Formation of Li+ and Cd2+ Catenates, a Reaction with a Negative Enthalpy of Activation

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The mechanism of formation of Li+ and Cd2+ catenates involves two kinetically observable steps; the slower one consists of two processes and has a negative activation enthalpy, supporting a preequilibrium between two complexed species in the mononuclear rearrangement leading to the catenate structure.

We have recently studied the complexation reactions of interlocked macrocyclic ligands (catenands) by various cationic species.[1] Cu+ and Ag+ lead to a classical second-order rate law whereas Li+, Cd2+, Zn2+ and Co2+ catenates are formed in two distinct steps. We report here the temperature dependence of these two steps for the complexation reactions of Li+ and Cd2+ by the catenand **1**.

Surprisingly, the observed rate constant k_2 of the second step decreases as the temperature is increased. On the other hand, the first bimolecular step is normal, with a second-order rate constant, and follows a classical dependence on the

temperature. The kinetic parameters of the overall reaction (1) were determined in the range 15–30 °C in the ternary

$$1 + M^{n+} \rightleftharpoons 1 \cdot M^{n+} \qquad (1)$$
$$\text{catenand} \qquad \text{catenate}$$
$$M^{n+} = Li^+ \text{ or } Cd^{2+}$$
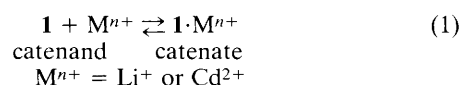
solvent MeCN–CH$_2$Cl$_2$–H$_2$O (80:10:10) by stopped-flow measurements.[1] Formation of the catenates **1·Li+** and **1·Cd2+** was monitored at 360 and 355 nm respectively. The reaction proceeds in two observable steps over the temperature range used. For the first step, a linear dependence of the experimental first-order rate constant k_{obs} on metal concentration was observed [eqn. (2)].[1] On the other hand,

$$-d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}] = k_1[M^{n+}][\mathbf{1}] \qquad (2)$$

the second step is independent of metal concentration. Each experiment was performed at least twice.

The variation of k_{obs} (first step) with metal concentration at various temperatures is represented in Fig. 1. The first step (k_1) corresponds to a classical bimolecular complexation reaction. It becomes faster as the temperature is increased as shown in Table 1.

Eyring's equation[2] was used to determine the activation parameters corresponding to both steps: [eqn. (3)]. The

$$\ln (k/T) = \ln (k_B/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT \qquad (3)$$
$$k = \text{rate constant}; \ k_B = \text{Bolzmann constant}$$

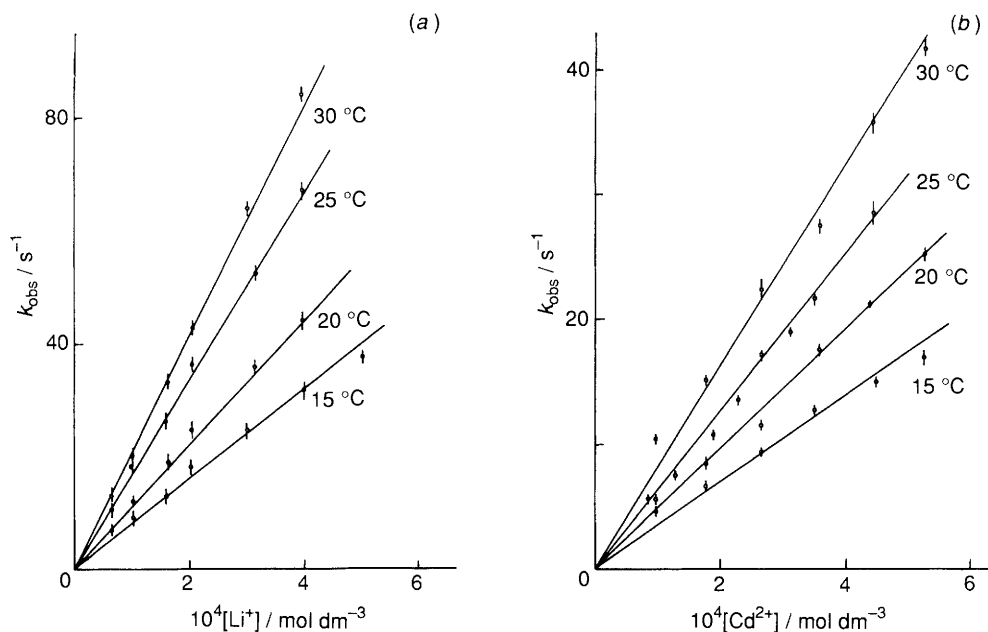variation of ln (k/T) as a function of T^{-1} for both steps is represented in Fig. 2.
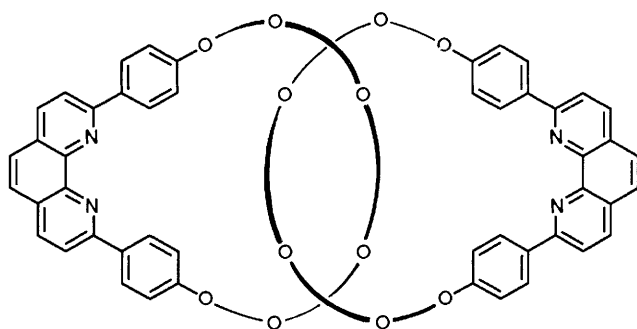
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Scheme 1

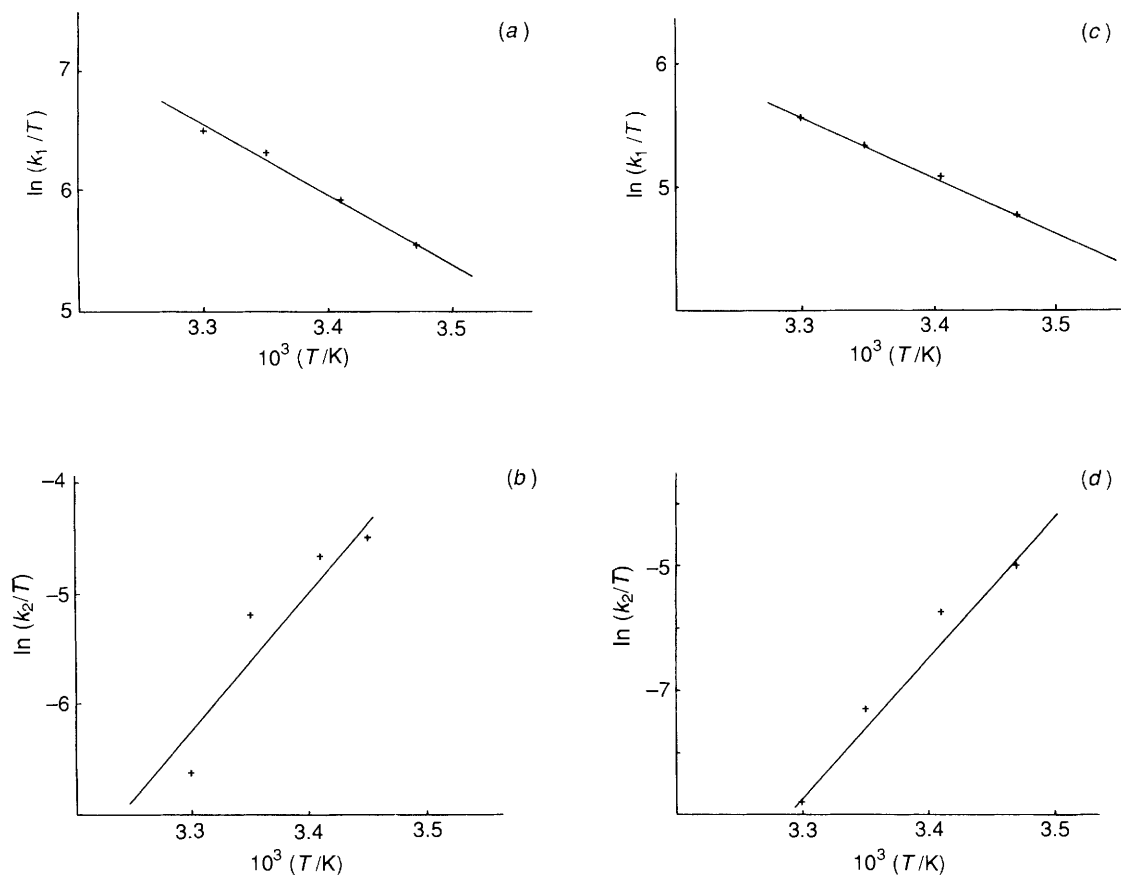**Fig. 1** k_{obs} (first step) as a function of metal concentration in the range 15–30 °C for (a) $1 \cdot Li^+$ and (b) $1 \cdot Cd^{2+}$

Fig. 2 Eyring's plots for k_1 and k_2; (a) and (b): $1 \cdot Li^+$; (c) and (d): $1 \cdot Cd^{2+}$

A linear plot is obtained for the k_1 values with a negative slope whereas the k_2 values lead to an Eyring plot with a positive slope and a relatively strong curvature. The activation parameters were obtained from these plots after linearisation (Table 2).

For Cd^{2+} the first step is relatively slow compared to the rate of reaction of 1,10-phenanthroline with the aquated ion in

water[3] ($k = 10^7$ dm^3 mol^{-1} s^{-1}). The macrocyclic structure of the ligand[4] and the hindered character of the chelate are probably responsible for the relatively slow rate observed.

The temperature dependence of the second step was highly unexpected. It implies that this step consists of two processes involving: (i) a preequilibrium (equilibrium constant K) between the first intermediate **II** obtained after the bimole-

Table 1 Kinetic data for the formation of Li^+ and Cd^{2+} catenates in the temperature range 15–30 °C[a]

$T/°C$	First step, $k_1 \times 10^{-4}/dm^3\,mol^{-1}\,s^{-1}$		Second step k_2/s^{-1}	
	Li^+	Cd^{2+}	Li^+	Cd^{2+}
15.0 ± 0.5	7.4 ± 0.2	3.4 ± 0.1	3.2 ± 0.5	1.95 ± 0.04
20.0 ± 0.2	10.9 ± 0.1	4.7 ± 0.1	2.7 ± 1.1	0.95 ± 0.05
25.0 ± 0.1	16.7 ± 0.3	6.2 ± 0.1	1.7 ± 0.5	0.18 ± 0.01
30.0 ± 0.1	20.1 ± 0.1	8.0 ± 0.1	0.4 ± 0.1	0.05 ± 0.01

[a] Solvent: $MeCN-CH_2Cl_2-H_2O$ (80:10:10); ionic strength = 0.1 adjusted with $Bu^n_4NClO_4$.

Table 2 Activation parameters for formation of the catenate $1 \cdot Li^+$ and $1 \cdot Cd^{2+}$ [a]

Catenate	First step (k_1) (bimolecular)		Second step (k_2) (unimolecular)	
	$\Delta H_1^{\ddagger b}$	$\Delta S_1^{\ddagger c}$	$\Delta H_2^{\ddagger b}$	$\Delta S_2^{\ddagger c}$
$1 \cdot Li^+$	11 ± 5	3 ± 1	-24 ± 20	-140 ± 80
$1 \cdot Cd^{2+}$	9 ± 2	-6 ± 1	-45 ± 35	-215 ± 150

[a] Same experimental conditions as for Table 1. The uncertainties have been calculated with a confidence interval corresponding to 95% probability. [b] Units kJ mol^{-1}. [c] Units J K^{-1} mol^{-1}.

cular step k_1 and a second transient species **III**, and (*ii*) a final first-order rearrangement step (rate constant k_3) affording the catenate structure **IV**. The putative mechanistic scheme represented in Fig. 3 may account for the observed temperature dependence.

The observed rate constant k_2 would then be the product of an equilibrium constant K and the rate constant k_3 [eqns. (4) and (5)].[5] If $\Delta H°$ is sufficiently negative, it may happen that

$$k_2 = K \times k_3 \tag{4}$$

$$\Delta H_2^{\ddagger} = \Delta H° + \Delta H_3^{\ddagger} \tag{5}$$

$\Delta H_2^{\ddagger}$ is also negative, as observed in the present case. In addition, if the reaction has a very strong and negative entropic contribution, K and subsequently k_2 may decrease with increasing temperature.

The formation of the intermediate complex **II** may involve the oxygen atoms of the pentaoxyethylene fragments coordinated to the metal. This intermediate could be geometrically relatively similar to the free ligand **I**. On the other hand, **III** may resemble the catenate **IV**, with possible stacking interactions between the aromatic subunits of each ring.[6]

Although the structure of the postulated intermediates **II** and **III** is not known, **III** must be much more rigid and organized than **II**. In addition, the reaction pathway converting **II** to **IV** is certainly extremely restricted. In other words, the formation of the catenate structure **IV**, with its two
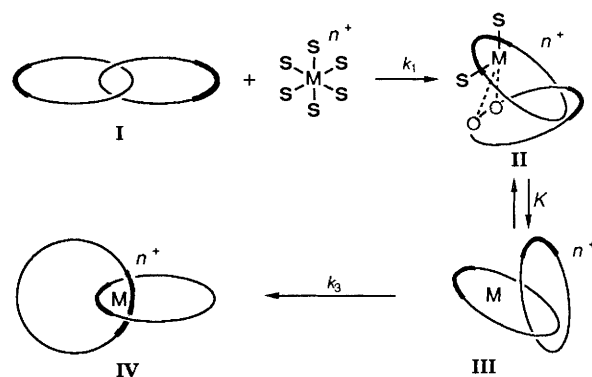
Fig. 3 A possible mechanistic scheme for the multistep formation of catenates $1 \cdot Li^+$ and $1 \cdot Cd^{2+}$ (S = solvent)

entwined rigid ligands, may be related to the cup-and-ball game; the more the player shakes the toy, the less likely it is that the hollow ball will fall on the post so as to be threaded by it.

Negative enthalpies of activation have only rarely been observed in the past. They usually involved electron transfer reactions between transition metal complexes,[7–9] with formation of an intermediate species containing the redox partners. An interesting example of a reaction in the gas phase with a negative activation energy and its theoretical treatment have also been reported.[10]

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