Kinetics of Acid-catalysed Dissociation of Tetraaza-macrocyclic Ligand Complexes of Copper(II)†

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The dissociation kinetics of copper(II) complexes of 1,4,7,10-tetraazacyclododecane ([12]aneN_4), 1,4,7,10-tetraazacyclotridecane ([13]aneN_4), 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4) and 1,5,9,13-tetraazacyclohexadecane ([16]aneN_4), have been studied spectrophotometrically in 0.015–2.50 mol dm^{-3} HNO_3 at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} (HNO_3 + $NaNO_3$). The rate law for the dissociation reaction of $[Cu([12]aneN_4)]^{2+}$ is rate = $(k_1[H^+]^2 + k_2[H^+])$ [complex] with $k_1 = (5.80 \pm 0.24) \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and $k_2 = (1.19 \pm 0.54) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. The rate law for the reaction of $[Cu([13]aneN_4)]^{2+}$ is rate = $k_3[H^+]$ [complex] with $k_3 = (7.99 \pm 0.07) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. The rate law for the reactions of $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$ is rate = $k_4[H^+][\text{complex}]/(1 + k_5[H^+])$; for the reaction of $[Cu([15]aneN_4)]^{2+}$, $k_4 = (1.42 \pm 0.34) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_5 = (9.91 \pm 1.65) \times 10^{-1}$ dm^3 mol^{-1}; for the reaction of $[Cu([16]aneN_4)]^{2+}$, $k_4 = 3.27 \pm 1.37$ dm^3 mol^{-1} s^{-1} and $k_5 = 6.96 \pm 2.04$ dm^3 mol^{-1}. The possible mechanisms for these reactions, the factors influencing the rates, and the factors affecting the relative importance of the solvation pathway and the protonation pathway are discussed.

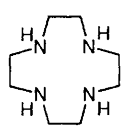
Previous papers in this series concerned the acid-catalysed dissociation of the copper(II) complexes of 14-membered macrocyclic tetraamine complexes.[1-4] In the current investigation, we have attempted to gain a more detailed understanding of the effects of macrocycle ring size on the dissociation kinetics of tetraamine macrocyclic ligand complexes of copper(II). To accomplish this, we have extended our studies to the dissociation reactions of copper(II) complexes of 1,4,7,10-tetraazacyclododecane, [12]aneN_4; 1,4,7,10-tetraazacyclotridecane, [13]aneN_4; 1,4,8,12-tetraazacyclopentadecane, [15]aneN_4; and 1,5,9,13-tetraazacyclohexadecane, [16]aneN_4, in moderately concentrated nitric acid solution, equation (1), where L is the macrocyclic ligand.

$$CuL^{2+} + 4H^+ \longrightarrow Cu^{2+} + H_4L^{4+} \qquad (1)$$

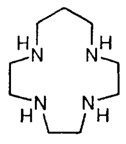
The reactivities of these copper(II) macrocyclic complexes are strongly influenced by the macrocycle ring; three types of rate laws are found for these reactions. However, these kinetic results can be explained by a general mechanism. The kinetics of the dissociation of $[Cu([12]aneN_4)]^{2+}$ in moderately concentrated perchloric acid solutions at I = 5.0 mol dm^{-3} ($NaClO_4$) has been reported by Hay and Pujari.[5] It is interesting that the rate law for this reaction in moderately concentrated perchloric acid solutions reported by Hay and Pujari[5] is significantly different from that in moderately concentrated nitric acid solutions obtained in this work.

Experimental

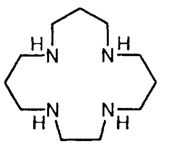
Reagents.—The macrocyclic ligands investigated were prepared through the Richman–Atkins procedure.[6-8] The complexes $[Cu([12]aneN_4)][ClO_4]_2$, $[Cu([13]aneN_4)][ClO_4]_2$, $[Cu([15]aneN_4)][ClO_4]_2$ and $[Cu([16]aneN_4)][ClO_4]_2$ were obtained by mixing hot equimolecular aqueous solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and the macrocyclic ligands. All other chemicals used in this work were of G. R. grade (Merck or Aldrich).



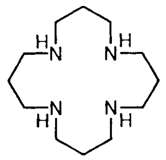
1,4,7,10-tetraazacyclododecane
[12]aneN_4



1,4,7,10-tetraazacyclotridecane
[13]aneN_4



1,4,8,12-tetraazacyclopentadecane
[15]aneN_4



1,5,9,13-tetraazacyclohexadecane
[16]aneN_4

Kinetic Measurements.—The kinetics of the acid-catalysed dissociation reactions of the copper complexes were followed at 25.0 ± 0.1 °C with the use of Hitachi U-3200 and U-3410 spectrophotometers. Absorbance *vs.* time data were collected at 584, 536 and 568 nm for the dissociation reactions of $[Cu([12]aneN_4)]^{2+}$, $[Cu([13]aneN_4)]^{2+}$ and $[Cu([15]aneN_4)]^{2+}$ respectively. The kinetics of the $[Cu([16]aneN_4)]^{2+}$ dissociation reaction were studied with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment with particular focus on 596 nm and temperature maintained at 25.0 ± 0.1 °C. Pseudo-first-order conditions were maintained by using at least a 10-fold excess of acid in each run. Good first-order kinetics were observed in all cases. The rate constants were obtained by linear least-squares fit for the data by using a computer.

Results

The visible absorption spectra were used to observe the dissociation reactions. The principal absorption band and

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† *Supplementary data available* (No. SUP 56975, 7 pp.): first-order rate constants and plots of k_{obs} *vs.* H^+. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Visible absorption bands of tetraazamacrocyclic ligand complexes of copper(II) in aqueous solutions at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} ($NaNO_3 + HNO_3$)

Complex	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
$[Cu([12]aneN_4)]^{2+}$	584	268
$[Cu([13]aneN_4)]^{2+}$	536	205
$[Cu([15]aneN_4)]^{2+}$	568	150
$[Cu([16]aneN_4)]^{2+}$	596	288

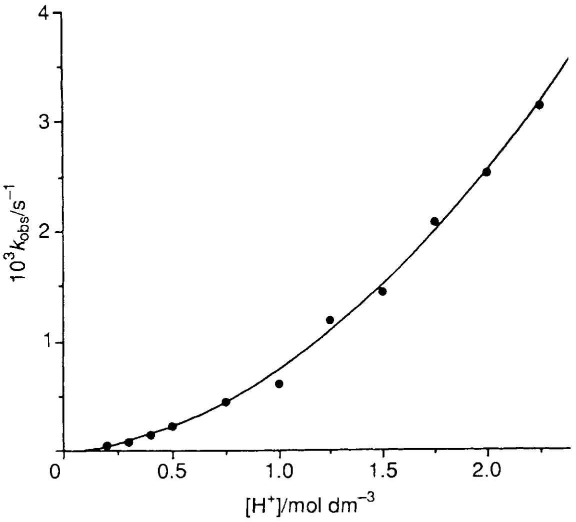

Fig. 1 Plot of k_{obs} *vs.* $[H^+]$ for the dissociation of $[Cu([12]aneN_4)]^{2+}$ at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} ($NaNO_3 + HNO_3$). The circles are the experimental results; the line is calculated from $k_{obs} = k_{67}K_{16}[H^+]^2 + (k_{68} + k_{69})[H^+]$ with $k_{67}K_{16} = (5.80 \pm 0.24) \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and $k_{68} + k_{69} = (1.19 \pm 0.54) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}

molar absorptivities of these copper(II) complexes in 5.0 mol dm^{-3} $NaNO_3$ at 25.0 ± 0.1 °C are given in Table 1. The kinetics of the dissociation reactions of these complexes were studied at 25.0 ± 0.1 °C with I = 5.0 mol dm^{-3} ($HNO_3 + NaNO_3$) and in 0.015–2.50 mol dm^{-3} HNO_3. Under these conditions, the dissociation reactions of these complexes were found to proceed to completion. In marked contrast to the behaviour of the (1,4,8,11-tetraazacyclotetradecane)copper(II) ion, $[Cu(cyclam)]^{2+}$, which involves consecutive processes with reversible steps as given in equation (2),[4] the dissociation

$$[Cu(cyclam)]^{2+} \underset{k_a}{\overset{k_a}{\rightleftharpoons}} [Cu(Hcyclam)]^{3+} \xrightarrow{k_b} H_4cyclam^{4+} + Cu^{2+} \quad (2)$$

processes of $[Cu([12]aneN_4)]^{2+}$, $[Cu([13]aneN_4)]^{2+}$, $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$ were found to occur by a single stage, and the rate equation can be expressed by equation (3).

$$\frac{-d[CuL^{2+}]}{dt} = k_{obs}[CuL^{2+}] \quad (3)$$

The observed first-order rate constants as a function of $[HNO_3]$ are given in SUP 56975 (Table 1S).

For the reaction of $[Cu(cyclam)]^{2+}$, a significant amount of the protonated intermediate $[Cu(Hcyclam)]^{3+}$ formed in the solution, therefore, this reaction was found to occur not in a single stage but in consecutive reversible steps. On the other hand, for the reactions of $[Cu([12]aneN_4)]^{2+}$, $[Cu([13]aneN_4)]^{2+}$, $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$, there is no significant amount of intermediate formed in the solutions; these complexes dissociated with the observed pseudo-first-order rate constants showing an acid dependence as given in equation (3).

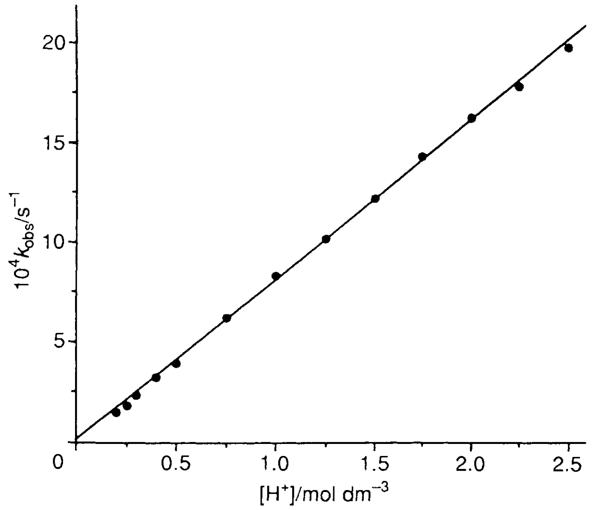

Fig. 2 Plot of k_{obs} *vs.* $[H^+]$ for the dissociation of $[Cu([13]aneN_4)]^{2+}$ at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} ($NaNO_3 + HNO_3$). The circles are the experimental results; the line is calculated from $k_{obs} = k_{23}K_{12}[H^+]$ with $k_{23}K_{12} = (7.99 \pm 0.07) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}

As shown in Fig. 1, the plot of the observed rate constant for the dissociation of $[Cu([12]aneN_4)]^{2+}$ *vs.* $[H^+]$ yields a curve concave to the axis of the rate constant and passing through the origin. A general rate law conforming to this situation is given by equation (4) or (5).

$$k_{obs} = k_1[H^+]^2 + k_2[H^+] \quad (4)$$

$$k_{obs}/[H^+] = k_1[H^+] + k_2 \quad (5)$$

A plot of $k_{obs}/[H^+]$ *vs.* $[H^+]$ gives a straight line (SUP 56975, Fig. 1S). The value of k_1 obtained from the slope of this plot is $(5.80 \pm 0.24) \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and the value of k_2 obtained from the intercept is $(1.19 \pm 0.54) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}.

As shown in Fig. 2, the plot of the observed rate constant for the reaction of $[Cu([13]aneN_4)]^{2+}$ *vs* $[H^+]$ is a straight line. This reaction obeys the simple rate law given in equation (6).

$$k_{obs} = (7.99 \pm 0.07) \times 10^{-4} [H^+] \quad (6)$$

As shown in Figs. 3 and 4, the observed rate constants for the reactions of $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$ increase with an increase in $[H^+]$ tending to attain limiting values at high acidities. These two reactions conform to the rate law given by equation (7) or (8).

$$k_{obs} = k_4[H^+]/(1 + k_5[H^+]) \quad (7)$$

$$\frac{1}{k_{obs}} = 1/k_4[H^+] + k_5/k_4 \quad (8)$$

The plots of k_{obs}^{-1} *vs.* $[H^+]^{-1}$ give straight lines for these two reactions (SUP 56975, Figs. 2S and 3S). The rate constants for the reactions of $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$ obtained from these plots are given in equations (9) and (10), respectively.

$$k_{obs} = \frac{(1.42 \pm 0.34) \times 10^{-2}[H^+]}{1 + (9.91 \pm 1.65) \times 10^{-1}[H^+]} \text{ s}^{-1} \quad (9)$$

$$k_{obs} = \frac{3.27 \pm 1.37[H^+]}{1 + (6.96 \pm 2.04)[H^+]} \text{ s}^{-1} \quad (10)$$

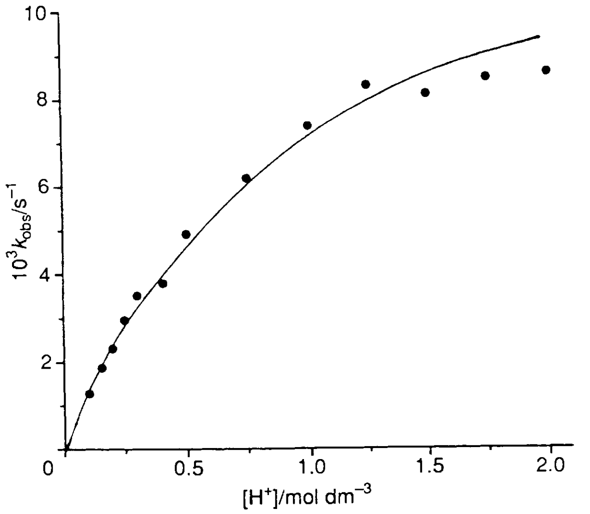

Fig. 3 Plot of k_{obs} *vs.* [H$^+$] for the dissociation of [Cu([15]aneN$_4$)]$^{2+}$ at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} (NaNO$_3$ + HNO$_3$). The circles are the experimental results; the line is calculated from $k_{obs} = k_{12}k_{23}[H^+]/(k_{21} + k_{23}[H^+])$ with $k_{12} = (1.43 \pm 0.24) \times 10^{-2}$ s^{-1} and $k_{23}/k_{21} = (9.91 \pm 1.65) \times 10^{-1}$ dm^3 mol^{-1}

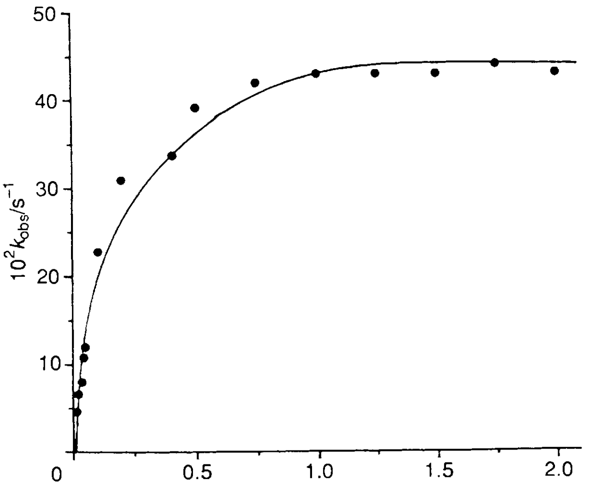

Fig. 4 Plot of k_{obs} *vs.* [H$^+$] for the dissociation of [Cu([16]aneN$_4$)]$^{2+}$ at 25.0 ± 0.1 °C and I = 5.0 mol dm^{-3} (NaNO$_3$ + HNO$_3$). The circles are the experimental results; the line is calculated from $k_{obs} = k_{12}k_{23}[H^+]/(k_{21} + k_{23}[H^+])$ with $k_{12} = 0.47 \pm 0.14$ s^{-1}, k_{23}/k_{21} = 6.96 ± 2.04 dm^3 mol^{-1}

Discussion

The mechanism of acid-catalysed dissociation of polyamine complexes has been studied in detail by Margerum and co-workers.[9,10] In the proposed pathway one nitrogen donor is dissociated from the metal ion without its replacement by a solvent molecule.[10] In this activated intermediate the chelate ring has not been opened sufficiently to move the nitrogen donor out of the first co-ordination sphere of the metal ion.[10] For the dissociation reaction of a macrocyclic tetraamine complex in moderately concentrated acid, such an activated intermediate is also expected to form, and the general mechanisn is shown in Fig. 5.[11] In this mechanism species **2** and **6** are activated intermediates which are in low, steady-state concentration, and are susceptible to protonation or replacement by a solvent molecule.

The experimental rate law for the dissociation of [Cu([12]-aneN$_4$)]$^{2+}$ [equation (4)] is in agreement with the following mechanism [equations (11)–(14)].

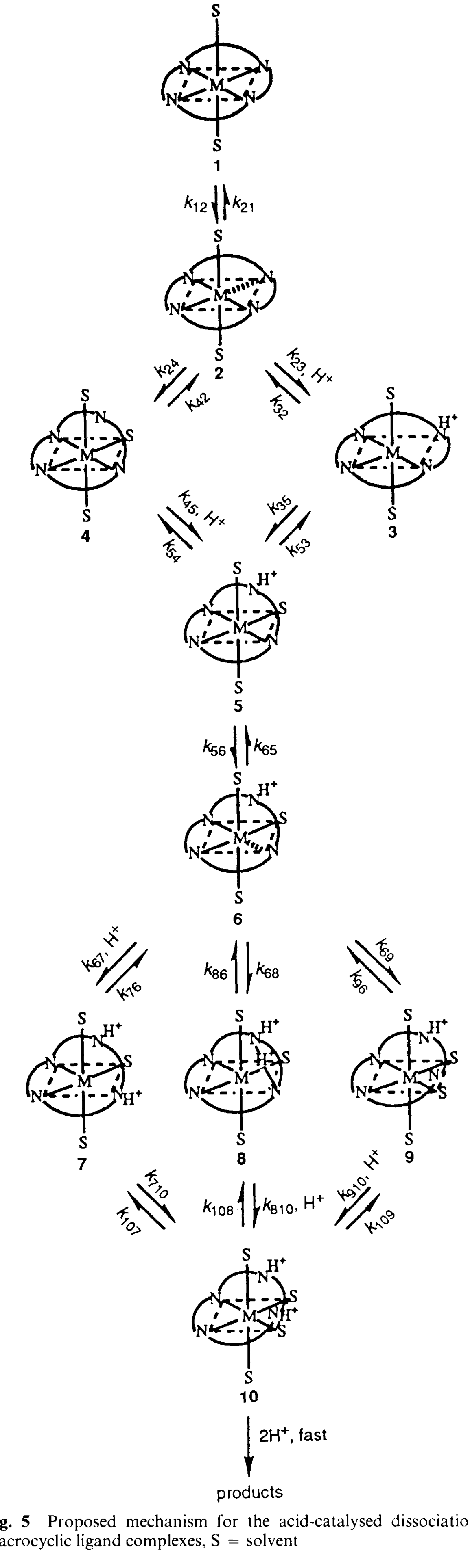

Fig. 5 Proposed mechanism for the acid-catalysed dissociation of macrocyclic ligand complexes, S = solvent

$$\mathbf{1} + \mathrm{H}^+ \underset{}{\overset{K_{16}}{\rightleftharpoons}} \mathbf{6} \qquad (11)$$

$$\mathbf{6} + \mathrm{H}^+ \xrightarrow{k_{67}} \text{products} \qquad (12)$$

$$\mathbf{6} \xrightarrow{k_{68}} \text{products} \qquad (13)$$

$$\mathbf{6} \xrightarrow{k_{69}} \text{products} \qquad (14)$$

For this mechanism, the simple rate law $k_{obs} = k_{67}K_{16}[H^+]^2 + (k_{68} + k_{69})[H^+]$ holds, with $k_{67}K_{16} = (5.80 \pm 0.24) \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and $k_{68} + k_{69} = (1.19 \pm 0.54) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. There is no detectable amount of intermediate found in the course of the dissociation of $[Cu([12]aneN_4)]^{2+}$, indicating that $[Cu(H[12]aneN_4)]^{3+}$ **5**, is relatively unstable as compared with $[Cu([12]aneN_4)]^{2+}$. In the monoprotonated intermediate, $[Cu(H[12]aneN_4)]^{3+}$, the distance between the unco-ordinated protonated amine group and the metal ion is very small due to the constraints of the cyclic ligand. The instability of $[Cu(H[12]aneN_4)]^{3+}$ is mainly due to the large electrostatic and inductive effects of the copper(II) ion.

For the reaction of $[Cu([13]aneN_4)]^{2+}$, the experimental rate law [equation (6)] is in accordance with the following mechanism [equations (15) and (16)]. This simple mechanism

$$\mathbf{1} \overset{K_{12}}{\rightleftharpoons} \mathbf{2} \qquad (15)$$

$$\mathbf{2} + \mathrm{H}^+ \xrightarrow{k_{23}} \text{products} \qquad (16)$$

$$\frac{-\mathrm{d}[Cu([13]aneN_4)^{2+}]}{\mathrm{d}t} = k_{23}K_{12}[H^+][Cu([13]aneN_4)^{2+}] \qquad (17)$$

leads to equation (17). Here $k_{23}K_{12}$ is $(7.99 \pm 0.07) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}.

The reported protonation constants, $CuL^{2+} + H^+ \longrightarrow Cu(HL)^{3+}$, for $[Cu([15]aneN_4)]^{2+}$ and $[Cu([16]aneN_4)]^{2+}$ indicate that $Cu(HL)^{3+}$ is more stable than CuL^{2+} in concentrated acid.[12,13] If the rate-determining step for the dissociation of $[Cu([15]aneN_4)]^{2+}$ or $[Cu([16]aneN_4)]^{2+}$ were the cleavage of the second M–N bond, significant amounts of $Cu(HL)^{3+}$ should form in the solution and this species would be expected to have a d–d absorption spectrum significantly different from that of the tetradentate CuL^{2+}.[14] Thus a large shift in the band maximum to low energy should be observed after mixing of CuL^{2+} and moderately concentrated acid.[14] This is not found experimentally. The experimental results indicate no detectable amount of $Cu(HL)^{3+}$ formed in the course of the dissociation of these two complexes, suggesting the rate-determining step should be prior to the formation of $Cu(HL)^{3+}$. In other words, the possible rate-determining step is $\mathbf{2} \longrightarrow \mathbf{4}$ or $\mathbf{2} + H^+ \longrightarrow \mathbf{3}$ in Fig. 5. The possible mechanism corresponding to the rate laws [equations (9) and (10)] for these two complexes is given by equations (18) and (19).

$$\mathbf{1} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathbf{2} \qquad (18)$$

$$\mathbf{2} + \mathrm{H}^+ \xrightarrow{k_{23}} \text{products} \qquad (19)$$

A steady-state treatment for **2** leads to rate law (20). For

$$k_{obs} = \frac{k_{12}k_{23}[H^+]}{k_{21} + k_{23}[H^+]} \qquad (20)$$

the reaction of $[Cu([15]aneN_4)]^{2+}$, $k_{12} = (1.43 \pm 0.24) \times 10^{-2}$ s^{-1}, $k_{23}/k_{21} = (9.91 \pm 1.65) \times 10^{-1}$ dm^3 mol^{-1}. For the reaction of $[Cu([16]aneN_4)]^{2+}$, $k_{12} = 0.47 \pm 0.14$ s^{-1}, $k_{23}/k_{21} = 6.96 \pm 2.04$ dm^3 mol^{-1}.

The complex $[Cu([16]aneN_4)]^{2+}$ contains four fused six-membered rings and is less inert than $[Cu([15]aneN_4)]^{2+}$ which contains one five- and three six-membered rings.[12,13] Thus, the dissociation of $[Cu([16]aneN_4)]^{2+}$ is faster than that of $[Cu([15]aneN_4)]^{2+}$.

The dissociation kinetics of copper(II) complexes with linear tetraamines, 1,4,7,10-tetraazadecane (2,2,2-tet), 1,4,8,11-tetraazaundecane (2,3,2-tet), 1,5,8,12-tetraazadodecane (3,2,3-tet) and 1,5,9,13-tetraazatridecane (3,3,3-tet) have been reported.[4,15] The rates of these reactions are much faster than for the corresponding macrocyclic tetraamine complexes owing to both the presence of the primary amines which protonate readily and the greater flexibility inherent in a non-ringed structure. The formation of an intermediate of type **2** for a macrocyclic complex involves some changes in bond angles and bond distances in two fused chelate rings; on the other hand, the formation of such an activated intermediate for an open-chain complex involves some changes in bond angles and bond distances in only one chelate ring. As a result, the dissociation rate of a macrocyclic complex is much slower than that of the corresponding open-chain complex.

For the dissociation reactions of the macrocyclic ligand complexes, the protonation pathway, $\mathbf{2} + H^+ \longrightarrow \mathbf{3}$, is much more important than the solvation pathway, $\mathbf{2} \longrightarrow \mathbf{4}$. Due to the constraint of the cyclic structure of the ligand, the unco-ordinated donor atom in **2** is strongly restricted and unable to move easily out of the first co-ordination sphere. In this case, the presence of acid has a very important effect. As a consequence, the protonation pathway is much more important than the solvation pathway. In marked contrast to these reactions, both the solvation pathway and the protonation pathway are important in the dissociation of the open-chain tetraamine complex, in which the unco-ordinated donor atom in the activated intermediate is relatively less restricted as compared to the macrocyclic complex and able to move out of the first co-ordination sphere. In this case, both solvation and protonation make contributions to the rate. For the dissociation of Cu^{II}–NH_3,[10] in which the donor atom in the activated intermediate is unrestricted and able to move very easily out of the first co-ordination sphere, the solvation pathway is much more important than the protonation pathway.[10]

Acknowledgements

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