(pK$_a$, 4.80)$^{(12)}$ was used for glycine, α-alanine, L-phenylalanine and L-valine, whereas bromothymol blue (pK$_a$, 7.0)$^{(12)}$ was used for β-alanine. Observations were made at 550 nm in systems having methyl red indicator and 620 nm in those having bromothymol blue indicator. The indicator concentration was $2 \cdot 10^{-5}$ M in all the cases. One of the two driving syringes of the flow module of the stopped flow system was filled with an aqueous solution of Ni(NTA)(H$_2$O)$_2^-$ (0.004 M) adjusted to the desired pH (5.5–6.9) and ionic strength (I) of 0.1 M with KNO$_3$, and the other was filled with the amino acid solution (I, 0.1 M with KNO$_3$) at the same pH buffered with HOAc (8×10^{-4} M) and requisite amount of NaOAc systems using methyl red and with phosphate buffer ([H$_2$PO$_4^-$], 1.2×10^{-3} M) and the requisite amount of HPO$_4^{2-}$ in the system using bromothymol blue indicator. Data from the absorbance *versus* time traces were analysed graphically by the method of least-squares using the relationship for *pseudo*-first-order reactions, since *pseudo*-first-order conditions were maintained in the experimental solutions.

Acknowledgements

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Acid Dissociation Kinetics of the Copper(II) Complex of 1,5,8,12-Tetra-azacyclo-octadecane ([18]aneN$_4$) and the Nickel(II) Complex of 1,5,8,12-Tetra-azacycloheptadecane ([17]aneN$_4$)

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Summary

The kinetics of the dissociation of [Cu([18]aneN$_4$9)]$^{2+}$ and [Ni([17]aneN$_4$8)]$^{2+}$ in acidic solution have been studied in detail. The dissociation of [Cu([18]aneN$_4$8)]$^{2+}$ displays saturation kinetics beyond 0.4 mol dm^{-3} HClO$_4$ with values of k$_{obs}$ becoming independent of [HClO$_4$]. The kinetic behaviour can be rationalised in terms of the scheme,

$$\mathrm{CuL^{2+} + H^+ \overset{K}{\rightleftharpoons} CuLH^{3+}}$$

$$\mathrm{CuLH^{3+} \xrightarrow{k} Cu^{2+}} + \text{protonated ligand}$$

with K = 64 dm^{3}mol^{-1} and k = 0.625 s^{-1} at 25 °C. Saturation kinetics are not observed in the dissociation of [Ni([17]aneN$_4$8)]$^{2+}$ and significant amounts of the protonated complex do not occur even in 0.5 mol dm^{-3} HClO$_4$. In this case protonation of the complex may be the rate-determining step. Dissociation of [Ni([17]aneN$_4$8)]$^{2+}$ is 10^{10}-fold faster than that of [Ni(cyclam)]$^{2+}$ at 25 °C.

Introduction

The dissociation of copper(II) and nickel(II) from 14-membered tetra-azamacrocycles such as cyclam (1,4,8,11-tetra-azacyclotetradecane) is extremely slow. Thus the half-life of [Ni(cyclam)]$^{2+}$ in 1 mol dm^{-3} HClO$_4$ is estimated to be 30 years at 25 °C$^{(1)}$ and the complex [Cu(cyclam)]$^{2+}$ dissociates extremely slowly even in 6 mol dm^{-3} HCl$^{(2)}$. However, complexes of the larger 17- and 18-membered tetra-aza-macrocycles dissociate quite readily in acidic solution$^{(3, 4)}$. The present paper discusses the kinetics of the acid dissociation of the cop-

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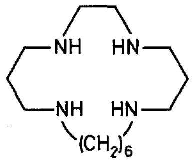
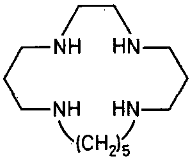
per(II) complex of 1,5,8,12-tetra-azacyclo-octadecane (*1*) and the nickel(II) complex of 1,5,8,12-tetra-aza-cycloheptadecane (*2*).



(*1*) = [18] aneN$_4$9



(*2*) = [17] aneN$_4$8

The use of tetra-aza-macrocycles in areas such as solvent extraction and hydrometallurgy requires rapid complexation and dissociation rates of the appropriate metal complexes, and for this reason it is important to investigate the various factors involved in these kinetic processes.

Experimental

The macrocyclic ligands 1,5,8,12-tetra-azacyclo-octadecane (*1*) and 1,5,8,12-tetra-azacycloheptadecane (*2*) were prepared by cyclisation of the tetratosylate of 1,10-diamino-4,7-diazadecane(3,2,3-tet)(5) and the ditosylate(6) of 1,6-hexanediol or 1,5-pentanediol in dimethylformamide (DMF) solution using NaH to generate the dianion of the tetratosylate. The general procedure used has been previously described(5). The cyclised products were recrystallised from formic acid and their purity monitored by i.r. spectroscopy. The absence of any ν(NH) band around 3200 cm^{-1} confirmed the purity of the product. The tetratosylates of the macrocycles were hydrolysed with concentrated H_2SO_4(5) and the macrocycles obtained by extraction with $CHCl_3$ after raising the pH of the solution to 14 with NaOH (yield *ca.* 40%).

[Cu([18]aneN$_4$9)] (ClO$_4$)$_2$

The macrocycle (20 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (20 mmol) were dissolved in MeOH (20 cm^3) and the solution heated on a steam bath until the volume was reduced to *ca.* 5 cm^3. $LiClO_4$ (0.5 g) was added and the solution allowed to stand for several h giving bright blue crystals of the complex. The complex was filtered off, washed with *i*-PrOH, then Et_2O and dried *in vacuo.* (Found: C, 32.2; H, 6.0; N, 10.6. $C_{14}H_{32}H_4O_8Cl_2Cu$ calcd.: C, 32.4; H, 6.2; N, 10.8%). The complex is a 2:1 electrolyte in water with Λ_M = 175 ohm^{-1}cm^{2}mol^{-1} at 25 °C.

[Ni([17]aneN$_4$8)](ClO$_4$)$_2$

The macrocycle (20 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (20 mmol) were dissolved in MeOH (20 cm^3) which had been acidified with a drop of conc · $HClO_4$. The solution was heated on a steam bath until the volume was reduced to *ca.* 5 cm^3. To this solution $LiClO_4$ (0.5 g) was added and the solution cooled to room temperature to give orange crystals of the product, which were filtered off, washed with i-PrOH then Et_2O and dried *in vacuo.* (Found: C, 31.0; H, 6.0; N, 11.2. $C_{13}H_{30}N_4O_8Cl_2Ni$ calcd.: C, 31.2; H, 6.05; N, 11.2%). The complex is a 2:1 electrolyte in water with Λ_M = 171 ohm^{-1}cm^{2}mol^{-1}. The blue [Ni([17]aneN$_4$8)(NCS)$_2$] and the green [Ni([17]aneN$_4$8)Cl$_2$] can also be characterised but rapidly give the orange complex on exposure to moisture.

Kinetics

The dissociation of [Cu([18]aneN$_4$9)]$^{2+}$ in $HClO_4$ solutions was monitored using a Durrum stopped-flow system interfaced with a transient-recorder and microcomputer. Measurements were made at 594 nm, and the quoted values of k_{obs} are the average of some six or eight kinetic runs. The ionic strength was maintained at 1.0 mol dm^{-3} using $NaClO_4$. Measurements using buffer solutions were carried out employing a Gilford 2400S spectrophotometer interfaced with an Apple IIe microcomputer. Citric acid/Na_2HPO_4 buffers were used adjusted to I = 0.1 mol dm^{-3} with $NaClO_4$. The dissociation of [Ni([17]aneN$_4$8)]$^{2+}$ was monitored at 462 nm using stopped-flow techniques, essentially as described for the copper complex.

Results and Discussion

[Cu([18]aneN$_4$9)] (ClO$_4$)$_2$

The dissociation of [Cu([18]aneN$_4$9)]$^{2+}$ was studied in the acidity range 0.01 to 0.50 mol dm^{-3} $HClO_4$ at 25 °C and I = 1.0 mol dm^{-3} by stopped-flow techniques, Table 1. A plot of k_{obs} (the observed first-order rate constant at constant acidity) *versus* the perchloric acid concentration displays "saturation kinetics" with k_{obs} becoming independent of [$HClO_4$] at high acidities, Fig. 1.

Additional experiments using citric acid buffers in the pH range 3.26 to 3.47, Table 2 established that there is no effective solvolytic reaction, Figure 1. The dissociation kinetics can be interpretated in terms of a rapid pre-equilibrium protona-

Table 1. Dissociation of [Cu([18]aneN$_4$9)]$^{2+}$ in perchloric acid solutions at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$).

[$HClO_4$] (mol dm^{-3})	10 k_{obs} (s^{-1})	[$HClO_4$] (mol dm^{-3})	10 k_{obs} (s^{-1})
0.01	2.4	0.15	5.6
0.015	3.1	0.30	5.9
0.02	3.4	0.40	6.1
0.03	4.1	0.50	6.3
0.05	4.8		

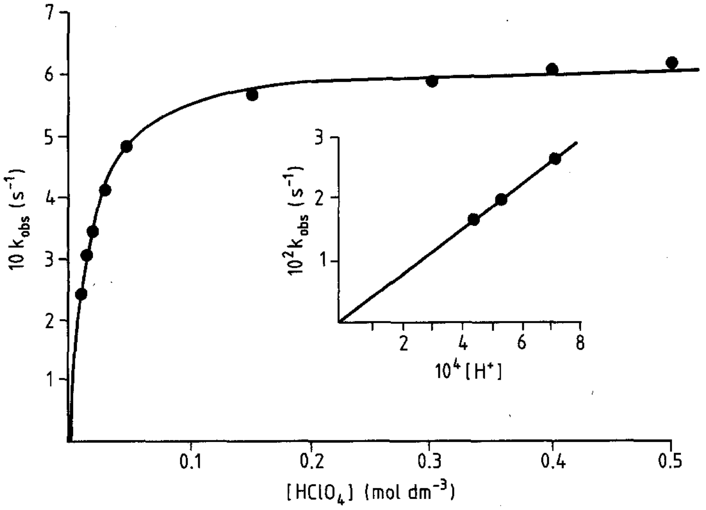


Figure 1. Acid dissociation of [Cu[18]aneN$_4$9)]$^{2+}$ in perchloric acid solutions at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$).

Table 2. Dissociation of $[Cu([18]andeN_4 9)]^{2+}$ in citric acid buffers at 25 °C and I = 0.1 mol dm^{-3} ($NaClO_4$).

pH	10^4 [H^+] (mol dm^{-3})	$10^2 k_{obs}$ (s^{-1})
3.26	7.12	2.72
3.39	5.28	2.04
3.47	4.39	1.71

tion (Equation 1) followed by rate-determining dissociation of the protonated complex (Equation 2).

$$CuL^{2+} + H^+ \overset{K}{\rightleftharpoons} CuLH^{3+} \qquad (1)$$

$$CuLH^{3+} \xrightarrow{k} \text{products} \qquad (2)$$

For such a reaction scheme, Equation (3) holds.

$$k_{obs}([CuL^{2+}] + [CuLH^{3+}]) = k[CuLH^{3+}] \qquad (3)$$

It can be readily shown that, Equation (4) is also valid.

$$k_{obs} = \frac{kK[H^+]}{(1 + K[H^+])} \qquad (4)$$

Rearrangement of Equation (4) gives (5).

$$\frac{1}{k_{obs}} = \frac{1}{kK[H^+]} + \frac{1}{k} \qquad (5)$$

A plot of $1/k_{obs}$ *versus* $1/[H^+]$ should thus be linear, of slope 1/kK and intercept 1/k. Such a plot is indeed linear over the complete acidity range studied, Figure 2, with a slope of 0.025 ± 0.02 and intercept 1.60 ± 0.02 (correlation coefficient 0.999). The value of k is 0.625 s^{-1} at 25 °C with K = 64 $dm^3 mol^{-1}$. The pK_a for the ionisation $CuLH^{3+} \overset{Ka}{\rightleftharpoons} CuL^{2+} + H^+$ can readily be calculated to be 1.8.

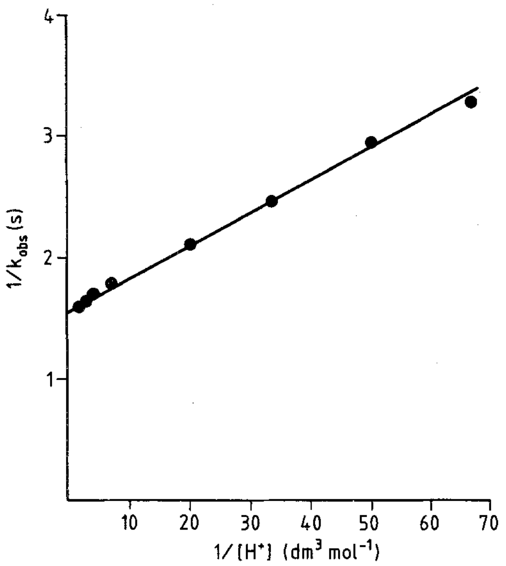
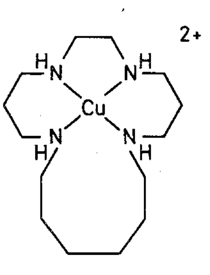
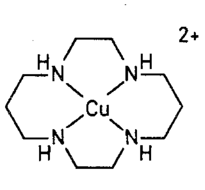


Figure 2. Double reciprocal plot for the dissociation of $[Cu([18]aneN_4 9)]^{2+}$ in $HClO_4$ solutions at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$). For clarity only the stopped-flow data are shown.

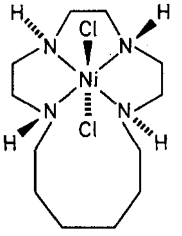


(3)

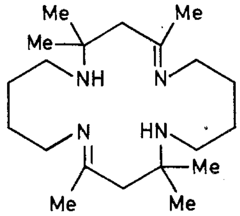


(4)

The high rate of dissociation of $[Cu([18]aneN_4 9]^{2+}$ (*3*) in acidic solution when compared with $[Cu(cyclam)]^{2+}$ (*4*) can be rationalised in terms of the strain introduced by the bulky 9-membered chelate ring. Recent crystallographic studies(7) on *trans*-$[Ni([16]aneN_4 9)Cl_2]$ (*5*) which contains a nine-membered chelate ring indicate considerable strain in the complex. Bite angles of the three five-membered rings are narrowed to 80.5°, while that of the nine-membered ring is opened out to 119.1°. Significantly, the Ni–N distance associated with the nine-membered ring is lengthened to 2.236 Å, while the Ni–N distance associated with the five-membered rings is within the "normal" range at 2.086 Å. As a result, relatively easy protonation of one of the nitrogens in the nine-membered ring of (*3*) is expected. The 14-membered cyclam ring system provides a good fit for the copper(II) ion leading to "normal" Cu–N bonds near 2.0 Å. Oversized rings result in markedly lower ligand-field strengths, Table 3, and more rapid dissociation rates.



(5)



(6)

The available kinetic data on the dissociation of copper(II) complexes of tetra-aza-macrocycles are summarised in

Table 3. The d-d spectra of copper(II) complexes of macrocyclic tetra-aza-ligands.

Complex	λ_{max} (cm^{-1})	Chelate Ring Sequence
$[Cu([14]aneN_4)]^{2+}$	19900	5, 6, 5, 6
$[Cu([16]aneN_4 8)]^{2+\,a)}$	18587	5, 6, 5, 8
$[Cu([17]aneN_4 9)]^{2+\,a)}$	17600	5, 6, 5, 9
$[Cu([17]aneN_4 8)]^{2+}$	17460	6, 5, 6, 8
$[Cu([18]aneN_4 9)]^{2+}$	16100	6, 5, 6, 9

a) Data from ref. 4.

Table 4. Dissociation rates (k) and equilibrium constants (K) for copper(II) complexes of tetra-aza-macrocycles at 25 °C.

Complex	k (s^{-1})	K ($dm^3 mol^{-1}$)	Ref.
[Cu(*trans*-Me_6[18]dieneN_4)]$^{2+}$	0.0048	10.2	3
$[Cu([16]aneN_4 8)]^{2+}$	0.48	2.7	5
$[Cu([17]aneN_4 9)]^{2+}$	0.53	1.3	5
$[Cu([18]aneN_4 9)]^{2+}$	0.625	64	This work

Table 4. For the saturated macrocycles it is noteworthy that values of k are all *ca.* 0.5 s^{-1} at 25 °C, while a much lower value of $k = 4.8 \times 10^{-3} s^{-1}$ is observed with the 18-membered diene ligand *trans*-Me_6[18]dieneN_4 (*6*). In the dissociation of the ligand a certain degree of folding is required(1, 8) which is presumably more difficult in the highly substituted and more rigid unsaturated ligand.

[Ni[17]aneN$_4$8]·(ClO$_4$)$_2$

The dissociation of $[Ni([17]aneN_48)]^{2+}$ was studied over the acidity range 0.015 to 0.50 mol dm^{-3} $HClO_4$ at 25 °C and I = 1.0 mol dm^{-3} by stopped flow techniques, Table 5.

Plots of k_{obs} *versus* [$HClO_4$] are linear over the complete acidity range, Figure 3, with $k_{obs}/[H^+] = k_H$ being 8.0 $dm^3mol^{-1}s^{-1}$ at 25 °C. Even in 0.5 mol dm^{-3} $HClO_4$ significant quantities of $NiLH^{3+}$ are not formed. The crystal structure(7) of the planar $[Ni([15]aneN_48)]^{2+}$ complex (*7*) containing an eight-membered chelate ring establishes that the Ni–N bond lengths in the eight-membered ring are equivalent at 1.905 Å, a quite typical value for low-spin nickel-amine complexes.

It appears that there is no significant weakening of any of the Ni–N bonds in complexes of this type so that protonation is therefore difficult, and may well be rate-determining.

Recent work by Billo(1) has established that dissociation of $[Ni(cyclam)]^{2+}$ probably involves folding to give the *cis*-complex with the RRRR(SSSS) configuration of the *sec*-NH centres. In 1 mol dm^{-3} $HClO_4$ the dissociation rate constant is $3 \times 10^{-6} s^{-1}$ for *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$, while for planar-$[Ni(cyclam)]^{2+}$ the dissociation rate constant is $8 \times 10^{-10} s^{-1}$ at 25°. Both reactions display a first-order dependence on [H^+] up to 3 mol dm^{-3} $HClO_4$, giving $k_H = 3 \times 10^{-6}$ $dm^3mol^{-1}s^{-1}$ for the planar species. On this basis the dissociation of $[Ni([17]aneN_48)]^{2+}$ (which is 100% square-planar in aqueous solution) is 10^{10} fold faster than that of $[Ni(cyclam)]^{2+}$.

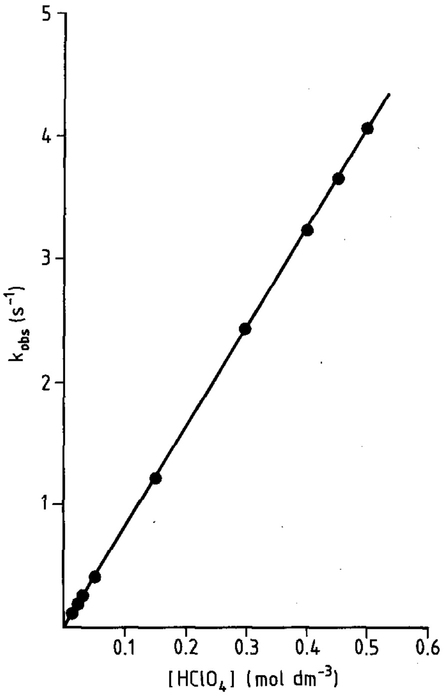
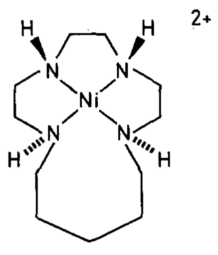


Figure 3. Acid dissociation of $[Ni[17]aneN_48]^{2+}$ in perchloric acid solutions at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$).



(*7*)

Table 5. Dissociation of $[Ni([17]aneN_48)]^{2+}$ in $HClO_4$ solutions at I = 1.0 mol dm^{-3} ($NaClO_4$) at 25 °C.

[$HClO_4$] (mol dm^{-3})	k_{obs} (s^{-1})	k_H a) ($dm^3mol^{-1}s^{-1}$)
0.015	0.11	7.3
0.02	0.16	8.0
0.03	0.24	8.0
0.05	0.40	8.0
0.15	1.21	8.1
0.30	2.42	8.1
0.40	3.22	8.0
0.45	3.63	8.1
0.50	4.03	8.1

a) $k_H = k_{obs}/[H^+]$.

Acknowledgement

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