1]	1	1.01	0.90	0.62	1.05[a]
	2	0.93	0.91	0.44	0.90[a]
	3	0.96	0.91	0.52	0.98[a]
	4	0.91	0.92	0.51	0.92[a]
	5	0.86	0.91	0.55	0.88[a]
 [2.2.1]	1	0.76	1.25	1.01	0.52
	2	0.75	1.06	0.89	0.53
	3	0.77	1.19	1.00	0.47
	4	0.72	1.19	1.06	0.49
	5	0.69	1.22	0.91	0.52
 [2.2.2]	1	0.83	0.54	1.00	0.96
	2	0.80	0.51	0.98	0.90
	3	0.69	0.55	0.94	0.97

[a] These relaxation time values correspond to those of the free ligand. Practically no salt dissolved in the ligand solution.

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