STUDIES ON COPPER(II), NICKEL(II) AND COBALT(III) COMPLEXES OF AZA MACROCYCLIC LIGANDS*

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An account of the acid-hydrolysis of some cobalt(III) macrocyclic complexes of the type [CoLCl₂]⁺ and acid catalysed dissociation of copper(II) and nickel (II) macrocyclic complexes of the type [CuL]³⁻ and [NiL]²⁺ has been presented here. The rate of acid-hydrolysis of cobalt(III) complexes is highly dependent on the ability of the macrocycle to fold. The reactions follow a dissociative path involving a square pyramid or a trigonal bipyramid intermediate depending on the configuration of the chiral N–H groups.

Acid catalysed dissociation of the copper(II) and nickel(II) tetraaza macrocyclic complexes shows a direct dependence on [H⁺] in the low concentration range and a limiting rate at high [H⁺] ion concentrations. A mechanism involving a pre-equilibrium protonation step has been proposed. A comparison of the data shows that the stability of these complexes is dependent on (i) the sequence in which the chelate rings occur (ii) size of the chelate rings and (iii) size of the macrocyclic ring. It is found that a 5,6,5 sequence of chelate rings is the most favoured one as it holds the four donor nitrogens in a “pre-oriented” geometry favourable for coordination. The dissociation of pentaza macrocyclic complexes shows a square dependence on [H⁺] and in the case of hexaza macrocyclic complexes a cube dependence on [H⁺]. Mechanisms for these reactions have been proposed on the basis of the kinetic data. These studies show that protonation of the equatorial plane nitrogen is a prerequisite for dissociation.

Key Words: Macroyclic Complexes; Acid Hydrolysis and Dissociation

INTRODUCTION

The importance of macrocyclic complexes as models for their natural counterparts is now well recognised.¹ As a result, a large amount of work has been carried out on such complexes. Broadly speaking, these studies have been largely centred on two aspects: (i) synthesis of a variety of azamacrocycles and (ii) studies on their reactivity. Herein, some aspects of acid hydrolysis of cobalt (III) complexes and acid catalysed dissociation of copper (II) and nickel (II) complexes, both falling under the latter category above, are presented.

RESULTS AND DISCUSSION

Acid Hydrolysis of [CoLCl₂]⁺ Type Complexes: Acid hydrolysis (auration) of an octahedral complex of the type [CoLCl₂]⁺ (where L is a tetra-aza-macrocycle) can be represented as:

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\[ \text{[CoLCl}_2\text{]}^+ + \text{H}_2\text{O} \rightarrow \text{[CoL(H}_2\text{O})\text{Cl]}^2+ + \text{Cl}^- \]  \(\text{(1)}\)

\[ \text{[CoL(H}_2\text{O})\text{Cl]}^2+ + \text{H}_2\text{O} \rightarrow \text{[CoL(H}_2\text{O})_2\text{]}^3+ + \text{Cl}^- \]  \(\text{(2)}\)

The first reaction is much faster than the second and hence can be easily followed in isolation, in a majority of the cases. Aquation proceeds through a dissociative path involving a square pyrimd or a triangular bipyramid intermediate. The latter is associated with an inversion of configuration and positive values of \(\Delta S^\ddagger\). Retention of configuration is associated with negative values of \(\Delta S^\ddagger\). However, this does not imply that negative values of \(\Delta S^\ddagger\) always involve a square pyramid intermediate. Distortion of the tetra-aza macrocycle toward a triangular pyramid structure followed by cis-attack can satisfactorily account for the aquation rates encountered for several cobalt (III) complexes which hydrolyse with retention of configuration.\(^{2,3}\) Out of the several factors which influence the rates of aquation in these complexes, folding of the macrocycle appears to play an important role in deciding the rate of aquation.

In the case of 13-and 14-membered tetra-aza macrocyclic ligands, the existence of a fold axis (I) is a prerequisite for the macrocycle to be able to fold. The macrocycle folds away from the direction in which the NH group lies. However, in the case of larger sized macrocycles, folding is possible even without the existence of a fold axis. Me$_6$[14] diene(II) can give rise to chiral NH isomers,\(^4\) N-racemic(III) and N-meso(IV).

In the case of the N-rac isomer, one chloro-ligand can be replaced by a nitrogen-group to give two isomers,\(^5\) syn-(IV) and anti-(VI).

The syn-isomer aquates slowly with \(k_{\text{aq}} \times 4.8 \times 10^{-4} \text{S}^{-1}\) at 25 °C while the anti-isomer aquates rapidly with \(t_{1/2} < 10S\). The marked difference in the reactivities of the two complexes can be rationalised in terms of the position of the leaving chloride with respect to the chiral NH groups. The high rate of aquation of the anti-isomer is a direct consequence of the steric compression on the leaving chloride due to the folding of the macrocycle (VI). In this case the axial methyils of the gem-dimethyl groups point towards the axial sites opposite to the chiral NH groups.\(^6\) Therefore, in addition to the folding of the macrocycle, the gem-dimethyl groups also exert a steric compression on the leaving chloride and hence contribute considerably to rate acceleration. The conversion of \(\text{trans-[CoMe}_6[14]\) diene Cl}_2]^+\) into the syn-and anti-isomers can be summarised as shown in Scheme 1.

The N-rac isomer has been prepared by treating the \(\text{cis-[CoMe}_6[14]\) diene CO$_3]^+\) complex with HCl. The carbonato complex has a folded macrocycle and hence an N-rac configuration.\(^5\) It is pertinent to note that epimerisation of the chiral N-H centres is possible only in basic solutions. Since in the above conversions, only acidic solutions have been used, the N-rac configuration in the starting cis-carbonato complex is retained unchanged all throughout.

Cyclam(VII) gives two \(\text{trans-[CoCyclam Cl}_2]^+\) isomers having an R, S, S, R (VIII) and R, R, R, S (S, S, S, S) ( IX) configuration. The R, S, S, R form is also referred to as the trans-III form.\(^7\) This configuration is thermodynamically the most
stable form of cyclam in which there is no strain in the ring with the 6-membered chelate rings is chair-form and the five-membered rings have a gauche conformation. The R, R, R, R configuration carries two fold axis. This configuration has been observed in the crystal structure of cis-[Co Cyclam Cl₂]Cl₈, (from which the R, R, R, R isomer is obtained) and cis-[Co Cyclam (en)] Cl₃.H₂O.⁹ The two trans-isomers are free from steric compression of ring substituents. The R, S, S, R isomer aquates¹⁰ with $k_{aq} = 1.10 \times 10^{-6} S^{-1}$ and the R, R, R, R isomer with $k_{aq} = 1.75 \times 10^{-3} S^{-1}$ at 25 °C. The rate enhancement of $1.6 \times 10^3$ for the isomer is evidently due to the folding of the macrocycle as this isomer carries two-fold axis.

The R, S, S, R isomer gives 100 per cent trans-[Co Cyclam Cl (OH)]²⁺ while the R, R, R, R isomer gives initially a mixture of 75 per cent trans- and 25 per cent cis-[Co Cyclam Cl(H₂O)]³⁺. The mixture then isomerises to the 100 per cent trans-[Co Cyclam Cl(H₂O)]²⁺. This case is the first example of stereochemical change in the aquation of 14-membered macrocyclic complex. These reactions are normally fully stereoretentive.
Reduction of Me₂[14] diene (X) gives two isomers, C-meso (XI) and C-rac (XII), which can be easily separated by fractional crystallisation from Xylene and diethylether. In the case of the C-meso isomer (L = XI) aeration of methanolic solutions of cobalt (II) chloride and the ligand followed by addition of HCl, then HClO₄ gives the α-trans-[CoLCl₂]⁺. The filtrate later yields the β-trans-[CoLCl₂]⁺ and finally a violet cis-[CoLCl₂]⁺ isomer. The cis-isomer on heating in dilute hydrochloric acid yields the green β-trans isomer. This is evidenced by the identical i, r. and aquation rates of the β-trans and the isomerised β-trans isomers.

Theoretically, the C-meso isomer is capable of yielding 10 diastereo isomers (Scheme 2). The equatorial and/or axial arrangement of the two ring methyl groups can be established by examination of molecular models. On the basis of ¹H nmr spectra and crystal structure studies on some cobalt(III) complexes, it has been established that an axial methyl gives a ¹H nmr signal as a doublet around δ 1.2 while and equatorial methyl gives doublet around δ 1.4. The ¹H nmr spectra of the α-trans and β-trans in (CD₃)₂SO as solvent gives single methyl doublets near δ 1.4 (Table I) indicating that both isomers should have a diequatorial arrangement of the two ring methyls. From Scheme 2, it can be concluded that this arrangement is present in structures (ii), (vi) and (ix). Since α-trans is the most stable form (isolated first of all), it is assigned structure (vi) corresponding to the most stable trans-III structure of cyclam. Further since the β-trans-isomer can be obtained from the cis-isomer, it must have a fold axis which is present in structure (ii) and not in structure (ix). Therefore, the β-trans-isomer is assigned structure (ii).
α-trans isomer aquates with $k_{aq} = 2.4 \times 10^{-4}S^{-1}$ and β-trans with $k_{aq} = 0.55 \times 10^{-4}S^{-1}$ at 25 °C. In this case the β-trans-isomer aquates a slower rate than α-trans-isomer, although the former has a fold axis.
### Table I

$^1$H nmr spectra of isomeric C-meso Me₂ane complexes\(^{14}\)

<table>
<thead>
<tr>
<th>Complex [CoLCl₅]ClO₄ isomer</th>
<th>δ/ppm(^a)</th>
<th>NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-trans</td>
<td>1.41 (d, $J = 7.3\text{Hz}$)</td>
<td>6.62 and 5.52</td>
</tr>
<tr>
<td>β-trans</td>
<td>1.40 (d, $J = 7.3\text{Hz}$)</td>
<td>6.63 and 5.52</td>
</tr>
</tbody>
</table>

\(^a\)in (CD₃)₂SO as solvent with TMS reference.
\(d\)—doublet.

### Table II

$^1$H nmr spectra of isomeric C-rac Me₂ane complexes\(^{14}\)

<table>
<thead>
<tr>
<th>Complex [CoLCl₅]ClO₄ isomer</th>
<th>δ/ppm(^a)</th>
<th>NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>1.39 (d, $J = 7.0\text{Hz}$)</td>
<td>6.62, 6.37, 5.40</td>
</tr>
<tr>
<td></td>
<td>1.22 (d, $J = 7.2\text{Hz}$)</td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td>1.40 (d, $J = 7.0\text{Hz}$)</td>
<td>6.62, 5.55</td>
</tr>
<tr>
<td>(D)</td>
<td>1.37 (d, $J = 7.2\text{Hz}$)</td>
<td>6.40, 5.76</td>
</tr>
</tbody>
</table>

\(^a\)in (CD₃)₂SO as solvent with TMS reference.
\(d\)—doublet

In the case of the C-rac Me₂ane (XII),\(^{14}\) aeration of methanolic solutions of cobalt(II) chloride followed by treatment with HCl, yields a violet cis-[CoL Cl₂]Cl isomer. Addition of HClO₄ to the filtrate and fractionation yields two trans-[CoLCl₅] ClO₄ isomers, (B) and(C). Isomerisation of the cis-isomer in hydrochloric acid yields a trans-isomer(D).\(^{15}\) $^1$H nmr spectra in (CD₃) SO (Table II) show that isomer(B) should have an axial-equatorial arrangement of the two methyl groups. This arrangement is present in structures (ii), (iv), (vi) and(ix) (Scheme 3). The thermodynamically stable trans-III configuration is present in structure (iv) and hence, the trans(B) isomer is assigned this structure. Both trans(C) and trans(D) isomer have a diequatorial arrangement, present in structure (x), (viii) and (x). Since isomer D is obtained from the cis-isomer, it must have N-(1)-N(8) fold axis similar to that established for the β-trans isomer with the C-meso ligand. Isomer D is therefore, assigned structure (v). Further, it is logical to assume that in going from isomer(B) to isomer(D), the conversion should involve epimerisation of only one chiral nitrogen at each stage (as observed with the C-meso ligand) as shown in Scheme 4. Therefore, isomer (C) should be assigned structure (viii). Isomer(B) aquates with a rate $k_{aq} = 4.5 \times 10^{-4}\text{S}^{-1}$ isomer(C) with $k_{aq} = 6.5 \times 10^{-4}\text{S}^{-1}$ and isomer(D) with $k_{aq} = 9.0 \times 10^{-4}\text{S}^{-1}$ at 25°C. Isomer(B) has no fold axis, isomer(C)—one-fold axis and isomer(D)—two-fold axis. Isomer
$D$ has a positive value of $S (S = 22 \pm 6 \text{ JK}^{-1} \text{ mol}^{-1})$, which is another example of aquation in these complexes accompanied by inversion. Isomer($D$) has two-fold axis and two twist-board six-membered chelate rings. In such a situation, isomerisation to a folded cis complex is thus quite probable during aquation.

The rates of aquation of the various macrocyclic cobalt (III) complexes (Table III) can be summarised as shown in Scheme 5.
These results show that complexes which carry a trans-III configuration (R, S, S, R) aquate very slowly. Rate enhancements are observed when the macrocycle is capable of folding towards the leaving group. The high rates of aquation observed for the 15- and 16-membered macrocyclic complexes, despite the absence of fold axis, is due to the fact that larger sized macrocycles can fold even against the chiral N-H groups.

In a dissociate process above, the geometries for a five coordinate intermediate are trigonal bipyramid (D$_{3h}$) (XIII) and square pyramid (C$_4$V) (XIV).
When viewed along the $C_2$ and $C_4$ axis, the two structures are very similar. If the macrocycle cannot fold, presumably the intermediate more closely resembles a square pyramid, which requires a higher free energy of activation. If the macrocycle can fold, then a trigonal bipyramid intermediate is possible.

The entering group X in this case can then retrace the path of the leaving group giving 100 per cent retention of configuration or take path indicated by arrows (XV) to give a cis-complex and lead to inversion of configuration. It is evident that some folding is required to reach the transition state for aquation. Presence of fold axis allows the transition state to be attained easily leading to rapid aquation.$^5$

**DISCUSSION OF THE COPPER (III) AND NICKEL (II) MACROCYCLIC COMPLEXES**

Formation and dissociation studies have been limited to only more labile metals, copper (II) and nickel (II). Formation studies have been possible largely with copper (II) due to the ease of incorporation of copper (II) into the macrocyclic cavity. On the other hand incorporation of nickel (II) requires elevated temperatures and hence, formation studies with nickel (II) have been very limited. Studies on copper (II) show that in tetragonal aqua copper (II) ligand substitution occurs via a dissociative path and formation of the second copper-nitrogen bond is rate determining.$^{16,17}$ In contrast, the dissociation studies are much more informative and give a better idea about the stability of these complexes.

Cabbiness and Margerum$^{18}$ while working on the dissociation of copper (II) complexes of 14-membered tetraaza macrocycles observed that these reactions are extremely slow.$^{19}$ The dissociation studies were, therefore, limited to the more labile triaza macrocycles.$^{19,20}$ During the course of our studies on larger ringed macrocycles, it was found that the copper (II) and nickel (II) complexes of the tetraaza macrocycle, Me$_8[18]$ diene (XVI), were quite labile in acidic solutions. This prompted us to take up detailed kinetic studies on the acid catalysed dissociation of these complexes. These studies were further diversified to cover other tetraaza diaza, pentaaza and hexaaza macrocycles.

The dissociation of $[\text{Cu (trans-Me}_8[18] \text{ diene)]}^{2+}$ in acidic solution$^{21}$ follows first order kinetics and gives a rate profile shown in Fig. 1. At low acidities plot of $k_{\text{obs}}$ vs $[H^+]$ is linear with a pronounced intercept attributed to a solvolytic dissociation path. The observed rate profile is consistent with kinetic scheme:

\[
\begin{align*}
\text{CuL}^{2+} + H^+ & \rightleftharpoons \text{CuLH}^{3+} & & K \\
\text{CuLH}^{3+} & \rightarrow \text{Cu}^{2+} + \text{HL}^+ & & k
\end{align*}
\]

The rate expression for this can be written as:

\[
k_{\text{obs}} = k_0 + \frac{kK[H^+]}{(1 + k[H^+]})
\]

... (5)
Equation (5) can be rearranged to give

\[
\frac{1}{(k_{\text{obs}} - k_0)} = \frac{1}{kK} \frac{1}{[H^+]} + \frac{1}{k} \tag{6}
\]

The plot of \( \frac{1}{k_{\text{obs}} - k_0} \) vs \( \frac{1}{[H^+]} \) is linear with an intercept equal to \( \frac{1}{k} \) and slope \( -\frac{1}{kK} \), and has been used to evaluate the values of \( K \) and \( k \). For comparing the stabilities of the various copper(II) complexes, a rate constant \( k_H \) can be defined as the slope of the linear plot between \( k_{\text{obs}} \) and \([H^+]\) at low acidities. The various parameters associated with these reactions are given in Table IV. A low value of \( K = 10.2 \text{M}^{-1} \) at 25 °C indicates a slow rate determining protonation step, at least in the low acidity range. Solvent deuterium isotope effects were also studied with the above complex, where reactions were monitored in DCl/D₂O and HCl/H₂O using low acidities. The ratio of \( k_H/k_D \) was found to be 2.0, which can be interpreted in terms of a slow proton transfer at these acidities and this step is at least partly rate-determining. It is possible that there is a change from rate-determining proton transfer step at low acidities to a rate-determining dissociation of CuLH³⁺ at high acidities.

The copper complex of cis-Me₆[18]diene (XVII), [Cu(cis-Me₆[18]dien)]²⁺, undergoes dissociation at a rate of about 700 times faster than the corresponding complex with trans-ligand. The much higher rate is due to the contorted conformation the cis-macrocycle adopts in its copper (II) complex in order to minimise angular, torsional and bond-length strain. This complex has a distorted tetrahedral geometry in contrast to the square planar geometry for other complexes. X-ray work²² has shown that the dihedral angle for the N(1) CuN(2)–N(3) CuN(4) planes is 36.6 °C.
Table IV

Dissociation rate data for tetraaza macrocyclic complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$k_H$ (M$^{-1}$S$^{-1}$)</th>
<th>$k_o$ (S$^{-1}$)</th>
<th>$k$ (S$^{-1}$)</th>
<th>$\Delta H^\ddagger$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (JK$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu (trans-Me$_6$[18] diene)]$^{2+}$</td>
<td>$3.6 \times 10^{-4}$</td>
<td>$8 \times 10^{-3}$</td>
<td>$4.0 \times 10^{-3}$</td>
<td>98.7</td>
<td>77.1</td>
</tr>
<tr>
<td>[Ni (trans-Me$_6$[18] diene)]$^{2+}$</td>
<td>$6.0 \times 10^{-4}$</td>
<td>$0.13 \times 10^{-3}$</td>
<td>$0.24 \times 10^{-3}$</td>
<td>51.9</td>
<td>85.3</td>
</tr>
<tr>
<td>[Cu (cis-Me$_6$[18] diene)]</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu tetra (cyanoethyl) cyclam]$^{2+}$</td>
<td>$2.24 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td></td>
<td>88.3</td>
<td>$-13.6$</td>
</tr>
<tr>
<td>[Cu[16] ane M$_8$]</td>
<td>1.13</td>
<td>0.027</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu[17] ane N$_4$]</td>
<td>0.60</td>
<td>0.122</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu (tetric)$_2$+ (red)]</td>
<td>$5.9 \times 10^{-8}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu (tetric)$_2$+ (unstable red)]</td>
<td>$7.0 \times 10^{-7}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu (tetric)$_2$+ (blue)]</td>
<td>$6.2 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu (2, 3, 2-tetra)]$^{2+}$</td>
<td>$6.7 \times 10^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the trans-ligand this angle is only 11.50. The dissociation reaction of the [Cu(cis-Me$_6$[18] diene)]$^{2+}$ complex is also subject to general acid catalysis. Therefore, $k_{obs} = k_H[H^+] + k_{HA}[HA]$, where [HA] is the concentration of a weak acid. The reaction was followed at pH 4.60 in acetic acid/sodium acetate buffers using different concentrations of acetic acid. A substantial catalysis by acetic acid was observed (Table V). A plot of $k_{obs}$ vs [HA] is linear with a positive intercept. The observation of general acid catalysis- indicates that the proton transfer step is rate determining.

The dissociation of [Ni (trans-Me$_6$[18] diene)]$^{2+}$ shows a similar rate profile (Fig. 2) to the one observed for the [Cu(trans-Me$_6$[18] diene)]$^{2+}$ complex. The lower values $k_H$ for this complex are in accord with the lower lability of the nickel(II) complexes. The low value of $K = 1.7$M$^{-1}$ supports a slow proton transfer step.

Table V

Acetic acid catalysis of dissociation of [Cu cis-Me$_6$[18] diene]$^{2+}$ at 25 °C,
$I = 0.1 M$(NaClO$_4$) and $pH = 4.60$

<table>
<thead>
<tr>
<th>$10^3$ [HOAc] (M)</th>
<th>$10^3$ $k_{obs}$ (S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.40</td>
</tr>
<tr>
<td>1.0</td>
<td>2.59</td>
</tr>
<tr>
<td>2.0</td>
<td>4.50</td>
</tr>
<tr>
<td>3.0</td>
<td>6.51</td>
</tr>
<tr>
<td>4.0</td>
<td>9.19</td>
</tr>
</tbody>
</table>

A ratio of 1 : 1 of sodium acetate-acetic acid was used.
On the basis of the observed kinetic data, the acid catalysed dissociation of the copper(II) and nickel(II) tetraaza macrocyclic complexes can be assigned a mechanism shown in Scheme 6.

The dissociation of the copper(II) complexes of two new 16- and 17-membered tetraaza macrocycles (XVIII, XIX) capable of generating 8- and 9-membered chelate rings has also been studied. The larger sized rings involve a stabilised strain, by analogy with cycloalkanes, but are stabilised to a considerable extent by the macrocyclic effect. The dissociation of these complexes show similar rate profiles to the ones observed for the Me₆[18] diene complexes. These two complexes show a considerably higher \( k_R \) values (Table IV) by virtue of the larger strain introduced by the 8- and 9-membered chelate rings. It is interesting to note that the rate of dissociation of the 16-membered macrocycle (XVIII) is higher than of the 17-membered macrocycle (XIX) with a 9-membered chelate ring.

X-ray analysis of the nickel(II) complex of an analogues macrocycle (XX) shows that all the carbons of the 8-membered chelate ring lie on one side of NiN₄ plane and the ring is severely distorted and is intermediate between boat-boat and crown conformations. In a similar situation, the 8-membered chelate ring of XVIII lies on one

### Table VI

*Dissociation rate data for polyaza macrocyclic complexes at 25 °C*

<table>
<thead>
<tr>
<th>Complex</th>
<th>( k_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni[15] ane N₈]⁺⁺</td>
<td>0.63 M⁻² S⁻¹</td>
</tr>
<tr>
<td>[Cu [15] ane N₈]⁺⁺</td>
<td>0.049 M⁻² S⁻¹</td>
</tr>
<tr>
<td>[Cu [16] ane H₈]⁺⁺</td>
<td>4.85 M⁻¹ S⁻¹</td>
</tr>
<tr>
<td>[Cu [17] ane N₉]⁺⁺</td>
<td>( 1.18 \times 10^9 ) M⁻³ S⁻¹</td>
</tr>
<tr>
<td>[Ni [18] ane N₉]⁺⁺</td>
<td>( 2.58 \times 10^9 ) M⁻³ S⁻¹</td>
</tr>
</tbody>
</table>
side of the NiN₄ plane. The six-membered ring lies on the other side of the Ni N₄ plane. The five-membered rings have an eclipsed conformation. With this kind of distortion, higher rate of dissociation of the copper complex of XVIII is expected.

In a similar situation, the copper(II) complex of tetra(cyano ethyl) cyclam (XXI) (a 14-membered macrocycle) also shows a high rate of dissociation. The four cyanoethyl arms lie on the same side of the N₄ plane. In the complex, copper 'sits atop' the N₄ plane, which weakens the CuN bond and makes it more susceptible to protonation.

The stability of tetraaza macrocyclic complex with copper(II) and nickel(II) has been observed to depend on the size of the chelate rings and size of the macrocyclic cavity. However, later work with tetraaza macrocycles carrying larger
chelate rings, has shown that in addition to the above two factors, the sequence in which the chelate rings occur has a marked influence on their stability. Comparison of the available data shows that a 5, 6, 5 chelate ring sequence is ideal for coordination. This sequence holds the four nitrogen donor in a 'pre-oriented' geometry favourable for coordination.

The acid catalysed dissociation of [Ni([8] ane N₂)]²⁺ (an eight-membered diaza-macrocycle, XXII) is very slow²⁷ and was followed at 60 °C (k₀ = 2 × 10⁻² S⁻¹ and k₉ = 2.0 × 10⁻³M⁻¹S⁻¹ at 60 °C). The rate profile is shown in Fig. 3. The dissociation should follow the pathway

\[ \frac{K}{NiL₄²⁺ + H^+ \rightarrow NiL₂H³⁺} \]  \hspace{1cm} \text{...(7)}

\[ \frac{k}{NiL₂H³⁺ + H₂O \rightarrow Ni²⁺ (aq)} \]  \hspace{1cm} \text{...(8)}

The overall rate expression will take the same form as in equation (5) when \( K[H^+] \ll 1 \), the reaction shows a direct dependence on \([H^+]\) and \( k₉ = kK \). In the

![Fig 3](image-url)  
**Fig 3** Dissociation of [Ni[18] ane N₉]²⁺ in HClO₄.
above scheme, step (8) is slow and hence rate-determining. The dissociation mechanism for this reaction can be proposed as shown in Scheme 7. The complex has a ‘twin butterfly’ shape (XXIII) with nickel sandwiched between the two macrocycles. The eight-membered ring is folded across the N, N-axis. The C₃ and C₇ protons shield the axial sites which prevent an octahedral geometry and likewise protects protonation of the nitrogens, resulting in low dissociation rates.

![Scheme 7](image)

In the case of copper(II) and nickel(II) complexes of pentaaza macrocycles, (XXIV, XXV, XXVI) the rate shows a square dependence on [H⁺] with no intercept.₂⁸⁻²⁹ This is the first example of a second order dependence on [H⁺] for the macrocyclic complexes. The transition state for this reaction should involve the complex and two protons. This kinetic behaviour can be represented as :

\[
\text{CuL}^{2+} + \text{H}^+ \rightleftharpoons k_{1}\text{Cu(HL)}^{3+}
\]  

\[
\text{Cu(HL)}^{3+} + \text{H}^+ \rightleftharpoons k_{3}\text{Cu(H}_2\text{L)}^{4+}
\]  

\[
\text{Cu(H}_2\text{L)}^{4+} \rightarrow k\text{Cu(aq)}^{2+} + \text{H}_2\text{L}^{2+}
\]

The rate law for this behaviour can be written as :

\[
\text{Rate} = \frac{kK_1K_2[\text{CuL}^{2+}][\text{H}^+]^2}{1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+]^2}
\]

\[
\text{...(9)}
\]

\[
\text{...(10)}
\]

\[
\text{...(11)}
\]

\[
\text{...(12)}
\]
Under the conditions of the studies done, $K_1[H^+] + K_2K_3[H^+]^{2+} \ll 1$, hence $k_H = kK_1K_2$. The $k_H$ values (Table VI) for the 15-, 16-, and 17-membered pentaaza macrocycles shows that the rate of dissociation increases with an increase in cavity size.

In order to check the validity of the above kinetic scheme, the dissociation of the nickel(II) complex of a hexaaza macrocycles(XXVII) was studied, which should show a cube dependence on $[H^+]$. The kinetic data indeed showed a cube dependence on $[H^+]$. Applying a similar treatment as above, a further equilibrium step in addition to steps (9) and (10) can be introduced.

$$Ni(H_2L)^{4+} + H^+ \rightleftharpoons Ni(H_3L)^{5+} \quad \ldots(13)$$

This gives the value of $k_H = kK_1K_2K_3 = 2.58 \times 10^2 \text{ dm}^9 \text{ mol}^{-3} \text{ S}^{-1}$. A mechanism for the dissociation of these complexes (taking the pentaaza macrocycles as representative) can be proposed as shown in Scheme 8. The first attack would be expected at the apical nitrogen because the axial copper-nitrogen bond is expected to be weaker due to Jahn-Teller distortion. In Scheme 8, species (2) has been introduced because it is improbable that a proton can attack a fully coordinated nitrogen. Arguments in favour of a partly bonded species rather than a completely broken copper-nitrogen bond as an intermediate for proton attack have been put forward by Margerum et al. It can also be concluded from these studies that
protonation of an equatorial plane nitrogen is a prerequisite for dissociation of the complex to take place.

REFERENCES