A Thermochemical Cycle for the Heat of Complexing of Na^+ and K^+ Cations with Cryptand 222 in Water and Methanol

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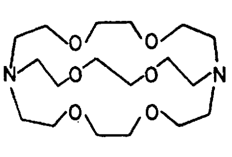
Summary Measurements of the enthalpy of transfer of cryptand 222 (I) and of the Na^+ and K^+ cryptates have been combined with heats of complex formation in water to yield by a thermochemical cycle the heats of complex formation in methanol.

Although the cryptands (macrobicyclic ligands) have been considered as models for cation carriers across regions of low dielectric constant, thermochemical measurements have been confined to water and aqueous methanolic solvents.[1] We now report the direct calorimetric determination of the enthalpy of transfer, ΔH_t°, from water to methanol of cryptand 222 (I) itself and of the cryptates, [Na^+ 222] and [K^+ 222],† in which the cations are contained within the ligand cage. There is an extraordinarily large ΔH_t° value for the ligand of nearly 14 kcal mol^{-1} (Table 1);‡ the ΔH_t° values for the two cryptates, although also large, are in the range expected for hydrophobic cations of considerable molar volume. In terms of enthalpy, the two cryptates, like the tetra-alkylammonium cations, are less stable in methanol than in water.



Cryptand 222
(I)

The ΔH_t° values for the cryptand and for the cryptates may be combined with the enthalpy changes for complex formation in water to yield a thermochemical cycle for the corresponding enthalpy changes in methanol (Table 2). For both cations Na^+ and K^+, complex formation is enthalpically favoured in methanol; this is entirely due to the

Table 1. Enthalpies of transfer from water to methanol, in kcal mol^{-1} at 298 K.[a]

Cryptand 222	Na^+	K^+	Et_4N^+	Pr_4N^+	Bu_4N^+	[Na^+222]	[K^+222]	Ph_4As^+
13·9	−4·9	−4·5	2·2	3·8	4·9	5·6	4·3	−0·4

[a] Values for the uncomplexed cations from M. H. Abraham, *J.C.S. Faraday I*, 1973, **69**, 1375, adjusted so that $\Delta H_t^\circ(Ph_4As^+) = \Delta H_t^\circ(Ph_4B^-)$.

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† No ΔH_t° values for any cryptands or cryptates have hitherto been reported for any pair of solvents.

‡ 1 Calorie = 4·184 joule.

TABLE 2. Thermochemical cycle for the heat of complexing of Na$^+$ and K$^+$ with cryptand 222 in water and methanol, in kcal mol^{-1} at 298 K[a].

	ΔH^0	
	$M^+ = Na^+$	$M^+ = K^+$
M^+ (aq) + 222 (aq) → [M^+222] (aq)	−7·6	−11·6
[M^+222] (aq) → [M^+222] (methanol)	5·6	4·3
222 (methanol) → 222 (aq)	−13·9	−13·9
M^+ (methanol) → M^+ (aq)	4·9	4·5
M^+ (methanol) + 222 (methanol) → [M^+222] (methanol)	−11·0	−16·7

[a] All measurements were carried out during this work, except M^+ (methanol) → M^+ (aq) (*cf.* Table 1).

effect of solvent on the cryptand 222 ligand, since the solvent effects on M^+ and on [M^+ 222] both act in the opposite direction. We can check the entire cycle (Table 2) by a direct calorimetric determination of the heat of complexing in methanol, for Na$^+$ and K$^+$. We find for Na$^+$ that the indirect cycle value is −11·0 ± 0·3 kcal mol^{-1} and the direct thermochemical value is −10·6 ± 0·1 kcal mol^{-1}. For K$^+$ the indirect value is −16·7 ± 0·3 kcal mol^{-1} and the direct value is −17·0 ± 0·1 kcal mol^{-1}. The validity of all the measurements that make up the cycle is thus confirmed, and the cycle can therefore be considered as a reliable method of indirectly determining heats of complex formation. Alternatively and probably more usefully, the cycle can be used in reverse to obtain enthalpies of transfer of cryptates, [M^+ 222].

Enthalpies of transfer were obtained from heats of solution of the cryptand and cryptate salts in water and methanol. Enthalpies of complex formation were determined by measurement of the heat of solution of the cryptand in the appropriate solvent and then in the solvent containing the metal cation. All experiments in aqueous solution were carried out in presence of OH$^-$ to suppress hydrolysis of the cryptand and cryptates.

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[1] J.-M. Lehn and J.-P. Sauvage, *J. Amer. Chem. Soc.*, 1975, **97**, 6700; G. Anderegg, *Helv. Chim Acta*, 1975, **58**, 1218; E. Kauffman, J.-M. Lehn, and J.-P. Sauvage, *ibid.*, 1976, **59**, 1099; M. H. Abraham, A. F. Danil de Namor, and W. H. Lee, unpublished work.