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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 $[CoLCl_2]^+$ and acid catalysed dissociation of copper(II) and nickel (II) macrocyclic complexes of the type $[CuL]^{2+}$ 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 is a "pre-oriented" geometry favourable for coordination. The dissociation of pentaaza macrocyclic complexes shows a square dependence on $[H^+]$ and in the case of hexaaza 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 : **Macrocyclic 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 azamacrocyclics 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 $[CoLCl_2]^+$ *Type Complexes*: Acid hydrolysis (aquation) of an octahedral complex of the type $[CoLCl_2]^+$ (where L is a tetra-aza-macrocycle) can be represented as:

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$$[CoLCl_2]^+ + H_2O \longrightarrow [CoL(H_2O)Cl]^{2+} + Cl^- \quad ...(1)$$

$$[CoL(H_2O)Cl]^{2+} + H_2O \longrightarrow [CoL(H_2O)_2]^{3+} + Cl^- \quad ...(2)$$

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 prymid 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 triagular 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.

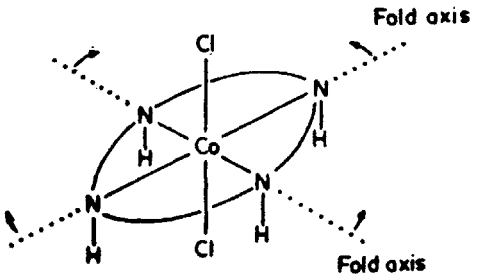
In the case of 13-and 14-membered tetra-aza macrocyclic ligands, the existence of a fold axis (I) is a prerequisite for the macrocycle to be able to fold. The macrocycle folds away from the direction in which the NH group lies. However, in the case of larger sized macrocycles, folding is possible even 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 nitro-group to give two isomers,[5] syn-(IV) and anti-(VI).

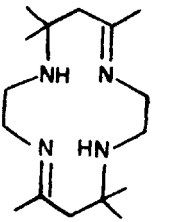
The syn-isomer aquates slowly with $k_{aq} \times 4.8 \times 10^{-4} S^{-1}$ at 25 °C while the anti-isomer aquates rapidly with $t_{1/2} < 10S$. The marked difference in the reacti vities of the two complexes can be rationalised in terms of the position of the leaving chloride with respect to the chiral 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 methyls 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 *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 *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.

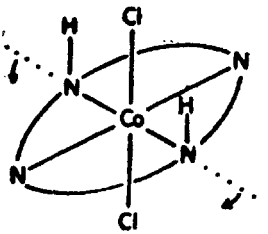
Cyclam(VII) gives two *trans*-[CoCyclam Cl_2]$^+$ isomers having an R, S, S, R (VIII) and R, R, R, R (S, S, S, S) (IX) configuration. The R, S, S, R form is also referred to as the *trans*-III form.[7] This configuration is thermodynamically the most



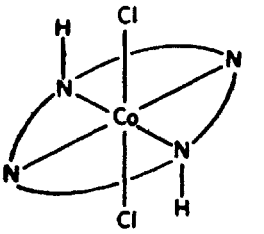
I



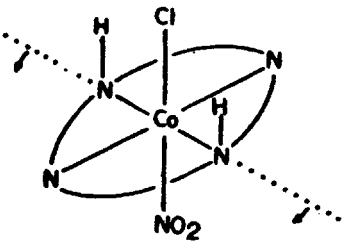
II



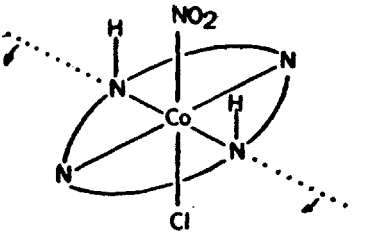
RR (S,S)
N-racemic
III



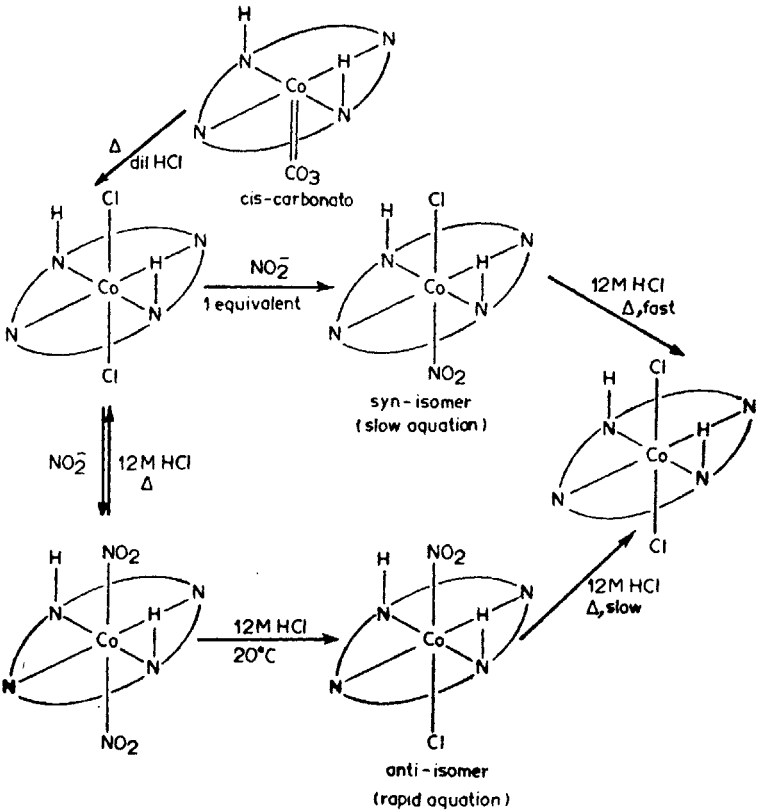
R,S
N-meso
IV



Syn-isomer
V



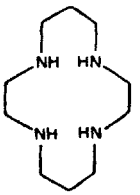
anti-isomer
VI



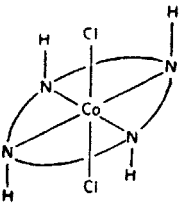
SCHEME 1

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 crytal structure of *cis*-[Co Cyclam Cl_2]Cl[8], (from which the R, R, R, R isomer is obtained) and *cis*-[Co Cyclam (en)] $Cl_3.3H_2O$.[9] The two *trans*-isomers are free from steric compression of ring substituents. The R, S, S, R isomer aquates[10] 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 1.6×10^3 for the isomer is evidently due to the folding of the macrocycle as this isomer carries two-fold axis.

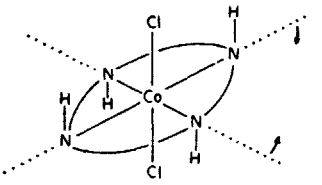
The R, S, S, R isomer gives 100 per cent trans-[Co Cyyclam Cl (OH)]$^{2+}$ while the R, R, R, R isomer gives initially a mixture of 75 per cent *trans*- and 25 per cent *cis*-[Co Cyclam Cl(H_2O)]$^{2+}$. The mixture then isomerises to the 100 per cent *trans*-[Co Cyclam Cl(H_2O)]$^{2+}$. This case is the first example of stereochemical change in the aquation of 14-membered macrocyclic complex. These reactions are normally fully stereoretentive.



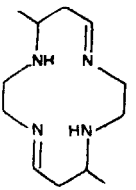
Cyclam
VII



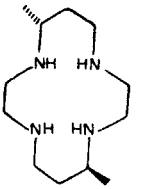
R, S, S, R
VIII



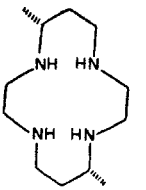
R,R,R,R (S,S,S,S)
IX



Me_2[14] diene
X



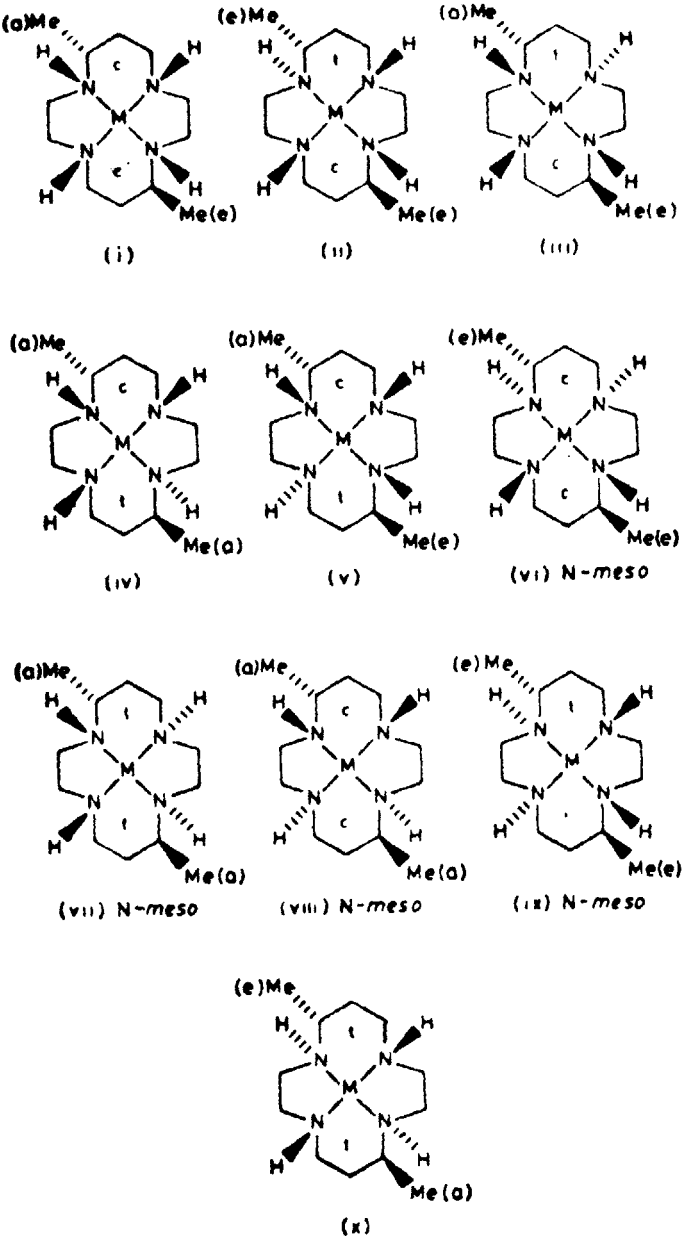
C-meso
XI



C-roc
XII

Reduction of Me_2[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.[11,12] 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 $HClO_4$ gives the α-*trans*-$[CoLCl_2]^+$. The filterate later yields the β-*trans*-$[CoLCl_2]^+$ and finally a violet *cis*-$[CoLCl_2]^+$ isomer.[13] 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 ^{1}Hnmr spectra and crystal structure studies on some cobalt(III) complexes,[14] it has been established that an axial methyl gives a ^{1}H nmr signal as a doublet around δ 1.2 while and equatorial methyl gives doublet around δ 1.4. The ^{1}H nmr spectra of the α-*trans* and β-*trans* in $(CD_3)_2SO$ 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). The



SCHEME 2

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

^1H nmr spectra of isomeric C-meso Me_2 ane complexes[14]

Complex $[CoLCl_2]ClO_4$ isomer	δ/ppm[a] CH_3	NH
α-*trans*	1.41 (*d*, J = 7.3Hz)	6.62 and 5.52
β-*trans*	1.40 (*d*, J = 7.3Hz)	6.63 and 5.52

a—in $(CD_3)_2SO$ as solvent with TMS reference.
d—doublet.

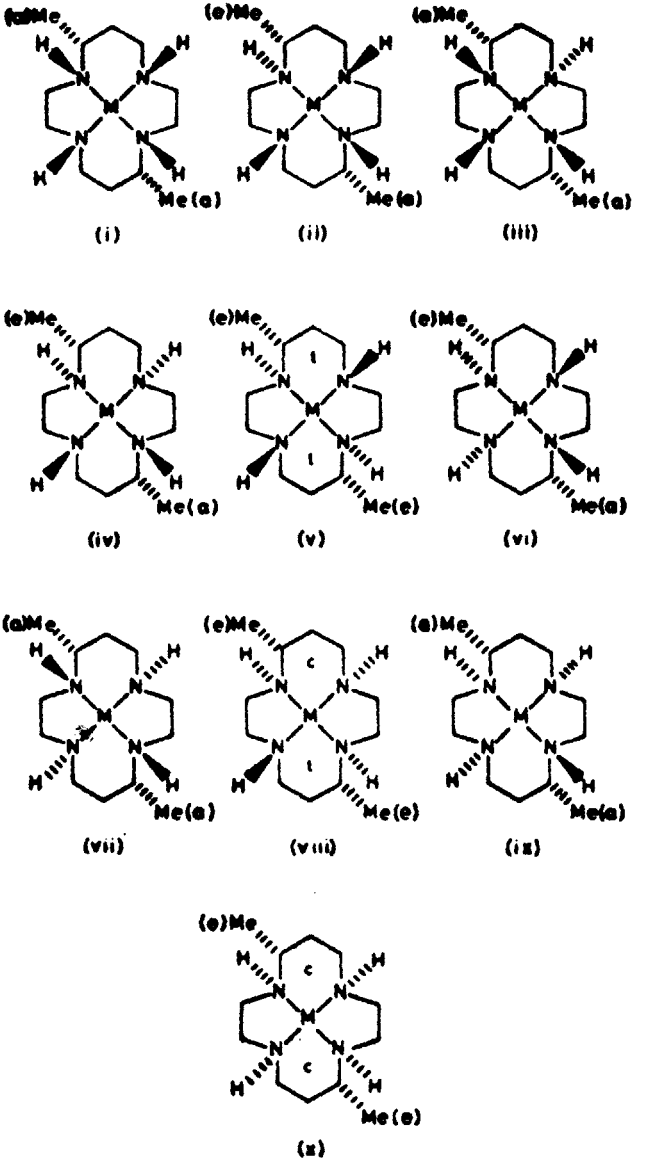
TABLE II

^1H nmr spectra of isomeric C-rac Me_2 ane complexes[14]

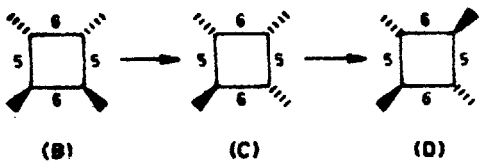
Complex $[CoLCl_2]ClO_4$ isomer	δ/ppm[a] CH_3	NH
(B)	1.39 (*d*, J = 7.0Hz) 1.22 (*d*, J = 7.2Hz)	6.62, 6.37, 5.40
(C)	1.40 (*d*, J = 7.0Hz)	6.62, 5.55
(D)	1.37 (*d*, J = 7.2Hz)	6.40, 5.76

a—in $(CD)_3$ SO as solvent with TMS reference.
d—doublet

In the case of the C-rac Me_2 ane (XII),[14] aeration of methanolic solutions of cobalt(II) chloride followed by treatment with HCl, yields a violet *cis*-$[CoL\ Cl_2]Cl$ isomer. Addition of $HClO_4$ to the filterate and fractionation yields two *trans*-$[CoLCl_2]\ ClO_4$ isomers, (B) and(C). Isomerisation of the *cis*-isomer in hydrochloric acid yields a *trans*-isomer(D).[15] ^1H nmr spectra in (CD_3) 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 $k_{aq} = 4.5 \times 10^{-4} S^{-1}$ isomer(*C*) with $k_{aq} = 6.5 \times 10^{-4}\ S^{-1}$ and isomer(*D*) with $k_{aq} = 9.0 \times 10^{-4} S^{-1}$ at 25 °C. Isomer(*B*) has no fold axis, isomer(*C*)—one-fold axis and isomer(*D*)—two-fold axis. Isomer



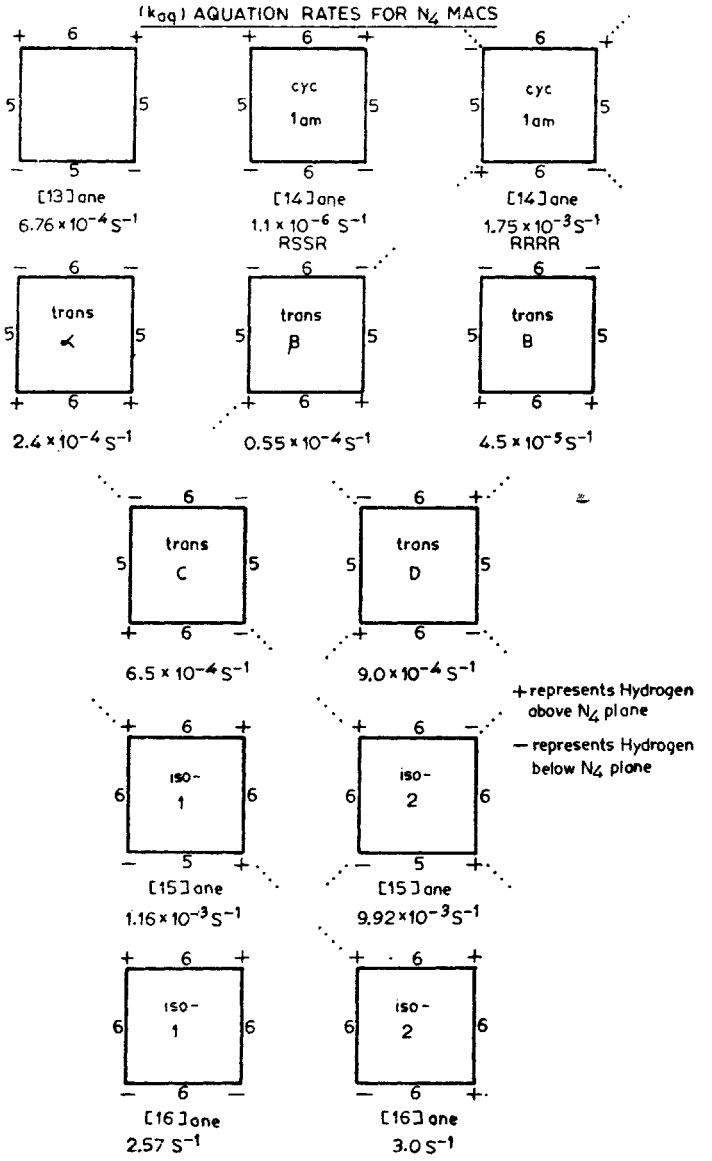
SCHEME 3



SCHEME 4

D has a positive value of S ($S = 22 \pm 6$ JK^{-1} 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.



SCHEME 5

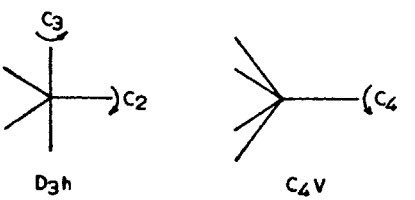
TABLE III

Aquation data at 25 °C for cobalt (III) tetraaza macrocyclic complexes $[Co(N_4)Cl_2]^+$

N_4 Ligand	Isomeric form	R_{aq} (S^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})
trien	*cis*-α	1.5×10^{-4}	90.0	− 25
$(en)_2$	*cis*	2.4×10^{-4}	90.0	− 17 to + 70
cyclen	*cis*	4.5×10^{-3}	78.2	− 21
[13] ane N_4	*trans*	6.76×10^{-4}	81.6	− 29
cyclam	*cis* R, R, R, R	1.6×10^{-2}	76.6	− 25
cyclam	*trans* R, R, R, R	1.75×10^{-3}	101.3	+ 42
cyclam	*trans* R, S, S, R	1.10×10^{-6}	103	− 12
C-meso Me_2[14] ane	α-*trans*	2.4×10^{-4}	69	− 84
C-meso Me_2[14] ane	β-*trans*	0.55×10^{-4}	76	− 72
C-meso Me_2[14] ane	*cis*	8.7×10^{-2}	103	+ 80
C-rac Me_2[14] ane	*trans* (B)	4.5×10^{-5}	96.7	− 4
C-rac Me_2[14] ane	*trans* (C)	6.5×10^{-4}	80.6	− 35
C-rac Me_2[14] ane	*trans* (D)	9.0×10^{-4}	96.9	+ 22
C-rac Me_2[14] ane	*cis*	5.5×10^{-2}	83.9	+ 12
[15] ane N_4	*trans* I	1.16×10^{-3}	72.4	− 59
[15] ane N_4	*trans* II	9.92×10^{-3}	61.5	− 75
[16] ane N_4	*trans* I	2.5	—	—
[16] ane N_4	*trans* II	3.0	—	—

These results show that complexes which carry a *trans*-III configuration (R, S, S, R) aquate very slowly.[5] 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 bipryamid (D_{3h}) (XIII) and square pyramid (C_4V) (XIV).



XIII XIV XV

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 intermidiate 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 case 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_6[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.

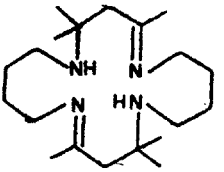
The dissociation of [Cu (*trans*-Me_6[18] diene]$^{2+}$ in acidic solution[21] follows first order kinetics and gives a rate profile shown in Fig. 1. At low acidities plot of k_{obs} *vs* [H^+] is linear with a pronounced intercept attributed to a solvolytic dissociation path. The observed rate profile is consistent with kinetic scheme:–

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

$$CuLH^{3+} \overset{k}{\rightarrow} Cu^{2+} + HL^+ \qquad \ldots(4)$$

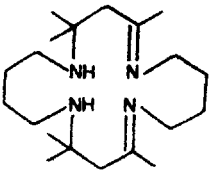
The rate expression for this can be written as:

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



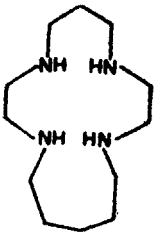
trans - Me_6 [18] diene

XVI

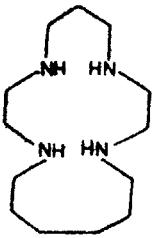


Cis - Me_6 [18] diene

XVII



XVIII



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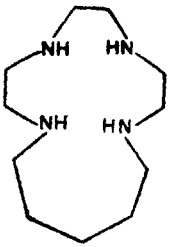

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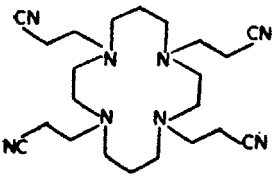
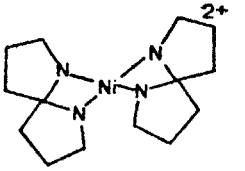


XXI

XXII



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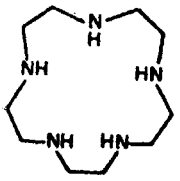

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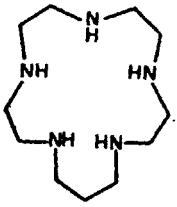

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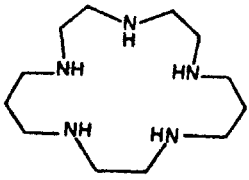

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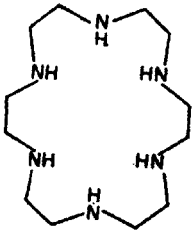


XXVII

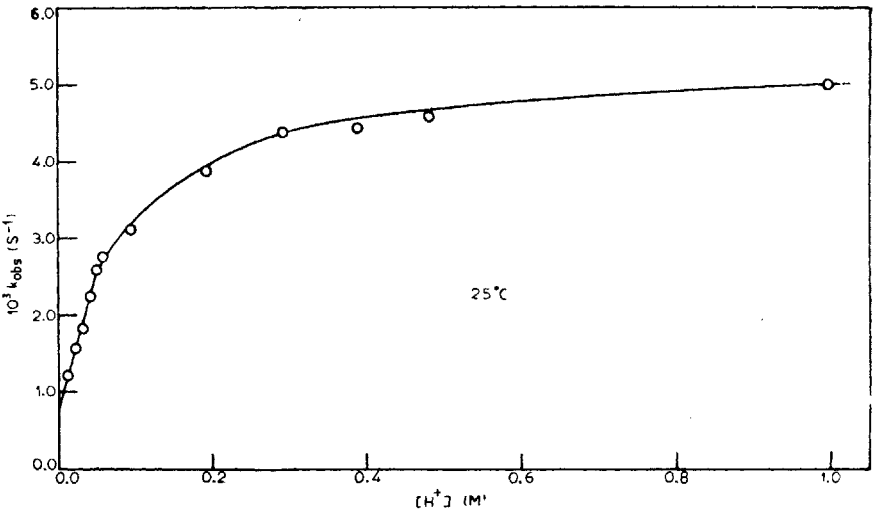


FIG 1 Dissociation of [Cu (*trans*-Ms_6 [18] diene N_4)]$^{2+}$ in $HClO_4$.

Equation (5) can be rearranged to give

$$\frac{1}{(k_{obs} - k_o)} = \frac{1}{kK}\frac{1}{[H^+]} + \frac{1}{k} \qquad \ldots(6)$$

The plot of $\frac{1}{k_{obs} - k_o}$ *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_{obs} and $[H^+]$ at low acidities. The various parameters associated with these reactions are given in Table IV. A low value of $K = 10.2M^{-1}$ 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/D_2O and HCl/H_2O 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 $CuLH^{3+}$ at high acidities.

The copper complex of *cis*-Me_6[18] diene (XVII), [Cu(*cis*-Me^6[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, tor sional and bond-length strain. This complex has a distorted tetrahedral geometry in contrast to the square planar geometry for other complexes. X-ray work[22] 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

Complex	rate			$\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$) for		$\Delta S^{\ddagger}$ ($JK^{-1}\ mol^{-1}$) for	
	k_H ($M^{-1}S^{-1}$)	k_0 (S^{-1})	k (S^{-1})	k_0	k	k_0	k
[Cu (*trans*-Me_6[18] diene)]$^{2+}$	3.6×10^{-2}	8×10^{-3}	4.0×10^{-3}	98.7	77.1	−18	−32
[Ni (*trans*-Me_6[18] diene)]$^{2+}$	6.0×10^{-4}	0.13×10^{-3}	0.24×10^{-3}	51.9	85.3	−145	−29
[Cu (*cis*-Me_6[18] diene)]	25	—	—	—	—	—	—
[Cu tetra (cyanoethyl) cyclam]$^{2+}$	2.24×10^{-2}	1.4×10^{-3}	—	88.3	—	−13.6	—
[Cu[16] ane $M_4$8]	1.13	0.027	0.48	—	—	—	—
[Cu[17] ane $N_4$9]	0.60	0.122	0.53	—	—	—	—
[Cu (tetra)]$^{2+}$ (red)	5.9×10^{-8}	—	—	—	—	—	—
[Cu (tetra)]$^{2+}$ (unstable red)	7.0×10^{-7}	—	—	—	—	—	—
[Cu (tetra)]$^{2+}$ (blue)	6.2×10^{-4}	—	—	—	—	—	—
[Cu (2, 3, 2-tetra)]$^{2+}$	6.7×10^{-1}	—	—	—	—	—	—

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 *p*H 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 $K = 1.7M^{-1}$ 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 = 0.1M($NaClO_4$) and *p*H = 4.60

10^2 [HOAc] (M)	$10^3\ k_{obs}$ (S^{-1})
0.5	1.40
1.0	2.59
2.0	4.50
3.0	6.51
4.0	9.19

A ratio of 1 : 1 of sodium acetate-acetic acid was used.

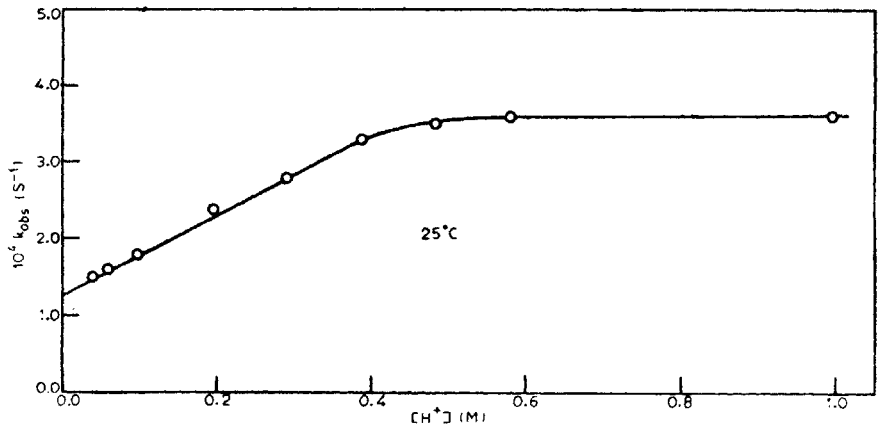


FIG 2 Dissociation of [Ni (*trans*-Me_6 [18] diene N_4)]$^{2+}$ in HNO_3.

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.

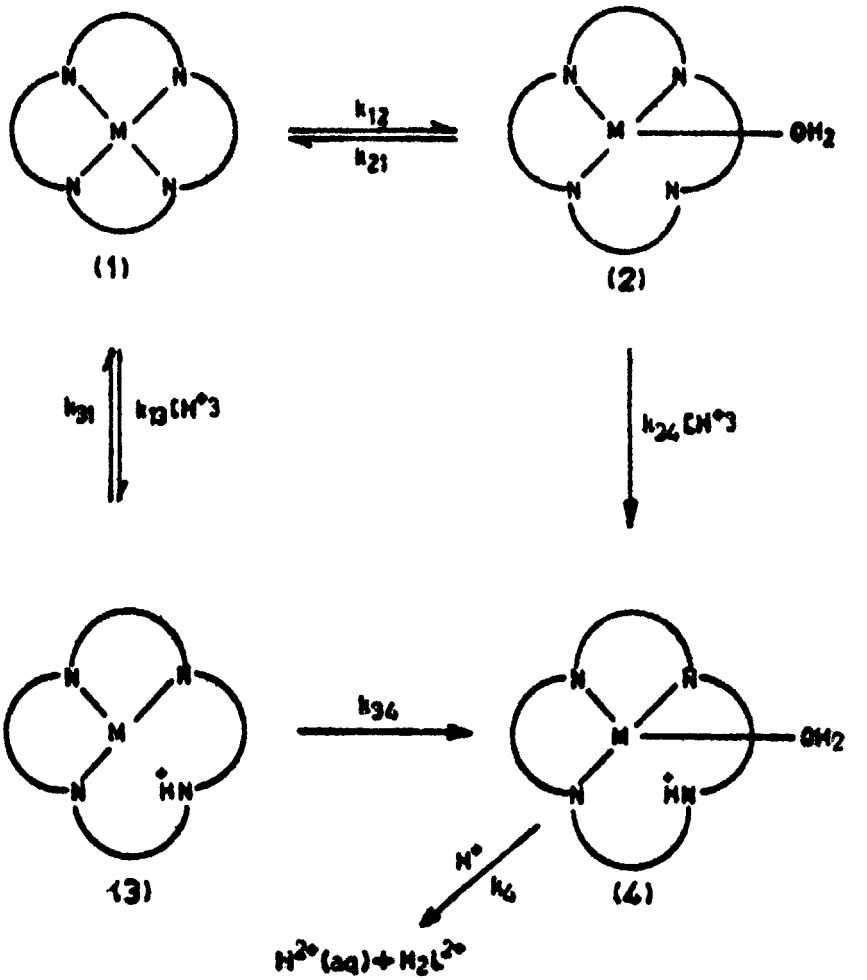
The dissociation of the copper(II) complexes of two new 16- and 17-membered tetraaza macrocycles(XVIII, XIX) capable of generating 8- and 9-membered chelate rings has also been studied.[23] The larger sized rings involve a stabilised strain, by analogy with cycloalkanes, but are stabilised to a considerable extent by the macrocyclic effect. The dissociation of these complexes show similar rate profiles to the ones observed for the Me_6[18] diene complexes. These two complexes show a considerably higher k_H 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[24] 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 NiN_4 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

Complex	k_H
[Ni [15] ane N_5]$^{2+}$	0.63 M^{-2} S^{-1}
[Cu [15] ane N_5]$^{2+}$	0.049 M^{-2} S^{-2}
[Cu [16] ane H_5]$^{2+}$	4.85 M^{-2} S^{-1}
[Cu [17] ane N_5]$^{2+}$	1.18 × 10^3 M^{-2} S^{-1}
[Ni [18] ane N_6]$^{2+}$	2.58 × 10^2 M^{-2} S^{-1}



SCHEME 6

side of the NiN_4 plane. The six-membered ring lies on the other side of the Ni N_4 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.[25] The four cyanoethyl arms lie on the same side of the N_4 plane. In the complex, copper 'sits atop' the N_4 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.[26] This sequence holds the four nitrogen donor in a 'pre-oriented' geometry favourable for coordination.

The acid catalysed dissociation of $[Ni([8]\ ane\ N_2)]^{2+}$ (an eight-membered diazamacrocycle, XXII) is very slow[27] and was followed at 60 °C ($k_0 = 2 \times 10^{-5}\ S^{-1}$ and $k_H = 2.0 \times 10^{-5} M^{-1} S^{-1}$ at 60 °C). The rate profile is shown in Fig. 3. The dissociation should follow the pathway

$$NiL_3^{2+} + H^+ \overset{K}{\rightleftharpoons} NiL_2H^{3+} \qquad ...(7)$$

$$NiL_2H^{3+} + H_2O \overset{k}{\rightarrow} Ni^{2+}(aq) \qquad ...(8)$$

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 $k_H = kK$. In the

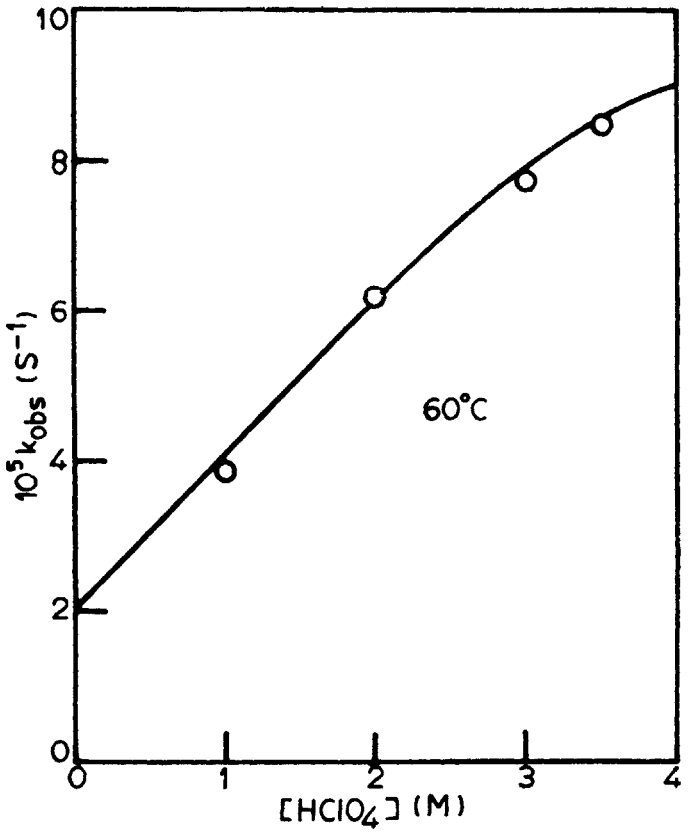
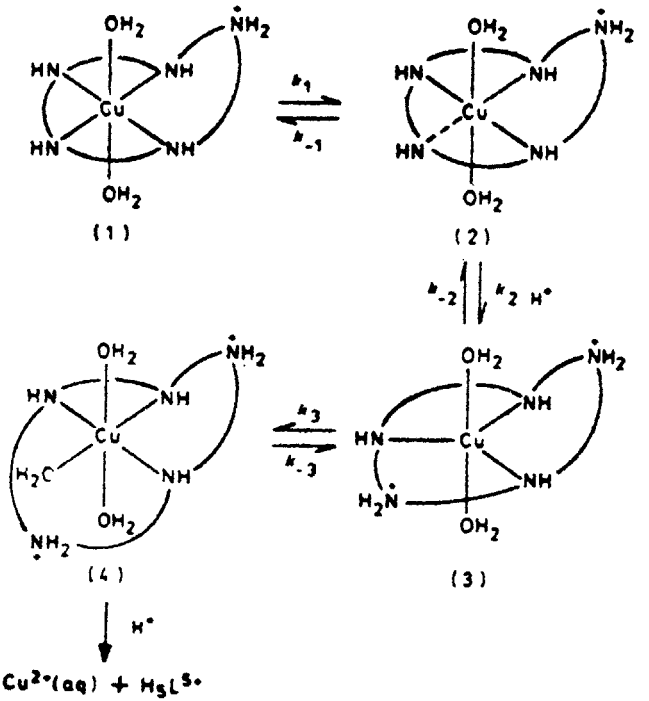


FIG 3 Dissociation of $[Ni\ [18]\ ane\ N_3)_2]^{2+}$ in $HClO_4$.

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 C_3 and C_7 protons shield the axial sites which prevent an octahedral geometry and likewise protects protonation of the nitrogens, resulting in low dissociation rates.



SCHEME 7

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 :–

$$Cu L^{2+} + H^+ \overset{k_1}{\rightleftharpoons} Cu(HL)^{3+} \quad \ldots(9)$$

$$Cu(HL)^{3+} + H^+ \overset{k_2}{\rightleftharpoons} Cu(H_2L)^{4+} \quad \ldots(10)$$

$$Cu(H_2L)^{4+} \overset{k}{\rightarrow} Cu(aq)^{2+} + H_2L^{2+} \quad \ldots(11)$$

The rate low for this behaviour can be written as :

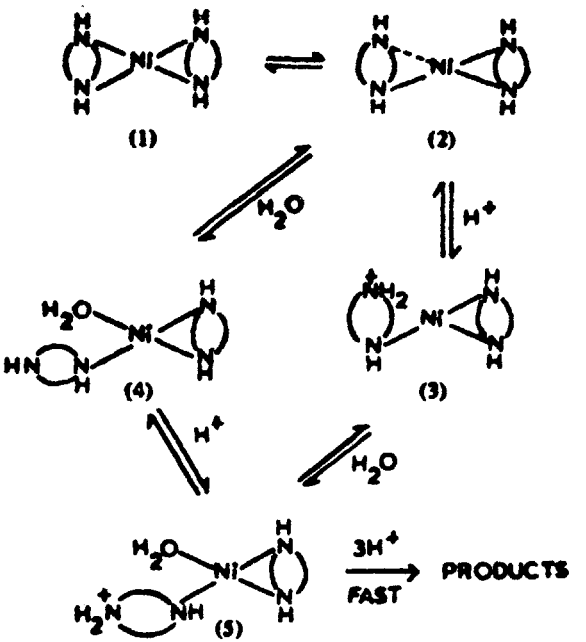
$$\text{Rate} = \frac{kK_1K_2[CuL^{2+}]\,[H^+]^2}{1 + K_1[H^+] + K_1K_2[H^+]^2} \quad \ldots(12)$$

Under the conditions of the studies done, $K_1[H^+] + K_1K_2[H^+]^{2+} \ll 1$, 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,[28] 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.

$$Ni(H_2L)^{4+} + H^+ \overset{k_3}{\rightleftharpoons} Ni(H_3L)^{5+} \qquad \ldots(13)$$

This gives the value of $k_H = kK_1K_2K_3 = 2.58 \times 10^2$ dm^9 mol^{-3} 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



SCHEME 8

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.*[30] 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.

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