

# Complexation of cobalt(II), nickel(II) and copper(II) by the pendant arm macrocyclic ligand *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane

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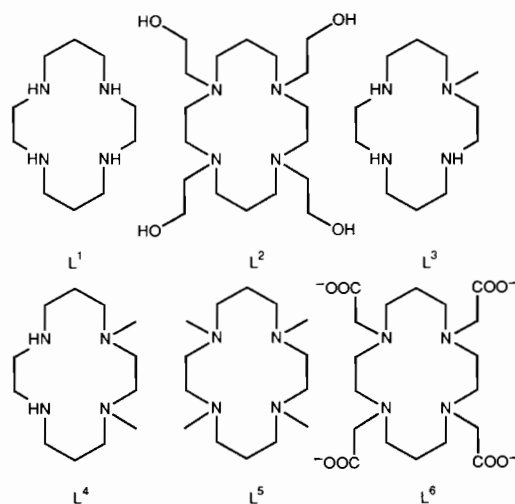
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## Abstract

A stopped-flow spectrophotometric study of the complexation of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  by the pendant arm ligand, *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane ( $\text{L}^2$ ), in aqueous solution at pH 6.80,  $I = 1.50$  ( $\text{NaNO}_3$ ) and 298.2 K yields the rate constants,  $k_{\text{LH}} = 880$  and  $116 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the complexation of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , respectively, by the monoprotonated ligand,  $\text{L}^2\text{H}^+$ . In aqueous  $\text{HNO}_3$ , the decomplexation of  $[\text{ML}^2]^{2+}$  is characterized by:  $k_{\text{obs}} = k_0 + k_1 K_{1a} [\text{H}^+] / 1 + K_{1a} [\text{H}^+]$  where at 298.2 K,  $k_0 = 0.21$ ,  $\approx 0$  and  $\approx 0 \text{ s}^{-1}$ ,  $k_1 = 151$ , 0.160 and  $6.07 \text{ s}^{-1}$ , and  $K_{1a} = 5.2$ , 83 and  $0.67 \text{ dm}^3 \text{ mol}^{-1}$ , respectively, when  $\text{M}^{2+} = \text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The effect of the pendant arms on the complexation and decomplexation processes are considered through a comparison of these data with those for 1,4,8,11-tetraazacyclotetradecane and related ligands.

## Introduction

The complexation of metal ions by pendant arm tetraazacycloalkanes is a subject of current interest because an appropriate combination of selectivity and lability in such reactions may render these ligands suitable for metal ion sensor or scavenging applications [1–7]. Thus, an understanding of the manner in which pendant arms modify the complexation characteristics of the parent tetraazacycloalkane is of importance. Such understanding is sought here through a comparison of the complexation of the parent 1,4,8,11-tetraazacyclotetradecane,  $\text{L}^1$ , its pendant arm derivative *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane,  $\text{L}^2$  [8–12], and the related ligands  $\text{L}^3$ – $\text{L}^6$  (Scheme 1). Studies of the complexation of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  by  $\text{L}^2$  indicate that significant selectivity between these metal ions exists, and that the complex stability constants,  $K$ , are decreased by more than an order of magnitude by comparison with those for the complexes formed by  $\text{L}^1$ , and the rate of complexation is increased by comparison with that of  $\text{L}^1$  [8]. In this study the kinetic characteristics of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  complexes of  $\text{L}^2$  have been subjected to detailed investigation



Scheme 1.

to determine the effect of the pendant hydroxyethyl arms on the complexation process.

## Experimental

### Materials

*N,N',N'',N'''*-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane was prepared as previously de-

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scribed [8]. Metal nitrates were either prepared from metal carbonates through reaction with the stoichiometric amount of HNO<sub>3</sub>, or were purchased. In either case they were twice recrystallized from water, and were dried and stored over P<sub>2</sub>O<sub>5</sub> under nitrogen. Water was ultrapurified with a MilliQ-Reagent system to produce water with a specific resistance of > 15 MΩ cm. The metal nitrate, HNO<sub>3</sub> and NaOH (all with *I* adjusted to 1.50 with NaNO<sub>3</sub>) titration solutions were prepared under nitrogen and were standardized by conventional methods.

#### Potentiometric titrations

Potentiometric titrations were carried out using a Metrohm E665 Dosimat autoburette interfaced to a Laser XT/3-8086 PC in conjunction with an Orion SA720 potentiometer and an Orion Ross Sureflow combination electrode. The electrode was standardized using standard buffer solutions. All titrations were performed at 298.2 ± 0.05 K in a water jacketted vessel which was closed apart from a vent to allow egress of nitrogen. A stream of nitrogen was passed through the titration solution to exclude atmospheric carbon dioxide, and the solution was stirred using a magnetic stirrer. The instrumentation was calibrated by titration of 0.100 mol dm<sup>-3</sup> NaOH from the autoburette against 0.004 mol dm<sup>-3</sup> HNO<sub>3</sub> (10.00 cm<sup>3</sup>). The protonation constants of L<sup>2</sup> were determined by titration of a solution (10.00 cm<sup>3</sup>) 0.004 and 0.001 mol dm<sup>-3</sup> in HNO<sub>3</sub> and L<sup>2</sup>, respectively, with 0.100 mol dm<sup>-3</sup> NaOH. The stability constants of [ML<sup>2</sup>]<sup>2+</sup>, [ML<sup>2</sup>-H]<sup>+</sup> (M<sup>2+</sup> = Co<sup>2+</sup>, Ni<sup>2+</sup> or Cu<sup>2+</sup>) were determined by titrations of solutions (10.00 cm<sup>3</sup>) 0.004, 0.001 and 0.00085 mol dm<sup>-3</sup> in HNO<sub>3</sub>, L<sup>2</sup> and M(NO<sub>3</sub>)<sub>2</sub>, respectively, with 0.100 mol dm<sup>-3</sup> NaOH. All titrations were carried out in duplicate at least. The protonation constants and apparent stability constant values were determined using the program MINQUAD [13].

#### Stopped-flow spectrophotometry

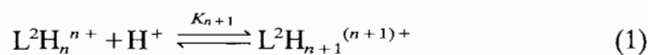
Kinetic studies were carried out on degassed solutions using a stopped-flow UV-Vis spectrophotometer similar to that described in the literature [14] constructed in our laboratories. The drive syringes and mixing chambers were thermostatted to ±0.05 K. Kinetic data were collected at 550, 365 and 630 nm close to the absorbance maxima of [CoL<sup>2</sup>]<sup>2+</sup>, [NiL<sup>2</sup>]<sup>2+</sup> and [CuL<sup>2</sup>]<sup>2+</sup>, respectively, whose spectra in aqueous 1.50 mol dm<sup>-3</sup> NaNO<sub>3</sub> ([CoL<sup>2</sup>]<sup>2+</sup>: λ<sub>max</sub> = 488 and 538 with ε<sub>max</sub> = 15.1 and 14.9 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively, observed for a solution 0.020 mol dm<sup>-3</sup> in [Co<sup>2+</sup>] and [L<sup>2</sup>] at pH 6.80; [NiL<sup>2</sup>]<sup>2+</sup>: λ<sub>max</sub> = 366 and 588 with ε<sub>max</sub> = 29.2 and 12.9 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively, observed for a solution 0.010 mol dm<sup>-3</sup> in [Ni<sup>2+</sup>] and [L<sup>2</sup>] at pH 6.80; and [CuL<sup>2</sup>]<sup>2+</sup>: λ<sub>max</sub> = 638 with ε<sub>max</sub> = 363 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively;

observed for a solution 0.002 mol dm<sup>-3</sup> in [Cu<sup>2+</sup>] and [L<sup>2</sup>] at pH 6.20) were consistent with those previously reported [8, 10]. Kinetic traces were digitized on a Datalab DL 905 data logger. Typically 10–12 such traces were signal averaged and fitted to a first order rate equation through a Laser Turbo XT PC interfaced to a Sun 3/60 work station. The solutions for complexation studies were buffered with 0.3 mol dm<sup>-3</sup> PIPES buffer (Cal Biochem) adjusted to the desired pH with NaOH or HNO<sub>3</sub>. An *I* = 1.50 was maintained by adjustment with NaNO<sub>3</sub> in both the complexation and decomplexation studies. The reactant concentrations are given below.

## Results and discussion

#### Ligand protonation constants and complex stability constants

The kinetic studies of the complexation of metal ions by L<sup>2</sup> required an *I* = 1.5 to allow sufficient variation of reactant concentration. Therefore, it was necessary to redetermine the protonation constants of L<sup>2</sup> and the stability constants of its complexes. The four protonations of L<sup>2</sup>:



where *n* = 0, 1, 2 or 3 are characterized by *K*<sub>*n*+1</sub>:

$$K_{n+1} = \frac{[\text{L}^2\text{H}_{n+1}^{(n+1)+}]}{[\text{L}^2\text{H}_n^{n+}][\text{H}^+]} \quad (2)$$

whose magnitudes appear in Table 1, together with data for other *I* values and related ligands [8, 10, 15, 16]. It is seen that *K*<sub>1</sub> and *K*<sub>2</sub> for L<sup>2</sup> increase with *I*, and are substantially smaller than those for L<sup>1</sup>, but are similar to those for L<sup>5</sup>, reflecting the change from a secondary amine to a tertiary amine donor set. The similar *K*<sub>1</sub> and *K*<sub>2</sub> are assigned to amine groups *trans* to each other where the interactions between their protonations are minimized. The much smaller *K*<sub>3</sub> and *K*<sub>4</sub> characterize protonations at the remaining amine

TABLE 1. Protonation constants of L<sup>2</sup> and related ligands at 298.2 K and various *I*

L	log <i>K</i> <sub>1</sub>	log <i>K</i> <sub>2</sub>	log <i>K</i> <sub>3</sub>	log <i>K</i> <sub>4</sub>
L <sup>2a</sup>	9.25 ± 0.02	8.79 ± 0.03	3.31 ± 0.06	2.88 ± 0.03
L <sup>2b</sup>	8.80	8.24	2.69	~1.20
L <sup>2c</sup>	8.83	8.30	2.65	<2.0
L <sup>1d</sup>	11.59	10.62	1.61	2.42
L <sup>5e</sup>	9.34	8.99	2.58	2.25
L <sup>5d</sup>	9.70	9.31	3.09	2.64

<sup>a</sup>This work, *I* = 1.50 (NaNO<sub>3</sub>) <sup>b</sup>Ref 8, *I* = 0.1 (NaNO<sub>3</sub>). <sup>c</sup>Ref 10, *I* = 0.1 (NaClO<sub>4</sub>). <sup>d</sup>Ref. 15, *I* = 0.5 (KNO<sub>3</sub>) <sup>e</sup>Ref. 16, *I* = 0.1 (NaNO<sub>3</sub>).

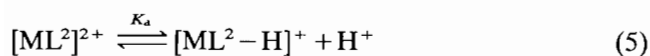
sites which interact substantially with the protonated *cis* amine groups.

Within the total  $[M^{2+}]$ , total  $[L^2]$  and pH ranges studied, the following equilibria characterize the metal ion complexation process:



where

$$K_{ML} = \frac{[ML^2]^{2+}}{[M^{2+}][L^2]} \quad (4)$$



where

$$K_a = \frac{[ML^2-H]^+[H^+]}{[ML^2]^{2+}} \quad (6)$$

When  $M^{2+} = Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ ,  $\log K_{ML} = 5.87 \pm 0.08$  (6.10),  $7.96 \pm 0.06$  (7.31, 7.45), and  $16.7 \pm 0.1$  (15.7, 16.2), respectively, at 298.2 K and  $I = 1.50$  ( $NaNO_3$ ), and the first and second figures in brackets are  $\log K_{ML}$  values reported for  $I = 0.1$  ( $NaNO_3$ ) and  $I = 0.1$  ( $NaClO_4$ ), respectively [8, 10]. It is seen that the magnitude of  $K_{ML}$  varies qualitatively as anticipated from the Irving-Williams series [17, 18]. When  $M^{2+} = Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ ,  $pK_a = 6.82 \pm 0.05$ ,  $9.22 \pm 0.05$  and  $10.1 \pm 0.05$ , respectively, ( $\log K_w = 13.7 \pm 0.05$ .)

#### Complexation of $Co^{2+}$ and $Ni^{2+}$ by $L^2$

It is desirable to compare the complexation of different  $M^{2+}$  under identical reaction conditions. Thus, in addition to this requirement, the previously discussed protonation of  $L^2$  and deprotonation of  $[ML^2]^{2+}$  necessitated the buffering of the system at a pH at which substantial complexation of  $M^{2+}$  occurred and precipitation of metal hydroxides did not interfere with observation of the rate process. The large value of  $K_{ML}$  characterizing  $[CuL^2]^{2+}$ , causes  $> 50\%$  of  $Cu^{2+}$  to be complexed at  $pH \geq 3$  (total  $[Cu^{2+}]$  and total  $[L^2] = 10^{-3}$  mol dm $^{-3}$  each), whereas the substantially lower values of  $K_{ML}$  for  $[CoL^2]^{2+}$  and  $[NiL^2]^{2+}$ , cause negligible percentages of  $Co^{2+}$  and  $Ni^{2+}$  to be complexed at  $pH = 5$ . At  $pH 6.80$  c. 100, 75 and 20% of  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Co^{2+}$ , respectively, are complexed and in principle this is a suitable pH for comparative kinetic studies. However, at the  $\geq 10$ -fold excess  $[M^{2+}]$  required to ensure pseudo first order kinetics for the approach to equilibrium, uncomplexed  $Cu^{2+}$  precipitates as the hydroxide at  $pH 6.80$ , and as a consequence only the complexation of  $Co^{2+}$  and  $Ni^{2+}$  were studied.

The variation of the magnitude of the pseudo first order rate constant,  $k_{obs}$ , for the approach to equilibrium with excess  $[Co^{2+}]$  (Fig. 1) is consistent with

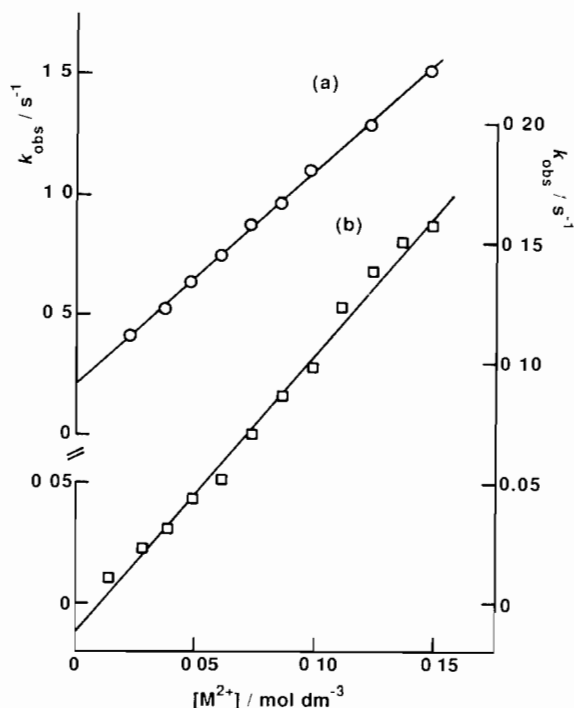


Fig. 1. The variation of  $k_{obs}$  for the complexation of  $M^{2+}$  by  $L^2$  with variation of  $[M^{2+}]$  at  $pH 6.80$  and  $I = 1.5$  ( $NaNO_3$ ) and 298.2 K. (a)  $M = Co$  and the total  $[L^2] = 2.5 \times 10^{-3}$  mol dm $^{-3}$ , (b)  $M = Ni$  and the total  $[L^2] = 1.5 \times 10^{-3}$  mol dm $^{-3}$ . The curves through the data points represent the least-squares fits to eqn. (8) in both cases

$$k_{obs} = k_c[Co^{2+}] + k_d \quad (7)$$

such that the slope of the graph gives an overall complexation rate constant,  $k_c = 8.93 \pm 0.11$  dm $^3$  mol $^{-1}$  s $^{-1}$ , and the intercept gives the decomplexation rate constant for  $[CoL^2]^{2+}$ ,  $k_d = 0.21 \pm 0.01$  s $^{-1}$ . A similar variation of  $k_{obs}$  with excess  $[Ni^{2+}]$  is also observed (Fig. 1) and  $k_c = 1.17 \pm 0.03$  dm $^3$  mol $^{-1}$  s $^{-1}$  and  $k_d = -0.012 \pm 0.003$  s $^{-1}$  were derived for this system. The negative value for  $k_d$  in the latter case is attributed to experimental error in the  $k_{obs}$  data, and also indicates that  $k_d$  is small in magnitude.

As both hexaqua  $Co^{2+}$  and  $Ni^{2+}$  undergo ligand substitution through dissociatively activated mechanisms [19–22], the second order  $k_c$  values reflect the fast formation of an encounter complex, characterized by  $K_o$ , prior to the substitution of the aqua ligands through an  $I_d$  mechanism. Thus, in the presence of excess  $[M^{2+}]$ ,  $k_{obs}$  is of the form:

$$k_{obs} = k_c[M^{2+}] + k_d = \frac{k_c'K_o[M^{2+}]}{1 + K_o[M^{2+}]} + k_d \quad (8)$$

where  $k_c'$  characterizes the interchange of the substituting ligand between the first and second coordination spheres of  $M^{2+}$ . Under the limiting condition:  $K_o[M^{2+}] \ll 1$ ,  $k_{obs} \approx k_c'K_o[M^{2+}] + k_d$ , and  $k_c'K_o \approx k_c$ , con-

sistent with the linear variation of  $k_{\text{obs}}$  with  $[\text{M}^{2+}]$  seen in Fig. 1. The significance of these observations is discussed below.

The predominant form of the free ligand over the pH range studied in the formation of  $[\text{NiL}^{2+}]^{2+}$  is  $\text{L}^2\text{H}_2^{2+}$ . When total  $[\text{L}^2]$  and  $[\text{Ni}^{2+}] = 1.5 \times 10^{-3}$  and  $7.5 \times 10^{-2}$  mol dm<sup>-3</sup>, respectively, the variation of  $k_{\text{obs}}$  with pH is:  $0.030 \pm 0.001$  (6.52),  $0.047 \pm 0.001$  (6.67),  $0.070 \pm 0.001$  (6.80),  $0.123 \pm 0.001$  (6.94), and  $0.204 \pm 0.004$  (7.12) where the first figure is  $k_{\text{obs}}$  (s<sup>-1</sup>) at 298.2 K, and pH is quoted in parentheses. (The pH range was constrained at the low end by the decreased amount of  $[\text{NiL}^{2+}]^{2+}$  formed and the resulting small absorbance change, and at the high end by precipitation of  $\text{Ni}(\text{OH})_2$ .) This variation of  $k_{\text{obs}}$  with the degree of protonation of  $\text{L}^2$  may be expressed as:

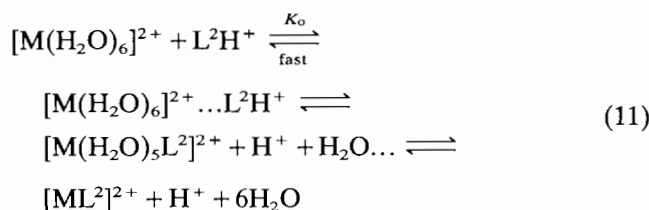
$$k_{\text{obs}} = \frac{k_{\text{L}}[\text{L}^2] + k_{\text{LH}}[\text{L}^2\text{H}^+] + k_{\text{LH}_2}[\text{L}^2\text{H}_2^{2+}]}{[\text{L}^2]_{\text{total}}} + k_{\text{d}} \quad (9)$$

where  $k_{\text{d}} \approx 0$ , only the  $\text{L}^2$ ,  $\text{L}^2\text{H}^+$  and  $\text{L}^2\text{H}_2^{2+}$  forms of the ligand are considered, and the pH dependence of  $k_{\text{obs}}$  is given by:

$$k_{\text{obs}} = \frac{k_{\text{L}}K_1K_2 + k_{\text{LH}}K_2[\text{H}^+] + k_{\text{LH}_2}[\text{H}^+]^2}{K_1K_2 + K_2[\text{H}^+] + [\text{H}^+]^2} \quad (10)$$

A least-squares fit of these  $k_{\text{obs}}$  data to eqn. (10) yields the pseudo first order  $k_{\text{L}} = 340 \pm 288$  s<sup>-1</sup>,  $k_{\text{LH}} = 8.23 \pm 2.75$  s<sup>-1</sup> and  $k_{\text{LH}_2} = -0.023 \pm 0.016$  s<sup>-1</sup>. The uncertainty in  $k_{\text{L}}$  is a consequence of the vanishingly small proportion of  $\text{L}^2$  existing as the unprotonated form over the pH range studied, and the small negative value of  $k_{\text{LH}_2}$  is consistent with  $\text{L}^2\text{H}_2^{2+}$  making a negligible contribution to the overall  $k_{\text{obs}}$  by comparison with that of  $\text{L}^2\text{H}^+$ . On this basis it is concluded that  $\text{L}^2\text{H}^+$  is the dominant substituting ligand, such that eqn. (9) becomes:  $k_{\text{obs}} \approx k_{\text{LH}}[\text{L}^2\text{H}^+]/[\text{L}^2]_{\text{total}}$ . A second order rate constant may be derived for substitution by  $\text{L}^2\text{H}^+$  by dividing  $k_{\text{LH}}$  by the total  $[\text{Ni}^{2+}]$  ( $7.5 \pm 10^{-2}$  mol dm<sup>-3</sup>) to give  $k_{\text{LH}'} = 110$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> =  $k_{\text{c}}[\text{L}^2]_{\text{total}}/[\text{L}^2\text{H}^+]$ . Independently,  $k_{\text{LH}'} = 116$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the  $\text{Ni}^{2+}$  system is obtained from  $k_{\text{c}}$  determined from the data in Fig.1 through the relationship:  $k_{\text{LH}'} = k_{\text{c}}[\text{L}^2]_{\text{total}}/[\text{L}^2\text{H}^+]$ . A value of  $k_{\text{LH}'} = 880$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> is similarly derived for the  $\text{Co}^{2+}$  system.

The sequential displacement of the six aqua ligands by multidentate  $\text{L}^2\text{H}^+$  may be expressed:



where the substitution of any one of the six aqua ligands may be rate determining. If this step is the substitution of the first aqua ligand in  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $k_{\text{c}}' (= k_{\text{LH}'}K_{\text{o}})$  in eqn. (8) should be similar to the water exchange rate constants,  $k_{\text{ex}} = 3.18 \times 10^6$  and  $3.15 \times 10^4$  s<sup>-1</sup> at 298.2 K for  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , respectively [18, 19]. On this basis  $K_{\text{o}} = 2.8 \times 10^{-4}$  and  $3.5 \times 10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup> are calculated for the  $[\text{CoL}^{2+}]^{2+}$  and  $[\text{NiL}^{2+}]^{2+}$  systems, respectively, through eqn. (8). These low  $K_{\text{o}}$  values are qualitatively consistent with an interaction between species of similar charge, such as  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ , and  $\text{L}^2\text{H}^+$  or  $\text{L}^2\text{H}_2^{2+}$ , where the latter is the dominant ligand species at pH=6.80. However, they are substantially lower than  $K_{\text{o}} = 0.122$  and  $0.047$  dm<sup>3</sup> mol<sup>-1</sup> calculated from the Fuoss equation [23, 24] using an interaction distance of 5 Å between 2+ and 1+, and between 2+ and 2+ charged species, respectively, which indicates that either it is inappropriate to use the Fuoss equation for such systems, or the substitution of the first aqua ligand in  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  is not the rate determining step, but a later step is. On the latter basis the calculated  $K_{\text{o}}$  is the product of the true  $K_{\text{o}}$  and the equilibrium constants for the substitution of the aqua ligands preceding the rate determining step.

For  $\text{Ni}^{2+}$ ,  $k_{\text{LH}'}$  (298.2 K) varies in the sequence 53, 116, 55, 10, 1.4 and 25000 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively, for  $\text{L}^1$ - $\text{L}^6$  [25-27]; and for  $\text{Co}^{2+}$ ,  $k_{\text{LH}'}$  (298.2 K) varies in the sequence 1500, 880 and 16 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively, for  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^5$  [25, 28] where the data for  $\text{L}^2$  arise from this study. Thus, it is seen that for  $\text{Ni}^{2+}$  increasing methyl substitution on  $\text{L}^1$  at N decreases  $k_{\text{LH}'}$ , whereas hydroxyethyl substitution causes a c. two-fold increase in  $k_{\text{LH}'}$  which is moderate by comparison with the c. 500-fold increase caused by acetato substitution. If the increased stiffness of the macrocyclic ring caused by the hydroxyethyl groups of  $\text{L}^2$  has a similar substitution rate decreasing effect to that of the methyl groups of  $\text{L}^5$  [26], the c. 80-fold increased complexation rate of  $\text{L}^2$  over  $\text{L}^5$  is attributable to the coordinating ability of the hydroxo groups. This suggests that a prior coordination of  $\text{Ni}^{2+}$  involving one or more hydroxo groups of  $\text{L}^2\text{H}^+$  before coordination of  $\text{Ni}^{2+}$  by all four amine nitrogens is achieved. (Although it is thought that the acetate pendant groups of  $\text{L}^6$  coordinate  $\text{Ni}^{2+}$  in the initial stages of complexation, the large value of  $k_{\text{LH}'}$  cannot be solely attributed to this effect as the negative charge of  $\text{L}^6\text{H}^{3-}$  should greatly increase the magnitude of  $K_{\text{o}}$  in eqn. (8) for this system [27].), The  $k_{\text{LH}'}$  data for the analogous  $\text{Co}^{2+}$  systems are consistent with this interpretation also.

There are probably several conformers of  $\text{L}^2\text{H}^+$  in solution which need not correspond to the conformer in  $[\text{ML}^{2+}]^{2+}$ , as exemplified by the observation of the *trans* IV (*RSSR*) conformer of  $\text{L}^2$  in the solid state

[29]. To convert this conformation to the *trans* III (*RRSS*) conformation observed in  $[\text{NiL}^2\text{-H}]^+$ ,  $[\text{CdL}^2]^{2+}$ ,  $[\text{HgL}^2]^{2+}$  and  $[\text{PbL}^2]^{2+}$  [10–12], two nitrogen inversions are required which may represent major activation barriers in the formation of  $[\text{ML}^2]^{2+}$ . Similar considerations arise for the *trans* I (*RSRS*) and *trans* V (*RRRR*) conformers of  $\text{L}^2\text{H}^+$ , and also the *cis* conformers. Evidence for a rate determining role for conformational change is presented in a study of the substitution of  $\text{L}^1$ ,  $\text{L}^3\text{-L}^5$  [25, 30], and the trimethyl analogue on  $\text{Ni}^{2+}$  in dimethylformamide where a second order substitution step was followed by a first order intramolecular process [30]. The rate determining step for the second order process is assigned to the formation of the second Ni–N bond and the rate of the slower first order process is thought to be controlled by a ligand conformational change.

#### $[\text{ML}^2]^{2+}$ decomplexation reactions in acid solution

The variation of the observed pseudo first order decomplexation rate constant for  $[\text{CoL}^2]^{2+}$ ,  $k_{\text{obs}}$ , with excess  $[\text{H}^+]$  is shown in Fig. 2, and is of the form:

$$k_{\text{obs}} = \frac{k_0 + k_1 K_{1a} [\text{H}^+]}{1 + K_{1a} [\text{H}^+]} \quad (12)$$

consistent with the decomplexation reactions:

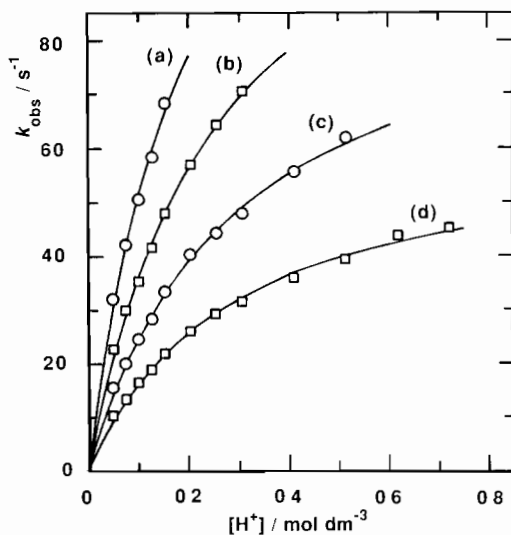
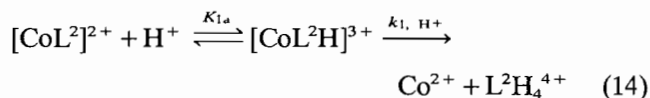
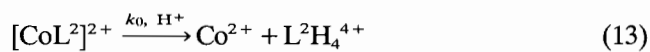


Fig. 2. The variation of  $k_{\text{obs}}$  for the decomplexation of  $[\text{CoL}^2]^{2+}$  (total  $[\text{Co}^{2+}] = \text{total} [\text{L}^2] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ) with  $[\text{HNO}_3]$  and  $I = 1.50$  ( $\text{NaNO}_3$ ) at: (a) 298.2, (b) 293.2, (c) 288.2 (d) 283.2 K. The solid curves represent the non-linear least-squares fits to eqn. (12).

where  $K_{1a}$  is a protonation constant and  $k_0$  and  $k_1$  are the rate constants for  $[\text{CoL}^2]^{2+}$  and  $[\text{CoL}^2\text{H}]^{3+}$ . Thus, when  $k_0$  is set equal to  $0.21 \pm 0.01 \text{ s}^{-1}$  at 298.2 K and 0 at the lower temperatures as is justified by the  $k_0 (=k_d) = 0.21 \pm 0.01 \text{ s}^{-1}$  (298.2 K) derived from the complexation data discussed above, the best fit  $k_1$  in Table 2 are obtained for which the Eyring equation yields the associated activation parameters. A combination of the requirement to maintain a 10-fold excess  $[\text{H}^+]$  over the total  $[\text{CoL}^2]^{2+}$ , and the magnitude of the molar absorbance of  $[\text{CoL}^2]^{2+}$  precludes study of this system at  $[\text{H}^+] < 0.0493 \text{ mol dm}^{-3}$ .

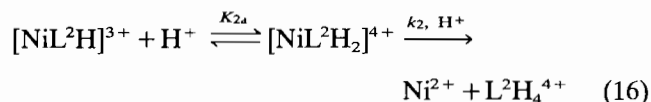
In the case of the less labile  $[\text{CuL}^2]^{2+}$ , the variation of  $k_{\text{obs}}$  with excess  $[\text{H}^+]$  (Fig. 3) is also consistent with eqn. (12), and  $k_0$  is indistinguishable from zero within experimental error. (Because the higher molar absorbance of  $[\text{CuL}^2]^{2+}$  makes it possible to work at excess  $[\text{H}^+] = 0.0078 \text{ mol dm}^{-3}$ , a more reliable estimate of the intercept  $k_{\text{obs}}$  value is obtained.) The best fit of  $k_{\text{obs}}$  to eqn. (12), and the derived  $k_1$  to the Eyring equation yields the parameters in Table 2. The data for the decomplexation of  $[\text{CuL}^2]^{2+}$  over a smaller  $[\text{H}^+]$  range from an earlier study [10] is compatible with the more extensive data presented here.

The fitting of the variation of  $k_{\text{obs}}$  for  $[\text{NiL}^2]^{2+}$  with  $[\text{H}^+]$  (Fig. 4) to eqn. (12) was carried out by setting  $k_0 (=k_d) \approx 0$  as is justified by the complexation data discussed above. The least-squares fit of the  $k_{\text{obs}}$  data to eqn. (12) yields the parameters in Table 2, and the least-squares fit of the derived  $k_1$  values to the Eyring equation yields the activation parameters. (A combination of the requirement to maintain a 10-fold excess  $[\text{H}^+]$  over the total  $[\text{NiL}^2]^{2+}$ , and the small magnitude of the molar absorbance of  $[\text{NiL}^2]^{2+}$  precludes study of this system at  $[\text{H}^+] < 0.0199 \text{ mol dm}^{-3}$ .)

The  $[\text{NiL}^2]^{2+}$   $k_{\text{obs}}$  data may also be fitted to:

$$k_{\text{obs}} = \frac{k_0 + k_1 K_{1a} [\text{H}^+] + k_2 K_{1a} K_{2a} [\text{H}^+]^2}{1 + K_{1a} [\text{H}^+] + K_{1a} K_{2a} [\text{H}^+]^2} \quad (15)$$

consistent with  $[\text{NiL}^2\text{H}_2]^{4+}$  providing an additional decomplexation path:



as shown in Fig. 4. The sums of the squares of the residuals divided by the number of degrees of freedom for this fitting are an order of magnitude less than for the fitting to eqn. (12) (Table 2), indicating that fitting of the  $k_{\text{obs}}$  data to eqn. (15) may be more appropriate, but the uncertainties associated with the magnitudes of  $k_2$  and  $K_{2a}$  are large. The simpler form of the  $k_{\text{obs}}$  variation with  $[\text{H}^+]$  in the cases of  $[\text{CoL}^2]^{2+}$  and  $[\text{CuL}^2]^{2+}$  does not preclude a  $k_2$  term becoming sig-

TABLE 2. Parameters for the decomplexation of  $[ML^2]^{2+}$  in excess  $HNO_3$  at  $I=1.50$  ( $NaNO_3$ )

$[ML^2]^{2+}$	$T$ (K)	$k_1$ ( $s^{-1}$ )	$k_2$ ( $s^{-1}$ )	$K_{1a}$ ( $dm^3 mol^{-1}$ )	$K_{2a}$ ( $dm^3 mol^{-1}$ )	$\Delta H_1^*$ ( $kJ mol^{-1}$ )	$\Delta S_1^*$ ( $J K^{-1} mol^{-1}$ )
$[CoL^2]^{2+}$	283.2	$62.7 \pm 1.4$		$3.47 \pm 0.17$		$38.8 \pm 5.0$	$-73 \pm 17$
	288.2	$95.0 \pm 2.9$		$3.50 \pm 0.21$			
	293.2	$127 \pm 6$		$3.98 \pm 0.30$			
	298.2	$151 \pm 19$		$5.2 \pm 1.0$			
$[CuL^2]^{2+}$	288.2	$2.29 \pm 0.11$		$0.76 \pm 0.05$		$58.9 \pm 4.2$	$-32.9 \pm 13.9$
	298.2	$6.07 \pm 0.29$		$0.67 \pm 0.04$			
	308.2	$14.5 \pm 0.6$		$0.64 \pm 0.03$			
	318.2	$24.9 \pm 1.2$		$0.82 \pm 0.06$			
$[NiL^2]^{2+a}$	288.2	$0.055 \pm 0.001$		$101 \pm 17$		$74.8 \pm 0.4$	$-9.1 \pm 1.6$
	298.2	$0.160 \pm 0.004$		$83 \pm 13$			
	308.2	$0.44 \pm 0.01$		$70 \pm 9$			
	318.2	$1.16 \pm 0.02$		$57 \pm 7$			
$[NiL^2]^{2+b}$	288.2	$0.046 \pm 0.001$	$0.098 \pm 0.027$	$301 \pm 53$	$0.66 \pm 0.48$	$75.5 \pm 0.8$	$-8.3 \pm 2.7$
	298.2	$0.132 \pm 0.004$	$0.31 \pm 0.13$	$216 \pm 35$	$0.55 \pm 0.52$		
	308.2	$0.370 \pm 0.015$	$0.73 \pm 0.29$	$139 \pm 21$	$0.69 \pm 0.80$		
	318.2	$0.99 \pm 0.03$	$4 \pm 13$	$101 \pm 14$	$0.16 \pm 0.74$		

<sup>a</sup>The sums of the squares of the residuals divided by the number of degrees of freedom (10) for fitting of the  $k_{obs}$  data to eqn (12) were:  $6.1107 \times 10^{-6}$ ,  $5.3125 \times 10^{-5}$ ,  $2.7098 \times 10^{-4}$  and  $1.8697 \times 10^{-2}$  in increasing magnitude of temperature. <sup>b</sup>The sums of the squares of the residuals divided by the number of degrees of freedom (8) for fitting of the  $k_{obs}$  data to eq. (15) were  $1.7433 \times 10^{-7}$ ,  $1.9249 \times 10^{-6}$ ,  $2.0148 \times 10^{-5}$  and  $1.7388 \times 10^{-4}$  in increasing magnitude of temperature.

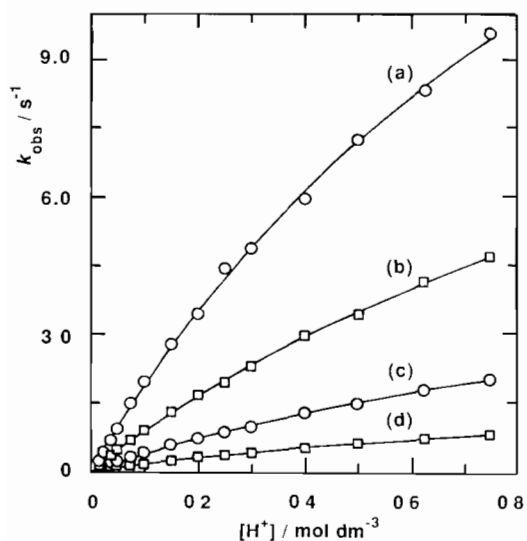


Fig. 3. The variation of  $k_{obs}$  for the decomplexation of  $[CuL^2]^{2+}$  (total  $[Cu^{2+}] = \text{total } [L^2] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) with  $[HNO_3]$  and  $I=1.50$  ( $NaNO_3$ ) at: (a) 318.2, (b) 308.2, (c) 298.2, (d) 288.2 K. The solid curves represent the non-linear least-squares fits to eqn. (12).

nificant at higher  $[H^+]$ , but a contribution to  $k_{obs}$  from this term was not detected in the  $[H^+]$  range studied.

#### Mechanistic considerations

The form of eqn. (12) requires the rapid breaking of an M-N bond prior to the rate determining step which is acid catalyzed by protonation of the amine group no longer bonded to  $M^{2+}$ . Ground state  $[ML^2]^{2+}$  may be in the *trans* III (*RRSS*) conformation with  $M^{2+}$

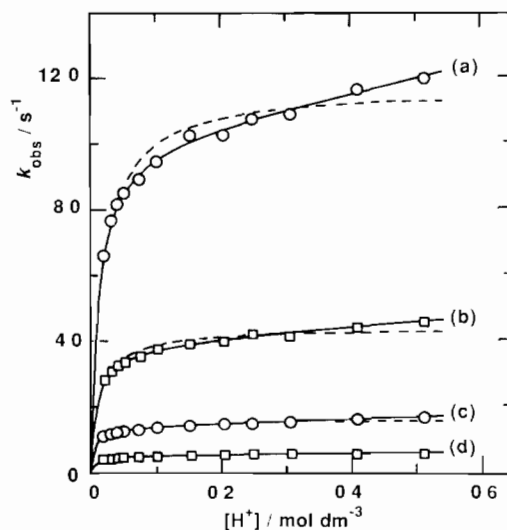


Fig. 4. The variation of  $k_{obs}$  for the decomplexation of  $[NiL^2]^{2+}$  (total  $[Ni^{2+}] = \text{total } [L^2] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$ ) with  $[HNO_3]$  and  $I=1.50$  ( $NaNO_3$ ) at: (a) 318.2, (b) 308.2, (c) 298.2, (d) 288.2 K. The solid and broken curves represent the non-linear least-squares fits to eqns (15) and (12), respectively. The latter curve is not shown for the data at 288.2 K as it closely approaches the curve representing the fit to eqn (15).

octahedrally coordinated by four coplanar nitrogens and two oxygens of hydroxyethyl arms diagonally opposed across the macrocyclic ring in *trans* related sites (as observed for  $[NiL^2-H]^+$ ) [10], or with two oxygens of adjacent hydroxyethyl arms bound to the 4, 8 nitrogens to give trigonal prismatic coordination (as observed for  $[CdL^2]^{2+}$ ,  $[HgL^2]^{2+}$  and  $[PbL^2]^{2+}$ ) [11, 12]. In the mechanistic scheme of Fig 5, these two alternative

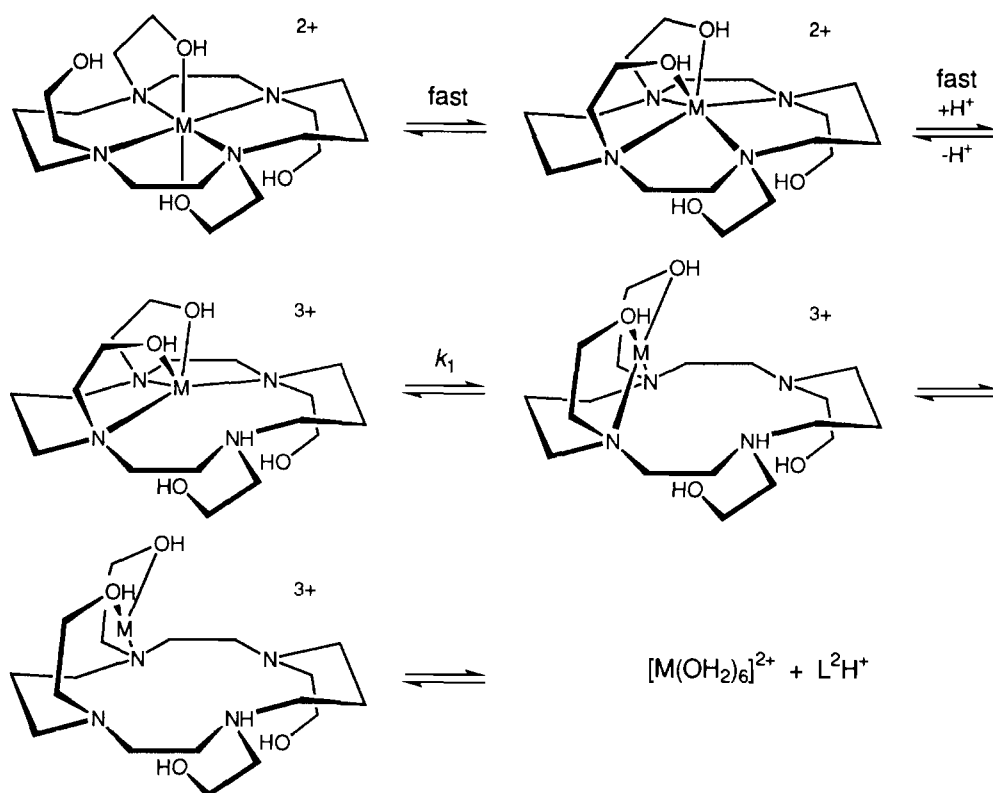


Fig. 5 A possible mechanism for the decomplexation of  $[ML^2]^{2+}$  through the  $k_1$  path. The *trans* III (*RRSS*) conformation is shown in all cases, but this does not infer that no conformational changes occur once M–N bonds are broken. Coordinated water is omitted.

ground states are shown in equilibrium prior to the rapid breaking of a M–N bond to produce an intermediate in which  $M^{2+}$  is coordinated by two hydroxo and three amine groups of  $L^2$  and a water (not shown). The rate determining steps characterized by  $k_0$  and  $k_1$  in eqn. (12) then occur through this unprotonated intermediate and its monoprotanated analogue. Consideration of the sequential decomplexation steps subsequent to the breaking of the first M–N bond is speculative, but a species in which  $M^{2+}$  is bound to  $L^2$  through two hydroxo groups is in accord with the expectation that the initial complexation of  $M^{2+}$  should also proceed through such an intermediate. The reverse of this sequence is the mechanism of complexation.

Should the alternative mechanism involving  $[ML^2H_2]^{4+}$  be operative, the rapid breaking of two M–N bonds would be required prior to the rate determining decomplexation steps characterized by  $k_0$ ,  $k_1$  and  $k_2$ .

The decrease in lability towards decomplexation at 298.2 K through the  $k_1$  path ( $[CoL^2H]^{3+} > [CuL^2H]^{3+} > [NiL^2H]^{3+}$ ) coincides with an increase in  $\Delta H_1^*$  in the order:  $[CoL^2H]^{3+} < [CuL^2H]^{3+} < [NiL^2H]^{3+}$ , and  $\Delta S_1^*$  becoming less negative in magnitude in the order:  $[CoL^2H]^{3+} > [CuL^2H]^{3+} > [NiL^2H]^{3+}$  (Table 2). The lability towards ligand substitution on the hexaqua metal

ions decreases in the sequence  $Cu^{2+} > Co^{2+} > Ni^{2+}$  and is explicable in terms of the larger ligand field activation energy (LFAE) of  $Ni^{2+}$  and the labilization of  $Cu^{2+}$  through a dynamic Jahn-Teller effect [31]. That this order of lability is not observed for  $[ML^2H]^{3+}$  indicates the superimposition of effects emanating from  $LH^+$  on lability. It may be that a combination of a departure from octahedral stereochemistry (as suggested above) and the dissimilarity of the tetraaza and hydroxo donor sets renders the lability relationships between the metal ions quite different from those observed for the hexaqua metal ions. The decrease in  $K_{1a}$  in the sequence:  $[NiL^2H]^{3+} > [CoL^2H]^{3+} > [CuL^2H]^{3+}$  indicates the greater effective basicity of the amine group of the first complex, which is a measure of the competition between the metal centre and the proton for the lone pair of electrons of the amine nitrogen. This variation is related to the lability of  $[ML^2H]^{3+}$  towards decomplexation, but in the absence of a knowledge of the stereochemistries of these species further discussion of the trends in the lability would be speculative.

The half life for the decomplexation of  $[NiL]^{2+}$  in acid solution is estimated to be *c.* 30 years [32] which emphasizes the labilization of  $[NiL^2]^{2+}$  towards decomplexation by the hydroxyethyl pendant arms of  $L^2$ . A more quantitative comparison is possible with

$[\text{ML}^5\text{H}]^{3+}$  for which  $k_1K_{1a} = 2.5, 2.9 \times 10^{-2}$  and  $6.7 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, when  $\text{M}^{2+} = \text{Co}^{2+}, \text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  [28], which compare with  $k_1K_{1a} = 785, 28.5$  and  $4.07 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, for  $[\text{ML}^2\text{H}]^{3+}$  when  $\text{M}^{2+} = \text{Co}^{2+}, \text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  at 298.2 K. As  $\text{L}^2\text{H}^+$  is of similar acidity to  $\text{L}^5\text{H}^+$  (Table 1) it is probable that  $K_{1a}$  for  $[\text{ML}^2\text{H}]^{3+}$  is similar to  $K_{1a}$  for  $[\text{ML}^5\text{H}]^{3+}$ , and therefore that  $k_1$  for  $[\text{ML}^2\text{H}]^{3+}$  is several orders of magnitude greater than that for  $[\text{ML}^5\text{H}]^{3+}$ . Thus the hydroxyethyl arms labilize  $[\text{ML}^2\text{H}]^{3+}$  towards decomplexation by comparison with  $[\text{ML}^1\text{H}]^{3+}$  and  $[\text{ML}^5\text{H}]^{3+}$ , consistent with coordinating hydroxyethyl groups stabilizing a structure with  $\text{M}^{2+}$  out of the plane of the macrocyclic ring as described for the decomplexation mechanism proposed above. When considered in conjunction with the complexation data, it is seen that the hydroxyethyl arms cause  $[\text{ML}^2\text{H}]^{3+}$  to be less stable than their  $[\text{ML}^1\text{H}]^{3+}$  and  $[\text{ML}^5\text{H}]^{3+}$  analogues largely because they labilize  $[\text{ML}^2\text{H}]^{3+}$  towards decomplexation.

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