68. Natural Abundance ^{17}O-NMR. Study of Some Macrocyclic Complexes with Alkali Metal Cations

by **Alexander I. Popov** and **Alfred J. Smetana**

Michigan State University, Department of Chemistry, East Lansing, Michigan 48824

and **Jean-Pierre Kintzinger**[1]) and **Thi Thanh-Tâm Nguyên**

Institut de Chimie Organique, Université de Lausanne, 2, rue de Barre, CH-1005 Lausanne, Switzerland

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Summary

Complexation between crown ethers 12C4, 15C5, 18C6 and cryptand 222, and alkali cations Li^+, Na^+, K^+ in various solvents were studied by ^{17}O-NMR. spectroscopy. Small diamagnetic shifts arising from the cation electric field are observed. They increase according to the sequence $K^+ < Na^+ < Li^+$. ^{17}O-linewidth are discussed and compared to the ^{13}C relaxation times. Linewidth modification results mainly from modifications of the effective correlation time. In general, for crown ethers, considerable line broadening occurs when the cation fits well into the cavity but line narrowing occurs when the cation is much smaller than the cavity.

Introduction. - The popularity of physicochemical studies of macrocyclic complexes has grown rapidly during the past decade [1]. One of the most useful techniques for such studies seems to be NMR. spectroscopy. Cation-ligand interactions can be studied by observing the magnetic resonance of the nuclei of the ligand and/or the cations. In the first case ^{1}H- and ^{13}C-NMR. measurements were widely used since the 'early' days of macrocyclic complexes. While the resonance frequencies of both nuclei are sensitive to the complexation reaction, the nuclei themselves do not participate directly in the formation of the complex.

Obviously, it would be interesting to examine the influence of complexation on the NMR. of the ligand atoms which interact directly with the cation. Evidently, ^{17}O-nucleus would be a good candidate for such a study: it has a wide range of chemical shifts (>1500 ppm) and despite the low natural abundance and low sensitivity of this nucleus, a number of NMR. studies have been carried out on reactions of oxygen-containing compounds, albeit of enriched samples [2] [3]. We are aware, however, of only one study involving metal complexes with the acetate and citrate ions [4] where the carboxylate groups were enriched to $\sim 5\%$ ^{17}O. The addition of calcium(II)-ion to these solutions did not induce any shift in the ^{17}O resonance.

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[1]) Author to whom correspondence should be addressed. Present address: Institut Le Bel, Université Louis Pasteur, 1, rue Blaise-Pascal, B.P. 296/R8, F-67000 Strasbourg, France.

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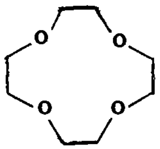
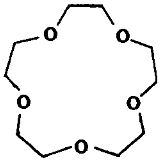


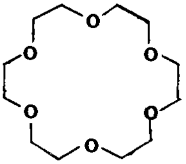
12C4

I



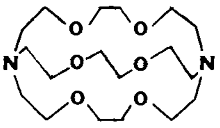
15C5

II



18C6

III



222

IV

It was of interest to us therefore, to investigate the possible use of ^{17}O-NMR. as a probe of the complexation reaction of the macrocyclic polyethers I-III and of the cryptand IV with alkali metal ions.

The work described in this paper was initiated independently in the two laboratories. Since the results dovetail so well, a joint publication seemed reasonable.

Experimental Part

Experimental conditions were slightly different at the Michigan State University (MSU) and at the University of Lausanne (UL).

At MSU, solvents were purified and dried before use. *Karl Fischer* titration showed a water content of less than 100 ppm. Salts were also dried and the crown ethers *(Aldrich)* were either redistilled under reduced pressure (I and II) or recrystallized as the acetonitrile complex (III) [5]. Crown ether solutions in the 0.5 to 1.0M concentration range were prepared in a glove box under nitrogen atmosphere.

Natural abundance ^{17}O-NMR. measurements were made at 24.399 MHz at a field of 42.3 kgauss in the pulsed *Fourier* transform mode on a *Bruker* WH-180 superconducting spectrometer. Due to the broadness of the resonances, only 1024 data points were used for data acquisition with a sweep of 20,000 Hz in the quadrature detection mode. In order to increase the signal to noise ratio, the lines were artificially broadened by 50 Hz by exponential multiplication of the free induction decay before *Fourier* transformation of data. A 50 µs pulse was used with a predelay time of 500 µs in order to avoid pulse feed through. Using these acquisition and data manipulation parameters, a good signal (signal to noise ratio ~5) could be obtained with ~500,000 pulses (~4.3 h). Because of the length of time needed to obtain a single measurement, the data obtained were, of necessity, not plentiful. The samples were contained in 15 mm o.d. NMR. tubes which were fitted inside 20 mm o.d. non-spinning NMR. tubes which contained acetone-d$_6$ *(Stohler)* which served as a lock compound and as a secondary external reference. All measurements were made at ambient temperature (~25°) and all ^{17}O-NMR. chemical shifts are referenced to pure distilled water.

At UL, commercial crown ethers I to III *(Fluka)*, cryptand IV *(Merck)* and spectral grade solvents were used without further purification. For NMR. measurements solutions were made by adding the theoretical amount of perchlorate salt to chloroform solutions of the ligand (concentration range 0.75 to 3M). Nitromethane (5% by weight) was added as an internal reference. All ^{13}C- and ^{17}O-NMR. measurements were made at 55°. ^{17}O-NMR. measurements were obtained with a *Bruker* WP 200 superconducting spectrometer operating at 27.145 MHz. Typical experimental conditions are given in *Figure 1;* ^{13}C- and ^{1}H-NMR. spectra were obtained at UL at 15 and 80 MHz respectively.

Results and Discussion. - From the results given in *Table 1*, it can be seen that the ^{17}O chemical shifts of the free crown ethers I and III in solution show only a small dependence on the nature of the solvent. All the shifts are near the value measured for pure 1,4-dioxane. The paramagnetic shift of the ^{17}O resonance of 18C6 in acetonitrile can be related to the existence of the acetonitrile-18C6 complex [5]. Linewidth variations roughly follow the viscosities of the solvents and the concentration of the ligands. Extremely broad lines were observed for the very viscous pure ligands I and II (1200 and 1700 Hz respectively).

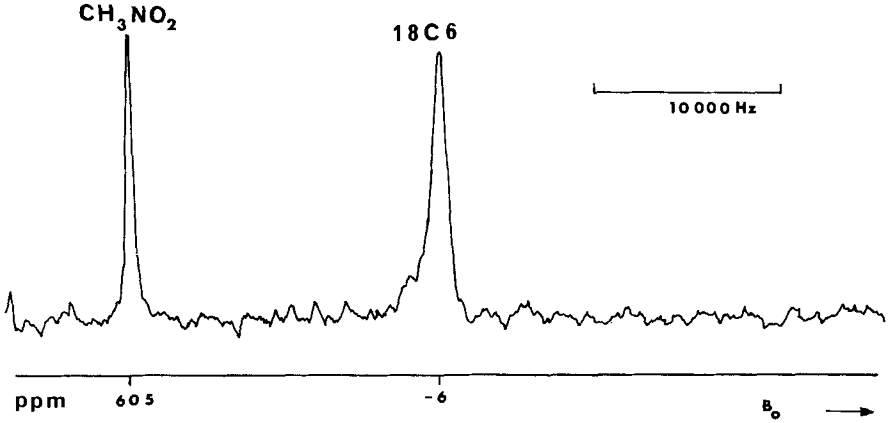


Figure. ^{17}*O-NMR. spectrum of the crown ether 18C6* (3 M in chloroform containing 5% CH_3NO_2 by weight) at 55° and 24.147 MHz. *Fourier* Transform mode with quadrature detection. Sweep-width: 50,000 Hz; Pulse-width: 30 µs (~90°). Pre-delay time: 40 µs, Sampling of 1024 points. Acquisition time: 10 ms. Number of scans: 92,000. Total acquisition time: 16 min; Broadening due to exponential multiplication. 200 Hz; zero filling to 8192 points before *Fourier* Transform.

Diamagnetic ^{17}O shifts are generally induced by the addition of alkali metal perchlorate salts to the solutions of free ligand. Since the addition of a salt with a large non-complexable cation, tetrabutylammonium perchlorate, does not change the ^{17}O chemical shift of the ligand, the observed shifts must be due to the complexation reaction. Furthermore in the MSU series of measurements the resonance of the perchlorate counterion, which is split into a quadruplet by the ^{35}Cl, was centered at 291 ppm in excellent agreement with the literature value of 290 ppm [6]. At UL, this quadruplet splitting was not observed due to the extensive line broadening. In every case, the position of the nitromethane and perchlorate ion resonance was unchanged.

The ^{17}O-NMR. chemical shifts for the free and complexed 12C4 in various solvents are shown in *Table 1.* As stated above, neat 12C4 gave a very broad resonance line. Dilution of neat 12C4 with a solvent of lower viscosity drastically reduces the linewidth of the signal. The addition of an equimolar amount of lithium perchlorate to the solution of this crown ether shifts the ^{17}O resonance upfield by ~10 ppm. Previous ^{7}Li-NMR. studies on the Li^+-12C4 system [7] showed the existence of $(12C4)_2 \cdot Li^+$ and $(12C4) \cdot Li^+$ complexes in solution and that while the $(12C4) \cdot Li^+$ complex is quite stable in nitromethane and acetonitrile solutions ($\log K_f > 4$) the stability decreases considerably in pyridine and acetonitrile solutions. These differences are less apparent from the ^{17}O-shifts. However, the existence of the two complexes is confirmed by the ^{17}O-NMR. since the ^{17}O chemical shift reverses direction (upfield to downfield) when the Li^+/12C4 mol ratio increases beyond 1:1.

The variation of the cavity size of ligands I to IV allows selective complexation of the Li^+, Na^+ and K^+ cations which is readily shown by the ^{7}Li-, ^{23}Na- and ^{39}K-NMR. [1]. However, the magnitude of the induced ^{17}O shifts are more dependent on the nature of the cation than on the cavity size of the ligand. The largest

Table 1. *^{17}O-NMR. chemical shifts and linewidths of crown ethers and of their complexes with perchlorate salts*

Ligand	Solvent	Free crown		Cation	( )b)	Complexed crown	
		δ(ppm)a)	$\Delta\nu_{1/2}$(Hz)a)			δ(ppm)a)	$\Delta\nu_{1/2}$(Hz)a)
Dioxane	None	-6					
12C4	Nitromethane	-8	490	Li^+	(0.33)	-14	625
				Li^+	(0.50)	-15	500
				Li^+	(1.0)	-21	620
				Li^+	(2.0)	-18	600
				NBu_4^+	(1.0)	-5	575
	Acetonitrile	-7	250	Li^+	(1.0)	-17	390
	Pyridine	-5	735	Li^+	(1.0)	-13	625
				NBu_4^+	(1.0)	-6	400
	Acetone	-5	245	Li^+	(1.0)	-13	650
				Na^+	(1.0)	-14	375
	Chloroform	-8	350	Li^+	(0.5)	-17	800
15C5	Nitromethane	-3	675	Li^+	(1.0)	-13	500
	Acetonitrile	-3	500	Li^+	(1.0)	-13	475
	Pyridine	-2	575	Li^+	(1.0)	-18	400
	Acetone	-3	375	Li^+	(1.0)	-13	375
				Na^+	(1.0)	-13	450
	Chloroform	-5	550	Na^+	(1.0)	-15	1000
18C6	Acetonitrile	$+3$	550	Li^+	(1.0)	-14	425
				Na^+	(1.0)	-9	600
				K^+	(1.0)	$+2$	1050
	Chloroform	-6	650	K^+	(1.0)	-9	1500
	Acetone	0	525	Li^+	(1.0)	-16	400
				Na^+	(1.0)	-12	575
				K^+	(1.0)	$+3$	775
222	Chloroform	-1	1200	K^+	(1.0)	$+1$	1300

a) Chemical shifts are accurate to ± 2 ppm and linewidths to about 10%.
b) Value of the cation/crown mol ratio.

chemical shift of -8 to -17 ppm was observed in the case of the lithium ion, followed by a -9 to -12 ppm shift for Na^+ and $+2$ to -3 shift for K^+ *(Table 1)*. These shifts are extremely small with respect to the overall ^{17}O chemical shift scale. They could arise either from conformational changes of the ligand following complexation reaction [9] or from the electrostatic interaction between the O-atoms and the metal cation [10] [11]. The knowledge of the vicinal $^3J_{HH}$ coupling constants in the $-OCH_2CH_2O-$ fragment would shed some light on the average conformation along the C,C-bonds. These couplings are obtained from the *AA'XX'*-type ^{13}C proton satellite spectra of the crowns I-III, as has been shown previously for the 1,4-dioxane molecule [12].

The data shown in *Table 2*, indicate that the average conformation along the C,C-bonds for all these ethers is a more or less deformed gauche conformation. It should also be noted that the changes in the $^3J_{HH}$ coupling constant following the complexation are not greater than the changes in the $^3J_{HH}$ among the different crown ethers. As the conformational changes do not modify the ^{17}O-shifts of the free crown ethers, there is no reason to expect that they would be more effective on complexation. Therefore, one can conclude that the observed ^{17}O-shifts on com-

Table 2. *^{13}C-, ^{17}O-chemical shifts and $^3J_{HH}$ coupling constants for various ligands and complexes in chloroformic solutions*[a])

	Compound	δ ^{17}O	$\Delta\nu_{1/2}$	δ ^{13}C	T_1 ^{13}C	$^3J_{HH}$
	Dioxane	-6	-	67.4	-	6.1; 2.7
(I)	12C4	-8	350	70.9	2.86	6.1; 2.1
	(12C4)Li^+ (2/1)	-17	800	67.1	0.67	6.65; 3.05
(II)	15C5	-5	550	70.8	2.44	6.1; 3.0
	(15C5)Na^+ (1/1)	-15	1000	68.3	0.63	6.4; 2.7
(III)	18C6	-6	650	70.6	2.26	6.05; 2.95
	(18C6)K^+ (1/1)	-9	1500	69.7	0.65	6.3; 2.1
(IV)	222	-1	1200	55.9	1.25	-
				69.6	1.36	-
				68.7	1.32	-
	(222)K^+ (1/1)	$+1$	1300	52.7	0.80	-
				69.3	0.85	-
				66.4	0.83	-

[a]) Concentrations for ^{17}O measurements are 3M for I, II and III and 1.5M for ^{13}C- and ^{1}H-measurements. Concentration of 222 is 0.75M for ^{17}O- and ^{13}C-NMR. spectra.

plexation are mainly electrostatic in origin, and are created by the electric field generated by the cations. Theoretical chemical shift calculations [13] predict a high field shift for the O-atom of the water molecule interacting with a Li^+-cation. Likewise experimental results obtained from measurement of ^{17}O chemical shifts of water in aqueous solutions of electrolytes show [14] [15] high field ionic molal shifts for the Li^+-, Na^+- and K^+-cations.

Linewidth variations are somewhat unexpected as one observes either a broadening or a narrowing of the resonance line following the complexation. Broadening occurs for the (12C4) · Li^+, (15C5) · Na^+, (18C6) · K^+ complexes but line narrowing is observed for (15C5) · Li^+ and (18C6) · Li^+. Since the linewidth measurements are relatively inexact (particularly for the cryptand 222), some ^{13}C-T_1-relaxation times were also determined *(Table 2)*. Taking into account the fact that the concentration of the solutions used in ^{17}O- and ^{13}C-NMR. were different, these T_1-relaxation times confirm the general trends depicted by the ^{17}O-linewidths and also confirm that the linewidth variations are not due to the modification of the ^{17}O nuclear quadrupole coupling constant. Linewidth variations can therefore be interpreted in terms of effective correlation times which are related to the overall reorientation of the ligands and to the local motions. Insertion of a metal cation into the center of a molecular cavity can, by itself, only slightly affect the overall reorientations since the size of the molecule remains essentially unchanged. Complexation of a cation by a flexible ligand, whose cavity size is consonant with the ionic radius produces a considerable rigidification of the ligand [9] due to the disappearance of the conformational equilibrium [16] present before complexation. The effective correlation time increases and broad lines (short relaxation time) are seen, as in the case of the (12C4) · Li^+, (15C5) · Na^+ and (18C6) · K^+ complexes.

Inclusion of a cation within a relatively rigid ligand can induce only small modifications in the correlation times. It has been shown that the conformational change in the free cryptands are relatively slow [17], and, therefore, cannot affect the effective correlation time. In this work we observe a slight decrease in T_1 of ^{13}C for the (222)K^+-system but previous measurements on the (222)Na^+-system in methanol/water solutions (95/5) [18] showed that the ^{13}C-T_1's were increased by complexation (from 0.60 to 1.05). These small modifications of correlation times could be indicative of a different solvation of the free cryptand and for the cryptate.

Complexation of cations by a crown ether with a cavity larger than the size of the complexed ion cannot freeze the precomplexation conformational process but it is likely that this kind of complexation creates additional conformational processes therefore reducing the effective correlation time, as observed for the (15C5) · Li^+- and (18C6) · Li^+-complexes.

Conclusion. - As a result of the electrostatic origin of the complexation process between polyethers and alkali cations, only small chemical shifts result in ^{17}O-NMR. Similar results were obtained by *Foster & Roberts* with ^{15}N-NMR. study of cryptates [19] where the ^{15}N-resonance also seems to be quite insensitive to complexation. However, in some cases, qualitative information concerning complexation can be extracted from the ^{17}O-shifts. For example, the addition of silver perchlorate to 18C6 in acetone produces a ^{17}O high field shift of -13 ppm, indicative of a (18C6) · Ag^+-complex in this solvent; but in acetonitrile the strong CH_3CN-Ag^+ interaction [20] and the 18C6–CH_3CN interaction prevents the formation of a (18C6)Ag^+ complex ($\delta_0 = +6$ ppm).

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