METAL ION COMPLEXING BY CRYPTAND 222 IN SOLUTIONS. A THERMODYNAMIC APPROACH

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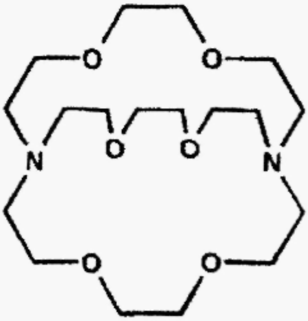
Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8.8.8) hexacosane) is a well known sequestering agent for metal ions in solution. Thermodynamic data concerning the ligand itself and its metal complexes in various solvents enable the understanding of the ability of cryptand 222 to complex preferentially certain cations and of how solvents affect these preferences. Some comments on the possibility of employing the "cryptate assumption" for obtaining individual ion thermodynamic properties are presented.

1. INTRODUCTION

Ligands that are able to "hide" metal cations from the solution in a selective manner play an important role in analytical chemistry. They enable the determination by various methods of a given cation in the presence of interfering cations or group of cations. Since the discovery of the polyoxadiazamacrobicyclo ligands known as cryptands by Lehn and coworkers /1/, a considerable amount of work has been published on the complexing abilities of these ligands for metal cations. Prominent among the workers have been the groups of Buschmann /2/, Danil de Namor /3/, Cox and Schneider /4/, Arnaud-Neu and Schwing-Weil /5/ and Kolthoff /6/ among others, and some of these have continued working in this area till today. Comprehensive tables summarising up to 1995 the complex stabilities of metal ions with various ligands of this kind were published by Izzat and coworkers /7/ but with few comments on the reported thermodynamic quantities. Among the cryptant ligands, the particular complexing agent 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8.8.8)hexacosane, CA registry

23978-09-8, Scheme 1, known as cryptand 222 (abbreviated in the following to C222) has been studied extensively. It is also known, commercially, as Kryptofix 222, and has found wide application in analytical chemistry (e.g., /8/) and other fields of chemistry. Of the >1000 references in Chemical Abstracts to C222, some 200 are labelled "uses in analysis".



Scheme 1: Structural formula of cryptant 222.

In C222 the two tertiary amine nitrogen atoms are connected by three $-C_2H_4OC_2H_4OC_2H_4-$ chains enclosing a cage, in which metal cations can be enclosed, coordinated by up to eight donor atoms: six oxygen and two nitrogen ones. The chains are sufficiently flexible to allow fairly large cations to enter and the conformations available bring the donor atoms with the highest affinity for the metal cation to its vicinity for effective bonding. The cation inside the cage is more or less shielded from the surrounding solvent, and its interaction with the donor atoms of the ligand is at the expense of its lost solvation. The C222 cryptand is known to exist in three conformations: the exo-exo, exo-endo, and endo-endo ones, depending on the positions of the unshared electron pairs on the tertiary nitrogen atoms, whether outside (exo) the cavity or inside (endo) it. These conformations depend on the environment (crystalline compounds or solutions) and conversion among them is time-dependent though rapid. Some cations, however, cannot enter the cage because of their excessive size or other causes, but may still be complexed by the ligand in a so-called "exclusive" position, and then the cation does not lose all or most of its solvation sphere. All these phenomena and effects can be elucidated by studying the thermodynamics of the association equilibria.

The metal ion complexing abilities of C222 have been more extensively studied than those of the similar bicyclic ligands cryptand 221 and cryptand 211 that have one or two of the chains between the nitrogen atoms shorter ($-C_2H_4OC_2H_4-$ instead of $-C_2H_4OC_2H_4OC_2H_4-$) or similar monocyclic ligands with fewer chains altogether: cryptands 22 and 21. Therefore only cryptand 222 is reviewed in the present article. In order to understand better the capabilities of C222 to complex metal cations the thermodynamic properties of C222 and the thermodynamics of its metal binding equilibria are discussed in the following sections of this review.

2. SOLUTION THERMODYNAMICS OF THE CRYPTAND C222

2.1 Solubilities and enthalpies of solution

The cryptand C222 is very soluble in water, due to ready accessibility of its six etheral oxygen and two tertiary amine nitrogen atoms to hydrogen bonding by the water molecules. The tertiary amine nitrogen atoms make the compound a fairly strong base. Some hydrolysis, i.e., protonation of at least one of the nitrogen atoms, takes place in water and other protic solvents, unless some small amount of uncomplexable base, such as tetraethylammonium hydroxide, is added. However, no recorded value for the solubility of C222 in water could be found. Its solubility in other solvents than water is considerably lower, but again, except for two hydrocarbon solvents immiscible with water, only values for distribution ratios between a solvent, S, and water were reported, see Section 2.2 below. The solubilities of C222 at 25 °C in cyclohexane (0.238 M) and in tetradecane (0.086 M) ($1\ M = 1\ mol\ dm^{-3}$) reported by Cox and Schneider /9/ and the partition coefficients of C222 between these solvents and water, corrected for hydrolysis, and reported by Abraham *et al.* /10/, 0.0249 and 0.0129, respectively, permit the calculation of its solubility in water. The resulting values for the solubility of C222 in water at 25 °C are: 9.5_6 and 6.6_7 M or an average of 8.1±1.4 M (in agreement with the standard molar Gibbs energy of solution deduced from these data /9/, $\Delta_{Solution}G^\circ = -5.0\pm0.7\ kJ\ mol^{-1}$, within the wide uncertainty limits).

The standard molar enthalpies of solution of the cryptand C222 in water and in other solvents are measurable calorimetrically. That in water is $\Delta_{solution}H^\circ = -24.73\pm0.17\ kJ\ mol^{-1}$ /10/, but those in other solvents, mainly aprotic ones, are generally positive, e.g., 34.47 kJ mol^{-1} in propylene carbonate and 32.93 kJ mol^{-1} in acetonitrile /11/, see also Section 2.2. Values of $\Delta_{\text{solution}}H°$ in other solvents are readily calculated from $\Delta_{\text{solution}}H°(\text{S}) = \Delta_{\text{solution}}H°(\text{water}) + \Delta_t H°(\text{C222, water}\rightarrow\text{S})$ and the values of the enthalpies of transfer, $\Delta_t H°$, listed in Table 1.

2.2 Gibbs energies, enthalpies, and entropies of transfer

The standard molar Gibbs energy of transfer of the cryptand C222 from one solvent, e.g., water, to another solvent, S, i.e., $\Delta_t G°(\text{C222, water}\rightarrow\text{S})$ could, in principle, be obtained from its solubilities in the two solvents. The provision is that the cryptand does not form crystal solvates, hence is the same chemical substance in equilibrium with the two solvents. A further condition is that the solubilities are sufficiently low for the activities of C222 to be adequately represented by its concentrations. In the case of water as the solvent the latter condition is, obviously, not met in view of the very large solubility (see above). Under these circumstances, the transfer Gibbs energy of C222 could, again in principle, be obtained from partition experiments between two completely immiscible solvents. A good approximation to such a pair is the system water + tetradecane and indeed such data are available /10/. Hexadecane was used as an "intermediate" for obtaining the partition ratios of C222 between the two miscible solvents methanol and N-methylpyrrolidin-2-one and their mixtures /12/. Alternatively, the solubilities of a metal cryptate salt, $\text{MC222}^+\text{A}^-$, in water and the non-aqueous solvent, yielding $\Delta_t G°(\text{MC222}^+\text{A}^-, \text{water}\rightarrow\text{S})$, combined with the values of the single ion transfer Gibbs energies $\Delta_t G°(\text{M}^+, \text{water}\rightarrow\text{S})$ and $\Delta_t G°(\text{A}^-, \text{water}\rightarrow\text{S})$ obtained by the use of a suitable extra-thermodynamic assumption, such as the TATB one, and the complexation equilibrium constants of M^+ with C222 (see Section 3.1 below) result in the value of $\Delta_t G°(\text{C222, water}\rightarrow\text{S})$. This round-about method was used to give $\Delta_t G°(\text{C222})$/kJ mol^{-1} values for water-miscible solvents, such as ethanol (4.35) and 1-propanol (4.44). On the basis of this and similar systems the data for $\Delta_t G°(\text{C222, water}\rightarrow\text{S})$ are shown in Table 1.

On the other hand, if the partition takes place between partially mutually soluble solvents /13/, such as water and nitromethane or water and any of the higher alcohols, 1-butanol to 1-decanol, completely different values are obtained, since they pertain to mutually saturated liquid phases. When the water content of the non-aqueous solvent is > 3 mol kg^{-1} the partition constant of the cryptand is near unity (it 'sees' mainly the water in the water-

Table 1

Thermodynamic functions of transfer of the cryptand C222 from water to other pure solvents or water-saturated solvents (marked by *) at 25 °C.

Solvent	$\Delta_t G°$/ kJ mol^{-1}	$\Delta_t H°$/ kJ mol^{-1}	$\Delta_t S°$/ J K^{-1} mol^{-1}
MeOH	4.73	58.24	180
EtOH	4.35		
1-PrOH	4.44		
1-BuOH*	–0.24		
1-PeOH*	–0.08		
1-HxOH*	–0.04		
1–HpOH*	0.29		
1-OcOH*	0.92		
1-DcOH*	1.42		
t-PeOH	0.77		
c-Hexanol	1.10		
PhCH$_2$OH	0.80		
2-PhC$_2$H$_4$OH	0.96		
PhOMe	0.92		
PhOEt	0.26		
c-Hexanone	3.44		
PhC(O)Me	2.53		
PC	7.95	59.20	172
DMSO	6.44	60.33	181
DMF	6.53	59.28	177
NMPy	2.63		
MeNO$_2$	7.07	56.15	164
MeCN	4.60	57.66	178
iPrCN	1.57		
PhCH$_2$CN	2.09		
NCC$_4$H$_8$CN	2.67		
PhCN	7.24	56.36	165
CHCl$_3$	–5.71		
CH$_2$Cl$_2$	–3.99		

rich solvent phase) and the absolute value of $\Delta_t G°$(C222, water→S) /kJ mol^{-1} is < 0.3. When, however, the water content is lower, larger positive values of $\Delta_t G°$(C222, water→S)/kJ mol^{-1} are obtained, e.g., 0.92 for 1-octanol, 1.42 for 1-decanol, and 9.2 for nitromethane. Except for the hydrocarbons mentioned above and chloroform and dichloromethane, where the directly measured distribution ratios between these solvents and water is <<1, most of the other solvents have distribution ratio values <1, hence positive values of $\Delta_t G°$.

Values for the enthalpies of transfer from water into non-aqueous solvents, $\Delta_t H°$(C222, H_2O→S) are shown in Table 1. These have been obtained from the enthalpies of solution, to form dilute solutions in the respective solvents. Also shown in this Table are the standard molar entropies of transfer $\Delta_t S°$(C222, H_2O→S) obtained from the enthalpies and Gibbs energies: $\Delta_t S°(\text{C222, H}_2\text{O}\rightarrow\text{S}) = [\Delta_t H°(\text{C222, H}_2\text{O}\rightarrow\text{S}) - \Delta_t G°(\text{C222, H}_2\text{O}\rightarrow\text{S})]/T$. In all cases, it is seen, the enthalpy changes control the transfer thermodynamics, but they are largely compensated by the entropy changes. The water molecules released from hydrogen-bonding on the transfer of C222 from water to the target solvent S are not completely replaced for solvating the C222 by the non aqueous solvent molecules, which, on the other hand, are able to interact by van-der-Waals forces with the ethylene groups of the cryptand. Conformational changes of the cryptand also take place when this is transferred from water to non-aqueous solvents and these contribute to the entropy changes.

2.3 Hydration of the cryptand

The conformations taken up by the cryptand C222 in the isolated form, i.e., in the gas phase, were explored by high temperature annealed molecular dynamics simulations /14/. The cryptand was found to be rather flexible, but in condensed phases it adopted conformations induced by the molecular environment, e.g., by a protic solvent such as water. Further molecular dynamics simulations in the presence of >800 water molecules per C222 molecule (i.e., in dilute aqueous solution) showed that a conformation (called **K**) not favoured in the gas phase had a significantly better interaction with water than other ones, including the one (called **I I**, for in-in) in which the crystalline C222 is present before dissolution in water. This **K** conformation has three water molecules outside the cage, bridging by hydrogen bonds with D_3 symmetry between the three etheral chains, rather than being located inside the cage. The total water binding energy, −331 kJ mol^{-1}, arises mainly as the sum of the energy of binding to the six oxygen atoms of the cryptand, −372 kJ mol^{-1}, with a small contribution from the binding to the two nitrogen atoms, −38 kJ mol^{-1}, and a repulsive contribution of the 18 $-CH_2-$ groups, 79 kJ mol^{-1} /14/. The conformational fluctuations in aqueous solutions are significantly reduced by the bridging water molecules, in comparison with the isolated cryptand molecule. The water, thus, stabilises a conformation (the **K** one, see below) that is suitable for metal ion complexation.

2.4. Thermodynamics of Protonation of the Cryptand

The cryptand C222 is a relatively strong base, due to its two tertiary amine nitrogen atoms. It is protonated (hydrolyzed, solvolyzed) to some extent in protic solvents, in particular water, and extensive protonation takes place in the presence of a not too weak acid in the solution. This protonation occurs in two separate stages, to form the monoprotonated, $HC222^+$ and the diprotonated H_2C222^{2+} species. They have distinct pK values for the dissociation of the protonated species: pK_1 for $HC222^+ \rightarrow H^+ + C222$ and pK_2 for $H_2C222^{2+} \rightarrow H^+ + HC222^+$.

Lehn and Sauvage /15/ and Anderegg /16/ determined the prononation equilibrium constants of the two stages of C222 in aqueous solutions at 25 °C in good agreement with each other's results. An ionic medium of 0.05 or 0.10 M tetramethylammonium chloride or bromide was used. The values are shown in Table 2. Somewhat higher pK values (by ~0.3 units) were obtained by them and others when the ionic medium was 0.10 M tetramethylammonium perchlorate or 0.25 M background salt. Anderegg /16/ also determined calorimetrically the enthalpy of the protonation, hence derived the entropy of protonation, also shown in Table 2. Recent re-determinations /17/ of the pK values and the enthalpies of protonation of C222 in aqueous solutions yielded somewhat higher values. Values in only a few other solvents have subsequently been determined, see Table 2.

The conformations of the protonated C222 species are not clear from the magnitudes of these thermodynamic quantities. It was suggested that the first proton is attached to the nitrogen atom in the exo position but that the second one is located inside the cavity, bonding to the two nitrogen atoms in the endo conformation. This is compatible with the relatively small negative enthalpy and large positive entropy accompanying the conformational change for the second protonation, compared with non- and mono-cyclic diamines /16/. However, other interpretations have also been suggested, i.e., that the

Table 2

Thermodynamic functions for the protonation of the cryptand C222 at 25 °C.

Protonation reaction	pK^{a}	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	$\Delta C_p°$/J K^{-1} mol^{-1}	$\Delta V°$/cm^3 mol^{-1}
	Solvent: water^{b,c}					
$H^+ + C222 \rightarrow HC222^+$	9.71	−55.42	−45.2	34.3	−60	−2
	10.21	−58.28	−51.9	21.5		
$H^+ + HC222^+ \rightarrow H_2C222^{2+}$	7.31	−41.72	−18.3	76.6	−102	4
	7.55	−43.09	−29.9	43.6		
	Solvent: methanol^{d}					
$H^+ + C222 \rightarrow HC222^+$	10.72	−51.19				
$H^+ + HC222^+ \rightarrow H_2C222^{2+}$	9.03	−51.54				
	Solvent: acetonitrile^{e}					
$H^+ + C222 \rightarrow HC222^+$	18.6					
	Solvent: benzonitrile^{f}					
$H^+ + C222 \rightarrow HC222^+$	18.40					
$H^+ + HC222^+ \rightarrow H_2C222^{2+}$	15.18					

[a] For the reverse, deprotonation reaction. [b] Values of pK, $\Delta G°$, $\Delta H°$, and $\Delta S°$ from /16/, upper values, and from /17/, lower values. [c] Values of $\Delta C_p°$ and $\Delta V°$ from /18/. [d] From /39/. [e] From /8/. [f] A.F. Danil de Namor *et al.*, *J. Chem. Soc. Faraday Trans.* 1993, **89**, 2727.

first protonation takes place in the endo-endo form, whereas repulsion between the positive charges causes the diprotonated species to be in the exo-exo form. An attempt to resolve this question by means of the heat capacity and volume change measurements /18/, shown in Table 2, was unsuccessful. However, molecular dynamics simulations /14/ provided an answer. It was found that intrinsically (i.e., for an isolated molecule) endo-protonation was favoured over exo-protonation due to internal N–H···O hydrogen bonding that makes the cage more rigid. In an aqueous solution the mono-protonated $HC222^+$ endo conformation binds one water molecule, which is hydrogen bonded inside the cage (compared with the three water molecules outside the cage of the neutral cryptand /14/).

3. THERMODYNAMICS OF METAL ION COMPLEXATION

3.1. Gibbs energies of complex formation

For the complexation reaction:

$$M^{n+}{}_S + C222_S \leftrightarrows [MC222]^{n+}{}_S \tag{1}$$

where subscript S denotes a solvent, the standard molar Gibbs energies, $\Delta_{comp}G°$, are generally obtained from the corresponding equilibrium constant $K(M^{n+}, S)$ from $\Delta_{comp}G° = -RT \log K$. Since equilibrium (1) is reached without a change in the charges, it should depend only slightly on the ionic strength when the latter is <0.1 mol dm^{-3}, hence the value of K at finite concentrations is commonly taken to represent the infinite dilution or standard value. It is often tacitly assumed that no ion pairs of $M^{n+}{}_S$ and of $[MC222]^{n+}{}_S$ with the anion present are formed, or else such large anions (as BF_4^-, ClO_4^-, or $CF_3SO_3^-$) are explicitly chosen that do not tend to form ion pairs in sufficiently dilute solutions.

Buschmann /17/ discussed the merits and disadvantages of the various methods for the determination of K. The direct potentiometric determination with an ion selective electrode appears to be the most accurate, permitting standard errors of ±0.01 in log K to be attained with careful work. This then leads to $\Delta_{comp}G°/kJ\ mol^{-1}$ values known to ±0.06 or to one to two decimals. Conductometric determinations of K incur larger errors, in spite of the high precision of the conductivity measurements, due to the implicit dependence of the conductivity on K and the participation of both $M^{n+}{}_S$ and $[MC222]^{n+}{}_S$

in the conductance. The same is true of the calorimetric titration technique, useful when $1 < \log K < 6$, where the estimated standard errors are ±0.05 in log K (leading to ±0.28 in $\Delta_{\text{comp}}G°/\text{kJ mol}^{-1}$), but the added bonus is the simultaneous determination of the standard molar enthalpy of equilibrium (1) (see below). Still less accurate are the methods using the displacement of cation M_2^{n+} by cation M_1^{n+}, where equilibria of the type:

$$M_1{}^{n+}\text{s} + [M_2\,C222]^{n+}\text{s} \rightleftarrows [M_1\,C222]^{n+}\text{s} + M_2{}^{n+}\text{s} \qquad (2)$$

are followed potentiometrically or calorimetrically and where K of M_2 is known and used to determine that of M_1. The displaced or displacing cation M_2 commonly used is either H^+ in a pH-metric titration or Ag^+ in a potentiometric titration. The lower accuracy is due partly to the slowness of such displacements, so that long times for equilibration are required, and partly to the accumulation of errors. Values of $\Delta_{\text{comp}}G°/\text{kJ mol}^{-1}$ are then obtainable to no better than ±0.5 (one decimal).

Some further methods, not considered by Buschmann /17/, are spectroscopic and extraction measurements. The former include nmr of suitable metal nuclei, notably Cs^+, where the chemical shift of the solvated and complexed cation contribute proportionately to the observed chemical shift /19/. UV-vis spectrophotometry is advantageously combined with extraction, if a second ligand, such as *p*-nitrophenoxide, that forms complexes with the metal cations absorbing light differently from the free ligand and that can be readily extracted into an immiscible solvent, is added /13/. Extraction, however, need not be used, as was the case for the competitive complexation of C222 and murexide /20/. The accuracy attainable with these methods is generally inferior to those obtained by potentiometry.

Selected values of $-\Delta_{\text{comp}}G°/\text{kJ mol}^{-1}$ of uni-, di- and tri-valent metal cations in water and various non-aqueous solvents, calculated from log K values available in the literature till the end of 2003, are shown in Table 3. The $-\Delta_{\text{comp}}G°/\text{kJ mol}^{-1}$ for the alkali metal cations are also shown in Fig. 1, where the solvents are arranged in a series according to increasing strength of complexaton of K^+ by C222 (more negative values of $\Delta_{\text{comp}}G°$). It is seen that the other alkali metal cation complexes have lower stabilities and generally follow suit in the series of solvents, that the values for Na^+ and Rb^+ are quite similar, as are also those of Li^+ and Cs^+, but less so. Outstanding outlyers are the values for Li^+ and Na^+ in nitromethane. It should be noted that the K and

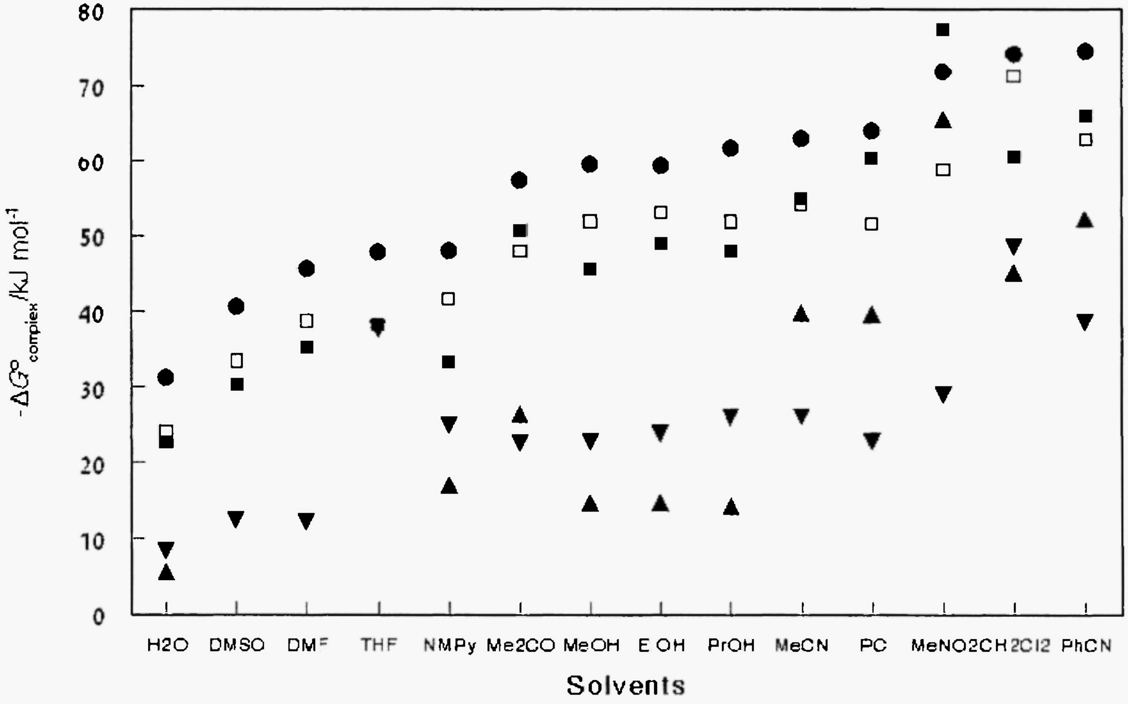


Fig. 1: The Gibbs energy of complexation, $-\Delta_{\text{complex}}G^\circ$, of the alkali metal cations with cryptand C222 at 25 °C in diverse solvents, ordered in ascending order of stabilities of the potassium complexes. The symbols are: ▲ Li^+, ■ Na^+, ● K^+, □ Rb^+, and ▼ Cs^+.

Table 3

Selected values of $-\Delta_{complex}G°/\mathrm{kJ\ mol^{-1}}$ of cations with cryptand 222 at 25 °C

Cation	H_2O	MeOH	EtOH	PrOH	Me_2CO	PC	NMP	DMSO	DMF	$MeNO_2$	MeCN	PhCN	CH_2Cl_2
Li^+	5.59 ^{a}	14.8 ^{e}	14.67 ^{h}	14.21 ^{j}	26.37 ^{d}	39.61 ^{a}	16.95 ^{a}	<6 ^{a}		65.48 ^{h}	39.84 ^{h}	52.17 ^{h}	45.1 ^{m}
Na^+	22.72 ^{a}	45.55 ^{a}	48.92 ^{a}	47.89 ^{j}	50.74 ^{d}	60.16 ^{a}	33.28 ^{t}	30.37 ^{a}	35.22 ^{a}	77.40 ^{h}	54.97 ^{h}	65.98 $^{h\ h}$	60.5 ^{m}
K^+	31.22 ^{a}	59.42 ^{a}	59.93 ^{a}	61.65 ^{l}	57.31 ^{d}	63.87 ^{a}	~48 ^{a}	40.58 ^{a}	45.55 ^{a}	71.81 ^{h}	62.85 ^{h}	74.55 ^{h}	74.2 ^{m}
Rb^+	24.20 ^{a}	51.94 ^{f}	52.97 ^{a}	51.92 ^{j}	47.89 ^{d}	51.49 ^{a}	41.55 ^{a}	33.39 ^{a}	38.70 ^{a}	58.79 ^{h}	54.23 $^{h\ h}$	62.79 ^{h}	71.3 ^{m}
Cs^+	8.39 ^{a}	22.83 ^{f}	23.80 ^{a}	25.97 ^{j}	22.60 ^{d}	22.83 ^{a}	~25 ^{a}	12.50 ^{d}	12.33 ^{a}	29.11 ^{h}	26.09 ^{a}	37.62 ^{h}	48.5 ^{m}
Cu^+								23.00 ^{j}			10.85 ^{j}	17.01 ^{h}	
Ag^+	54.8 ^{b}	69.64 ^{g}	65.70 ^{a}	62.79 ^{j}	77.86 ^{p}	92.87 $^{p\ p}$	50.29 ^{p}	41.90 ^{p}	56.62 ^{p}	101.09 ^{h}	50.69 ^{p}	56.91 ^{p}	
Tl^+	37.90 ^{a}	57.36 ^{f}	63.01 ^{a}		62.10 ^{p}	68.15 ^{t}		35.4 ^{k}	46.01 ^{t}		70.21 ^{t}		
NH_4^+	28.5 ^{r}								36.90 ^{u}				
Mg^{2+}	<11.4 ^{e}	27.63 ^{i}											
Ca^{2+}	26.09 ^{b}	46.46 ^{f}			73.63 ^{d}	61.47 $^{a\ f}$		10.90 ^{l}	21.92 ^{a}		59.9 ^{a}		
Sr^{2+}	47.15 ^{b}							30.02 ^{a}	41.67 ^{a}				
Ba^{2+}	53.97 ^{b}	73.58 ^{f}				97.61 ^{d}		36.30 ^{h}	45.92 ^{h}		102.18 $^{h\ h\ h}$		
Co^{2+}	16.0 ^{d}										18.38 ^{w}		
Ni^{2+}	25.1 ^{d}										26.02 ^{w}		
Cu^{2+}	38.87 ^{c}	49.03 ^{c}						29.1 ^{k}			101.6 ^{k}		
Zn^{2+}	16.0 ^{d}	<23.4 ^{c}											
Cd^{2+}	38.8 ^{h}	59.42 ^{c}						20.5 ^{k}			113.0 ^{k}		
Hg^{2+}	103.9 ^{b}					131.3 ^{s}		86.2 ^{k}			119.3 ^{k}		
Pb^{2+}	70.55 ^{b}	73.92 ^{d}						41.27 ^{l}			150.1 ^{k}		

Table 3 (continued)

Cation	H_2O	MeOH	EtOH	PrOH	Me_2CO	PC	NMP	DMSO	DMF	$MeNO_2$	MeCN	PhCN	CH_2Cl_2
Sm^{2+}						100.5 [q]			75.3 [i]				
Eu^{2+}	59.8 [y]								84.5 [i]		73.6 [i]		
Yb^{2+}									81.6 [i]				
UO_2^{2+}						44.0 [t]							
La^{3+}	36.82 [o]					91.9 [i]					85.96 [x]		
Ce^{3+}						81.0 [n]							
Pr^{3+}	36.36 [o]					90.3 [i]		18.38 [l]			87.61 [x]		
Nd^{3+}						91.27 [h]		18.61 [l]			84.13 [x]		
Sm^{3+}	33.90 [o]					98.7 [i]			15.4 [i]				
Eu^{3+}	33.68 [o]					98.2 [i]			18.72 [x]		80.60 [x]		
Gd^{3+}						95.9 [i]		19.69 [l]	18.78 [x]		82.42 [x]		
Tb^{3+}						95.1 [i]			17.58 [x]		78.20 [x]		
Dy^{3+}						97.6 [i]							
Pr^{3+}	36.36 [o]					90.3 [i]		18.38 [l]			87.61 [x]		
Nd^{3+}						91.27 [h]		18.61 [l]			84.13 [x]		
Sm^{3+}	33.90 [o]					98.7 [i]			15.4 [i]				
Eu^{3+}	33.68 [o]					98.2 [i]			18.72 [x]		80.60 [x]		
Ho^{3+}	35.4 [o]							19.81 [l]			85.62 [x]		
Er^{3+}						95.9 [i]					79.22 [x]		
Yb^{3+}						99.4 [i]		23.46 [l]	17.98 [x]		80.67 [x]		

[a] ref. 31. [b] ref 16. [c] ref. 39. [d] ref. 17. [e] ref. 15. [f] ref. 6. [g] ref. 21. [h] ref. 10. [i] ref. 22. [j] ref. 29. [k] ref. 23. [l] ref. 20. [m] ref. 11. [n] ref. 43. [o] ref. 40. [p] ref. 25. [q] ref. 42. [r] ref. 44. [s] ref. 45. [t] ref. 46. [u] ref. 26. [v] ref. 48. [w] ref.47. [x] ref. 49. [y] ref. 24.

$\Delta_{\mathrm{comp}}G°$ listed in Table 3 do not distinguish between various conformations of the $[\mathrm{MC222}]^{n+}{}_\mathrm{S}$ complex, i.e., whether "inclusive" or "exclusive". These terms refer respectively to the cation being completely shielded from the solvent by the cryptand or, when it is too large for the cavity in the cryptand, to its being partly exposed to the solvent.

There are values of $-\Delta_{\mathrm{comp}}G°/\mathrm{kJ\ mol^{-1}}$ not shown in Table 3, i.e., for solvents not listed there. These are notably for K^+ in various (water-saturated) solvents /13/: 38.13 in *t*-pentanol, 41.61 in *c*-hexanol, 45.26 in benzyl alcohol, 46.35 in *c*-hexanone, 47.83 in benzyl cyanide, 50.57 in hexanenitrile, 50.74 in 2-phenylethanol, 53.03 in *i*-butanenitrile, and 55.42 in acetylacetone, obtained from extraction equilibria of the *p*-nitrophenoxide salts. Other values are 35.8 and 30.4, respectively /21/, for Ag^+ and Tl^+ in hexamethyl phosphoric triamide, 32.0 for Na^+ and 54.2 for Ag^+ in tetramethylurea /23/, 13.41 for Cs^+ in N-methylformamide and 10.39 in N,N-dimethylacetamide from NMR chemical shifts /19/, 21.01 in the latter solvent and 104.17 in tetramethylene sulphone for Cu^{2+} and 12.44 in propanenitrile and 13.36 in butanenitrile for Cu^+ from potentiometry /25/ and for Ag^+ 47.43 in N,N-dimethylacetamide /25/ and 21.98 for Cs^+ in chloroform /26/.

The values of $-\Delta_{\mathrm{comp}}G°$ due to the work of different authors are generally in agreement within ±1 kJ mol^{-1}. This should be a realistic estimate of the accuracy attainable when $3 \leq \log K \leq 10$, very weak or very strong complexing posing special problems. In both cases the displacement method, eq. (2), have often been employed, but the equilibria are attained rather slowly. In view of this and the trends noted in Fig. 1, some reported values of $-\Delta_{\mathrm{comp}}G°$ should be discounted as probably unreliable. Thus, the estimates of the complex stabilities of Li^+ and Cs^+ in water by Morel *et al.* /18/ and of Tl^+ in water by Anderegg /16/ are particularly low and may be disregarded. In other cases this is more difficult to judge, the values being compared with those of other authors that are in better agreement. Notable outlyers are the high value for Sr^{2+} in methanol /27/, the low value for Tl^+ in PC /28/, the lower values for Cs^+ /19/ and for Ba^{2+} /20/ in DMSO, the higher values for Na^+ and Cs^+ /23,27/ and the lower value for K^+ /23,25/ in acetonitrile.

The solvent effects on the complex stabilities illustrated in Fig. 1 can be ascribed most directly to the de-solvation of the metal cations $M^{n+}{}_\mathrm{S}$ when they become complexed and embedded completely in the cryptate $[\mathrm{MC222}]^{n+}{}_\mathrm{S}$. Hence, the stronger the solvation the weaker the complexation, and the order of solvents should follow their 'basicities' or abilities to donate pairs of non-bonding electrons to the metal cations. This property is described by the Kamlet-Taft β_{KT} or the Gutmann *DN* parameters of the solvents that are in very good mutual correlation. The order of the solvents shown in Fig. 1 follows almost exactly the order of decreasing β_{KT} values, water being displaced to the head of the series, possibly due to its ability to multiply solvate the cations also in solvation shells beyond the first by hydrogen bonding. The alcohols, methanol, ethanol, and 1-propanol are somewhat displaced from their positions according to β_{KT} to the middle of the series with respect to the complexation of K^+. This is visually evident (Fig. 1) in particular for Li^+. Disruption of the hydrogen bonding structure of the alcohols as well as of water by the six bulky hydrophobic –CH_2CH2– groups of $[MC222]^{n+}{}_S$, compared with the more hydrophilic ligand $C222_S$ may be the cause.

The complex stabilities of various cations with C222 in a given solvent are dictated by the balancing of two trends. These are the de-solvation Gibbs energies of the cations and their abilities to be accommodated inside the cavity of the ligand and interact with all six oxygen atoms and eventually also with the two nitrogen atoms in the endo-endo conformation of the ligand. It is assumed that the energy invested in the de-solvation is recovered more or less fully by these interactions. The size of the cavity of C222 is given by its 'diameter', 0.28 nm /15/. The relative values for the alkali metal cations thus depend on the ability of the cation to fit snugly into the cryptand cage that is obviously best for K^+ with a diameter of 0.276 nm for the bare (unsolvated) cation. Similarly, among the alkaline earth cations it is Ba^{2+} (diameter 0.272 nm) that can be accommodated best. Somewhat smaller cations, such as Ag^+ (0.230 nm), Sr^{2+} (0.226 nm), and Pb^{2+} (0.236 nm), may not be able to interact closely with all six oxygen atoms and would be discriminated against. This becomes more pronounced with still smaller cations, such as Na^+ (0.204 nm), Ca^{2+}(0.200 nm), and La^{3+} (0.210 nm) and in particular Li^+ and divalent transition metal cations. It is interesting to note that the divalent lanthanide cations Sm^{2+}, Eu^{2+}, and Yb^{2+} are much more strongly complexed than their trivalent analogues in DMF. Another example for this effect is the greater stability of the Eu^{2+} (0.234 nm) than the Eu^{3+} (0.190 nm) complex in acetonitrile by a factor of ca. 3000 /22/. On the other hand, cations that are larger than the cavity are complexed "exclusively", hence do not interact with all the available binding sites, but need not lose all their solvation Gibbs energies. Thus, Rb^+ (0.294 nm), Tl^+ (0.300 nm), and in particular Cs^+ (0.340 nm) are too large to be completely enclosed by the ligand, hence their diminished complex stabilities. Tetraalkylammonium cations appear not to be complexed by C222 at all, hence their salts serve as background electrolytes in potentiometric or polarographic determinations.

3.2. Enthalpies of complex formation

The standard molar enthalpy changes, $\Delta_{comp}H°$, for reaction (1) can be obtained from the application of the van't Hoff relationship to equilibrium constants K determined at several temperatures /19,20/. This method, however, is much less accurate than the determination of $\Delta_{comp}H°$ by either calorimetric titration or from the enthalpies of solution of salts in the presence and absence of excess ligand /10,11,29/. In calorimetric measurements the time for reaching equilibrium is of importance, so that the method is less suitable if a replacement reaction (2) is needed, since this is notoriously slow. On the other hand, the enthalpies can be measured with good accuracy also for very strong complexes, where the determination of the stability constants may run into difficulties. However, small enthalpies of complexation, below, say, 5 kJ mol^{-1}, as is the case for Li^+ in DMF and DMSO, cannot be measured at all accurately by calorimetric titration. The standard molar enthalpies of solution of a salt of a given cation and its cryptate salt with the same anion, as well as that of the ligand C222 itself, in a given solvent S_1 provide a value of the enthalpy of complexation in this solvent if the corresponding data in another solvent, S_2 are known. The standard molar enthalpies of transfer, $\Delta_t H°(S_1 \rightarrow S_2) = \Delta_{Solution}H°(S_2) - \Delta_{Solution}H°(S_1)$ of all the species involved are used for this purpose.

The observed heats are practically all exothermic (Cd^{2+} in water and Co^{2+} and Ni^{2+} in methanol being apparent exceptions), and selected values of $-\Delta_{comp}H°$/ kJ mol^{-1} are listed in Table 4 as far as available in the literature by the end of 2003. These data are generally valid with one decimal, although in some cases only an approximate, integral value is available. In a few cases values have been reported to two decimals, this being hardly justified by the average standard errors of ±0.8 kJ mol^{-1} encountered in the determinations /10,11,29,30/.

The agreement among values of the enthalpies for given metal cation and solvent reported by different authors is considerably worse than for the Gibbs energies, being generally within 5 kJ mol^{-1}. In some cases, however, serious discrepancies are encountered, the most blatant ones being the following. The low value of $-\Delta_{comp}H°$/ kJ mol^{-1} = 23.4 of Sr^{2+} in water was obtained from the equilibrium constants in the range 15 to 35 °C calculated as the ratio of

Table 4

Selected values of $-\Delta_{\mathrm{complex}}H°/\mathrm{kJ\ mol^{-1}}$ of cations with cryptand 222 at 25°C

Cation	H_2O	MeOH	Me_2CO	PC	DMSO	DMF	$MeNO_2$	MeCN	PhCN
Li^+	5.9 [a]	7.0 [a]	23.9 [c]	36.4 [a]			59.1 [a]	29.8 [a]	47.0 [a]
Na^+	31.9 [a]	44.6 [a]	55.2 [c]	64.1 [a]	46.9 [a]	40.0 [a]	85.7 [a]	61.0 [a]	66.1 [a]
K^+	48.4 [a]	71.3 [a]	69.0 [c]	71.9 [a]	59.3 [a]	55.3 [a]	80.3 [a]	71.3 [a]	79.5 [a]
Rb^+	49.2 [a]	74.9 [a]	64.9 [c]	68.2 [a]	59.2 [a]	47.6 [a]	73.6 [a]	70.2 [a]	74.2 [a]
Cs^+	21.7 [a]	49.9 [a]	40.0 [c]	41.3 [a]	35.1 [a]	31.0 [a]	51.4 [a]	43.5 [a]	49.7 [a]
Ag^+	53.6 [a]	76.6 [a]	71.6 [h]	102.6 [h]	51.4 [a]	65.6 [a]	72.9 [f]	53.5 [a]	59.4 [a]
Tl^+	55.2 [b]					66.1 [e]			
Mg^{2+}									
Ca^{2+}	4.6 [m]	22.0 [c]	73.5 [c]						
Sr^{2+}	44.4 [b]	42.5 [c]	73.7 [c]						
Ba^{2+}	59.8 [b]	68.9 [c]	91.7 [c]	103.4 [a]	47.8 [a]	54.8 [h]		108.8 [a]	
Co^{2+}		−8.1 [c]							
Ni^{2+}		−13.5 [c]							
Cd^{2+}	−2.1 [b]								
Hg^{2+}	66.7 [b]								
Pb^{2+}	57.7 [b]	72.7 [c]							
La^{3+}				77.5 [a]				132.8 [i]	
Pr^{3+}				94.8 [a]				119.5 [i]	
Nd^{3+}				104.9 [a]				117.2 [i]	
Sm^{3+}								105 [g]	
Eu^{3+}	−16.7 [k]					29.6 [i]		136.8 [i]	
Gd^{3+}						23.5 [i]		113.6 [i]	
Tb^{3+}						18.1 [i]		148.6 [i]	
Ho^{3+}								99.2 [i]	
Er^{3+}				113.0 [d]				133.6 [i]	
Yb^{3+}						15.5 [i]		93.5 [i]	

[a] ref. 3. [b] ref. 16. [c] ref. 2. [d] ref. 5. [e] ref. 21. [f] ref. 4. [g] ref. 22. [h] ref. 26 [i] ref. 49. [j] ref. 41. [k] ref. 48. [l] ref. 44. [m] ref. 50.

the forward to backward rate constants. This method is not as accurate as the calorimetric method employed /16,25/ to obtain the higher value, 44.4, that ought to be preferred (the same applies to Ca^{2+}, although there the discrepancy is not so large). It is much more difficult to decide between the values for Na^+ and Ag^+ in methanol, where the values reported by Buschmann /27/ are 7-8 kJ mol^{-1} lower than those reported by Abraham /10/, and Danil de Namor *et al.* /11,29,30/, and for Ag^+ these are still lower than those reported by Cox, Schneider *et al.* /21,30/. For the alkali metal cations in acetone, the $\Delta_{comp}H^\circ$ data of Buschmann /27/ follow the $\Delta_{comp}G^\circ$ data, so that the more negative value ascribed to Cs^+ by Popov and coworkers /19/ from the temperature dependence of nmr data appears to be unreliable. In the cases of Pr^{3+} in PC and Ag^+ in DMF, the later calorimetric $-\Delta_{comp}H^\circ$ values /4,5/ should be preferred, since the earlier values were obtained from the van't Hoff relation applied to the stability constants over a relatively short range of temperatures /16,20/. It should be noted that the value $-\Delta_{comp}H^\circ$/ kJ mol^{-1} = 38.2 reported for Rb^+ in PC by Izatt *et al.* /7/ is a misprint of the correct value 68.2 /29/.

The enthalpies of complexation with the cryptand C222 of series of cations in a given solvent are rather close to the corresponding Gibbs energies, although showing a somewhat less pronounced maximum for K^+ for the alkali metal cations. What was said above concerning the compensation of the de-solvation and interaction Gibbs energies applies to the enthalpies too. Since enthalpy data are available for fewer solvents than Gibbs energy data, the dependence on solvent properties is less clear cut. However, the differences between $-\Delta_{comp}H^\circ$ values for a given cation, say K^+, are smaller than between the $-\Delta_{comp}G^\circ$ values (the slope of a plot of $-\Delta_{comp}H^\circ$ vs. $-\Delta_{comp}G^\circ$ for this cation is 0.745), so that the entropy of complexation (see below) does play a role in the selectivity of C222 for various cations in different solvents.

3.3 Entropies of complex formation

The entropy of the complexation reaction (1) necessarily obeys the relation $\Delta_{comp}S^\circ = (\Delta_{comp}H^\circ - \Delta_{comp}G^\circ)/T$, hence, rather than report here the original $\Delta_{comp}S^\circ$ values published by diverse authors, they were calculated as averages from the selected more reliable entries in Tables 3 and 4. Table 5 shows these values of $\Delta_{comp}S^\circ$/J K^{-1} mol^{-1}, which, in view of the probable errors mentioned above, should be taken to be valid to no better than ±10 J

K^{-1} mol^{-1}. They are reported, therefore, as integral values only. A striking feature of Table 5 is that there are both positive and negative entries, in contrast to the almost universally exoergic entries in Tables 3 and 4.

Most of the entries show reasonable systematics: the values for the alkali metal cations become increasingly negative from Li^+ to Cs^+ (or have a negative extremum at Rb^+). The values for Ag^+ are generally in between those for Na^+ and K^+ (as are the ionic radii of these cations). The values for the divalent cations are generally positive but decrease (and may become negative) as the size of the cations increase, and the few data for the trivalent

Table 5

Selected values of $\Delta_{complex}S°/J\ K^{-1}\ mol^{-1}$ of cations with cryptand 222 at 25 °C

	H_2O	MeOH	Me_2CO	PC	DMSO	DMF	$MeNO_2$	MeCN	PhCN
Li^+	-1	23	8	7			21	34	17
Na^+	-31	3	-15	-13	-55	-16	-28	-20	0
K^+	-58	-40	-39	-27	-63	-33	-29	-28	-16
Rb^+	-85	-77	-57	-56	-87	-30	-50	-54	-10
Cs^+	-45	-92	-58	-58	-77	-63	-75	-58	-4
Ag^+	9	-23	-19	-27	-81	-27		-7	-8
Tl^+	-58					-74			
NH_4^+		-71							
Mg^{2+}				74					
Ca^{2+}	78	82		-9					
Sr^{2+}	9	82		-10					
Ba^{2+}	-19	16		-19	-39	-16		-22	
Cd^{2+}	137								
Hg^{2+}	125								
Pb^{2+}	50	4							
La^{3+}				48				-56	
Pr^{3+}				-13				-101	
Nd^{3+}				-46				-138	
Sm^{3+}								-143	
Eu^{3+}	169							-122	
Er^{3+}				-57					

lanthanides are also fairly systematic. In some cases, however, there are departures from a smooth variation that may point to inadequacies in the $\Delta_{comp}H^{\circ}$ and $\Delta_{comp}G^{\circ}$ data. Such cases may include the highly negative $\Delta_{comp}S^{\circ}$ values for Rb^+ in water and DMSO and the insufficiently negative value for this cation in DMF.

It is difficult to detect any systematics in the $\Delta_{comp}S^{\circ}$ values for a given cation in the various solvents or to indicate a dominant solvent property that affects these values. Although the $\Delta_{comp}S^{\circ}$ values are small with respect to the entropies of solvation of the cations in the various solvents, when the former are added to the latter they lead to the entropies of the following process:

$$M^+_g + C222_S \rightarrow [MC222^+]_S \qquad (4)$$

for the combined complexation and solvation of the gaseous alkali metal cations and Ag^+, M^+_g. These values (in J K^{-1} mol^{-1}) are practically independent of the cation and the solvent for the dipolar aprotic solvents PC (–216±10), DMSO (–228±9), DMF (–218±8), nitromethane (–218±5), and acetonitrile (–226±8) /11,29,30/. Entropies of solvation of these cations in (or transfer from water into) acetone and benzonitrile are unfortunately not available for extending this generalisation. The corresponding values for the protic solvents water (–156±18) and methanol (–155±15) are different, and in each solvent show greater variability.

The entropies of complexation are due to balancing the numbers of solvent molecules released from the solvation shells of the cation and the ligand on complexation with the donor atoms that are immobilised in the cavity of the cryptate and the solvent molecules that are immobilised by solvating the complex. A negative inherent entropy change, $-R \ln 2 = -6$ J K^{-1} mol^{-1}, due to the diminution of the number of particles in solution by the complexation must also be taken into account. For most of the trivalent lanthanides the field generated by the cation inside the cavity is sufficiently large for the complex to be still solvated by many solvent molecules, hence the entropies are negative. For most of the divalent cations the balance is the other way around, indicating that complete de-solvation of the cation on complexation cannot be compensated by solvation of the complex, leading to positive entropies. For the less strongly solvated alkali metal cations the binding to the six oxygen atoms of the cryptand overshadows the de-solvation, hence the negative entropies.

3.4. Heat capacities and volumes of complexation

The heat capacity changes of the complex formation reaction (1) have been studied essentially by just one research group, that of Morel-Desrosier and Morel /32/, and in only two solvents: water and methanol. That the ligand itself is solvated – and to different extents – in these two solvents is indicated by the different values of the standard partial molar heat capacity at constant pressure, C_p^{∞}/J K^{-1} mol^{-1} of C222: 1050±6 and 727+6, in water and methanol, respectively. The values reported for the complexation reaction, $\Delta_{\mathrm{compl}}C_p^{\circ}$, have been written /32/ in terms of the electrolytes MCI and MCl_2 for the alkali metal and alkaline earth metal chlorides, rather than in terms of the cations. Since the electrolytes and the cryptates are completely ionically dissociated in water at infinite dilution and presumably also in methanol at 0.05 mol kg^{-1} (at which concentration they were reported), the values shown in Table 6 are written in terms of the cations.

It was pointed out by Morel *et al.* /32/ that the heat capacity and entropy changes are well correlated in aqueous solutions except for Ca^{2+} (but there were no data for Li^+ and Cs^+, that might also have been out of line), see Fig. 2. This was ascribed to the predominance of 'internal' changes of the

Table 6

$\Delta_{\mathrm{complex}}C_p^{\circ}$/J K^{-1} mol^{-1} and $\Delta_{\mathrm{complex}}V^{\circ}$/cm^3 mol^{-1} of cations with cryptand 222 at 25 °C /18/.

	$\Delta_{\mathrm{complex}}C_p^{\circ}$/J K^{-1} mol^{-1} [a]		$\Delta_{\mathrm{complex}}V^{\circ}$/cm^3 mol^{-1} [b]	
	H_2O	MeOH	H_2O	MeOH
Li^+		2	-4±4, (0.7)[c]	-1.8
Na^+	71	-34	8±1, 14.2	10.6, 15[d]
K^+	39	-88	22±1, 17.4	15.9, 16,[d] 13[d]
Rb^+	11	-82	24±1, 14.2	13.1
Cs^+		-26	19±3, (1.4)[c]	7.4, 7,[d] 10[d]
Ca^{2+}	-27	-343	26.1	10.0
Sr^{2+}	125	-89	26.6	14.6
Ba^{2+}	77	-245	28.3	9.7

[a] Average standard error ±4 J K^{-1} mol^{-1}. [b] Average standard error ±0.6 cm^3 mol^{-1}. [c] Estimated, see text. [d] Ref. /33/.

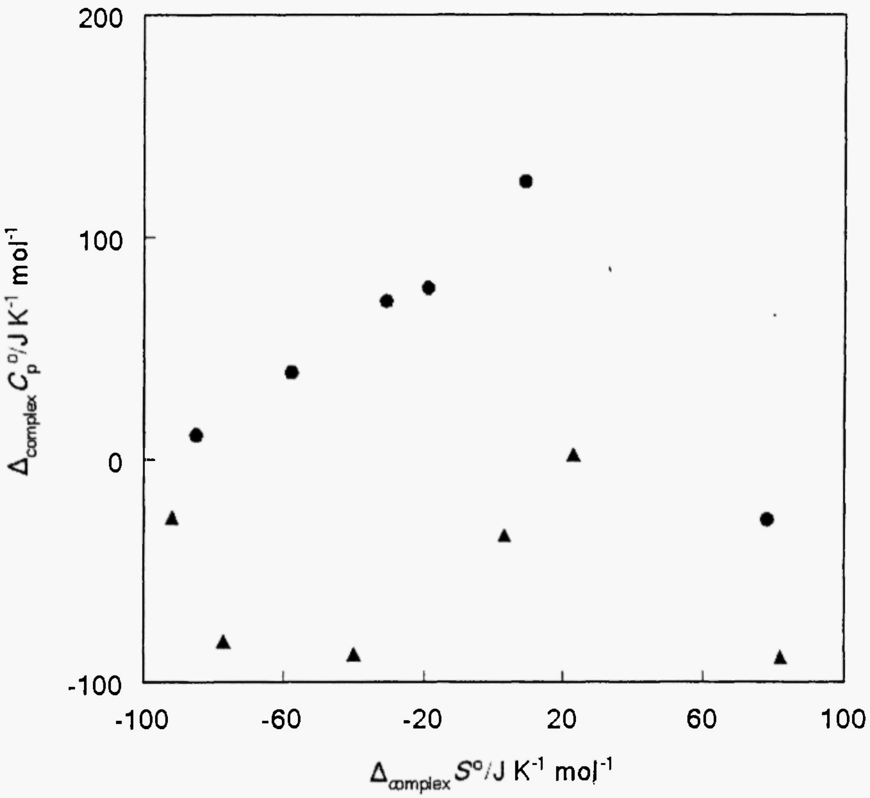


Fig. 2: Plots of the heat capacities, $\Delta_{complex}C_p{}^o$, and entropies, $\Delta_{complex}S^o$, of complexation of alkali and alkaline earth metal cations with cryptand C222 at 25 °C in water (●) and methanol (▲).

cryptand itself, which are of the same sign (negative) for the entropy and heat capacity. This picture becomes less clear when the data for the methanol solutions are added, since then not only does Ca^{2+} deviate from a simple correlation but also Ba^{2+} and possibly also Sr^{2+}. The explanation proposed /32/ for Ca^{2+} in terms of the different conformation of its cryptate is inadequate, since that should be independent of the solvent, so why do Sr^{2+} and Ba^{2+} obey the linear correlation in water but not in methanol? More data, preferably corroborated by work from other research groups, are needed in order to understand heat capacity changes for the complexation reaction (1).

The standard partial molar volume of the cryptand C222 in water, V^∞, is 315.5±0.5 cm^3 mol^{-1}, provided that protonation is prevented by the addition of a low concentration of base (Et_4NOH), as found by Morel-Desrosiers and Morel /18/. The values of V^∞ in methanol, acetonitrile and DMSO are 322.5, 329.8, and 340.8 $cm^3\ mol^{-1}$, respectively, and values in other solvents have been shown in a diagram to depend on the molar volumes of the solvents themselves, increasing with the latter but in an irregular manner /33/.

Complexation of the alkali metal cations in water /18/ causes expansion that reaches a maximum with K^+, Table 6. The entries there for $\Delta_{compl}V^\circ$ differ from earlier data of the same authors /18/ ($\Delta_{compl}V^\circ/\ cm^3\ mol^{-1}$ = 8 for Na^+, 22 for K^+, and 24 for Rb^+) who also gave values for Li^+ (−4) and Cs^+ (19), albeit all with a larger standard error than the later data. The latter, given only for Na^+, K^+, and Rb^+, are more consistent with $V^\infty(MC222^+,Cl^-)$ − $V^\infty(M^+,Cl^-)$ − $V^\infty(C222)$, so that this expression can be used with $V^\infty(MC222^+,Cl^-)$ of the earlier publication to yield the estimates for Li^+ and Cs^+ shown in Table 6. The $\Delta_{compl}V^\circ$ data for the alkaline earth complexes in Table 6 are compatible with the same value of $V^\infty(C222)$ and values of $V^\infty(MC222^{2+},2Cl^-)$ reported later on for Ca^{2+} and Ba^{2+}, showing that Ca^{2+} does not exhibit, as far as the volume is concerned, the extraordinary behaviour ascribed to it /32/ regarding the entropy and heat capacity.

Little can be said about the volume changes found /32/ in methanol on complexation and shown in Table 6. Although $V^\infty(M^+,Cl^-)$ in methanol is available for the alkali metal chlorides from their ionic volumes of transfer from water to methanol, no corresponding values for the alkaline earth metal chlorides are available. A few data of $\Delta_{compl}V^\circ$ in other solvents are available: they are 25, 16, and 11 $cm^3\ mol^{-1}$ for sodium, potassium and cesium in acetonitrile and 2, 1, and 3 $cm^3\ mol^{-1}$ for these cations in DMSO (in both solvents as iodides).

The positive values of $\Delta_{compl}V^\circ$ in water and methanol but non-monotonous with the ionic sizes, Table 6, showing a balance between de-solvation, possible adjustments of cavity size to the cation size, and interactions in the cavity, again show that the complexation process is far from being a simple one. Thus, it is not only the de-solvation of the cation to be complexed, with its concomitant removal of the electrostriction of the solvent surrounding it, that affects $\Delta_{compl}V^\circ$, but also conformation changes of the cryptand. This is contrary to what was assumed by Letcher and co-workers /33/, requiring monotonous decrease of $\Delta_{compl}V^\circ$ with increasing cation sizes. Molecular dynamics simulation /14/ yielded radial distribution functions from which the radius of gyration of the complexes formed in water could be estimated. According to this method there should be a difference of

26.1 cm^3 mol^{-1} between the volumes of the sodium and potassium cryptates in water. The experimental value of this difference is only 3.2 cm^3 mol^{-1} (Table 6), showing that the radii of gyration are not a reliable indicator of the relative sizes of the cryptates.

3.5 Molecular dynamics simulations of the complexation energetics

Molecular mechanics calculations by Geue *et al.* /34/ showed four conformations of C222, two endo-endo, one endo-exo, and one exo-exo, of which the elongated endo-endo conformation had the least strain energy. Subsequently, Auffinger and Wippf /14/ in their comprehensive molecular dynamics simulation investigations showed that a certain conformation (called the **K** one) of the cryptand C222 is stabilised in aqueous solutions (see above) and that it is particularly suitable for the complexation of metal ions. Contrary to the expectation with regards to the shielding of the cations from the solvent by the cryptand, that does take place in aprotic non-aqueous solvents, in water the cryptates are hydrated. The radial distribution functions (rdf's) obtained from the simulation show that the cations are directly coordinated to water molecules. The total coordination number of the cation in the cryptate is the same as or larger than that in dilute aqueous solutions, their first shell hydration number. This coordination number is made up from the 6 oxygen atoms and 2 nitrogen atoms of the cryptant together with the oxygen atoms of the hydrating water molecules, Table 7. Furthermore, these

Table 7

Coordination numbers and interaction energies (in kJ mol^{-1}) of cations in aqueous solutions and in cryptates (with C222) /14/.

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Eu^{3+}
Hydration number	4.0	6.1	7.7	8.6	<10.8	7.9	8.9
Coordination number	10.0	8.9	9.3	9.3	9.3	11.0	11.9
Hydration energy	−577	−326	−310	−293	−285	−1678	−3728
Interaction energy[a]	−699	−427	−418	−423	−423	−1381	−3083

[a] This includes the direct cryptate-water and the cryptand cage-water interaction energies.

rdf's show that that the dislocation of the metal ion in the cryptate from the center-of-mass of the latter is small for the larger alkali metal ions (a distance of 0.02 nm for Cs^+) but large for Li^+ (0.16 nm), indicating that this cation is located in a facial rather than central position. Of the two water molecules that hydrate the Li^+ ion in the cryptate, one is held inside the cage by the ion and the other is outside it, the former resembling the hydration of $HC222^+$ (see above). No significant water structure beyond the first hydration shell of the alkali metal cryptates is indicated by the rdf's, but for the di- and trivalent cations water is "structured" in the second shell, i.e., between the etheral bridges and at larger distances, in the "hydrophobic $-CH_2-$ region" /14/.

When an aqueous cation is complexed by C222, the energy lost on partial dehydration is largely regained by the interaction of the cation with the donor atoms of the cryptand, but for the alkali metal cations there is further energy gain by the hydration of the cryptate, Table 7. On the other hand, for the multiply charged Ca^{2+} and Eu^{3+} cations stabilisation is achieved entropically, and only when hydration in the second and third shells around the cryptate is invoked, the enthalpy of complexation being near zero or positive /14/. However, the statement by Auffinger and Wipff /14/ that the entropy of complexation of cations in water is some 80 J K^{-1} mol^{-1} more positive than in other solvents is not borne out by the data shown in Table 5. Still, the uniqueness of water compared with other solvents is due to its small size and ability to penetrate into the cage and/or between the etheral chains of the cryptand and hydrogen bond to its oxygen (and nitrogen) atoms as well as hydrate the cations. This is consistent with the positive enthalpies and entropies of transfer of the cryptand C222 from water to other solvents, e.g., for transfer into methanol: 58 kJ mol^{-1} and 179 J K^{-1} mol^{-1}. Smaller values are found for transfer of the cryptates, since some solvation of the complexed cations by, e.g., methanol, has been indicated by the molecular dynamics simulations /14/. The speculation that primary amides, e.g., formamide, may also hydrogen bond to the cryptand (and bridge between two oxygen atoms by means of the $-NH_2$ group) as well as effectively solvate the cations inside the cage of the cryptates (by means of the carbonyl oxygen) is interesting in this respect, but has not so far been demonstrated experimentally.

4. THE CRYPTATE SINGLE-ION CONVENTION

Important analytical techniques, such as potentiometric determination by means of ion selective (or specific) electrodes, depend on the chemical potentials of individual ions. Whereas solute-solvent and solute-solute interactions pertain to the actual species in the solution, i.e., individual ions,. thermodynamic quantities are generally measurable only for electroneutral components, i.e., complete electrolytes. At infinite dilution the quantities for the individual ions, concern only ion-solvent interactions and are additive. Hence, the experimentally obtained standard molar thermodynamic quantities for electrolytes could be split into the single-ion contributions, provided that a method of doing so was available for any one electrolyte. Such a method cannot arise within the framework of thermodynamics itself, so that an extra-thermodynamic assumption or a convention must be adopted for obtaining the single-ion quantities.

For the thermodynamics of transfer of ions between different solvents many such assumptions have been proposed over the years as summarised by Marcus /35/ and several are in common use nowadays. These include the so-called ‘reference electrolyte’ assumption (mainly the TATB one, involving tetraphenylarsonium tetraphenylborate) and the ‘ion/molecule’ assumption (mainly the BBCr one, involving bisbiphenylchromium(I)/(0)). For the former assumption, thermodynamic quantities for the reference electrolyte (except for the partial molar volumes) are split evenly between the cation and the anion. The latter assumption maintains that the Gibbs energy of transfer of the complex ion, the single charge of which is well shielded from the solvent by the bulky ligand in which it is imbedded, equals that of the ligand itself. The justification of this assumption is as follows. The energy of the interaction with the solvent of the bulky ligand, whether alone or in the complex, is large. It takes place through dispersion (van-der-Waals) forces and should be independent of the presence or absence of the ion hidden inside the ligand. Compared with this interaction energy, that of the electrostatic interaction of the ion with the solvent through ion-dipole or ion-induced dipole interactions is small, due to the large distance between the imbedded ion and the solvent molecules, hence can be neglected.

Cryptands appear to be ideal ligands for the implementation of this idea. Villermaux and Delpuech /36/ were the first who suggested that a cryptand may be used for this purpose. The standard molar Gibbs energy of transfer of sodium chloride from water to aqueous methanol,

$\Delta_t G^\circ(\mathrm{NaCl,H_2O \rightarrow H_2O{+}MeOH})$, was obtained from the change in the composition of the vapour above the solutions when the electrolyte was added, following an experimental procedure proposed by Grunwald *et al.* /37/, in the presence of the cryptand (C221 was used). The assumption was made that since the sodium ions are shielded from the solvent, the measured quantity represents the transfer Gibbs energy of the chloride anion alone, $\Delta_t G^\circ(\mathrm{Cl^-,H_2O \rightarrow H_2O{+}MeOH})$. Similar measurements were made with sodium azide, to obtain $\Delta_t G^\circ(\mathrm{N_3^-,H_2O \rightarrow H_2O{+}MeOH})$. The results for both anions were tested against another commonly used extra-thermodynamic assumption, the TATB one, with satisfactory agreement. The authors concluded that "cryptates may open a route to a reliable scale of single-ion [free] energies of transfer".

Somewhat later, Lejaille *et al.* /23/ used the cryptand C222 with a much more convenient potentiometric titration method of the ligand with coulometrically generated silver ions. This procedure yielded the single-ion transfer activity coefficients of $\mathrm{Ag^+}$, ${}_t\gamma(\mathrm{Ag^+})$, using the assumption that ${}_t\gamma(\mathrm{AgC222^+}) = {}_t\gamma(\mathrm{C222})$ for transfer between methanol and water or non-aqueous solvents, where $RT \ln {}_t\gamma = \Delta_t G^\circ$ for any species. The alternative assumption, ${}_t\gamma(\mathrm{NaC222^+}) = {}_t\gamma(\mathrm{C222})$, obtained from competitive titration with silver ions in the presence of sodium ions, gave $\log {}_t\gamma(\mathrm{Ag^+})$ values in fair agreement (within 4.5 kJ mol^{-1} in $\Delta_t G^\circ$) with those determined from titrations in the absence of sodium ions. For transfer from methanol to water and to DMSO the results were also in similar agreement with those using the TATB assumption, but not so for transfer to acetonitrile (the difference in $\Delta_t G^\circ$ being 8.0 kJ mol^{-1}).

At about the same time Gutknecht *et al.* /21/ measured electrochemically the standard molar Gibbs energies and enthalpies of transfer of $\mathrm{Ag^+}$ and $\mathrm{K^+}$ from water to DMF, DMSO, PC, and acetonitrile, and $\Delta_t G^\circ$ for $\mathrm{Tl^+}$ to the former three solvents. They found that $\Delta_t G^\circ$ was independent of the cation and of the solvent within ±2.5 kJ mol^{-1} and that $\Delta_t H^\circ$ was independent of them within ±5.4 kJ mol^{-1}. Hence, for transfer of univalent cations between non-aqueous polar aprotic solvents (excluding transfers from water) the general assumptions:

$$\Delta_t G^\circ(\mathrm{MC222^+}) = \Delta_t G^\circ(\mathrm{C222}) \text{ and } \Delta_t H^\circ(\mathrm{MC222^+}) = \Delta_t H^\circ(\mathrm{C222}) \qquad (5)$$

could be formulated /21/ and taken as valid. Concerning the thermodynamics of the transfer of the ligand C222 itself see above, Section 2.2. The nmr chemical shifts of cations such as $^{7}Li^{+}$ and $^{205}Tl^{+}$ depend on the solvents in which they are situated, but cease to do so once completely shielded from the solvents by cryptands (C221 for Li^{+} and this as well as C222 for Tl^{+}, but not Cs^{+} /19/). These findings are in line with the abilities of cryptands to insulate cations from the solvents deduced from assumption (5).

The alternative assumption that $\Delta_t G°$(or $\Delta_t H°$)($MC222^{+}$) = 0, requiring that also $\Delta_t G°$(or $\Delta_t H°$(C222) = 0 within ±2.5 (or ±5.4) kJ mol^{-1}, was introduced too /21/. The latter, pertaining to an electroneutral species, can be tested experimentally without requiring an extra-thermodynamic assumption and was subsequently found by other workers to be more or less valid for the enthalpies. The standard molar heats of solution, $\Delta_{Solution}H°$(C222)/kJ mol^{-1} are 33.51 in methanol, 34.55 in DMF, 35.60 in DMSO, 34.47 in PC, 31.42 in nitromethane, 32.93 in acetonitrile, and 31.63 in benzonitrile /38/, averaging at 33.4±1.4 kJ mol^{-1}.

However, the general validity of the assumptions (5) was a subject of controversy and several groups of workers applied themselves to exploration of its limits. Abraham *et al.* /10/ extended this examination also to the derived entropies, i.e., $\Delta_t S°(MC222^{+}) = \Delta_t S°(C222)$, but limited it to transfer between water and methanol. They stressed in their test /10a/ that a necessary corollary to eq. (5) is that $\Delta_t G$(or H or S)°(M_1C222^{+}) = $\Delta_t G$(or H or S)°(M_2C222^{+}) for any two cations M_1^{+} and M_2^{+}, and since this was found *not* to be the case in transfers from water, assumption (5) was *not* generally valid for this solvent system. This discouraging result, concerning transfers from water as the reference solvent, was corroborated by Danil de Namor *et al.* /11, 29,30/, for transfers from water to DMF, DMSO, PC and acetonitrile. Kolthoff *et al.* /27/ explained the failure of eq. (5) for transfers involving *protic solvents*, in particular water, by the ready solvation (hydration) of the free cryptand C222 through hydrogen bonding to its six etheral oxygen atoms and two nitrogen atoms, which are not available to solvation once they are binding the cation in $MC222^{+}$. This is partly borne out by a molecular dynamics simulation study /14/ that, however, shows that not only the cryptant but also cryptated cations are hydrated to some extent, but in any case the cations are not at all adequately shielded from the aqueous solvent. A potentially protogenic solvents with a substantial Kamlet-Taft hydrogen bond donation parameter, α_{KT}, such as nitromethane, has also been found /3/ to cause failure of eq. (5) to hold for Ag^{+} cations.

Interestingly, for transfers of the alkali metal cations from methanol to DMF and to DMSO or between these two aprotic solvents eq. (5) was validated within ±1.5 k mol^{-1} for $\Delta_t G°$ and within ±6 kJ mol^{-1} for $\Delta_t H°$ /11,29,30/. Similarly, transfers from PC to these two aprotic solvents and to acetonitrile and nitromethane also validated assumption (5) within these limits for $\Delta_t G°$, $\Delta_t H°$, and $T\Delta_t S°$. It was further found that the single-ion values derived from the cryptate assumption agree well with those derived from the TATB one /11,29,30/. The same conclusion was reached by Kolthoff *et al.* concerning $\Delta_t G°$ for transfer of Na^+, K^+, Ag^+, and Tl^+ from PC to other polar aprotic solvents /27/.

The situation regarding divalent ions is less clear. With the cryptand C222 (but not C221) the assumption (5) was found /27/ to be "close to being valid" for Ba^{2+} for transfers from PC to DMF, DMSO, and methanol but this was not confirmed later. It was indeed found /30/ that $\Delta_t G°(BaC222^{2+}) \neq \Delta_t G°(C222)$ for transfers among methanol, DMSO and MeCN, and that $\Delta_t H°(BaC222^{2+}) \neq \Delta_t H°(C222)$ for transfers among these solvents as well as PC and DMF. Neither was assumption (5) valid for $\Delta_t G°$ of Cu^{2+} from methanol to DMSO /22/. For the trivalent lanthanides the enthalpies of transfer between PC and acetonitrile show even larger deviations from eq. (5). In fact, $\Delta_t H°(LnC222^{3+}) = \Delta_t H°(Ln^{3+})$, for Ln = La, Pr and Nd, meaning that the solvents discern enthalpy-wise the charge on the cation as if the cryptand were absent /30/.

In view of all this evidence it is clear that as long as the cations are monovalent, M^+, completely enclosed by the cryptand (i.e., being "inclusive"), and not requiring extensive conformational changes in the latter, dipolar aprotic solvents cannot distinguish between the free ligand C222 and the complex $MC222^+$ in terms of the thermodynamic functions of solvation. In some cases Li^+ and Cs^+ appear to be exceptions, being too small or too large for the cavity of C222, so that this conclusion is most generally valid for Na^+, K^+, and Ag^+. This still permits the assumption (5) to be employed by means of the convenient electrochemical titration method proposed by Lejaille *et al.* /23/ and by Gutknecht *et al.* /21/ with Ag^+ ions. Once the single-ion thermodynamic quantities have been determined for this one ion, those for all others, including anions and multivalent cations, are obtainable by application of the additivity principle to electrolyte transfer data. It is also convenient that the resulting values are in agreement with those obtained by the commonly used TATB method.

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