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Thermodynamic and Kinetic Studies on Complex Formation of Alkaline Earth Metal Ions with Diaza-Crown Ethers in Methanol*

B. G. COX

Department of Chemistry, University Stirling, Stirling FK9 4LA, U.K.

P. FIRMAN and H. SCHNEIDER

Max-Planck-Institut für Biophysikalische Chemie, 3400 Göttingen, F.R.G.

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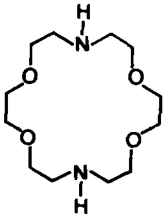
Stability constants K_s and rate constants of formation and dissociation of alkaline earth metal complexes with the diaza-crown ethers (2,2) and (2,2-Me_2) in methanol are reported, together with corresponding thermodynamic parameters. It is shown that it is possible to determine the dissociation rate constants k_d of these crown ether complexes from stopped-flow experiments. The values of K_s and k_d for (2,2) complexes are displaced parallel with respect to the corresponding values for (2,2-Me_2) complexes, and variations of K_s with metal ion radius are reflected in similar (inverse) variations of k_d. However, enthalpies and entropies of reaction and activation point to differences in the behaviour of the two ligands.

Introduction

The ability of macrocyclic ligands (*e.g.* crown ethers) to form inclusion complexes with metal ions, including alkali metal ions, whose stabilities are larger than those formed with open chain ligands of corresponding chemical structure, has attracted much interest in experimental studies of their chemical properties [1]. A variety of methods have been used to determine stability constants, K_s, of the complexes, the values of which range from log $K_s \sim 1$ to log $K_s > 15$, where the time required for equilibration in titration experiments may cause difficulties.

Comparatively few experimental data are available for the kinetics of formation of crown ether type complexes, most of which has come from ultrasonic relaxation and NMR measurements [2]. The rate constants are much too high for determination by fast-mixing experiments. However, in the present paper it is demonstrated that the dissociation rates of complexes formed between alkaline earth metal ions and monocyclic diaza-crown ethers (2,2) (I) and (2,2-Me_2) (II) are accessible by stopped-flow measurements in methanol. There is an inverse relationship between the variations in stability constants and dissociation rate constants with ionic radius of the metal ion, in agreement with earlier results for crown ether and cryptand complexes.



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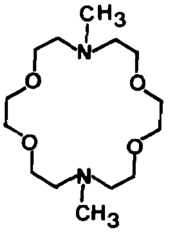

II

Unlike 18-crown-6, the diaza-crown ethers do not distinguish selectively between Sr^{2+} and Ba^{2+}, because the ring cavity diameter of the diaza-ligands is smaller than that of 18-crown-6, which forms the most stable alkaline earth metal complex with Ba^{2+}. An isokinetic correlation between activation entropies and activation enthalpies for the proton-catalysed dissociation process of (2,2-Me_2) complexes and of (2,2-Me_2) complexes suggest a constancy of the reaction mechanism throughout a series of complexes.

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*A complete list of experimental data is available on request.

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TABLE I. Stability Constants (log K_s) and Thermodynamic Parameters of Complexing of Alkaline Earth Metal Ions with Diaza-Crown Ethers in Methanol at 25 °C (K_s in M^{-1}).

ligand	ion	$\log K_s$[a]	$-\Delta H$/kJmol^{-1} [b]	$T\Delta S$/kJmol^{-1} [c]
(2,2)	Ca^{2+}	3.5	<12.0	
(2,2)	Sr^{2+}	5.7	11.3	21.2
(2,2)	Ba^{2+}	5.9	13.4	20.2
(2,2-Me_2)	Ca^{2+}	4.2	15.6	8.6
(2,2-Me_2)	Sr^{2+}	6.5	25.0	12.1
(2,2-Me_2)	Ba^{2+}	6.9	34.6	4.7

[a] Errors ± 0.1 in $\log K_s$. [b] Errors ± 2.1 kJmol^{-1}. [c] Errors ± 2.7 kJmol^{-1}.

Experimental and Results

Materials

The ligand 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, (2,2) was purchased from Merck and used without further purification. The ligand 4,13-dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, (2,2-Me_2) was synthesized from ligand (2,2) using the procedure of Clark [3]. An aqueous solution of 35% formaldehyde (0.02 mol) was mixed together with 3 g (0.01 mol) ligand (2,2) and a solution of 95% formic acid (0.05 mol). The reaction mixture was refluxed for 12 h under heating. The heating was continued for several hours after addition of concentrated hydrochloric acid. The mixture was then made strongly basic with NaOH, and extracted with chloroform. After drying over sodium sulfate the extract was distilled under vacuum (with Buechi Kugelrohr Destille). The purity was then checked by acid titration (>99%) and NMR. The transparent viscous substance dissolved in $CDCl_3$ has NMR signals: $-CH_2-N$: 2.70 ppm (Triplet), $N-CH_3$: 2.32 ppm (Singlet), $-CH_2-O$: 3.65 ppm (Singlet + Triplet), Dried methanol (Merck, max 0.01% H_2O) was used as solvent. Inorganic salts: $Sr(NO_3)_2$ (Merck) and $Ba(ClO_4)_2$ (Merck) were dried before use. A stock solution of $Ca(NO_3)_2 \cdot 4H_2O$ was prepared and dried over molecular sieves (3 Å) for several days. Trifluoromethanesulfonic acid (EGA), anhydrous $AgClO_4$ (Alfa) and $(Et)_4NClO_4$ from Fluka were used as purchased.

Stability Constant Measurements

The stability constants of the alkaline earth metal ion complexes, ML^{2+}, listed in Table I, were determined by potentiometric titrations using the Ag/Ag^+ electrode to monitor the silver ion concentration in equilibrium (1), as previously described [4]. In each titration experiment

$$ML^{2+} + Ag^+ \rightleftharpoons M^{2+} + AgL^+ \qquad (1)$$

a solution of ligand L ($C_L = 5.0 \cdot 10^{-3}$ *M*) and cation M^{2+} ($C_M = 1.0 \cdot 10^{-2}$ *M*) was added to 10 ml of a silver salt solution ($C_{Ag} = 1.0 \cdot 10^{-3}$ *M*). The titrations were also repeated at a constant ionic strength I = 0.05 *M*, and the results obtained agree within an experimental error of ±0.1 in $\log K_s$. The stability constants of the silver ion complexes with ligand (2,2) ($\log K_s = 9.99 \pm 0.05$) and with ligand (2,2-Me_2) ($\log K_s = 9.69 \pm 0.05$) were determined from direct potentiometric measurements of silver ion concentrations in solution with the ligands. Tetraethylammonium perchlorate was used as supporting electrolyte and for the solution in the bridge (0.1 *M*) forming a connection to the reference cell (0.001 *M* Ag^+/Ag).

Heat of Reaction Measurements

The heats of complexation were measured using a calorimeter manufactured by Tronac Inc., model 450. Experimental data were treated according to the procedure described by Eatough *et al.* [5]. In a preliminary run the heat of dilution of the ligand solution ($C_L = 0.1$ *M*) which was added to the corresponding metal ion solution ($C_M = 0.01$ *M*; 40 ml) was found to be less than 2 kJ mol^{-1}, and was therefore neglected.

Kinetic Measurements

The dissociation reactions of the complexes were observed conductimetrically. For each run a mixture of the complex ($C_L = 2.0–10.0 \cdot 10^{-4}$ *M*, $C_M = 6.0–20.0 \cdot 10^{-4}$ *M*) was reacted with a large excess of trifluoromethanesulfonic acid ($1.0–10.0 \cdot 10^{-3}$ *M*). The observed rates were always first order, and were treated by standard methods. In all cases the experimental dissociation rate constants, k_e, were found to be linearly dependent on the proton concentration, namely on the mean value $[H^+]$ between the concentration at the beginning of the replacement reaction and at its end (eqn. (2)).

$$k_e = k_d + k_H[H^+] \qquad (2)$$

TABLE II. Dissociation Rates, k_d, and Protonation Catalysis Constants, k_H, of Complexes between Alkaline Earth Metal Ions and the Ligands (2,2) and (2,2-Me$_2$) in Methanol.[a]

T/°C	Ca^{2+}-(2,2)		T/°C	Ca^{2+}-(2,2-Me$_2$)	
	k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$		k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$
−5	10.4	262	−10	4.2	1414
0	15.1	356	−5	6.0	1793
5	21.6	480	0	8.6	2241
10	30.4	699	5	11.6	2777
15	42.7	835	25	38.4[b]	6150[b]
25	80.3[b]	1489[b]		$r^2 = 0.999$[c]	$r^2 = 0.999$[c]
	$r^2 = 0.999$[c]	$r^2 = 0.996$[c]			

T/°C	Sr^{2+}-(2,2)		T/°C	Sr^{2+}-(2,2-Me$_2$)	
	k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$		k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$
5	0.49	109	10	0.18	70
10	0.89	139	15	0.28	107
15	1.7	156	20	0.40	153
20	2.7	200	25	0.58	223
25	4.2	249		$r^2 = 0.999$[c]	$r^2 = 0.999$[c]
	$r^2 = 0.997$[c]	$r^2 = 0.994$[c]			

T/°C	Ba^{2+}-(2,2)		T/°C	Ba^{2+}-(2,2-Me$_2$)	
	k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$		k_d/s^{-1}	$k_H/M^{-1}\ s^{-1}$
0	1.4	341	10	0.37	52
5	2.0	452	15	0.58	62
10	2.9	595	20	0.90	69
15	4.1	762	25	1.4	72
20	5.8	971		$r^2 = 0.999$[c]	$r^2 = 0.962$[c]
25	8.0[b]	1240[b]			
	$r^2 = 0.999$[c]	$r^2 = 0.999$[c]			

[a] $\Delta k_d = \pm 5\%$; $\Delta k_H = \pm 10\%$. [b] Extrapolated. [c] r^2 = correlation coefficient for lnk *vs.* 1/T.

The dissociation constant k_d of the uncatalyzed path was obtained by extrapolation of k_e towards $[H^+] = 0$. An ionic strength, I, correction was applied to ($k_e - k_d$), the contribution of the acid catalysed dissociation path of k_e [6], using activity coefficients $\gamma_\pm$ calculated from the Davies equation [7]:

$$-\log \gamma_\pm = \frac{A\sqrt{I}}{1 + \sqrt{I}} - 0.3AI \tag{3}$$

The final values of k_d and k_H were determined from a plot of the corrected k_e values, $k_e\ (I = 0) = k_d + (k_e(I \neq 0) - k_d)\gamma_\pm^4$, *vs.* $[H^+]$. Several further iterations were found to be necessary since the change in k_d between first and second treatment was around 5%. However, k_H was reduced by a factor of 0.2 to 0.5 as result of the ionic strength correction.

Values of k_d and k_H at the temperatures of the experiments are listed in Table II. The rate constants for dissociation, k_d and k_H values at 25 °C, together with the enthalpies and entropies of activation, given in Table III, were obtained from appropriate Arrhenius plots. The rate constants for complex formation, k_f, were calculated from k_d and the corresponding stability constant, K_s, using eqn. (4).

$$k_f = K_s \cdot k_d \tag{4}$$

Discussion

In X-ray diffraction studies it has been shown that the macrocyclic crown ethers 18-crown-6 (18C6) and the two related compounds, monoaza-18-crown-6 and 1,10-diaza-18-crown-6, (2,2), in which one or two ether oxygens of 18C6 are replaced by nitrogen (NH), form ring cavities of similar sizes. The ionic radii of K^+, Ag^+, and Ba^{2+} match best the cavity size of the ligands and, for example, the complex

TABLE III. Dissociation and Formation Rates and Activation Parameters for Complexes between Alkaline Earth Metal Ions and Diaza-Crown Ethers in Methanol at 25 °C.

Ligand	Ion	k_d/s^{-1} [a]	$k_f/M^{-1}\ s^{-1}$	$k_H/M^{-1}\ s^{-1}$ [b]	$(k_Hk_d^{-1})/M^{-1}$
(2,2)	Ca^{2+}	80.3	$2.5 \cdot 10^5$	1489	20.9
(2,2)	Sr^{2+}	4.2	$2.1 \cdot 10^6$	249	59.3
(2,2)	Ba^{2+}	8.0	$6.4 \cdot 10^6$	1240	155
(2,2-Me_2)	Ca^{2+}	38.4	$6.1 \cdot 10^5$	6150	160
(2,2-Me_2)	Sr^{2+}	0.58	$1.8 \cdot 10^6$	223	384
(2,2-Me_2)	Ba^{2+}	1.4	$1.1 \cdot 10^7$	72	51.3

Ligand	Ion	$\Delta H_d^{\ddagger}$/kJ mol^{-1} [c]	$T\Delta S_d^{\ddagger}$/kJ mol^{-1} [d]	$\Delta H_H^{\ddagger}$/kJ mol^{-1} [e]	$T\Delta S_H^{\ddagger}$/kJ mol^{-1} [f]
(2,2)	Ca^{2+}	42.8	−19.3	36.1	−18.9
(2,2)	Sr^{2+}	72.7	+3.4	25.3	−34.1
(2,2)	Ba^{2+}	45.0	−22.9	32.4	−23.0
(2,2-Me_2)	Ca^{2+}	38.7	−25.3	24.9	−26.5
(2,2-Me_2)	Sr^{2+}	51.8	−22.5	51.4	−8.3
(2,2-Me_2)	Ba^{2+}	59.1	−13.1	12.5	−49.8

[a] Error ± 5%. [b] Error ± 10%. [c] Error $\leqslant \pm 2.5$ kJ mol^{-1}. [d] Error $\leqslant \pm 3.0$ kJ mol^{-1}. [e] Error $\leqslant \pm 5.0$ kJ mol^{-1}. [f] Error $\leqslant \pm 6.0$ kJ mol^{-1}.

stability of K^+ with a given ligand is larger than those formed with either larger or smaller alkali metal cations. Similarly, among the alkaline earth cations, Ba^{2+} forms the most stable complex. The interactions of these ions with the donor atoms of the ligands are primarily of a simple electrostatic nature, whereas covalent bonding is involved in Ag^+ complexing. The difference is reflected strongly in the effect of replacing an oxygen atom in 18C6 by nitrogen, which has been shown by Frensdorff [8] and Izatt *et al.* [9] to weaken appreciably the complexing of K^+ ($\Delta \log K_s = -2.2$ in methanol), but to increase the stability constants of Ag^+ complexes ($\Delta \log K_s = +1.7$ in water). These trends continue when the stabilities of complexes of (2,2) with K^+ and Ag^+ are included. However, the stabilities of the corresponding Ba^{2+} complexes are less sensitive to the replacement of O by N in 18C6 (Table I and [10–12]).

A comparison of alkaline earth metal complexes of (2,2) with those of (2,2-Me_2) shows an almost constant difference in $\log K_s$ of 0.7–0.9, presumably because of the greater availability of electrons in $N{-}CH_3$ than N–H. This is reflected also in the pK_a values of the first protonation, which are larger for (2,2-Me_2) than for (2,2) both in water and methanol [13].

The variation of $\log K_s$ with the radius of the alkaline earth metal ions indicates that the cavity radius of the two diaza-crown ethers lies between the ionic radii of Sr^{2+} and Ba^{2+}, and is smaller than that of 18C6. The stability constants of these two ions are amost equal for (2,2) complexes and also for (2,2-Me_2), while the stability of $Ba(18C6)^{2+}$ is larger than that of $Sr(18C6)^{2+}$ [11]. This conclusion is supported by the results of X-ray diffraction studies. Comparison of the free ligands is less appropriate, because of an elliptical arrangement of the oxygen atoms in 18C6 [14] and an almost planar circular arrangement of the heteroatoms in (2,2) [15], but a clearer picture emerges from the structures of the corresponding K^+ complexes. X-ray diffraction studies on $K(18C6)^+$ complexes show a circular cavity with a diameter of 2.74–2.86 Å [16]. The cavity diameter of $K(2,2)^+$ is smaller, due to the larger van der Waals' radius of the nitrogen atom [17], and the distance between K^+ and N in $K(2,2)^+$ corresponds to a cavity diameter value of 2.71 Å. In view of this we assume that Sr^{2+} is located centrosymmetrically in the ring cavities of (2,2) and (2,2-Me_2) while Ba^{2+}, which is too large to be properly accommodated by the cavities, occupies a site somewhat displaced from the plane of the heteroatoms. On the other hand, Ca^{2+} is too small to completely fill the cavity of the ligands in a planar conformation and the heteroatoms may wrap around Ca^{2+} in order to increase their interaction with Ca^{2+} (*cf.* $Na(18C6)^+$) [18]. The higher solvation energy of Ca^{2+} compared to that of Sr^{2+} and Ba^{2+}, and the energy necessary to distort the ligands, both contribute to the small stability constants of $Ca(2,2)^{2+}$ and $Ca(2,2\text{-}Me_2)^{2+}$.

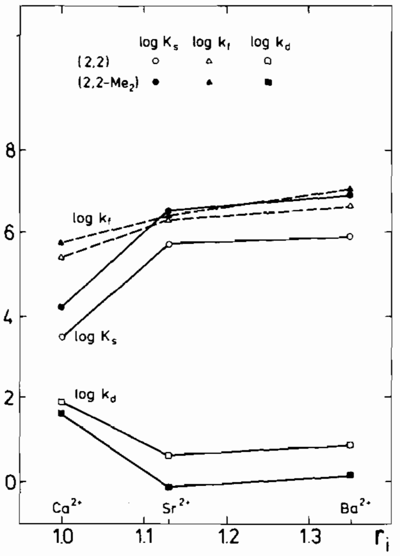

Fig. 1. Stability constants (K_s) and rates of dissociation (k_d) and formation (k_f) of alkaline earth metal complexes with (2,2) and (2,2-Me$_2$) in methanol at 25 °C.

The dissocation rate constants, k_d, in Table III support the interpretation given for the variation of $\log K_s$ with ionic radii and ligand type. Figure 1 shows that $\log k_d$ changes mirror those in $\log K_s$ for each of the ligands: the dissociation rate constants of (2,2-Me$_2$) are smaller than those of the (2,2) complexes and changes in log k_d values between Sr^{2+} and Ba^{2+} are insignificant. The formation rate constants, k_f, calculated from K_s and k_d values using eqn. (4), show a linear but slight dependence upon the reciprocal radii of the metal ions. Values of k_f lie between $2 \cdot 10^5$ and $1 \cdot 10^7$ M^{-1} s^{-1} and are very similar in magnitude to k_f values for several quite different macrocyclic ligands such as dibenzo-18-crown-6 (Sr^{2+}, $k_f = 9.6 \cdot 10^4$ M^{-1} s^{-1} at -15 °C) [19], antamanide (Ca^{2+}, $k_f = 4.9 \cdot 10^3$ M^{-1} s^{-1} at 25 °C) [20] or the macrobicyclic (2,2,2) (Sr^{2+}, $k_f = 5.4 \cdot 10^4$ M^{-1} s^{-1} at -15 °C) [19]. The similarity of the k_f values for these ligands of widely differing structure suggest that the stepwise desolvation of the ions during complex formation, and not conformational pre-equilibria of the ligands (perhaps except for antanamide) [20], is the rate determining process.

In the experimental procedure used to obtain dissociation rate constants [21] an excess of acid was mixed with a solution of a metal complex, and the decrease in concentration of the metal complex with time was observed conductimetrically. This is possible because the proton mobility is much larger than the mobility of the liberated metal or the protonated complex. The observed dissociation rate constants, k_e, were found to be dependent upon the proton concentration as in eqn. (2), where k_d is the rate constant for direct dissociation of a complex and k_H represents a proton catalyzed path. In experiments with macrobicyclic cryptand ligands it was found that k_H and k_H/k_d values decrease with increasing stability constant (and hence decreasing k_d values) for ions smaller than the cavity size, and become negligibly small when the ion size matches or exceeds the cavity size [6, 21, 22]. For these cryptate complexes a proton will only interact with the nitrogen atom of the cryptand when the electron lone pair of the nitrogen atom is in an exo-conformation, so that the exo–endo equilibrium determines the contribution of k_H to the total dissociation process. When the metal ion equals or exceeds the cavity in size, an exo-conformation is very unlikely, if only because of the reduction in distance between the oxygen atoms in different chains accompanying an endo–exo conversion. For much more flexible ligands such as (2,2) and (2,2-Me$_2$) no such simple relation exists between k_H/k_d and k_d. This may be seen from the data in column six of Table III where variations in k_H/k_d contrast sharply with the known behaviour of cryptates [6, 21, 22]. Only the k_H values for (2,2-Me$_2$) and the k_H/k_d values for (2,2) change monotonically with ionic radius. Only the Sr^{2+} complexes have k_H values of comparable magnitude. In the Ba^{2+} complexes, the metal ion is displaced from the plane of the heteroatoms, as discussed above, and a proton may attack a nitrogen atom from the opposite side, perhaps hindered more by the CH_3 group than by the N–H proton. On the other hand, protonation of nitrogen in the Ca^{2+} complexes probably requires an endo-exo conformational change and this should be easier in the N–CH_3 than in the N–H system [23]. The bulky CH_3 group also presumably reduces the residual metal ion-ligand contact more strongly then the N–H proton in (2,2).

While the stability constants and rates of formation and dissociation emphasise the similarities between the (2,2) and (2,2-Me$_2$) complexes, the corresponding thermodynamic parameters point to some quite significant differences. Inspection of Table I shows that enthalpies and entropies of complexation contribute additively to the magnitude of $\log K_s$, but in different proportions for (2,2) and (2,2-Me$_2$). In the case of (2,2) the entropic contribution dominates for Sr^{2+} and Ba^{2+}, and $\log K_s$, ΔH and ΔS values are very similar for the two cations. The large positive ΔS values may be mainly a result of the desolvation of the metal ions since the solvation entropies ($T\Delta S$) of Sr^{2+} and Ba^{2+} in methanol are -46 kJmol^{-1} and -34 kJmol^{-1} [24]. Just the opposite behaviour is observed for (2,2-Me$_2$) complexes, where ΔH values make the major contribution to $\log K_s$. The enthalpies of complex formation become substantially more negative with

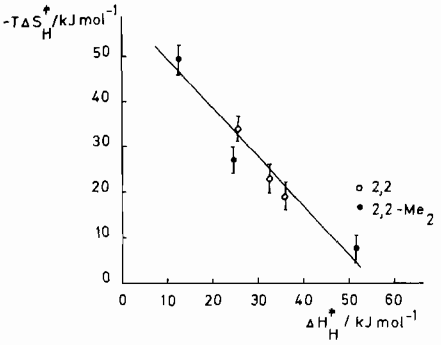

Fig. 2. $T\Delta S^{\ddagger}_{H}$ *vs.* $\Delta H^{\ddagger}_{H}$ for the proton catalysed dissociation of alkaline earth metal complexes with (2,2) –○– and with (2,2-Me_2) –●– in methanol.

increasing ionic radii, and the similar $\log K_s$ values for Sr^{2+} and Ba^{2+} in this case is a result of compensating ΔS values. Alkaline earth complexes with 18C6 in methanol show similar variations in ΔH with cation size, and as expected from $\log K_s$, $Ba(18C6)^{2+}$ has the most negative ΔH value. In the absence of suitable data in the literature it is difficult to interpret the compensating ΔS values for (2,2-Me_2) complexes of Ba^{2+} and Sr^{2+}, and the much more positive entropies of complexation for (2,2).

Differences between (2,2) and (2,2-Me_2) are further demonstrated by the activation enthalpies and entropies, $\Delta H^{\ddagger}_{d}$ and $T\Delta S^{\ddagger}_{d}$, in Table III. Except for $Sr(2,2)^{2+}$, $\Delta H^{\ddagger}_{d}$ and $\Delta S^{\ddagger}_{d}$ contribute additively to $\log k_d$, with $\Delta H^{\ddagger}_{d}$ being the dominant quantity. The activation parameters for the proton catalysed dissociation pathway (Table III) for complexes of (2,2) and (2,2-Me_2) show a single linear dependence of $T\Delta S^{\ddagger}_{H}$ on $\Delta H^{\ddagger}_{H}$, with a slight deviation of the data for $Ca(2,2\text{-}Me_2)^{2+}$. The existence of an isokinetic correlation (Fig. 2) may be evidence for a constant mechanism throughout a series.

Conclusion

In the present paper experiments are described which demonstrate that it is possible to determine dissociation rate constants for alkaline earth metal complexes with diaza-crown ethers from stopped-flow experiments. The similarities between K_s and k_d and the monotonic dependence of $\log k_f$ on ionic radius suggest a similarity in behaviour of alkaline earth metal complexes with (2,2) and (2,2-Me_2). However, thermodynamic and activation parameters point to differences between the two diaza-crown ethers and the data for (2,2-Me_2) complexes, which show some similarities to corresponding data for 18C6 complexes, appear to be simpler to interpret. Solvation of the metal complexes has not been specifically taken into account to date, and it is possible that this makes a major contribution to the differences between the (2,2) and (2,2-Me_2) complexes. Thus the N–H bond should be strongly polarised in the presence of an M^{2+} ion, leading to significant interactions involving the hydrogen atom and solvent molecules. Two recent studies have provided evidence of strong H-bonding interactions between amine hydrogens of coordinated NH_3 or ethylenediamine ligands and solvent molecules [25, 26] and similar effects may be operating here.

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