state generated compared wtih one cathodic electron per excited state for the annihilation system. The observed ratio between these systems corresponds to these expectations and implies that losses in the $S_2O_8^{2-}$ system, e.g., by direct reduction of SO_4^-· at the electrode (eq 9), by reaction of SO_4^-· with solvent, or by oxidation of $Ru(bpy)_3^+$ in side reactions, are small.

Note also that the observed intensities in the $S_2O_8^{2-}$ system can be much higher than those in the 1+/3+ system because of the higher reactant concentrations that can be employed in the $MeCN-H_2O$ solvent.

Chemiluminescent Systems. Chemiluminescence can also be generated in a $MeCN-H_2O$ solution containing $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ when a strong reductant capable of producing $Ru(bpy)_3^+$ is added to the solution. Thus, when Mg powder or turnings were added to a $MeCN-H_2O$ solution mixture of 1 mM $Ru(bpy)_3^{2+}$ and 20 mM $S_2O_8^{2-}$, a bright orange emission resulted that was easily visible under room light and persisted for several hours. The production of luminescence presumably follows a pathway similar to that discussed for the ecl, with the external circuit and electrode replaced by a strong electron donor. Addition of $S_2O_8^{2-}$ or Mg to the solution after the luminescence had decayed to low levels resulted again in a bright emission, indicating that the system is limited by consumption of Mg or $S_2O_8^{2-}$. Analogous chemiluminescent systems involving $Ru(bpy)_3^{2+}$, oxalate, and a strong oxidant have been reported.[2c] An interesting aspect of this system is that no apparent reaction occurs when Mg, $S_2O_8^{2-}$, and $Ru(bpy)_3^{2+}$ are mixed in MeCN alone. This is probably due to the low solubility of $(NH_4)_2S_2O_8$ and the Mg oxide coating in MeCN. The reactants can be mixed in MeCN and stored for long durations (>50 h) with no or very low emission detected. However, the bright chemiluminescence is observed simply upon addition of water, which dissolves the reactants. In carrying out this reaction, means of venting the H_2 produced by the Mg reaction must be provided. Similar experiments were performed with Me_2SO replacing water. Although H_2 evolution was eliminated under these conditions, the observed emission was not as intense as in the $MeCN-H_2O$ system, probably because of the lower solubility of the $(NH_4)_2S_2O_8$ in this medium

Conclusion

The chemical or electrochemical reduction of $S_2O_8^{2-}$ produces a strongly oxidizing intermediate, SO_4^-·, that generates a very intense emission in the presence of electrogenerated $Ru(bpy)_3^+$. The ecl mechanism involves several reaction pathways and includes the quenching of $Ru(bpy)_3^{2+*}$ by $S_2O_8^{2-}$ to produce several strong oxidants also capable of generating the excited state. The ecl and chemiluminescent intensity of this system is several times larger than that of previously reported systems based on $Ru(bpy)_3^{2+}$ and may be useful in practical devices. Other ecl and chemiluminescent systems based on reaction of the intermediate SO_4^-· with suitable reduced species, A^-· (e.g., radical anions of aromatic hydrocarbons), to produce A* have also been studied. These will be the subject of a separate communication.

(14) **Note Added In Proof:** Findings similar to those reported here have just appeared: Bolletta, F.; Ciano, M.; Balzani, V.; Serpone, N. *Inorg. Chim. Acta* **1980**, *62*, 207–213.

Solution Thermodynamic Studies. 6.[1] Enthalpy–Entropy Compensation for the Complexation Reactions of Some Crown Ethers with Alkaline Cations: A Quantitative Interpretation of the Complexing Properties of 18-Crown-6

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Abstract: The interactions of 18-crown-6, 15-crown-5, and 12-crown-4 with Na^+ and K^+ were studied in methanol and water as solvents at 25 °C. $\Delta G°$ values for both 1:1 and 2:1 complexation reactions were determined by potentiometric titrations. Used in conjunction with these values, calorimetric measurements led to $\Delta H°$ and $\Delta S°$ values. The thermodynamic parameters obtained cannot be correlated with the cations or the crown ethers "hole" sizes in any 1:1 or 2:1 reactions. Moreover, the $\Delta G°$ values are the result of quite different but permanently compensating combinations of the $\Delta H°$ and $\Delta S°$ values. These arise from several thermodynamic processes in which the role of the solvent must be considered. In the case of 18-crown-6, we present a quantitative interpretation in which this crown ether develops interactions that are stronger with Na^+ than with K^+.

Since Pedersen's pioneering work,[2] the interest in complexing agents like crown ethers and cryptands has increased considerably. These complexing agents are known to effect a dramatic change in the interactions of cations with their counterions and give rise to the so-called "naked anions"[3] for instance. The association properties of crown ethers with alkaline cations have been mainly described in terms of similarities between cation size[4-7] and the size of the inner "hole" of the crown ether. This kind of oversimplified qualitative description does not take into account the role of the solvent.[8,9]

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In order to obtain a more realistic description, we planned to perform a quantitative study of the complexing properties of three crown ethers (18-crown-6, 15-crown-5, and 12-crown-4) and two alkaline chlorides (NaCl and KCl). Numerous thermodynamic parameters for this kind of reaction have already been published in the literature,[4-9] but few of them have been measured by using the same experimental procedure. In our work we decided to measure $\Delta G°$ and $\Delta H°$ in order to deduce $T\Delta S°$ for reactions 1 and 2 (where CE and M^+ stand for the crown ethers and the

$$CE + M^+ \rightleftharpoons CEM^+ \tag{1}$$

$$CEM^+ + CE \rightleftharpoons (CE)_2M^+ \tag{2}$$
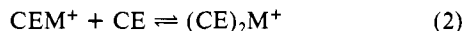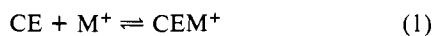
cations, respectively) in two solvents (methanol and water) at 25 °C. The measurements were obviously made at variable (but very low) ionic strength. Without exception, the measured quantities were partial molar quantities, depending on the experimental conditions, but they can safely be considered as being identical with standard quantities. Great care was exercized with the experimental measurements and data treatment in order to obtain accurate thermodynamic parameters. These parameters are discussed at the end of the paper.

Products

The cyclic polyether 18-crown-6 (purity 99%) was purchased from Merck. The 12-crown-4 and 15-crown-5 ligands were synthesized by cationic cyclooligomerization of ethylene oxide[10] (Borregaard Industries Ltd., Sarpsborg). Cyclic and acyclic impurities were removed by complexation with KBF_4 or $NaBF_4$ and by the distillation of the pyrolysis product. Both the suprapure NaCl and the suprapure KCl and the dry methanol (max 0.01% H_2O) were purchased from Merck.

Methods

Potentiometric Titration. For the determination of the equilibrium constants of reactions 1 and 2, 25 mL of various electrolyte solutions were placed in a thermostated glass cell ($T = 25$ °C) equipped with a magnetic stirrer and two electrodes. One of the electrodes was Ag/AgCl (Tacussel Io Model 158891) and the other was glass (Tacussel PMEV Model 70086). Before undertaking the measurements in anhydrous methanol, we pretreated the glass electrode by soaking it for a week in this solvent in order to prevent erratic responses. The emf was read on an electronic millivolt meter coupled with a pH meter (Orion Digital Ionalyster Model 601). The variation of this emf was measured as a function of the amount of crown ether solution added to the electrolyte solution. In a typical titration experiment, the fraction of complexed cation ranged from 0% to more than 65%, so that 70% to 90% of the theoretical maximum information[11] could be obtained. The relationships in eq 3 and 4 give the

$$K_1 = c_{CEM^+}/(c_{M^+}c_{CE}) \tag{3}$$

$$K_2 = c_{(CE)_2M^+}/(c_{CEM^+}c_{CE}) \tag{4}$$

stepwise equilibrium ratios, where c stands for the molar concentration ($L \cdot mol^{-1}$) of the species considered. The activity coefficient of the free cyclic polyether was assumed to be equal to 1, taking into account the low analytical crown ether concentrations (less than $\sim 10^{-3}$ M for 18-crown-6 and less than $\sim 4 \times 10^{-2}$ M for 12-crown-4). Considering the low ionic force of the solution ($\mu \sim 10^{-3}$), the activity coefficients of charged species (including M^+, CEM^+, and $(CE)_2M^+$) could be estimated by following the Debye–Hückel limit law:

$$\log \gamma = -A(\mu)^{1/2} \tag{5}$$

where A assumes the value of 1.89 and 0.51 with the methanol and water as solvents, respectively ($T = 25$ °C).[12] Relationship 5 is valid for any charged species and, therefore, γ does not appear in the expressions of the equilibrium constants (relationships 3 and 4).

The relationship between the measured emf and the unknown free-cation concentration is given by

$$\Delta E_i = \left(\omega \frac{RT}{F} \ln \frac{c_{M^+_i}}{c_{M^+_0}}\right) + \left(\frac{RT}{F} \ln \frac{c_{Cl^-_i}}{c_{Cl^-_0}}\right) \tag{6}$$

where i refers to the electrolyte solution after the ith addition of the crown ether solution. Parameter ω takes into account the non-Nernstian slope of the glass-electrode response. The ω value, which had been measured by previous calibration experiments, remained slightly different from 1.

After a rough graphical evaluation, the values of the equilibrium constants were improved by a nonlinear regression analysis. These values were such as to minimize the quantity

$$U = \sum_i (\Delta E_i^m - \Delta E_i^c)^2 \tag{7}$$

where ΔE_i^m and ΔE_i^c are respectively the measured and calculated values of the emf variations. ΔE_i^c can be calculated on the basis of stoichiometric equations, provided that the equilibrium constants K_1 and K_2 are known. The equilibrium $M^+ + Cl^- \rightleftharpoons MCl$, characterized by $K_{assoc} \simeq 10$ $L \cdot mol^{-1}$,[13a] was also considered, with methanol as solvent. Following a referee's comment, we have carefully tested the choice of a K_{assoc} value as regards the final results. It can be effectively argued that KCl and NaCl are unassociated in methanol,[13b] even if a very recent work substantiates a small but definitely non-zero K_{assoc} value for potassium chloride.[13c]

It is important to note that the terms in the summation in (7) must not be weighted by the square inverses of the error on the measured quantities (namely, ΔE_i^m). The omission of the weighting factors, required by the Gaussian approximation of regression analysis,[14] could in some cases lead to biased estimates of the unknown parameters (this was previously shown for both calorimetric titration[15] and the determination of longitudinal relaxation times by the FIRFT method[16]). However, it is not the case in our treatment, since the error on ΔE_i^m (of approximatively 0.1 mV) remained constant in the course of the titration experiments.

The minimum of function U was obtained by "pit-mapping",[17,18] and this also led to the estimation of the confidence intervals on K_1 and K_2 via the "D boundary" technique. Results were calculated for a confidence level of 95%.

Finally, we took into account the possible presence of a contaminant that might complex the cation in the same way as the titrant crown ether. The treatment remained essentially the same. It was completed by the introduction of the prescribed parameters, i.e., the amount of the hypothetical contaminant and its complexation equilibrium constants (under discussion). The numerical treatments were performed on CDC 6500 and 6600 computers. The programs were written in Fortran IV language.

Calorimetric Measurements. The values of $\Delta H°_1$ and $\Delta H°_2$ were obtained by measuring the molar specific dissolution heat (Q) of the crown ether in the electrolyte solution. It is easy to show that Q is expressed by

$$Q = \delta H^r + (\alpha_1 + \alpha_2)\Delta H°_1 + \alpha_2\Delta H°_2 \tag{8}$$

where δH^r is the molar specific heat of dissolution of the polyether in the pure solvent. Molar fractions, α_1 and α_2, of 1:1 and 2:1 complexed crown ethers were calculated by using the previously determined K_1 and K_2 values. Dissolution heats were measured on a LKB 8700 calorimeter. The uncertainties in $\Delta H°$ and $T\Delta S°$ are due to the experimental errors in the measurement of Q and to the errors in α_1 and α_2.

Results and Discussion

The $\Delta G°$, $\Delta H°$, and $T\Delta S°$ values of reactions 1 and 2 are given in Table I. The results obtained for the reactions of 12-crown-4 with K^+ in methanol illustrate the advantage of performing potentiometric titrations (leading to K_1 and K_2 values) together with calorimetric measurements (leading to the $\Delta H°_1$ and $\Delta H°_2$ values) in order to obtain significant results. The K_2 value is remarkably

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Table I. $\Delta G°$, $\Delta H°$, and $T\Delta S°$ Values (kcal/mol) of Reactions 1 and 2[a]

| | | | methanol | | | | | water | |
		ref	(1) M⁺ = K⁺	(2) M⁺ = K⁺	(1) M⁺ = Na⁺	(2) M⁺ = Na⁺	ref	(1) M⁺ = K⁺	(1) M⁺ = Na⁺
18-crown-6	$\Delta G°$	b	−8.40 ± 0.05		−5.95 ± 0.04		b	−2.92 ± 0.03	
		8	−8.27 ± 0.04		−5.95 ± 0.03		7	−2.77 ± 0.14	−1.09 ± 0.14
		6	−8.32 ± 0.05		−5.89 ± 0.05		6	−2.81 ± 0.05	
							9	−2.79 ± 0.00	−1.12 ± 0.03
	$\Delta H°$	b	−12.70 ± 0.10		−7.50 ± 0.07		b	−5.60 ± 0.20	
		8	−13.41 ± 0.06		−8.4 ± 0.3		7	−6.21 ± 0.01	−2.25 ± 0.10
	$T\Delta S°$	b	−4.30 ± 0.15		−1.55 ± 0.11		b	−2.68 ± 0.23	
		8	−5.14		−2.4		7	−3.4	−1.1
15-crown-15	$\Delta G°$	b	−4.90 ± 0.02	−1.8[c]	−4.27 ± 0.04	−3.2 ± 0.8	7	−1.01 ± 0.11	−0.95 ± 0.14
		8	−5.13 ± 0.24	−3.70 ± 0.04	−4.75 ± 0.01		9	−1.04 ± 0.03	−0.92 ± 0.04
	$\Delta H°$	b	−7.70 ± 0.05		−5.50 ± 0.20		7	−4.10 ± 0.10	−1.50 ± 0.04
		8	−7.70 ± 0.30	−8.10 ± 0.50	−4.99 ± 0.03				
	$T\Delta S°$	b	−2.80 ± 0.07		−1.23 ± 0.24		7	−3.1	−0.54
		8	−2.57	−4.40	−0.24				
12-crown-4	$\Delta G°$	b	−2.16 ± 0.02	−0.76 ± 0.2	−2.0 ± 0.03	−3.11 ± 0.03			
	$\Delta H°$	b	−5.10 ± 0.35		−3.0 ± 0.30	−6.7 ± 1.8			
	$T\Delta S°$	b	−2.94 ± 0.37		−1.0 ± 0.33	−3.6 ± 1.8			

[a] 1 kcal = 4.184 kJ. $T = 25$ °C. $K_{assoc} = 10$ L·mol⁻¹. [b] This work. The uncertainties on the estimated parameters are defined in the text under methods. In particular, those that are associated with $\Delta G°$ values are deduced from standard deviations for the stepwise equilibrium ratios multiplied by the value of the t-Student variable, t, which defines a probability equal to 0.975 ($t_{0.975} > 2$). [c] For this reaction, the uncertainty on K_2 is higher than the K_2 value.

Table II. Effect of Taking Into Account a Contaminant as Regards the K_1, K_2, and U^a Values Associated with the 12-Crown-4 with K⁺

contaminant	quantity,[c] %	K_1, L·mol⁻¹	K_2, L·mol⁻¹	U,[a] mV²
none		38.9	3.9	0.86
18-crown-6	0.1	39.0	3.8	0.86
	0.5	39.2	3.5	0.86
	1.0	39.2	3.7	0.87
	1.5	39.2	3.7	0.97
	2.0	39.2	3.6	0.88
15-crown-5	0.5	39.1	3.7	0.86
	1.0	39.3	3.8	0.90
	1.5	39.2	3.5	0.87
	2.0	39.1	3.8	0.88

[a] Defined by relation 7. Methanol, $T = 25$ °C, $K_{assoc} = 10$ L·mol⁻¹.[b] [b] The results of this table are essentially unaffected if K_{assoc} is 0 instead of 10 L·mol⁻¹. [c] Expressed as the molar fraction of the contaminant in the 12-crown-4.

Table III. Cationic Diameters and Cavity Sizes of Crown Ethers[a]

cation	diameter, Å	crown ether	"hole diameter", Å
Na⁺	1.94	12-crown-4	<1.2–1.5[b]
K⁺	2.66	15-crown-5	1.7–2.2
		18-crown-6	2.6–3.2

[a] Reference 19. The upper and lower limits of the "hole" diameter are estimated according to the atomic models of Korey–Koltun and Fisher-Hirschfelder-Taylor. [b] Values for 14-crown-4.

low, and the amount of 2:1 complexes in titration experiments is small. The information concerning reaction 2 obtained from such experiments is obviously sparse. Table II shows the effect of the presence of a hypothetical contaminant on K_1 and K_2 values. As can be predicted, the U values are higher in the presence of contaminant, but it is interesting to note that the K_1 and K_2 values are not at all sensitive to the presence of a contaminant. If reaction 2 is disregarded, the U values are higher, and this proves that the simulation is worse.

Table I clearly shows that Christensen's $|\Delta G°|$ values for 15-crown-5 complexation reactions are significantly higher than ours. According to Clechet,[15] the Gaussian approximation cannot be used in Christensen's least-squares treatment. This latter treatment might thus lead to an overestimation of the $|\Delta G°|$ and $|\Delta H°|$ values as compared with our values, which are compatible with the Gaussian approximation (see Methods section). At all events, the results in Table I show that a given value of the equilibrium constant, or of $\Delta G°$, at a single temperature is uninformative by itself since it is the result of quite different combinations of enthalpy and entropy terms. Furthermore, the interactions of crown ethers and cations as measured by $\Delta G°$ for reaction 1 do not correlate with the size of the hole in the crown or with cation size (cf. Tables I and III).

The $\Delta H°$ and $\Delta S°$ values for reaction 1 in methanol lead to the following important, and in some respects unexpected, features: (i) the selectivity of crown ethers relative to the cations is enthalpy

driven, (ii) the largest $|\Delta H°|$ values are found with K⁺, regardless of the crown ether, and (iii) for each cation, the $|\Delta H°|$ value decreases according to the decrease in ring size.

The interpretation of $\Delta H°$ and $\Delta S°$ values is a somewhat complex task because these values arise from a combination of various phenomena that, taken together, control complexation equilibria. Such processes will feature in the following discussions. The first of these discussions concerns the variations of the $\Delta S°$ and $\Delta H°$ values for reaction 1 in going from K⁺ to Na⁺ with 18-crown-6 as ligand. These variations are rigorously given by relationships 8 and 9 (where CE = 18-crown-6). The first

$$\Delta S°(M⁺ = Na⁺) - \Delta S°(M⁺ = K⁺) = [S°_{K⁺} - S°_{Na⁺}] + [S°_{CENa⁺} - S°_{CEK⁺}] \quad (9)$$

$$\Delta H°(M⁺ = Na⁺) - \Delta H°(M⁺ = K⁺) = [H°_{K⁺} - H°_{Na⁺}] + [H°_{CENa⁺} - H°_{CEK⁺}] \quad (10)$$

bracketed term on the right-hand side of these relationships corresponds to the desolvation of the cation upon complexation. The complete or partial substitution of the cation solvation shell by the cyclic polyether has already been pointed out as an important factor in the complexation equilibria.[8,9] As regards the estimation of the $\Delta S°$ variation, interactions of the complexed cation with solvent molecules would contribute to making the $S°_{CENa⁺}$ and $S°_{CEK⁺}$ unequal. However, such a situation is not expected with the large ligand 18-crown-6, which is able to encage Na⁺ and K⁺ completely. Volume and compressibility measurements have shown that the complexes of 18-crown-6 should not be surrounded, if at all, by a very structured solvation shell in an aqueous solution.[9,20] Moreover, in a ¹H NMR study of the complexes of dibenzo-18-crown-6, the substitution of K⁺ by Ba²⁺ (whose ionic radii are nearly equal) led to virtually identical incremental shifts (which can be correctly estimated according to the Buckingham treatment) in methanol and acetone.[21] This

(20) Høiland, H.; Ringseth, J. A.; Vickingstad, E. *J. Solution Chem.* **1978**, 7, 515–520.

meant that solvent effects were ruled out.[21] These results lead to the view that the complexes of 18-crown-6 with Na$^+$ and K$^+$ are characterized by similar interactions with the solvent, and it is therefore tempting to make the assumption

$$S^\circ_{\text{18-crown-6-Na}^+} \simeq S^\circ_{\text{18-crown-6-K}^+} \qquad (11)$$

This assumption is a priori a very rough approximation especially as regards water, for which solvent minor changes induce non-negligible entropy variations. In the early stages, however, it is rewarding to use this approximation, whose validity will be discussed later. In this way, (9) becomes

$$\Delta S^\circ(M^+ = Na^+) - \Delta S^\circ(M^+ = K^+) =$$
$$[\delta S^t(K^+)_{\text{solvent}\leftarrow\text{gas}} - \delta S^t(Na^+)_{\text{solvent}\leftarrow\text{gas}}] + 1.6 \text{ eu} \quad (12)$$

where the term 1.6 eu stands for the difference between gas-phase translational entropies of cations K$^+$ and Na$^+$.

The contribution $\delta S^t(M^+)_{\text{solvent}\leftarrow\text{gas}}$ (M$^+$ = Na$^+$ or K$^+$) is more negative for the smaller cation. According to the data corresponding to K$^+$ and Na$^+$,[12,22] (12) leads to an estimated ΔS° variation that is equal to 10.4 eu in methanol. This value corresponds very well to the observed increase in the ΔS° values in going from K$^+$ to Na$^+$ (9.2 eu) for reaction 1 with 18-crown-6 as ligand. In water, the corresponding entropy increase going from K$^+$ to Na$^+$ is equal to 7.7 eu. Once again, this value is consistent with the estimation provided by the transfer entropies of the cations[12] according to (12), i.e., 10.1 eu. Enthalpy variation associated with the desolvation of the cations (i.e., [$\delta H^t(K^+)_{\text{solvent}\leftarrow\text{gas}} - \delta H^t(Na^+)_{\text{solvent}\leftarrow\text{gas}}$]) also contributes to the difference between the ΔH° values measured for reaction 1 with K$^+$ and Na$^+$. However, in this case and contrary to what has been observed for entropy, desolvation is largely compensated for by the cation–crown ether interactions that are present in the complexes. These interactions have been assumed to be stronger for K$^+$ than for Na$^+$ when the ligand is 18-crown-6.[4-7] However, the opposite has also been claimed, especially for dibenzo-18-crown-6.[23] As we shall see, our results confirm that, in the case of 18-crown-6, the interactions are indeed stronger for Na$^+$ than for K$^+$. The difference between solvation enthalpies of cations Na$^+$ and K$^+$ [$\delta H^t(K^+)_{\text{solvent}\leftarrow\text{gas}} - \delta H^t(Na^+)_{\text{solvent}\leftarrow\text{gas}}$] amounts to -20.7 and -20.2 kcal/mol with methanol and water as solvents, respectively.[12,22] According to (10), the difference [$H^\circ_{\text{CENa}^+} - H^\circ_{\text{CEK}^+}$] (CE = 18-crown-6) assumes the values of -15.5 and -16.2 kcal/mol when methanol and water are used as solvents, respectively. This enthalpy difference is therefore almost solvent independent and reflects the intramolecular interactions within the complexes. These interactions seem to be very different for the complexes of Na$^+$ and K$^+$. They are stronger in the case of the smaller cation.

In this context, it is interesting to question the assumption (eq 11) that lies behind the discussion concerning the comparison of the ΔS° and ΔH° values.

Indeed, $S^\circ_{\text{CEK}^+}$ cannot be strictly equal to $S^\circ_{\text{CENa}^+}$ if $H^\circ_{\text{CEK}^+}$ and $H^\circ_{\text{CENa}^+}$ do not assume the same value. However, as we will demonstrate, the equality of the two entropy terms can be considered to be a rough approximation in solution. We can factorize these entropy terms according to the relationship

$$S^\circ_{\text{CEM}^+} =$$
$$S^\circ_{\text{libr,CEM}^+} + S^\circ_{\text{tr,CEM}^+} + S^\circ_{\text{rot,CEM}^+} + S^\circ_{\text{mix,CEM}^+} + S^\circ_{\text{solv,CEM}^+} \quad (13)$$

(where CE = 18-crown-6, M$^+$ = Na$^+$ or K$^+$). The first term on the right-hand side of this relation is associated with the libration motion of the cations within their complexes. The frequencies of the quantized motions of ions Na$^+$ and K$^+$ encaged in dibenzo-18-crown-6 were measured at 214 and 168 cm^{-1}, respectively.[24] The vibrational entropies associated with these frequencies can be estimated to be equal to 2.0 and 2.5 eu according

to the harmonic oscillator approximation. These values lead to a difference of -0.5 eu in going from K$^+$ to Na$^+$. As regards the $S^\circ_{\text{libr,CEM}^+}$ variation, this difference has to be doubled since the displacements of the cation in the "plane" of polyether oxygen atoms depend on at least two normal coordinates. Therefore, $S^\circ_{\text{libr,CEM}^+}$ makes a contribution to [$S^\circ_{\text{18-crown-6-Na}^+} - S^\circ_{\text{18-crown-6-K}^+}$] that is less than -1 eu. The entropies $S^\circ_{\text{tr,CEM}^+}$ associated with the translation motion of the complexes only differ by $(3/2)R \ln [m_{\text{18-crown-6-Na}^+}/m_{\text{18-crown-6-K}^+}]$ (where m stands for the molecular mass), i.e., -0.2 eu. Moreover, this value is certainly overestimated, because it corresponds to the perfect gas-phase situation. The same remark is partially valid for the rigid-rotation entropy contribution. The products of the principal inertia moments are similar for the two complexes, i.e., 4.17×10^9 amu^3 Å^6 for CENa$^+$ and 7.26×10^9 amu^3 Å^6 for CEK$^+$ (these values being calculated on the basis of the solid-state geometry of the complexes[25,26]). The corresponding contribution to [$S^\circ_{\text{18-crown-6-Na}^+} - S^\circ_{\text{18-crown-6-K}^+}$] is only -0.6 eu, and considering the overestimation previously emphasized, this contribution is also very small. However, symmetry plays an important role at the level of the rigid-rotation entropy contribution, and this is true independent of the physical state. The symmetry number of the CEM$^+$ complex is 6 in the case of K$^+$ but 1 in the case of Na$^+$, at least in the solid phase.[25,26] Moreover, the Na$^+$ complex is chiral, and a mixing entropy term, $S^\circ_{\text{mix,CEM}^+}$ (i.e., $+R \ln 2$), characterizes this complex. The sum of these two contributions to [$S^\circ_{\text{18-crown-6-Na}^+} - S^\circ_{\text{18-crown-6-K}^+}$] is therefore equal to ($R \ln 6 + R \ln 2$), i.e., 4.9 eu.

Taking into account all the terms given in (13) except $S^\circ_{\text{solv,CEM}^+}$, which will be discussed later, it appears that [$S^\circ_{\text{18-crown-6-Na}^+} - S^\circ_{\text{18-crown-6-K}^+}$] is equal to -1.2 or $+3.1$ eu, depending on whether we consider a similar symmetry for the two complexes in solution or two different symmetries as they appear in the crystal. In the first case, $\Delta S^\circ(Na^+) - \Delta S^\circ(K^+)$ can be estimated to be 8.9 and 9.2 eu in water and methanol, respectively. In the second case, however, we obtain 13.2 and 13.5 eu in the two solvents (by way of comparison, the same differences based on assumption 11 are 10.1 eu in water and 10.4 eu in methanol). All these values are not very different from the experimental values (7.7 ± 1.3 eu in water and 9.2 ± 0.9 eu in methanol). It would be easy to choose any set of calculated values and to justify the incongruity with respect to the experimental values by an ad hoc selection of the solvation entropy contributions, $S^\circ_{\text{solv,CEM}^+}$. Taking into account the great difficulty in estimating the $S^\circ_{\text{solv,CEM}^+}$ terms, even roughly, we prefer to conclude that at the level of accuracy we are dealing with, these contributions are similar for the two solvents and more or less independent of the nature of the cation. Further calculation could lead to the conclusion that this description is more valid for methanol than for water.[27]

Now we are therefore able to present a general description of the behavior of the two alkaline cations Na$^+$ and K$^+$ relative to 18-crown-6. The large difference between the ΔH° terms associated with the 1:1 complex formation is due to the desolvation of the cation and to the crown ether–cation interactions. These interactions are stronger with Na$^+$ than with K$^+$. The complex is such that the interactions with the solvent appear not to be very important or, at least, to be more or less independent of the nature of the cation and of the solvent. At the level of ΔS°, the largest contribution is associated with the desolvation process, which is obviously solvent and cation dependent. After careful analysis, the rough assumption expressed by (11), i.e., $S^\circ_{\text{18-crown-6-Na}^+} \simeq S^\circ_{\text{18-crown-6-K}^+}$, in methanol or water appears valid, but this con-

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(27) In the case of water as a solvent, the great difficulty of estimating entropy variations, even roughly, has already been pointed out. Furthermore, it is interesting to note that the transfer enthalpies of methanol → water of both 18-crown-6 complexes virtually assume the same values; since they are deduced from the measured value of δH^t(18-crown-6)$_{\text{water}\leftarrow\text{methanol}}$, i.e., -13.6 kcal/mol, and from the $\delta H^t(M^+)_{\text{water}\leftarrow\text{methanol}}$, i.e., $+4.9$ kcal/mol for Na$^+$ and $+4.4$ kcal/mol for K$^+$,[22] they are equal to -2.6 and -2 kcal/mol for the Na$^+$ and K$^+$ complexes, respectively.

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Table IV. $\Delta G°$, $\Delta H°$, and $T\Delta S°$ Values (kcal/mol) of Reactions 1 and 2[a]

		methanol					water		
		ref	(1) M+ = K+	(2) M+ = K+	(1) M+ = Na+	(2) M+ = Na+	ref	(1) M+ = K+	(1) M+ = Na+
18-crown-6	$\Delta G°$	b	−8.42 ± 0.05		−5.94 ± 0.04		b	−2.92 ± 0.03	
		8	−8.27 ± 0.04		−5.95 ± 0.03		7	−2.77 ± 0.14	−1.09 ± 0.14
		6	−8.32 ± 0.05		−5.89 ± 0.05		6	−2.81 ± 0.05	
							9	−2.79 ± 0.00	−1.12 ± 0.03
	$\Delta H°$	b	−12.70 ± 0.10		−7.50 ± 0.07		b	−5.60 ± 0.20	
		8	−13.41 ± 0.06		−8.4 ± 0.3		7	−6.21 ± 0.01	−2.25 ± 0.10
	$T\Delta S°$	b	−4.28 ± 0.15		−1.56 ± 0.11		b	−2.68 ± 0.23	
		8			−2.4		7	−3.4	−1.1
15-crown-15	$\Delta G°$	b	−4.90 ± 0.02	−2.0[c]	−4.26 ± 0.04	−3.6 ± 0.9	7	−1.01 ± 0.11	−0.95 ± 0.14
		8	−5.13 ± 0.24	−3.70 ± 0.04	−4.75 ± 0.01		9	−1.04 ± 0.03	−0.92 ± 0.04
	$\Delta H°$	b	−7.70 ± 0.05		−5.50 ± 0.20				
		8	−7.70 ± 0.30	−8.10 ± 0.50	−4.99 ± 0.03		7	−4.10 ± 0.10	−1.50 ± 0.04
	$T\Delta S°$	b	−2 80 ± 0.07		−1.24 ± 0.24				
		8	−2.57	−4.40	−0.24		7	−3.1	−0.54
12-crown-4	$\Delta G°$	b	−2.16 ± 0.02	−0.78 ± 0.2	−1.95 ± 0.03	−3.16 ± 0.03			
	$\Delta H°$	b	−5.1 ± 0.35		−3.0 ± 0.30	−6.7 ± 1.8			
	$T\Delta S°$	b	−2.94 ± 0.37		−1.05 ± 0.33	−3.54 ± 1.8			

[a] 1 kcal = 4.184 kJ. $T = 25$ °C, $K_{assoc} = 0$ L·mol⁻¹. [b] This work. The uncertainties on the estimated parameters are defined in the text under Methods. In particular those that are associated with $\Delta G°$ values are deduced from standard deviations for the stepwise equilibrium ratios multiplied by the value of the t-Student variable, t, which defines a probability equal to 0.975 ($t_{0.975} > 2$). [c] For this reaction, the uncertainty on K_2 is higher than the K_2 values.

clusion cannot be generalized to other systems. As we stated in our experimental section, we have tested the influence of the association constants of KCl and NaCl in methanol on the complexation thermodynamic parameters. As it is obvious from Table IV (compared to Table I), all the thermodynamic quantities are quite unsensitive to the choice of K_{assoc} (10 or 0 L·mol⁻¹). However, according to a very recent work,[13c] in the case of potassium chloride it seems that the most reliable results are those obtained for $K_{assoc} \simeq 10$ L·mol⁻¹. This is the reason why we consider the values given in Table I to be our best,[28] at least in the case of the potassium cation.

Turning to the complexing properties of 12-crown-4 and 15-crown-5, it is important to note that cation complexation by such small crown ethers does not completely remove the cation solvation shell, and this was especially shown by volume and compressibility measurements in the case of 15-crown-5 complexes in aqueous solution.[9] The interpretation of the thermodynamic parameters is more complicated in this case. Work is in progress in our laboratory to find a general explanation for the experimental values we have found. The formation of the 2:1 complexes that we have observed with 15-crown-5 and 12-crown-4 supports the view that

in the 1:1 complexes the presence of cyclic polyether does not exclude specific interactions of the cation with other ligands, i.e., another crown ether molecule or solvent molecules. The $\Delta H°$ and $\Delta S°$ values of reaction 2 (solvent:methanol) also compensate in the same way as in reaction 1. Given the loss of three additional rigid-rotation degrees of freedom, the $\Delta S°_2$ values are noticeably lacking in negativity as compared to those measured for reaction 1. Also interesting is the preferential formation of 2:1 complexes with the smaller cation Na⁺ in place of K⁺. This is consistent with the contribution of a cavity term[29] to the chemical potential of solutes: the larger the solute, the more positive the contribution. It is not surprising that the formation of 2:1 complexes is not subordinate to the relative sizes of the crown hole and of the cation. This has been shown in another way in a recent study of Na⁺ complexes with dicoronands in pyridine as a solvent.[30] "O₆–O₄" spirobis(crown ether) has indeed been shown to form 2:1 complexes in which the Na⁺ ion is bound to at least one O₆ ring.[30]

At all events, the thermodynamic study of complexation equilibria 1 and 2 shows that crown-ring and cation sizes must be abandoned as correct predictors of the selectivity of crown ethers toward alkaline cations in solution.

(28) In order to test other possible causes of inaccuracy, we have also checked the influence on the final results of the use of Debye–Hückel's law in its complete form

$$\log \gamma = (-A(\mu)^{1/2})/(1 + aB(\mu)^{1/2}) \qquad (14)$$

where A has previously been defined and where a is the distance of closest approach of the ions and B a function of the solvent and temperature. For $a = 5$ Å, which is considered to be a reasonable assumption,[12] the thermodynamic parameters are essentially unaffected if (14) is used in place of (5) (cf., Table IV).

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