Solvent Dependence of Kinetics and Equilibria of Thallium(I) Cryptates in relation to the Free Energies of Solvation of Thallium(I)

Brian G. Cox*

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

Jadwiga Stroka

University of Warsaw, Institute of Fundamental Problems of Chemistry, Warsaw, Poland

Irmgard Schneider and Hermann Schneider

Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, Federal Republic of Germany

Stability constants and dissociation rate constants of thallium(I) cryptates have been measured in several solvents at 25 °C. The Tl+ cryptates are more stable and less sensitive to ligand cavity size than the corresponding complexes of the alkali-metal cations. The stability constants vary strongly with solvent, and the solvent dependence of the complex stabilities appears to reflect mainly changes in the solvation of Tl+. It is shown that free energies of transfer of the solvated Tl+ among non-aqueous solvents calculated on the assumption that the difference in the free energies of transfer of the Tl+ cryptates and the corresponding cryptands is zero are in good agreement with literature data. Changes in the stability constants with solvent and ligand are reflected in changes in both dissociation and formation rate constants, but more so in the former. Thus the solvation of the transition state, $(Tl^{+}\cdots Cry)^{\ddagger}$, is rather closer to that of the reactants, and includes additional solvent interactions compared with the stable cryptate complex, $TlCry^{+}$.

The solvent dependence of the stability constants of inclusion complexes formed between metal ions and macrobicyclic diazapolyethers, cryptands (Cry), contains potentially important information on the solvation free energies of ions. This follows from eqn (1), which relates stability constants (K_s)

$$- RT \, \ln[K_s(S)/K_s(R)] = \Delta G_{tr}(MCry^{n+}) - \Delta G_{tr}(Cry) - \Delta G_{tr}(M^{n+}) \qquad (1)$$

for a given cryptate $MCry^{n+}$ in two solvents S and R (= reference) to the free energies of transfer from R to S of the species involved in the complexation equilibrium

$$M^{n+} + Cry \rightleftharpoons MCry^{n+} \qquad (2)$$
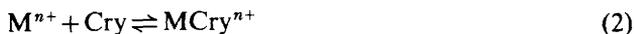
$$K_s = [MCry^{n+}]/[M^{n+}][Cry]. \qquad (3)$$

In a recent study Chantooni and Kolthoff[1] concluded that in dipolar aprotic solvents the first two terms on the right-hand side of eqn (1) cancel or nearly so, provided that the ion size is not greater than that of the cavity of the cryptand, *i.e.* the cations are shielded from direct interaction with the solvent. The relationship

$$\Delta G_{tr}(MCry^{n+}) - \Delta G_{tr}(Cry) = 0 \qquad (4)$$

was proposed previously,[2,3] and when introduced into eqn (1) leads to the assumption

$$RT \ln [K_s(S)/K_s(R)] = \Delta G_{tr}(M^{n+}) \tag{5}$$

which can be used to estimate the transfer free energies for solvated metal ions from the determination of stability constants. Danil de Namor and coworkers have also confirmed that for some alkali-metal cryptates in a range of aprotic solvents eqn (4) and (5) may be used to estimate $\Delta G_{tr}(M^+)$ with a reliability comparable to that of other commonly used extrathermodynamic assumptions,[4-6] and that similar conclusions hold for $\Delta H_{tr}(M^+)$ values obtained from heats of cryptate formation.[7-9]

Closer inspection of the results in the treatment of Chantooni and Kolthoff[1] indicates that for Tl$^+$ eqn (4) is rather more general and holds even when the size of Tl$^+$ is larger than that of cavity of the ligand. This method then may be very convenient for the study of the properties of Tl$^+$ in different media. Results for both the complexation and the transfer free energies of Tl$^+$ are of particular interest because of its importance as a probe for the role of alkali-metal cations, especially K$^+$, in biological systems.[10-14] Therefore in this paper we present stability constants and dissociation rate constants for complexes of Tl$^+$ with several cryptands (see scheme 1) in water, dipolar aprotic solvents and protic solvents.

(I) $(2, 1, 1)$ $m = 0, n = 0$
(II) $(2, 2, 1)$ $m = 1, n = 0$
(III) $(2, 2, 2)$ $m = n = 1$

(IV) $(2_B, 2, 2)$ **(V)** $(2_B, 2_B, 2)$

Scheme 1.

The transfer free energies of solvated Tl$^+$ calculated using eqn (5) are found to be in good agreement with values from several sources in the literature. Furthermore, the variation of the calculated $\Delta G_{tr}(Tl^+)$ values with cavity size of the ligand is insignificant and irregular in the different solvents, and covers a range similar to or smaller than that of the literature data. It seems that the higher polarizability of Tl$^+$ allows it to adjust to the structures of the different ligand cavities more readily than alkali-metal cations of similar size. The latter ions, for example, show larger differences between log K_s values for (2,1,1) and (2,2,2) cryptates[15] than Tl$^+$.

Table 1. Stability constants (log K_s) of Tl^+ cryptates at 25 °C

solvent	(2,1,1)	(2,2,1)	(2,2,2)	$(2_B,2,2)$	$(2_B,2_B,2)$
H_2O	3.19^a	6.8^b	$6.64;^c\ 6.4;^b\ 5.5;^d\ 6.3^e$	5.84^a	4.61^f
MeOH	$5.6_5{}^a$	$10.7_6{}^a$	$10.2_8;^b\ 10.1;^g\ 10.0_5{}^f$	$8.7_1{}^a$	$8.30;^c\ 7.9^h$
EtOH	$5.1_2{}^a$	$11.0_1{}^a$	$11.0_4{}^c$	8.58^a	$8.5_9{}^c$
AN	$7.0_2{}^i$	$11.9_2{}^i$	$12.3_0;^j\ 13.4^k$	$10.2_4{}^i$	$10.2_3{}^i$
PC	$6.5_8{}^h$	$12.1_3{}^h$	$11.7_8;^l\ 11.9^j$	$10.7_3{}^a$	$9.8_1{}^h$
DMF	$3.1_5{}^h$	$8.6_1{}^h$	$8.06;^h\ 7.7^l$	6.79^a	$6.1_4;^h\ 6.1_6{}^c$
DMSO	$1.4_4{}^h$	$6.8_0{}^h$	$6.3;^l\ 6.2;^k\ 6.1^g$	$4.6_7{}^c$	$4.5_8{}^h$

Abbreviations: MeOH, methanol; EtOH, ethanol; AN, acetonitrile; PC, propylene carbonate; DMF, dimethylformamide; DMSO, dimethyl sulphoxide. [a] This work, error in log $K_s \pm 0.10$. [b] P. Gresser, D. W. Boyd, A. M. Albrecht-Gary and J. P. Schwing, *J. Am. Chem. Soc.*, 1980, **102**, 651. [c] This work; error in log $K_s \pm 0.05$. [d] G. Anderegg, *Helv. Chim. Acta*, 1985, **58**, 1218. [e] J-M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, 1975, **97**, 6700. [f] M. K. Chantooni Jr and I. M. Kolthoff, *Proc. Natl Acad. Sci. USA*, 1981, **78**, 7245. [g] E. Lee, J. Tabib and M. J. Weaver, *J. Electronanal. Chem.*, 1979, **96**, 241. [h] M. K. Chantooni Jr and I. M. Kolthoff, *J. Soln Chem.*, 1985, **14**, 1. [i] B. G. Cox, J. Stroka and H. Schneider, to be published. [j] I. M. Kolthoff and M. K. Chantooni Jr, *Proc. Natl Acad. Sci. USA*, 1980, **77**, 5040. [k] M. Lejaille, M. Livertoux, C. Guidon and J. Bessière, *Bull. Soc. Chim. Fr.* 1978, I–373. [l] J. Gutknecht, H. Schneider and J. Stroka, *Inorg. Chem.*, 1978, **17**, 3326.

The rate constants for cryptate dissociation (k_d) and formation (k_f), on the other hand, show a more complex dependence upon size and solvent than the equilibrium quantities. Both k_d and k_f values for the Tl^+ cryptates depend upon the ligand cavity size, but the former more so than the latter. The transition states for complex formation all lie closer to the reactants than to the product complexes, but the difference between the transfer free energies of the transition state and the reactants show a correlation with the solvent donor numbers.

Experimental and Results

Materials

The cryptands (2,1,1), (2,2,1), (2,2,2), $(2_B,2,2)$ and $(2_B,2_B,2)$ were commercial samples (Merck) and were used without further purification. The purities of the cryptands used were determined from the equivalent points in pAg potentiometric titrations of silver with the respective cryptands, in conjunction with the determination of stability constants. In all cases the purity was found to be better than or equal to that of the manufacturer's specification. Solvents were purified by fractional distillation under vacuum[15] or, when sufficiently pure, used as supplied. $AgClO_4$ was dried under vacuum at 80 °C for at least 12 h. $TlClO_4$ was prepared from Tl_2CO_3 and $HClO_4$ by metathesis in water, recrystallized twice from water and dried under vacuum.[16] Tetraethylammonium perchlorate (TEAP) was purified as described previously.[3]

Stability Constants

The stability constants of Tl^+ cryptates were determined by a disproportionative reaction of Tl^+ cryptates with Ag^+ and calculated using the stability constant of the respective Ag^+ cryptate.[3,17] Total metal concentrations were $(1–5) \times 10^{-3}$ mol dm^{-3} and total cryptand concentrations $5 \times 10^{-4}–2 \times 10^{-3}$ mol dm^{-3}. Where not available the stability constants of Ag^+ cryptates were determined additionally (total Ag^+ concentration $= 5 \times 10^{-5}–1 \times 10^{-4}$ mol dm^{-3}, total cryptand concentration $= 5 \times 10^{-4}–2 \times 10^{-3}$ mol dm^{-3}). No activity coefficient corrections were necessary in the calculation of stability constants from potentiometric data because the ionic strength was constant

Table 2. Stability constants (log K_s) of Ag$^+$ cryptates at 25 °C used in this work for the determination of stability constants of Tl$^+$ cryptates (table 1)

solvent	(2,1,1)	(2,2,1)	(2,2,2)	(2$_B$,2,2)	(2$_B$,2$_B$,2)
H$_2$O	8.5^a	—	9.6^a	9.2$_5{}^b$	—
MeOH	10.6$_0{}^a$	14.6$_4{}^a$	12.2$_0{}^a$	11.4$_2{}^b$	11.8$_5{}^d$
EtOH	9.70^a	13.8$_4{}^a$	11.5$_1{}^a$	10.2$_8{}^b$	10.8$_5{}^b$
PC	—	—	—	—	15.5$_4$;^{b,c} 15.4$_6{}^e$
DMF	—	—	—	—	9.3$_1$;^{b} 9.4$_7{}^f$
DMSO	—	—	—	—	6.8$_4{}^b$

^{a} B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103**, 1384. ^{b} This work, error in log $K_s \pm 0.05$. ^{c} log $K_s \pm 0.1$. ^{d} B. G. Cox, D. Knop and H. Schneider, *J. Phys. Chem.*, 1980, **84**, 320; B. G. Cox, P. Firman, I. Schneider and H. Schneider, *Inorg. Chim. Acta*, 1981, **49**, 153. ^{e} B. G. Cox, Ng van Truong and H. Schneider, *J. Am. Chem. Soc.*, 1984, **106**, 1273. ^{f} B. G. Cox, J. Garcia-Rosas and H. Schneider, *Ber Bunsenges. Phys. Chem.*, 1982, **86**, 293.

($I \leqslant 0.10$ mol dm^{-3}). Where the liquid junction potential was sufficiently stable over 1 h and the potential reading during a titration remained undisturbed, no TEAP was added to maintain constant ionic strength. In order to avoid the necessity of activity coefficient corrections in these cases, equal volume increments of a metal cryptate solution and an equilmolar metal ion solution were added simultaneously to the two half-cells, which contained equal amounts of a silver-ion solution. Otherwise the ionic strength was maintained constant at 0.05 or 0.10 mol dm^{-3} in the two half-cells and the salt bridge. The variation of log K_s with I was found to be smaller than the experimental error. In table 1 the stability constants of Tl$^+$ cryptates determined in this study, as well as values obtained from the literature, are collected. In the course of this work several previously unreported stability constants of Ag$^+$ complexes were also determined, and these are listed in table 2.

Kinetic Measurements

The dissociation reactions of Tl$^+$ cryptates were followed conductimetrically in stopped-flow experiments using an all-glass apparatus. The variations in conductance, which followed from protonation of the uncomplexed cryptands [resulting in loss of highly mobile H$^+$ (protic solvents) or increased dissociation of weak acids (aprotic solvents)], were monitored with a Wheatstone bridge operating at 40 kHz. An equilibrium mixture of Tl$^+$ cryptate, with a concentration ratio of Tl$^+$ to cryptand always > 1, was mixed with an excess of acid.[18] The pseudo-first-order rate constant k_e was found to be linearly dependent on the acid concentration. In protic solvents strong acids (HClO$_4$, CF$_3$SO$_3$H) were used as scavengers, and k_e depends on the H$^+$ concentration in the following way:[18]

$$k_e = k_d + k_H [\text{H}^+]/\gamma_\pm^2. \tag{6}$$

The mean molar activity coefficients, $\gamma_\pm$, were calculated by using the Davies equation.[19]

In dipolar aprotic solvents a weak acid (dichloroacetic acid or trifluoroacetic acid) was used as scavenger and the dependence of k_e on the acid concentration is given by[20, 21]

$$k_e = k_d + k_{HA}[\text{HA}]. \tag{7}$$

Table 3. Rates of dissociation (k_d/s^{-1}) of Tl$^+$ cryptates at 25 °C

solvent	(2,1,1)	(2,2,1)	(2,2,2)	(2$_B$,2,2)	(2$_B$,2$_B$,2)
H$_2$O		1.10×10	5.99	8.06×10	1.6×10^2
MeOH		2.58×10^{-2}	5.21×10^{-2}	1.24	4.32
EtOH	$\leqslant 4.10^{-3}$	5.99×10^{-3}	1.34×10^{-2}	0.28	0.99
AN		4.28×10^{-4a}	1.16×10^{-3a}	2.63×10^{-3a}	5.32×10^{-2a}
PC	15.9	6.22×10^{-3}	1.34×10^{-2}	1.88×10^{-2}	2.51×10^{-2}
DMF		1.41×10^{-1}	1.82×10^{-1}	4.07	2.10×10
DMSO		2.03	1.87	8.6	*ca.* 0.3

[a] B. G. Cox, J. Stroka and H. Schneider, to be published.

The rate constants k_d of the uncatalysed dissociation were determined by extrapolation of k_e to zero acid concentration and are listed in table 3. These values may be combined with the stability constants in table 1 to determine k_f values for cryptate formation $(K_s = k_f/k_d)$.

Discussion

Thallium(I) is a $d^{10} s^2$ ion, and has an ionic radius of 1.44 Å, which is only slightly smaller than that of rubidium(I), 1.48 Å.[22] It is strongly poisonous for man because Tl$^+$ may substitute for K$^+$ in cells. With respect to Pearson's hard-acid – soft-base classification,[23] the behaviour of Tl$^+$ corresponds to that of a soft acid, although not strongly so, and it has properties which are characteristic of both the hard acid potassium(I) and the soft acid silver(I).[24] Because of the ease with which Tl$^+$ can be monitored by spectroscopic,[25,26] fluorescence,[27] n.m.r.[28,29] and polarographic[30,31] methods, in sharp contrast to the alkali-metal cations, this ion is very appropriate for a variety of experimental investigations, and it has been used as a probe for the role of K$^+$ in biological systems.[10-14] In fact, Tl$^+$ is found to activate a number of K$^+$-activated enzymes.[32]

Complexes of Tl$^+$ with macrocyclic ligands which are able to wrap around the ion and to shield it partly or completely from the solvent have been studied frequently alongside those of the alkali-metal cations. The data available for 15-crown-5, 18-crown-6 and their benzo-derivatives show that log K_s values for the three ions K$^+$, Tl$^+$ and Ag$^+$ are of similar magnitude, and larger than those of both Na$^+$ and Rb$^+$.[33] The introduction of nitrogen donor atoms to form the diaza-18-crown-6 ligand (2,2), however, leads to a strong differentiation in the behaviour of the ions. The stabilities of complexes of (2,2) decrease strongly in the series Ag$^+ \gg$ Tl$^+ \gg$ alkali-metal ions.[34] A strong and specific interaction of Ag$^+$ with the two nitrogen atoms of (2,2) results in the extraordinary large stability of the Ag$^+$ complexes, and this is also observed in silver complexes with the bicyclic cryptands. The decrease in stability of the alkali-metal complexes of (2,2) compared with Tl$^+$ seems to result mainly from a strong preference of these cations for oxygen donor atoms $[K_s(^{18}c^6) \gg K_s(2,2)]$ rather than from any particularly strong interaction of Tl$^+$ with the nitrogen donor atoms, as found for Ag$^+$ complexes.

Considering now the results for the cryptate complexes, there are again some noticeable differences between the behaviour of the complexes of Tl$^+$ and those of the alkali-metal cations. The relative stability constants of the alkali-metal cryptates are strongly determined by the ligand cavity size, apart from a general shift towards higher stabilities for complexes of the smaller cations in poorly solvating media. Thus the most stable complexes of (2,1,1) and (2,2,1) are formed with Li$^+$ and Na$^+$, respectively, in all solvents, and of (2,2,2) with K$^+$ in all except nitromethane.[4] The Tl$^+$ cryptate stabilities, however, are less strictly determined by the ligand's cavity size, as shown by the
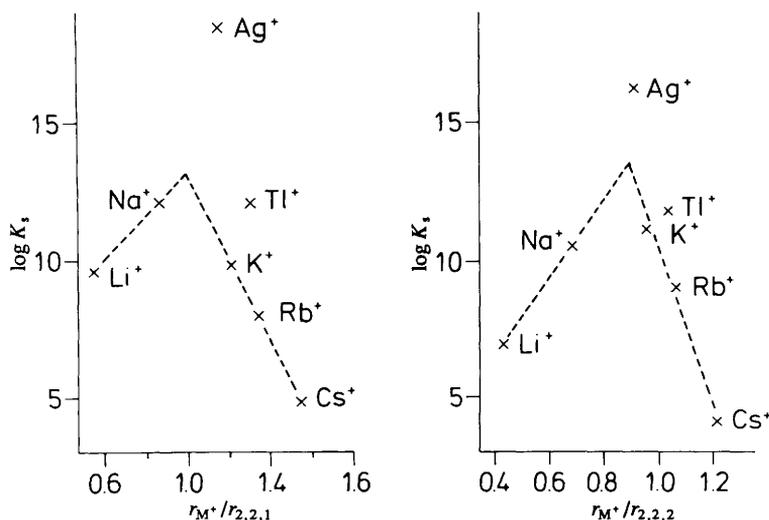
Fig. 1. Stability constants of (2,2,1) and (2,2,2) cryptates with alkali-metal ions and with Tl^+ in propylene carbonate at 25 °C.

sequences of log K_s values for complexes of Tl^+ and the larger alkali-metal cations in different solvents:[33]

$$(2,1,1): Na^+ > Tl^+ > K^+ > Rb^+ (> Cs^+)$$
$$(2,2,1): Tl^+, Na^+ > K^+ > Rb^+ > Cs^+$$
$$(2,2,2): Tl^+ > K^+ > Rb^+ > Na^+ > Cs^+.$$
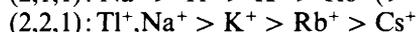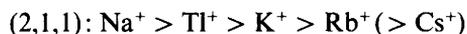
A further comparison is provided in fig. 1, which shows stability constants of (2,2,1) and (2,2,2) cryptates of Tl^+, alkali-metal cations and Ag^+ in propylene carbonate. The results, which are plotted against the ratio of cation size to cavity size, clearly show the ordering of the alkali-metal cations according to the criterion of optimal matching of ion and cavity size, and the different behaviour of Tl^+ and especially Ag^+. For Tl^+, log K_s is similar to that of Na^+ for (2,2,1) and to that of K^+ for (2,2,2), despite having an ionic size close to that of Rb^+. Taken together, these stability constant comparisons show that (i) there is an extra stability of up to five orders of magnitude, depending upon the solvent, for cryptates of Tl^+ compared to those of Rb^+, the alkali-metal cation of closest size, and (ii) Tl^+ seems to be able to adjust its ionic shape and surface charge distribution to the structures of the cavities of the cryptands much more readily than the alkali-metal cations. However, there is no clear evidence for Tl^+ of the remarkably specific and (probably) covalent interactions with the ligand donor atoms shown by Ag^+ (*e.g.* fig. 1).

Across the range of solvents studied the stability constants of Tl^+ cryptates vary by over 12 orders of magnitude (table 1), but the selectivity pattern among the various ligands is remarkably independent of solvent. This is illustrated in fig. 2, which shows that in the different solvents the log K_s values change in a clearly parallel manner, with the sequence for different ligands $(2,2,1) \geqslant (2,2,2) > (2_B,2,2) > (2_B,2_B,2) > (2,1,1)$.

The free energies of the cryptate formation reaction [eqn (2)] may be calcuated from the stability constants in table 1 and used to discuss the free energies of transfer [eqn (1)] among the various solvents. For this propylene carbonate has been chosen as reference solvent because of its high dielectric constant, aprotic nature and lack of specific interactions with solutes.[35] The results $\{-RT\ln[K_s(S)/K_s(PC)]\}$ are listed in table 4, together with the free energies of transfer of solvated Tl^+, $\Delta G_{tr}(Tl^+)$, taken from the literature, and are shown in fig. 3.

The transfer free energies of cryptate formation are strikingly independent of crypt-
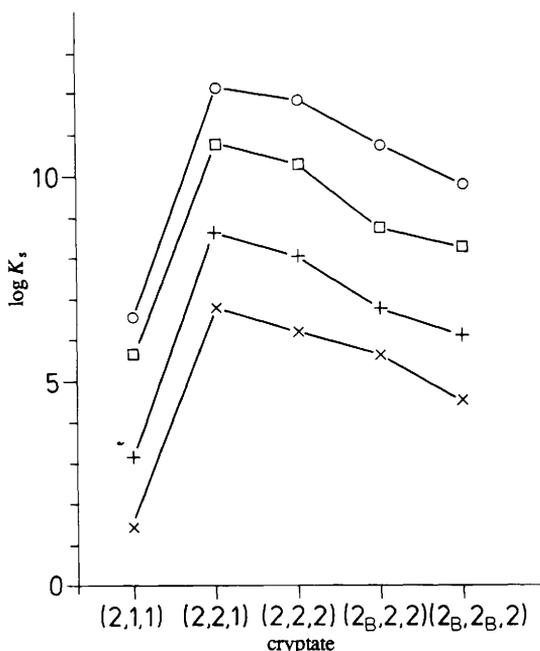
Fig. 2. Stability constants of Tl^+ cryptates at 25 °C: ○, PC; □, MeOH, +, DMF; ×, DMSO.

Table 4. Transfer free energies of complex formation and of Tl^+ solvation in kJ mol^{-1} at 25 °C

| solvent, S | $-RT \ln [K_s(S)/K_s(PC)]^a$ | | | | | mean value | $\Delta G_{tr}(Tl^+)$ |
	(2,1,1)	(2,2,1)	(2,2,2)	$(2_B,2,2)$	$(2_B,2_B,2)$		
H_2O	19.4	30.4	29.3	27.9	29.7	—	$-8.37;^b -11^c$
MeOH	5.3	7.8	8.6	11.5	8.6	8.4 ± 2.2	$-4.2;^b -6.0;^d -6.9^c$
EtOH	8.3	6.4	4.2	12.3	7.0	7.6 ± 3.0	$-9.7;^e -4.0^c$
AN	-2.5	1.20	-3.0	2.8	-2.4	-0.8 ± 2.6	$0.84;^b -3.9;^e -0.86;^d -3.0^c$
DMF	19.6	20.1	21.2	22.5	21.0	20.9 ± 1.1	$-20.1;^b -26.1;^e -21.4;^d$ -22.5^c
DMSO	29.3	30.4	31.3	34.6	29.9	31.1 ± 2.1	$-33.5;^b \cdot-32.9;^e -30.5;^d$ -32.4^c

^{a} In the calculations always the first $\log K_s$ value from several ones in table 1 has been taken. ^{b} Ref. (29) (B. G. Cox, TATB assumption). ^{c} Ref. (33) (Y. Marcus, average values). ^{d} Ref. (1) (M. K. Chantooni Jr and I. M. Kolthoff, TATB assumption). ^{e} Ref. (32) (G. Gritzner, bisbiphenyl-chromium assumption).

and structure [apart from (2,1,1) in water] and show no systematic trends when considered over the range of solvents. Furthermore, a comparison with $\Delta G_{tr}(Tl^+)$ shown on the right-hand scale of fig. 3 demonstrates clearly the agreement between Bressière's assumption [eqn (4)]^2 for Tl^+ cryptates and other well accepted extrathermodynamic assumptions in these dipolar aprotic and protic, non-aqueous solvents. Except for water, the $\Delta G_{tr}(Tl^+)$ values determined from cryptate stabilities *via* eqn (5) show a scatter within a given solvent which is not larger than that of the various $\Delta G_{tr}(Tl^+)$ data from the literature. Even (2,1,1), the smallest of the cryptands studied, with a cavity size much

Solution Studies of Thallium(I) *Cryptates*
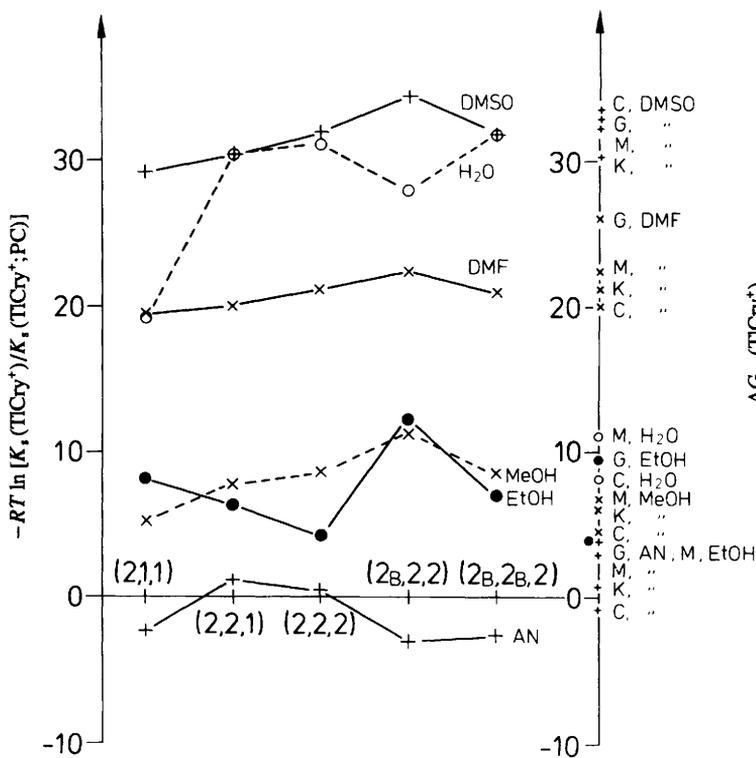
Fig. 3. Free energies of transfer of Tl^+ in kJ mol^{-1} at 25 °C. [C, Cox, ref. (37); G, Gritzner, ref. (40); K, Kolthoff, ref. (1); M, Marcus, ref. (41).]

smaller than the size of Tl^+, does not provide an exception to this behaviour. Therefore the free energy of transfer of Tl^+ estimated from the stability constants of Tl^+ cryptates may be used as an additional or alternative source of single-ion transfer free energies among non-aqueous solvents. The advantage of this method in comparison to other extrathermodynamic assumptions [tetraphenylarsonium/tetraphenylborate,[36,37] ferrocene/ferrocinium ion[38] bisbiphenylchromium $(0/1)$[39,40] or others[41,42]] lies in the various and relatively simple possibilities available for the determination of the stability constants of Tl^+ cryptates.

In water there is a significant difference, amounting to *ca.* 20 kJ mol^{-1}, between $\Delta G_{tr}(Tl^+)$ obtained from the Tl^+ cryptate stability constants and the literature data. Depending upon the reliability of assumptions such as $PhAs^+/BPh_4^-$, this indicates that ΔG_{tr} [$Tl(Cry^+)$] for transfer from propylene carbonate to water is *ca.* 20 kJ mol^{-1} more positive than that of the corresponding free ligand. This probably results from a stronger hydration of the nitrogen and oxygen atoms in the latter, which are not involved in ion binding. The smallness of the water molecules may also allow them to interact with the enclosed thallium (I) ion through the space between the arms of the cryptands, and this would also influence the observed complexation behaviour. Some evidence for this comes from n.m.r. studies of Tl^+ cryptates, which show that spin–spin splitting between Tl^+ and the protons in the (2,2,2) complex is observed in $CHCl_3$,[43] but not in water. Also the ^{205}Tl n.m.r. chemical shifts of Tl^+ cryptates in solution are independent of solvent for a given cryptand molecule, except when water is the solvent.[28] This, however, does not seem to be a major factor in determining the transfer free energies of the Tl^+ complex stabilities, as it would tend to produce a deviation in the opposite direction to that observed in fig. 3.
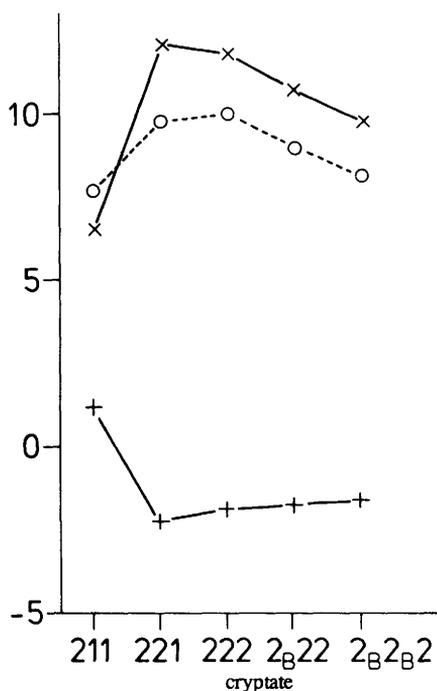
Fig. 4. Stability constants (log K_s; $\times$) and rate constants for formation (log k_f; $\bigcirc$) and dissociation (log k_d; $+$) of Tl$^+$ cryptates in propylene carbonate at 25 °C.

Table 5. Rates of formation (k_f/dm^3 mol^{-1} s^{-1}) of Tl$^+$ cryptates at 25 °C

solvent	(2,1,1)	(2,2,1)	(2,2,2)	(2$_B$,2,2)	(2$_B$,2$_B$,2)
H$_2$O	—	6.9×10^7	2.4×10^7	$5.5_8 \times 10^7$	6.5×10^6
MeOH	—	$1.4_9 \times 10^9$	$9.9_3 \times 10^8$	$2.1_1 \times 10^8$	$8.6_2 \times 10^8$
EtOH	$< 5.3 \times 10^2$	$6.1_3 \times 10^8$	$1.3_7 \times 10^9$	$2.5_5 \times 10^7$	$3.8_5 \times 10^8$
AN	—	$3.5_6 \times 10^8$	$2.1_2 \times 10^9$	$4.5_7 \times 10^7$	$9.0_4 \times 10^8$
PC	$6.0_5 \times 10^7$	$8.3_9 \times 10^9$	$8.0_7 \times 10^9$	$1.0_1 \times 10^9$	$1.6_2 \times 10^8$
DMF	—	$5.7_4 \times 10^7$	2.1×10^7	$2.5_1 \times 10^7$	$2.9_0 \times 10^7$
DMSO	—	$1.2_8 \times 10^7$	$3.7_3 \times 10^6$	$4.0_2 \times 10^5$	ca 1×10^4

Complexation Kinetics

The dissociation rate constants, k_d, of the Tl$^+$ cryptates (table 3) vary over about six orders of magnitude, compared with a range of about nine orders of magnitude for the corresponding stability constants (table 1). There is an evident correspondence in the variations of log k_d and $-$log K_s (*e.g.* fig. 4), although in general this is less strict than that observed for the alkali-metal cryptates.[18] For all of the cryptates k_d is highest in water, and it is also noticeable that in water k_d is a minimum for Tl(2,2,2)$^+$, whereas in all other solvents Tl(2,2,1)$^+$ dissociate most slowly. Both of these factors are probably related to the ability of water to form hydrogen bonds with the ligand donor atoms and to interact with Tl$^+$ even in the complex, as discussed above.

The formation rate constants vary over a smaller range than k_d values, and lie in the range 10^6–10^9 dm^3 mol^{-1} s^{-1}, except for the benzo-substituted cryptates in DMSO (table 5). In water, DMF and DMSO they are considerably below the diffusion-controlled
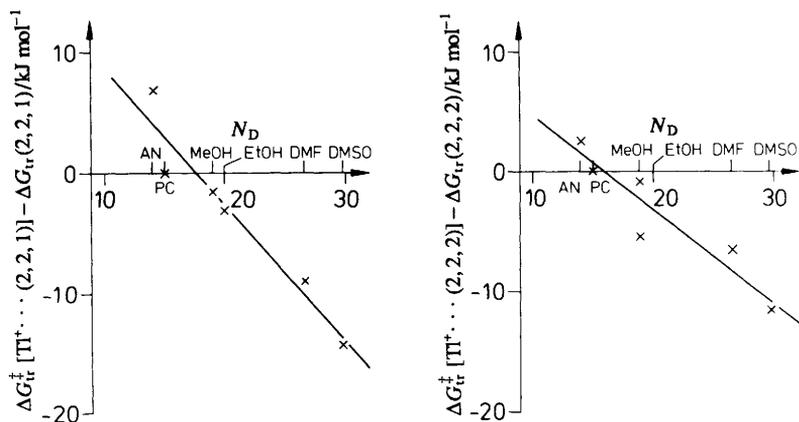
Fig. 5. Variation of free energies of transfer of Tl^+ cryptate transition states referred to the corresponding cryptand, $\Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry) - \Delta G_{tr}(Cry)$, with solvent donor number, N_D. [$\Delta G_{tr}(Tl^+)$ from ref. (1) and for EtOH from ref. (39).]

limit, but in the poorer cation solvents they approach the maximum values observed for multistep substitution complexations reactions.[44]

It is of interest to consider the variations in the free energies of the transition states for the various complexation reactions in a similar manner to that discussed above for the stable cryptate complexes. The stronger contribution of the dissociation rate constants to the observed variations in stability constants indicates that the transition state for complex formation lies closer to the reactants than to the products, and this might also be expected to show up in its solvation behaviour. The free energy of transfer of the transition state, $\Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry)$, referred to propylene carbonate as reference solvent (R) is related to the formation rate constants and the free energies of transfer of the reactants in solvent (S) by

$$-RT\ln[k_f(S)/k_f(R)] = \Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry) - \Delta G_{tr}(Cry) - \Delta G_{tr}(Tl^+). \qquad (8)$$

A comparable assumption to that in eqn (4) but involving the transition state rather than the stable complex, would result in a correlation between the left-hand side of eqn (8) and $\Delta G_{tr}(Tl^+)$. In fact, no such correlation is observed, and indeed it would require k_d to be independent of solvent, *i.e.* the free energy of transfer of the transition state is equal to that of the stable cryptate:

$$\Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry) = \Delta G_{tr}(TlCry^+) - RT\ln[k_d(S)/k_d(R)]. \qquad (9)$$

Thus in terms of solvation there is in the transition state an additional interaction between the solvent and Tl^+ and the ligand binding groups over that of the stable cryptate. This is consistent with the Tl^+ being at least partly outside of the ligand's cavity in the transition state. The specific solvent dependence of this interaction is illustrated in fig. 5, in which $\Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry) - \Delta G_{tr}(Cry)$ (calculated using eqn (8) and the data in tables 4 and 5) is plotted against the donor number of the solvents.[45] The linearity observed is independent of which of the extrathermodynamic assumptions are used to estimate $\Delta G_{tr}(Tl^+)$, and undoubtedly reflects mainly the (residual) interaction between Tl^+ in the transition state and the solvent. This is confirmed by a parallel behaviour with solvent of $\Delta G_{tr}(Tl^+)$ and $\Delta G^{\ddagger}_{tr}(Tl^+\cdots Cry)$ except for a change in the sequence of AN, MeOH and EtOH. This latter effect is indicative of the solvation of the transition state also involving the binding groups of the cryptands.

Conclusion

(i) Thallium(I) forms stable complexes with a range of cryptand ligands in water and non-aqueous solvents. The stability constants are very sensitive to solvent (variations over 12 orders of magnitude in the stability constants were observed in the different solvents). (ii) The Tl^+ complexes are more stable and less strongly dependent upon ligand cavity size than those of alkali-metal cations of similar ionic radii (K^+, Rb^+). The effects, however, are less marked than those of the corresponding Ag^+ complexes. (iii) The solvent dependence of the complex stabilities are governed mainly by changes in the solvation of Tl^+. In a range of dipolar aprotic and polar, protic solvents the assumption that changes in the free energies of the cryptate complexes and the free ligands are equal leads to values for $\Delta G_{tr}(Tl^+)$ among solvents which are in good agreement with literature values based on other commonly used extrathermodynamic assumptions. (iv) The formation rate constants normally lie in the range 10^6–10^9 dm^3 mol^{-1} s^{-1}, depending upon the solvent and ligand. The dissociation rate constants vary over a wider range, and correlate more closely with the complex stabilities.

References

1 M. K. Chantooni Jr and I. M. Kolthoff, *J. Soln Chem.*, 1985, **14**, 1.
2 M. E. Lejaille, M. H. Livertoux, G. Guidon and J. Bessière, *Bull. Soc. Chim. Fr. 1978*, I–373; J. Bessiere and M. F. Lejaille, *Anal. Lett.*, 1979, **12**, 753.
3 J. Gutknecht, H. Schneider and J. Stroka, *Inorg. Chem.* 1978, **17**, 3326.
4 A. F. Danil de Namor, L. Ghosaini and W. H. Lee, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2495.
5 A. E. Danil de Namor, H. Berroa de Ponce and E. C. Viguria, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2811.
6 A. F. Danil de Namor and H. Berroa de Ponce, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1569.
7 A. F. Danil de Namor and L. Ghosaini, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 781.
8 A. F. Danil de Namor, L. Ghosaini and T. Hill, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 349.
9 A. F. Danil de Namor and L. Ghosaini, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 3275.
10 R. J. P. Williams, *Q. Rev. Chem. Soc.*, 1970, **24**, 331.
11 J. P. Manners, K. G. Morallee and R. J. P. Williams, *J. Chem. Soc. D*, 1970, 965.
12 S. Krasne and G. Eisenman, in *Membranes, a Series of Advances*, ed. G. Eisenman (Marcel Dekker, New York, 1973), vol. 2, pp. 277–328.
13 A. G. Lee, *J. Chem. Soc. A*, 1971, 880; 2007.
14 C. H. Sueltor, in *Metal Ions in Biological Systems*, ed. H. Sigel (Marcel Dekker, New York, 1974), vol. III, p. 201.
15 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103**, 1384.
16 I. M. Kolthoff and M. K. Chantooni Jr, *J. Phys. Chem.*, 1972, **76**, 2024.
17 B. G. Cox, H. Schneider and J. Stroka, *J. Am. Chem. Soc.*, 1978, **100**, 4746.
18 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1981, **103**, 1054.
19 C. W. Davies, *Ion Association* (Butterworths, London, 1962).
20 B. G. Cox, J. Garcia-Rosas and H. Schneider, *J. Am. Chem. Soc.*, 1982, **104**, 2434.
21 B. G. Cox, W. Jedral, P. Firman and H. Schneider, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1486.
22 L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 3rd edn, 1960).
23 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533; *Science*, 1966, **151**, 172.
24 E. C. Taylor and A. McKillop, *Acc. Chem. Res.*, 1970, **3**, 338.
25 R. Gresser, D. W. Boyd, A. M. Albrecht-Gary and J. P. Schwing, *J. Am. Chem. Soc.*, 1980, **102**, 651.
26 B. G. Cox, J. Stroka and H. Schneider, unpublished work.
27 G. Cornelius, W. Gärtner and D. H. Haynes, *Biochemistry*, 1974, **13**, 3053.
28 D. Gudlin and H. Schneider, *Inorg. Chim. Acta*, 1979, **33**, 205.
29 J. F. Hinton and K. R. Metz, in *NMR of Newly Accessible Nuclei*, ed. P. Laszlo (Academic Press, New York, 1983), vol. 2, p. 367
30 H. Schneider and H. Strehlow, *J. Electroanal. Chem.*, 1966, **12**, 530.
31 E. L. Yee, J. Tabib and M. J. Weaver, *J. Electroanal. Chem.*, 1979, **96**, 241.
32 J. J. Dechter, *Progr. Inorg. Chem.*, 1982, **29**, 285.
33 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271.

34 B. G. Cox, P. Firman, H. Horst and H. Schneider, *Polyhedron*, 1983, **2**, 343.
35 H. L. Friedman and C. V. Krishnan, in *Water, A Comprehensive Treatise*, ed. F. Franks (Plenum Press, New York, 1973), vol. 3, pp. 1–118.
36 R. Alexander and A. J. Parker, *J. Am. Chem. Soc.*, 1967, **89**, 5549.
37 B. G. Cox, *Annu. Rep. Progr. Chem., Sect. A*, 1973, **70**, 249.
38 H. M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem.*, 1960, **64**, 483.
39 G. Gritzner, V. Gutmann and R. Schmid, *Electrochim. Acta*, 1968, **13**, 919.
40 G. Gritzner, *Inorg. Chim. Acta*, 1977, **24**, 5.
41 Y. Marcus, *Rev. Anal. Chem.*, 1980, **5**, 53.
42 O. Popovych, *Crit. Rev. Anal. Chem.*, 1970, **1**, 73.
43 J-M. Lehn, J. P. Sauvage and B. Dietrich, *J. Am. Chem. Soc.* 1970, **92**, 2916; E. Grell, personal communication.
44 R. Winkler, *Dissertation*, (Göttingen University 1969).
45 V. Gutmann and E. Eychera, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 257; V. Gutmann, *Coordination Chemistry in Non-aqueous Solutions* (Springer, Wien, 1968).