

²³Na NUCLEAR MAGNETIC RESONANCE STUDY OF THE COMPLEXATION OF SODIUM TETRAPHENYLBORATE BY [5,5]-DIBENZO-30-CROWN-10 IN NITROMETHANE, ACETONITRILE, ACETONE AND PYRIDINE

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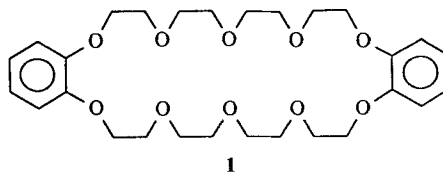
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The nature of the (Na-DB30C10)⁺ complex has been studied by ²³Na NMR in four non-aqueous solvents: nitromethane (NM), acetonitrile (AN), acetone (AC) and pyridine (PY). The equilibrium constant of formation (*K_f*) of (Na-DB30C10)⁺ in AC, AN and PY was determined at 300 K: log *K_f* = 3.9 ± 0.3, 3.4 ± 0.5 and 3.0 ± 0.1, respectively. In cases such as in pyridine, where exact values of the rate constants for the chemical exchange could not be calculated, limiting values were determined giving *k*₋₁ (the rate constant for complex dissociation) > 6.6 × 10⁻⁴ s⁻¹ and *k_c* (the rate constant for the formation of the complex) > 5 × 10⁷ l mol⁻¹ s⁻¹. Evidence was found for the formation of a 2:1 (Na₂-DB30C10)²⁺ complex in nitromethane. It has been previously shown that for (Na-DB24C8)⁺ the first coordination sphere of Na⁺ is exclusively filled by the oxygens of the crown ether, whereas for (Na-DB18C6)⁺ there is participation of at least one solvent molecule. The first coordination sphere of Na⁺ in (Na-DB30C10)⁺ consists of one or several molecules of solvent in addition to a number of oxygens from the crown ether. The *soft* wrapping of the Na⁺ by DB30C10 is in contrast with the *hard* wrapping of Na⁺ by DB24C8 and of K⁺ by DB30C10.

INTRODUCTION

The large crown ether [5,5]-dibenzo-30-crown-10 (6,7, 9, 10, 12, 13, 15, 16, 23, 24, 26, 27, 29, 30, 32, 33-hexadecahydrodibenzo[*b,q*] [1, 4, 7, 10, 13, 16, 19, 22, 25, 28] decaoxacyclotriacontin) (DB30C10, **1**) first reported by Pedersen¹ in 1967, is known to form stable complexes with a variety of cations, ranging from dicationic organic entities such as diquat^{2,3} to organometallic derivatives such as [Rh(cod)(NH₃)₂]⁴⁺ (cod = cyclooctadiene), inorganic complexes such as [Pt(bpy)(NH₃)₂]⁵⁺ or (UO₂)²⁺⁶ and alkaline earth⁷ or alkali metal⁸⁻¹¹ cations.

In the case of the alkali metal cations, complexation in methanol¹² shows a plateau selectivity since the equilibrium constant for the formation of (Na-DB30C10)⁺ is a factor of 400 lower than that of (K-DB30C10)⁺, which is in the same order as that of (Cs-DB30C10)⁺.¹² The formation constants of the



(Cs-DB30C10)⁺ complex were determined by ¹³³Cs NMR in five non-aqueous solvents by Shamsipur and Popov.¹³ At 30 °C, they are in a range between log *K_f* = 3.4 (acetonitrile) and 4.4 (pyridine). In all five cases, the complexes are enthalpy stabilized and entropy destabilized.¹³ These observations can be rationalized by the fact that DB30C10 is flexible enough to adapt its conformation to the size of the cation and to wrap around K⁺ or Cs⁺. Such 'wrap-around' structures of the KSCN-DB30C10¹⁴ and KI-DB30C10¹⁵ complexes have been determined in the solid state by x-ray crystallography and studied by CP-MAS ¹³C NMR.¹⁶ Live and Chan¹⁰ have shown that in solution the DB30C10 conformations of these complexes are similar

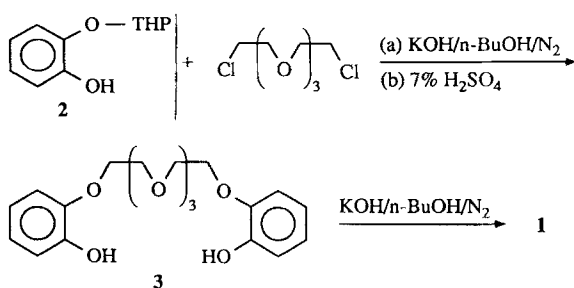
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to those in the crystal. Recently, our group has shown, by ^{39}K and ^{13}C NMR, that in non-aqueous solvents DB30C10 wraps around the potassium cation and expels the conjugate anion and the solvent molecules from the cation coordination sphere.¹⁷ This behaviour is very similar to the case of Na^+ -[4,4]-DB24C8 ([4,4]-dibenzo-24-crown-8 = 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b,n*] [1,4,7,10,13,16,19,22] octa-oxacyclotetrasin).¹⁸⁻²¹ However, if DB30C10 can form a cavity precisely adapted to the size of K^+ , then in the case of smaller cations such as sodium, it has been proposed that the cavity formed during the complexation process is not so perfectly adapted¹⁰ and that unfavourable non-bonding interactions would become important.²² The main result is a drop of the value of the equilibrium constant of formation on going from K^+ to Na^+ , and the possibility of formation of 2:1 sodium-DB30C10 complexes, as it has been shown in the solid state²² and in solution.^{13,23}

It is in this context that we decided to study, by ^{23}Na NMR, the nature of the $(\text{Na-DB30C10})^+$ complex in four non-aqueous solvents: nitromethane (NM), acetonitrile (AN), acetone (AC) and pyridine (PY). ^{23}Na NMR is an excellent probe of the close electronic environment of the sodium cation^{24,26} and is very sensitive to the nature of the sodium coordination shell.

EXPERIMENTAL

[5,5]-Dibenzo-30-crown-10 synthesis. [5,5]-DB30C10 was synthesized by a modification of Pedersen's method,¹ after monoprotection of catechol by tetrahydropyran (THP),²⁷ according to the following scheme:



2-[(Tetrahydro-2H-pyran-2-yl)oxy]phenol (2)²⁷. Compound 2 was synthesized following a modification of the previously published method,²⁷ as follows. A 18.5-g (0.22-mol) amount of dihydropyran dissolved in 50 ml of toluene containing 4–8 drops of concentrated HCl was added dropwise over 1 h at 0 °C to 22 g (0.20 mol) of catechol dissolved in 150 ml of toluene. After a standing period of 1 h, the toluene was extracted with 2 × 100 ml 10% NaOH. The aqueous phase was saturated with carbon dioxide until pH7 to generate the

monoprotected catechol. This two-phase mixture was extracted with 2 × 100 ml of dichloromethane. The dichloromethane solution was washed with 50 ml of water, then with 50 ml of saturated aqueous NaCl. The organic phase was dried over MgSO₄, filtered and the CH₂Cl₂ evaporated to afford 29.4 g of monoprotected catechol as a slightly golden liquid, with a yield of 76%. TLC (silica gel with 4:1 CH₂Cl₂–hexane as eluent) showed only a very slight contamination by catechol. (M^+ = 194; ^1H and ^{13}C NMR spectra were in perfect agreement with the structure).

2,2'-[oxybis(2,1-ethanedioxy-2,1-ethanedioxy)]bisphenol (3).^{3,28} A 9.12-g (0.047-mol) amount of monoprotected catechol 2 was dissolved in 110 ml of butan-1-ol with 5.28 g (0.094 mol) of KOH with reflux under nitrogen. After complete dissolution, 5.28 g (0.023 mol) of 1,11-dichloro-3,6,9-trioxaundecane in 30 ml of butan-1-ol were added dropwise over 1 h. The mixture was refluxed for 24 h and after filtration and solvent evaporation, the brown oil obtained was dissolved in 50 ml CH₂Cl₂ and extracted with 24 ml of 10% NaOH. After standard work-up procedures, the protected bisphenol was reacted with 25 ml of 7% H₂SO₄ for 2 h. The solution was then extracted with 2 × 50 ml of CH₂Cl₂ and, after work-up, 3.88 g of 3 were obtained as a brownish oil (yield 45%). The ^1H NMR data were in good agreement with the literature.³

[5,5]-DB30C10 (1).¹ A 0.66 g (0.0017 mol) amount of 2 was dissolved under nitrogen in a mixture of 50 ml of butan-1-ol and 0.23 g (0.041 mol) of KOH at reflux. After complete dissolution, 0.39 g (0.0017 mol) of bischlorotetraethylene glycol in 40 ml of butan-1-ol was added dropwise over 1 h and the solution obtained refluxed for 24 h. Then the butan-1-ol was removed by distillation with water addition, until the temperature remained at 100 °C for 10 min. [5,5]-DB30C10 crystallized out during the distillation. After recrystallization from ethyl acetate, 0.17 g of [5,5]-DB30C10 were obtained (yield 20%); m.p., 104–106 °C; lit.^{1,3} m.p., 104–106.5 °C. The ^1H NMR data were in good agreement with the literature,³ as also were the ^{13}C NMR.^{10,17}

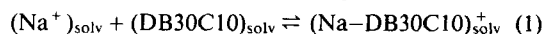
Materials and methods. Nitromethane (Aldrich, gold label) and acetonitrile (BDH, assured) were dried under reflux over calcium hydride, fractionally distilled and stored over 4 Å molecular sieves under argon. Pyridine (Aldrich, gold label) and acetone (Fisher, spectranalyzed) were stored over 4 Å molecular sieves under argon at least 2 days prior to use. The NMR tubes were tightly capped under argon. All the spectra were recorded within 24 h of preparation of the samples. [5,5]-Dibenzo-30-crown-10 was synthesized and purified as described above, or purchased from Parish Chemical. In the latter case, it was recrystallized from

a minimum volume of acetone; after cooling and washing with a few millilitres of acetone, it was dried at 60 °C under vacuum for several hours (m.p. 105–106 °C). Sodium tetraphenylborate (Aldrich, 99+ %) was dried over phosphorus pentoxide under vacuum for several hours prior to use.

The ^{23}Na NMR spectra were obtained at 79.346 MHz (Varian XL-300 spectrometer). The temperature was controlled at 300 ± 0.5 K. The chemical shifts were measured with respect to a 0.1 M NaCl solution in $\text{D}_2\text{O}-\text{H}_2\text{O}$ (10:90) and corrected for the bulk diamagnetic susceptibility of the solvent. The lineshapes were Lorentzian in all cases and the linewidths at half-height were measured graphically. The 90° pulse width, which was systematically controlled, depended on the experimental conditions and was in the range 20–30 μs . The T_1 measurements were done by an inversion-recovery $180^\circ-\tau-90^\circ$ pulse sequence and T_1 was obtained from a three-parameter non-linear regression analysis on at least nine experimental data points.

RESULTS

Figure 1 shows the ^{23}Na chemical shifts of a 0.010 M NaBPh_4 solution in four solvents [nitromethane (NM), acetonitrile (AN), acetone (AC) and pyridine (PY)] as a function of ρ , the ratio $[\text{DB30C10}]:[\text{NaBPh}_4]$. By coincidence, the chemical shifts of solvated and complexed sodium are almost identical in acetone and acetonitrile. In nitromethane there is evidence for the formation of an $(\text{Na}_2-\text{DB30C10})^{2+}$ complex.^{13,23} For pyridine, the data can be accounted for by the formation of a 1:1 complex. A non-linear regression analysis based on the equilibrium of the equation



gives $K_f = 2.8 \pm 0.1$ and a value for the characteristic chemical shift of the complex, δ_c , equal to -6.9 ± 0.3 ppm (Table 1). The values of the chemical shifts of the complex in the four solvents span a 3 ppm range (-7 to -10 ppm). The formation of the complex in acetone and acetonitrile can be followed through the relaxation rates. In the extreme narrowing limit, and in the absence of any contribution from chemical exchange, we have

$$T_{2,\text{obs}}^{-1} = T_{2,\text{inh}}^{-1} + T_{1,\text{obs}}^{-1} = \pi\nu_{1/2} \quad (2)$$

where $T_{2,\text{obs}}^{-1}$ is the observed transverse relaxation rate directly obtained from the linewidth of the signal, $\nu_{1/2}$, $T_{2,\text{inh}}^{-1}$ is the field inhomogeneity component and $T_{1,\text{obs}}^{-1}$ is the longitudinal relaxation rate which is measured independently and, in the case of a quadrupolar nucleus such as ^{23}Na ($Q = 0.12$ barn), is totally dominated by the quadrupolar relaxation²⁴⁻²⁶ ($T_{1,\text{obs}}^{-1} = T_{1,q}^{-1}$). We carefully checked that in all the cases of this study at 79.35 MHz, there was no exchange contribution to the observed transverse relaxation rate.

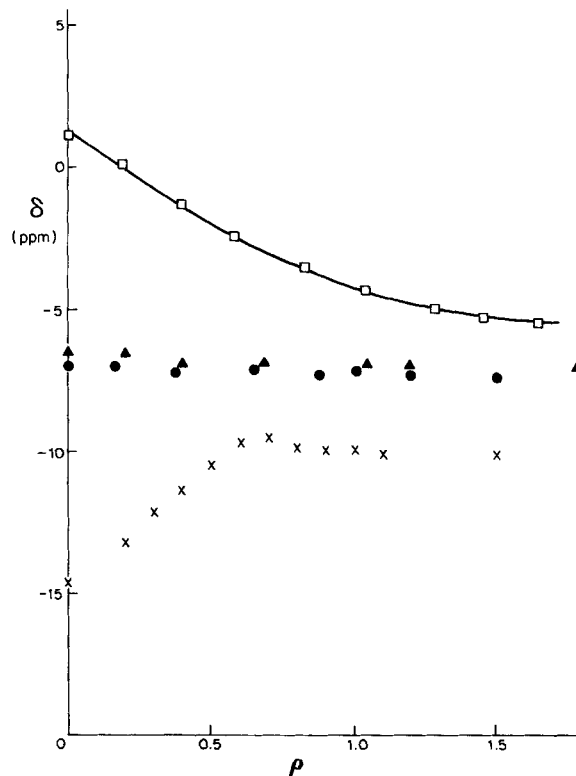


Figure 1. ^{23}Na chemical shifts as a function of the ratio $\rho = [\text{DB30C10}]/[\text{NaBPh}_4]$ in four solvents: (\square) pyridine; (\blacktriangle) acetonitrile; (\bullet) acetone; (\times) nitromethane. $[\text{NaBPh}_4] = 0.010$ M. The data in nitromethane are from Ref. 23. The data points are experimental and the line is calculated from the data in Table 1

This was verified by the fact that $T_{1,\text{obs}}^{-1}$ was typically lower than $T_{2,\text{obs}}^{-1}$ by 5–20 Hz, which is the expected order of magnitude for $T_{2,\text{inh}}^{-1}$. Under extreme narrowing conditions for a spin- $\frac{3}{2}$ nucleus, neglecting the asymmetry parameter, the quadrupolar longitudinal relaxation rate is given by the equation

$$T_{1,q}^{-1} = \frac{2\pi}{5} \chi^2 \tau_c \quad (3)$$

where τ_c is the correlation time characteristic of the quadrupolar relaxation and χ is the quadrupolar coupling constant (QCC), which is given by

$$\chi = \frac{e^2 q Q (1 + \gamma_\infty)}{h} \quad (4)$$

where Q is the ^{23}Na nuclear quadrupole moment, q is the electric field gradient at the quadrupolar nucleus site and $(1 + \gamma_\infty)$ is the Sternheimer antishielding factor. $T_{1,q}^{-1}$ therefore reflects, through its electric field

Table 1. ($^{23}\text{Na-DB30C10}$) $^+$ NMR characteristics and formation constants^a

Solvent	δ (ppm)	$\nu_{1/2}$ ^d (Hz)	T_1^{-1} ^e (Hz)	η ^f (mP)	Log K_f
NM	-10.2 ± 0.1 ^{b,c}	230 ± 10 ^b	^g	6.20	^g
AC	-7.4 ± 0.1 ^d	72 ± 2	201 ± 6	3.24	3.9 ± 0.3 ^h
AN	-7.1 ± 0.1 ^d	86 ± 2	280 ± 20	3.57	3.4 ± 0.5 ^h
PY	-6.9 ± 0.3 ^c	325 ± 5	1140 ± 30	9.52	3.0 ± 0.1 ^h 2.8 ± 0.1 ⁱ

^a Values of the ^{23}Na chemical shifts, linewidths and longitudinal relaxation rates for the complex (Na-DB30C10) $^+$ in nitromethane (NM), acetone (AC), acetonitrile (AN) and pyridine (PY). The viscosities of the four solvents are also indicated. $[\text{NaBPh}_4] = 0.010 \text{ M}$, unless indicated otherwise. $T = 294 \text{ K}$.

^b From Ref. 23; $\text{NaBPh}_4 = 0.050 \text{ M}$.

^c Calculated from a non-linear regression; see equation (1) and Figure 1.

^d Experimental value obtained for $\rho = [\text{DB30C10}]/[\text{NaBPh}_4] = 2.0$ (acetone: $\rho = 1.5$).

^e From non-linear regression analysis. See Figure 2.

^f From Ref. 17 and references cited therein.

^g Not determined.

^{h,i} Logarithm of the equilibrium constant of formation (300 K) of the complex determined from non-linear regression on the data shown in (h) Figure 2 (T_1^{-1}) and (i) Figure 1 (δ).

gradient term, the dissymmetry of the electronic distribution around the sodium cation. In the cases of ($^{23}\text{Na-DB24C8}$) $^+$ ¹⁸ and ($^{39}\text{K-DB30C10}$) $^+$,¹⁷ $T_{1,q}^{-1}$ was shown to be linearly related to the macroscopic viscosity of the solvent. This was rationalized on the basis of the Debye–Stokes–Einstein relationship, which relates the correlation time τ_c to the medium macroscopic viscosity, η :

$$\tau_c = \frac{4}{3} \pi a^3 \left(\frac{\eta}{kT} \right) f_r \quad (5)$$

where a is the molecular radius and f_r a microviscosity coefficient.^{24,25}

Equations (3)–(5) show that the ^{23}Na relaxation rate of a sodium complex in media of various viscosities is expected to be directly proportional to η , if the electric field gradient, q , is independent of the solvent. In this context, a convenient representation of the titration of Na^+ by DB30C10 as measured by the relaxation rates is to plot $T_{1,\text{obs}}^{-1}/\eta$ as a function of $\rho = [\text{DB30C10}]/[\text{NaBPh}_4]$ ²⁹ (Figure 2). The formation constants, $\log K_f$, could be determined in pyridine, acetonitrile and acetone from non-linear regression analysis [equation (1)] of the plots shown in Figure 2. The results are given in Table 1. The agreement between $\log K_f$ in pyridine determined independently from the chemical shifts and from the relaxation rates is good. In contrast with the case of the complexes (Na-DB24C8) $^+$ ¹⁸ and (K-DB30C10) $^+$,¹⁷ the relaxation rates of the complex are not perfectly proportional to the viscosity of the solvent. This is apparent from Figure 2, since the three titration curves do not give the same plateau value for T_1^{-1}/η .

A further insight into the nature of the sodium coordination shell with an eventual participation of the solvent can be gained from a study of the ^{23}Na chemical shift and relaxation rate variations of the complex in

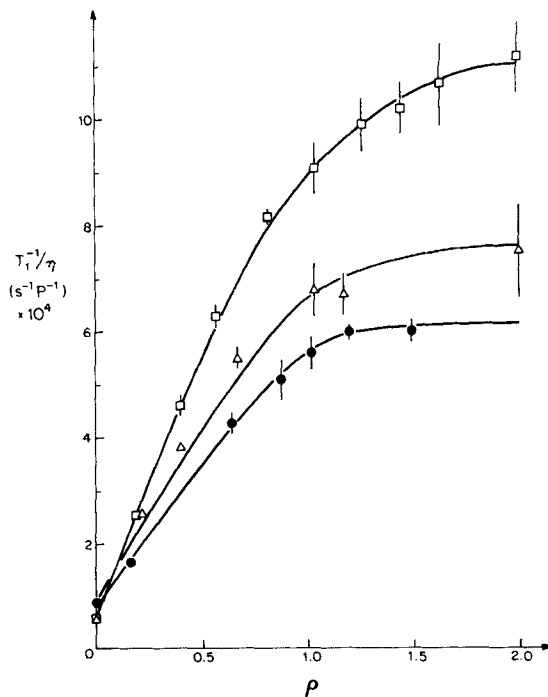


Figure 2. ^{23}Na longitudinal relaxation rate divided by the viscosity of the solution (T_1^{-1}/η) as a function of the ratio $\rho = [\text{DB30C10}]/[\text{NaBPh}_4]$ in three solvents: (\square) pyridine; (\triangle) acetonitrile; (\bullet) acetone. $[\text{NaBPh}_4] = 0.010 \text{ M}$. The data points are experimental and the three lines are calculated from the data given in Table 1

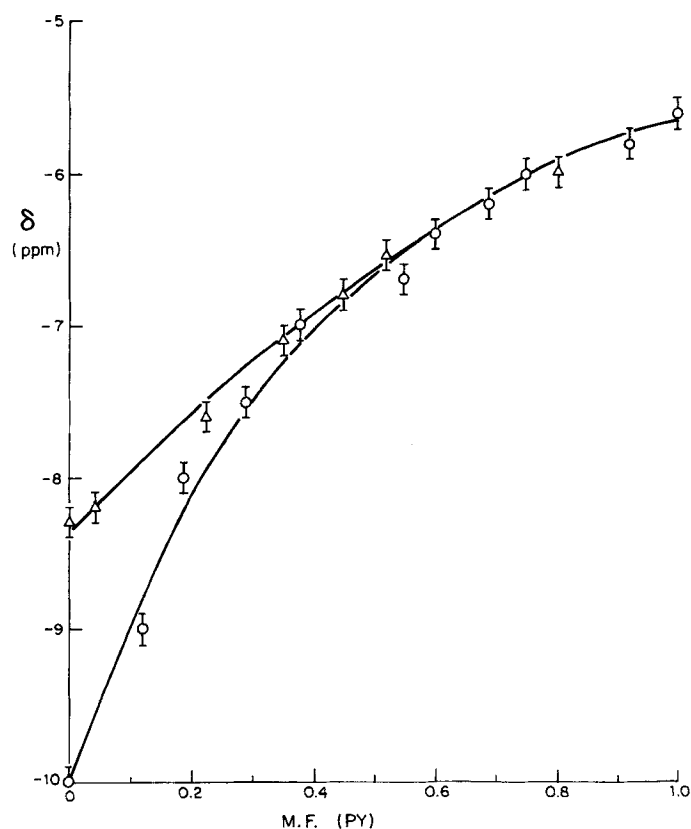


Figure 3. ^{23}Na chemical shifts as a function of the molar fraction of pyridine in two binary mixtures: (Δ) acetone-pyridine; (\circ) nitromethane-pyridine. For all the solutions $\rho = [\text{DB30C10}]/[\text{NaBPh}_4] \geq 2.0$ and $[\text{NaBPh}_4] = 0.010 \text{ M}$

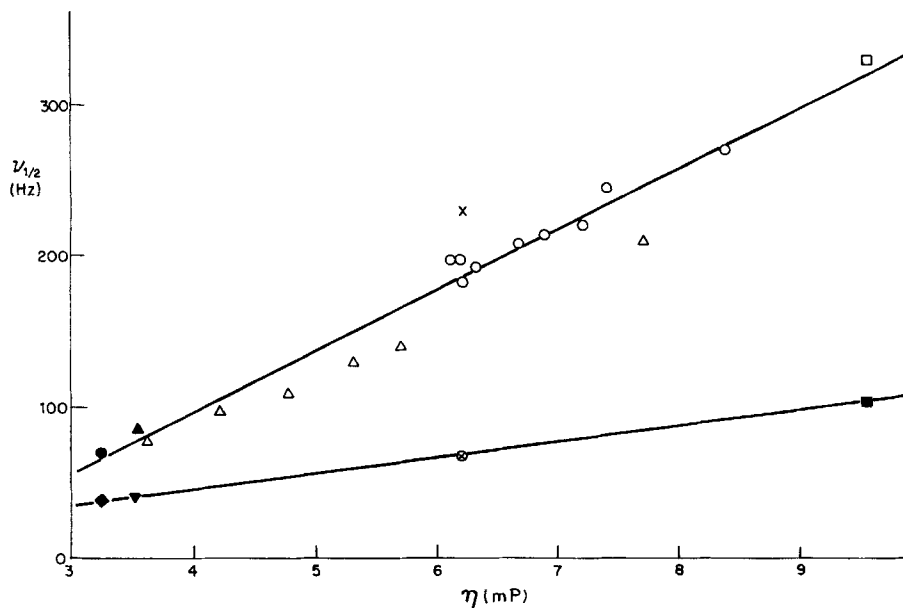


Figure 4. Linewidths at half-height of the ^{23}Na signals for the complex $(\text{Na-DB30C10})^+$ as a function of the solution viscosity. (\square) Pyridine; (\circ) binary mixtures of nitromethane and pyridine; (Δ) binary mixtures of acetone and pyridine; (\times) nitromethane; (Δ) acetonitrile; (\bullet) acetone. In all cases $\rho = [\text{DB30C10}]/[\text{NaBPh}_4] \geq 2.0$ and $[\text{NaBPh}_4] = 0.010 \text{ M}$. For comparison, the results for the complex $[\text{Na-DB24C8}]^+$ are also indicated: (\diamond) acetone; (∇) acetonitrile; (\otimes) nitromethane; (\blacksquare) pyridine

binary mixtures. Such variations are shown in Figure 3 for the binary mixtures NM-PY and AC-PY. A definite curvature is observed, showing preferential solvation of the complex by pyridine in both cases. Figure 4 shows the relationship between the observed linewidths of $(^{23}\text{Na-DB30C10})^+$ in the four solvents and the two binary mixtures as a function of the viscosity of the medium. The linear correlation coefficient of the DB30C10 plot is 0.97 for 19 experimental points. For comparison, the same relationship is shown in the case of $(\text{Na-DB24C8})^+$.¹⁸

DISCUSSION

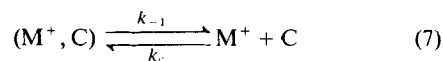
The equilibrium constant of formation (K_f) of $(\text{Na-DB30C10})^+$ could be determined at 300 K in acetone, acetonitrile and pyridine. Log K_f is lower in pyridine (2.9 ± 0.1) than in acetone or acetonitrile. One should note a discrepancy with the previously published value of log K_f in acetone, determined by ^1H NMR (log $K_f = 2.5$).¹⁰ This is perhaps due to a contamination by water of the acetone- d_6 used in the ^1H NMR study. The value determined in acetonitrile (log $K_f = 3.4 \pm 0.5$) is in good agreement with the value (3.6) determined by polarography at 295 K in the presence of $0.05 \text{ M Bu}_4\text{NClO}_4$.^{12,31}

In acetonitrile and acetone, the coincidental equality of the chemical shifts of the solvated and of the complexed sodium cation prevents any kinetic study. In pyridine, a limiting value for the exchange rate can be evaluated on the basis of the equation³²

$$T_{2,\text{ex}}^{-1} = 4p_A p_B \pi^2 (\nu_A - \nu_B)^2 (k_A + k_B)^{-1} \quad (6)$$

where $T_{2,\text{ex}}^{-1}$ is the exchange contribution to the transverse relaxation rate, A and B denote the two sites between which sodium exchanges in solution (solvated and complexed), p_A and p_B are the populations of the two sites, $(k_A + k_B)$ is the sum of the two pseudo-first-order rate constants for the exchange $\text{A} \rightleftharpoons \text{B}$ and $\nu_A - \nu_B$ is the difference (Hz) between the chemical shifts of $^{23}\text{Na}^+$ in the two sites. Equation (6) is valid under the conditions of moderately rapid exchange³² where the longitudinal relaxation rate is not affected by the exchange.³² The quadrupolar contribution to the relaxation rate is given by $T_{1,\text{obs}}^{-1}$ and if the difference $T_{2,\text{obs}}^{-1} - T_{1,\text{obs}}^{-1}$ is larger than the inhomogeneity contribution, $T_{2,\text{inh}}^{-1}$ [equation (2)], the excess can be attributed to $T_{2,\text{ex}}^{-1}$.^{33,34} The difference $T_{2,\text{obs}}^{-1} - T_{1,\text{obs}}^{-1}$ was measured to be 30 Hz for $\rho = 0.5$ in pyridine at 300 K. This value is of the same order of magnitude as the error limits ($T_{2,\text{obs}}^{-1} = 570 \pm 20 \text{ Hz}$) and of the inhomogeneity, but it gives a higher limit value for $T_{2,\text{ex}}^{-1}$. Knowing $\nu_A - \nu_B = 635 \text{ Hz}$, one can calculate that $(k_A + k_B) > 1.3 \times 10^5 \text{ s}^{-1}$. If the mechanism of exchange were

dissociative,³³ corresponding to the equation



then $(k_A + k_B) = k_{-1}(1 - \rho)^{-1}$ and $k_{-1} > 6.6 \times 10^{-4} \text{ s}^{-1}$. Since $K_f = k_c/k_{-1} = 7.9 \times 10^2$, a lower limit is known for $k_c > 5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. Since it is known for several crown ethers and cryptands in several aqueous and non-aqueous solvents that the rate constant for the formation of the complex with alkali metal cations is diffusion controlled,^{35,36} this lower value for k_c is very reasonable. Conversely, one could calculate, on the basis of $k_c = 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, that $T_{2,\text{ex}}^{-1}$ should be 15 Hz, which is in excellent agreement with the experimental data. This discussion does not preclude any competition from a fast associative mechanism of exchange, plausible in the case of a large crown ether.^{20,37} Recently, it has been shown by Shamsipur and Popov³⁸ that at temperatures below 263 K, the predominant mechanism for the exchange of the Cs^+ cation between the solvated and the DB30C10 complexed sites is associative in acetonitrile, propylene carbonate and methanol.

Table 2 gives the ^{23}Na NMR characteristics of the Na^+ complexes with [5,5]-DB30C10, [4,4]-DB24C8 and [3,3]-DB18C6 ([3,3]-dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*] [1,4,7,10,13,16] hexaoxacyclooctadecin). The data for [4,4]-DB24C8 have been published and analysed previously.¹⁸ In this case, both the chemical shifts and the linewidths divided by the solution viscosity ($\nu_{1/2}^*$) occupy a very narrow range of values. This is rationalized by the fact that during the formation of the $(\text{Na-DB24C8})^+$ complex, the solvent molecules are completely expelled from the sodium first coordination sphere, which is exclusively composed of ether oxygens from the large crown ether, wrapped around the cation.¹⁸ The same conclusion was reached for the complex $(\text{K-DB30C10})^+$.¹⁷ The data are very different in the case of DB18C6, for which a definite correlation can be noticed between the $(\text{Na-DB18C6})^+$ chemical shifts and the donicity number of the solvent. This correlation is similar, although less pronounced, to that shown by Erlich and Popov,³⁹ relating the donicity number of the solvent and the chemical shift of the solvated sodium cation. This is an indication that, in the case of $(\text{Na-DB18C6})^+$, at least one solvent molecule participates in the first coordination sphere of the cation. There is also a large variation of $\nu_{1/2}^*$, a parameter reflecting the dissymmetry of the electronic distribution around Na^+ [equations (2)–(5)], with the nature of the solvent. In the case of DB30C10, the situation is intermediate between DB24C8 and DB18C6. There is a definite variation of the $(^{23}\text{Na-DB30C10})^+$ chemical shift with the donicity number of the solvent, and the $\nu_{1/2}^*$ data depend on the nature of the solvent (see Figure 2 for the similar observation in the case of T_1^{-1} data).

Table 2. ($^{23}\text{Na-DB6nC2n}$) $^+$ ($n = 3, 4, 5$) NMR characteristics a

Compound	Parameter	NM	AN	AC	PY
[5,5]-DB30C10	D.N. c	2.7	14.1	17.0	33.1
[4,4]-DB24C8 b	$\nu_{1/2}^*$ d	370 \pm 30	241 \pm 6	222 \pm 6	341 \pm 5
[3,3]-DB18C6		103 \pm 5	109 \pm 5	129 \pm 5	127 \pm 5
[5,5]-DB30C10	δ^e	144 \pm 10	250 \pm 10	332 \pm 20	1260 \pm 50
[4,4]-DB24C8 b		-10.2	-7.1	-7.4	-6.9 \pm 0.3
[3,3]-DB18C6		-7.7	-8.4	-8.4	-8.8
		-17.0	-13.2	-14.1	-7.8

a Value of the ^{23}Na chemical shifts (δ) and reduced linewidths ($\nu_{1/2}^*$) for the complexes ($^{23}\text{Na-DB6nC2n}$) $^+$ ($n = 3, 4, 5$) in nitromethane (NM), acetonitrile (AN), acetone (AC) and pyridine (PY).

b From Ref. 18.

c Donicity number, from Ref. 30.

d Reduced linewidth: $\nu_{1/2}^* = \nu_{1/2}/\eta$, where $\nu_{1/2}$ is the observed linewidth and η the viscosity of the solvent.

e Unless indicated otherwise, the error in δ is ± 0.1 ppm.

This last point can be seen in Figure 4, where the correlation between $\nu_{1/2}$ and η in 19 different solutions of pure solvents and of binary mixtures shows some scatter. Also, the slope resulting from a linear regression on the data ($\nu_{1/2}, \eta$) in the case of DB30C10 is larger (41 Hz mP $^{-1}$) than that obtained in the case of DB24C8 (11 Hz mP $^{-1}$). The volume of the complex cannot explain such a large difference. On the basis of CPK models, one can roughly estimate a 10% increase of the volume going from (Na-DB24C8) $^+$ to (Na-DB30C10) $^+$. The slope indicates a mean value of the electric field gradient, q , at the $^{23}\text{Na}^+$ site of (Na-DB30C10) $^+$ larger by a factor of 3.7 than that of (Na-DB24C8) $^+$. We have previously shown 17 that the ratio of the electric field gradients for ($^{23}\text{Na-DB24C8}$) $^+$ and ($^{39}\text{K-DB30C10}$) $^+$ was 0.9 ± 0.1 .

All the observations that we have developed in this paper point to a structure of (Na-DB30C10) $^+$ incorporating one or several molecules of solvent in the first coordination sphere of the sodium cation, in addition to a number of oxygens from the crown ether. Since we do not observe any large variations of the chemical shift or of the relaxation rates with the concentration of the complex, since the data are very similar when PF $_6^-$ is the counter anion instead of BPh $_4^-$ and since it is generally known that ion pairing by BPh $_4^-$ is negligible at the concentrations of the study, 21 it is very improbable that the BPh $_4^-$ counter anion coordinates the sodium cation in the complex.

This ^{23}Na NMR study complements previous ^{13}C and ^1H NMR studies 10,13 which suggested that the solution conformation of the crown ether in (Na-DB30C10) $^+$ was different from that of (Na-DB24C8) $^+$. The ^{23}Na NMR data do not permit access to the conformation of the oligoethyleneoxy chain in solution, but definitely point to an incomplete desolvation of sodium during the complexation process. This is probably due, as was suggested by Owen and Truter, 22 to the fact that 'if the sodium ion, coordinated only by the ligand, were to oc-

cupy the central cavity with the usual Na—O (polyether) distances, very unfavourable non-bonded interactions would be induced in the molecule.' As a result, one or several ether oxygen sites remain uncoordinated, and can be involved in the formation of a 2:1 Na $^+$ -DB30C10 complex, 23 or in a fast associative exchange mechanism.

One could summarize by contrasting the *soft* wrapping of Na $^+$ by DB30C10 with the *hard* wrapping of K $^+$ by DB30C10 17 or of Na $^+$ by DB24C8. 18

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