Inorganica Chimica Acta, 62 (1982) 89–97

The Kinetics of the Acid-Catalysed Dissociation of the Macrocyclic Complexes $[\mathrm{Ni}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$, $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ and $[\mathrm{Cu}(\textit{cis}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ and the Kinetics of the Base-Catalysed Dissociation of the Copper(II) Complexes

ROBERT W. HAY and RAMESH BEMBI

Chemistry Department, University of Stirling, Stirling FK9 4LA, U.K.

Received March 4, 1982

The acid-catalysed dissociation of the copper(II) and nickel(II) complexes of trans-*Me_6[18]dieneN$_4$ (2,4,4,11,13,13-hexamethyltetra-azacyclo-octadeca-1,10-diene) and the copper(II) complex of* cis-*Me_6-[18]dieneN$_4$ (2,4,4,11,11,13-hexamethyltetra-aza-cyclo-octadeca-1,13-diene) have been studied kinetically. For the complexes of* trans-*Me_6[18]dieneN$_4$, the observed rate constant at constant hydrogen ion concentration (k_{obs}) is given by the expression (i), where k_o represents the solvolytic dissociation pathway*

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

The acid catalysed reactions of the trans-*diene complexes involve a rapid pre-equilibrium protonation step, followed by a slow loss of the metal ion from the protonated complex. Activation parameters for the k and k_o pathways have been determined.*

The acid-catalysed dissociation of the copper(II) complex of the cis-*diene, which is known to have pseudo-tetrahedral stereochemistry, is very much faster than that of the* trans-*diene which is essentially planar. This reaction shows no solvolytic pathway, but both general and specific acid catalysed pathways. Thus in the presence of acetic acid (HA) the rate expression at constant pH is given by*

$$k_{obs} = 25\ \mathrm{M}^{-1}\ s^{-1}[H^+] + 2.14 \times 10^{-1}\ \mathrm{M}^{-1}\ s^{-1}\ [HA]$$

at 25 °C and I = 0.1 M.

The kinetics of dissociation of the two copper(II) complexes in basic solution have also been studied in detail. For 1×10^{-2} to 5×10^{-2} M *hydroxide, the reactions show a second order dependence on the hydroxide ion concentration and the dissociation can be represented by the equations*

$$CuL^{2+} + OH^- \overset{K}{\rightleftharpoons} CuLOH^+$$

$$CuLOH^+ + OH^- \xrightarrow{k} Cu(OH)_2 + L$$

At high base concentrations the reactions show a first order dependence on [OH^-] (as all CuL^{2+} is converted to $CuLOH^+$). Values of K and k have been determined. The equilibrium $CuL^{2+} + N_3^- \rightleftharpoons [CuLN_3]^+$ has also been studied for the trans *diene, the equilibrium constant is 7.3* M^{-1} *compared with 0.27* M^{-1} *for the reaction with hydroxide ion at 25 °C.*

Introduction

Early workers with complexes of 14-membered macrocyclic tetra-aza ligands quickly recognised that these compounds were both unusually stable in the thermodynamic sense, and were inert towards ligand dissociation, even in very strong mineral acids.

The macrocyclic effect, in which the thermodynamic stability of metal complexes is enhanced by coordination to macrocyclic as opposed to analogous non-cyclic ligands of the same denticity was first reported in 1969 [1]. A great deal of interest has been shown in the thermodynamic origins of this additional stability [2–7]. The macrocyclic effect can also be considered in kinetic terms, as the formation constant for the equilibrium (1) is given by $K = k_f/k_r$

$$M^{2+}(solv) + MAC(solv) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} M(MAC)^{2+}(solv) \qquad (1)$$

The macrocyclic effect arises predominantly from the slower dissociation rate of the macrocyclic complex compared with its linear analogue [8]. Much of the previous kinetic work has been limited to the formation reaction and few studies have been made on the dissociation kinetics which are expected to be more influential than the formation kinetics in the determination of the stability of macrocyclic complexes.

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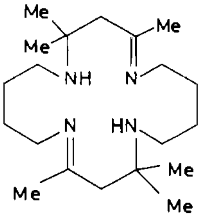
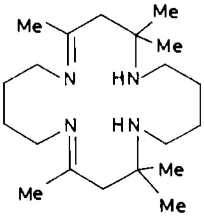
Little work on the dissociation kinetics of tetraaza macrocycles has been described [13, 14]. Cabbiness and Margerum [13] have carried out a brief investigation of the dissociation rates of 14-membered macrocyclic copper(II) complexes in 6.1 *M* HCl at 25 °C. Some of these reactions are extremely slow, with values of k_{obs} in the range 1.2 $\times 10^{-3}$ s^{-1} to 3.6 $\times 10^{-7}$ s^{-1} ($t_{1/2}$ 9.6 min to 22 days). As a result, attention has focussed on more labile systems including N_2O_2, N_2S_2, S_4 and N_3 donor macrocycles [9–12, 15–20]. Very recently [21], the dissociation and isomerisation kinetics of $[Cu(tet\ a)(blue)]^{2+}$ (tet *a* = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-aza-cyclotetradecane) in 1–5 *M* HNO_3 has been investigated. The cleavage of the second copper-nitrogen bond is considered to be rate determining.

Martell and coworkers [24] have recently reported the preparation of the copper(II) and nickel(II) complexes of *trans*-$Me_6[18]dieneN_4$ (I) and the copper(II) complex of *cis*-$Me_6[18]dieneN_4$ (II). These 18-membered macrocyclic complexes dissociate readily in weakly acidic and in basic solutions, and it is possible to study these reactions kinetically over a range of acid and base concentrations. The results of such experiments are described in the present paper.



(I)



(II)

Experimental

The macrocyclic ligand 2,4,4,11,13,13-hexamethyl 1,5,10,14-tetraazacyclooctadeca-1,10-diene dihydroperchlorate dihydrate, $H_2(trans\text{-}[18]dieneN_4)(ClO_4)_2 \cdot 2H_2O$ was prepared as follows*. Perchloric acid (72%, 83 cm^3, 1 mol) was added dropwise with continuous stirring to a cooled (ice-salt bath) solution of 1,4-diaminobutane (88 g, 1 mol) in methanol (800 cm^3). After completion of the addition, acetone (117 cm^3, 2 mol) diluted with an equal volume of methanol was added dropwise over a period of 2 hr, the reaction temperature being maintained between 0–5 °C (ice-salt bath). The resulting mixture was stirred for a further 4 hr during which time the temperature was slowly allowed to rise to ambient. The solution was stored overnight in a refrigerator and the colourless crystalline product was filtered off, washed with methanol then ether and dried *in vacuo* (yield 233 g, 42%). The dihydroperchlorate salt appeared quite stable and it has been stored for a period of several months in a dessicator with no apparent decomposition (other than a slight development of colour) (*Caution! great care should be exercised with amine hydroperchlorate salts since they can detonate with great violence on heating*). *Anal.* Calcd. for $C_{20}H_{40}N_4 \cdot 2HClO_4 \cdot 2H_2O$: C, 41.89; H, 8.08; N, 9.76. Found: C, 42.19; H, 7.86; N, 9.75%. The ligand has a broad νOH at 3500 cm^{-1}, νC=N at 1665 cm^{-1} (sp) and ClO_4 bands at 1100 cm^{-1} (br) and 625 cm^{-1}.

The complexes $[Cu(trans\text{-}Me_6[18]dieneN_4)](ClO_4)_2$, $[Ni(trans\text{-}Me_6[18]dieneN_4)](ClO_4)_2$, and $[Cu(cis\text{-}Me_6[18]dieneN_4)](ClO_4)_2$ were prepared essentially as previously described [22]. Satisfactory analytical data was obtained for all three complexes, Table I.

TABLE I. Analytical Data for the Complexes.

Complex^a	C (%)	H (%)	N (%)
$[CuL_1](ClO_4)_2$	40.39(40.10)	6.62(6.73)	8.92(9.35)
$[NiL_1](ClO_4)_2$	40.05(40.4)	6.79(6.79)	9.05(9.42)
$[CuL_2](ClO_4)_2$	40.40(40.10)	6.66(6.73)	8.96(9.35)

^{a}L_1 = *trans*-$Me_6[18]dieneN_4$; L_2 = *cis*-$Me_6[18]dieneN_4$. The calculated figures are given in parenthesis. $[CuL_1](ClO_4)_2$ = $C_{20}H_{40}N_4O_8Cl_2Cu$; $[NiL_1](ClO_4)_2$ = $C_{20}H_{40}N_4O_8Cl_2Ni$; $[CuL_2](ClO_4)_2$ = $C_{20}H_{40}N_4Cl_2O_8Cu$.

Kinetic Measurements

The acid catalysed dissociation of the nickel(II) and copper(II) complexes of *trans*-$Me_6[18]dieneN_4$ were studied using nitric acid and perchloric acid solutions respectively adjusted to I = 1.0 *M* with $NaNO_3$ or $NaClO_4$. The dissociation of $[Cu(cis\text{-}Me_6[18]dieneN_4)]^{2+}$ is quite rapid in acid solution and in this case the reaction was studied using 0.01 *M* acetate buffers adjusted to I = 0.1 *M* ($NaClO_4$).

All the reactions were monitored spectrophotometrically using a Gilford 2400S spectrophotometer.

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*There is some evidence that this perchlorate salt is in fact the monohydroperchlorate of the 9-membered diaza macrocycle, rather than the dihydroperchlorate salt of the 18-membered tetraaza macrocycle. Ring opening appears to take place in the presence of metal salts to give complexes of the 18-membered ring macrocycle. The nine-membered ring structure would account for the very slow formation of the nickel(II) complex which is observed.

TABLE II. The Acid-Catalysed Dissociation of $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ and $[\mathrm{Ni}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ at 25 °C and I = 0.97 *M*.

(a) $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ ($HClO_4$ solutions)

10^3 [H$^+$] (*M*)	10^3 k_{obs} (s^{-1})	10^3 [H$^+$] (*M*)	10^3 k_{obs} (s^{-1})
9.6	1.20	96.6	3.10
19.3	1.57	193.3	3.88
29.0	1.84	290.0	4.38
38.6	2.25	386.6	4.41
48.3	2.60	483.3	4.58
58.0	2.74	966.6	5.00

(b) $[\mathrm{Ni}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ (HNO_3 solutions)

10^3 [H$^+$]	10^3 k_{obs}	10^3 [H$^+$]	10^3 k_{obs}
38.7	0.15	386.6	0.33
58.0	0.16	483.3	0.35
96.6	0.18	580.0	0.36
193.3	0.24	996.6	0.36
290.0	0.28		

The dissociation of $[\mathrm{Ni}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ was monitored at 460 nm, $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ at 360 nm and $[\mathrm{Cu}(\textit{cis}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ at 290 nm. Plots of log (A_t – A_∞) *versus* time were linear for several half lifes, and the observed rate constants at constant pH (k_{obs}) were computed from this data.

The base catalysed dissociations of the copper(II) complexes were monitored spectrophotometrically at 300 nm (*cis*-diene) and 380 nm (*trans*-diene) using sodium hydroxide solutions in the range 1×10^{-2}–5×10^{-2} *M* adjusted to I = 0.1 *M* ($NaClO_4$).

At high base concentrations it was necessary to use stopped flow techniques. The reactions were monitored at 380 nm using sodium hydroxide solutions in the range 0.2–0.4 *M* adjusted to I = 0.5 *M* ($NaClO_4$). The reactions were studied using a Durrem-Gibson stopped flow system interfaced with a desk top computer. At least six kinetic runs were carried out at each sodium hydroxide concentration. Any reaction with a correlation coefficient (for first order dependence in the complex concentration) less than 0.999 was rejected. It is difficult to extend the measurements to higher sodium hydroxide concentrations due to the viscosity and density differences of the two solutions.

Results and Discussion

The purple $[\mathrm{Cu}(\textit{cis}\text{-}\mathrm{Me_6[18]dieneN_4})](\mathrm{ClO_4})_2$ and the red $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})](\mathrm{ClO_4})_2$ are both paramagnetic with magnetic moments (1.87 and 2.10 B.M. respectively at 300 K) [22] within the normal range for copper(II) complexes lacking metal–metal interactions. The large differences in the visible (d–d) metal ion spectra of the two complexes can be attributed to a change in coordination geometry from a distorted tetrahedron for the *cis*-ligand (λ_{max} = 582 nm) to a nearly planar arrangement for the *trans*-ligand (λ_{max} 483 nm). X-ray work [23] has established that for the *cis*-ligand the nitrogens coordinate copper(II) in a pseudotetrahedral manner with a dihedral angle of 36.6° between the N(1)CuN(2) and N(3)CuN(4) planes, while the *trans*-ligand leads to a small dihedral angle of 11.5°. Such marked differences in the coordination geometry are expected to be reflected in the relative dissociation rates of the two complexes. The dissociation of $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ was monitored at 360 nm over the nitric acid concentration range 9.6×10^{-3}–9.67×10^{-1} mol dm^{-3}. The observed first order rate constants k_{obs} obtained at 25 °C are listed in Table II. A plot of k_{obs} *versus* the hydrogen ion concentration is shown in Fig. 1. There is initially a linear dependence of k_{obs} on [H$^+$], but at higher hydrogen ion concentrations the reaction becomes independent of [H$^+$]. At low acidities a plot of k_{obs} *versus* $[H]^+$ is linear with a pronounced intercept which can be interpreted as a solvolytic pathway leading to metal dissociation. The acid catalysed pathway is consistent with the kinetic scheme,

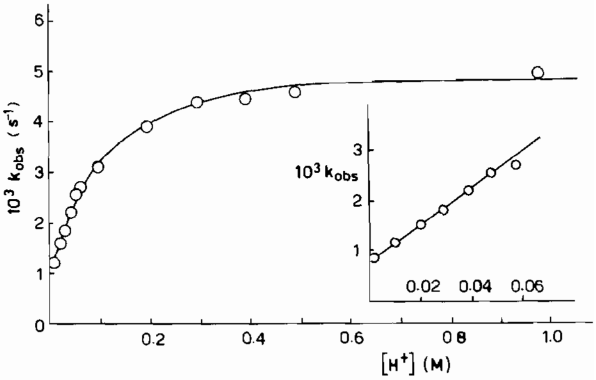


Fig. 1. The dissociation of $[\mathrm{Cu}(\textit{trans}\text{-}\mathrm{Me_6[18]dieneN_4})]^{2+}$ in perchloric acid solutions at 25 °C.

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

$$\mathrm{CuLH^{3+} \xrightarrow{k} Cu^{2+} + HL^+} \tag{3}$$

in which there is a rapid preequilibrium protonation of the copper(II) complex followed by a slow rate-determining dissociation step (eqn. 3).

The overall rate expression thus takes the form (eqn. 4),

TABLE III. Temperature Dependence of the Acid-Catalysed Dissociation of $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ and $[Ni(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ at I = 0.97 *M* ([H$^+$] = 0.97 *M*).

(a) $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$

Temp. (°C)	10^3 k_{obs} (s^{-1})	10^3 k_o (s^{-1})	10^3 k (s^{-1})
20	2.28	0.41	1.87
22.5	3.20	0.58	2.62
25	4.80	0.80	4.00
28	5.96	1.21	4.75
34	10.56	2.61	7.95

For k; $\Delta H^‡$ = 77.1 kJ mol^{-1}, $\Delta S^‡_{298}$ = −32 JK^{-1} mol^{-1}. k_o; $\Delta H^‡$ = 98.7 kJ mol^{-1}, $\Delta S^‡_{298}$ = +18 JK^{-1} mol^{-1}.

(b) $[Ni(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$

Temp. (°C)	10^3 k_{obs} (s^{-1})	10^3 k_o (s^{-1})	10^3 k (s^{-1})
25	0.36	0.13	0.24
29	0.58	0.17	0.41
32	0.82	0.21	0.61
36	1.10	0.27	0.83
42	2.00	0.41	1.59

For k; $\Delta H^‡$ = 85.3 kJ mol^{-1}, $\Delta S^‡$ = −29 JK^{-1} mol^{-1}. k_o; $\Delta H^‡$ = 51.9 kJ mol^{-1}, $\Delta S^‡$ = −145 JK^{-1} mol^{-1}.

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

where k_o represents the solvolytic reaction. At 25 °C, k_o is 8 × 10^{-4} s^{-1} and k is *ca.* 4.7 × 10^{-3} s^{-1}. Using eqn. (4) it can be readily shown that,

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

so that a plot of $1/(k_{obs} - k_o)$ *versus* $1/[H^+]$ should be linear of slope $1/kK$ and intercept $1/k$. Such a plot is indeed linear giving k = 4.8 × 10^{-3} s^{-1} and K = 10.2 M^{-1} at 25 °C. For comparative purposes it is useful to employ a k_H rate constant, defined as the slope of the plot of k_{obs} *versus* [H$^+$] at low acidities. In this case k_H = 3.6 × 10^{-2} M^{-1} s^{-1} at 25 °C. The temperature dependence of the reaction was also studied over the temperature range 20–34 °C. At 25 °C, k_o = 8 × 10^{-3} s^{-1} and at 32 °C, k_o = 20 × 10^{-3} s^{-1} giving Ea = 98.7 kJ mol^{-1}. This value of the activation energy was used to calculate values of k_o at the intermediate temperatures. Values of k_{obs} were obtained at [H$^+$] = 0.97 *M* where k_{obs} = k_o + k (*i.e.* $K[H^+] \gg 1$). The results obtained are summarised in Table III. For the acid catalysed dissociation of $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$, $\Delta H^‡$ = 77.1 kJ mol^{-1} and $\Delta S^‡_{298}$ = −32 JK^{-1} mol^{-1}.

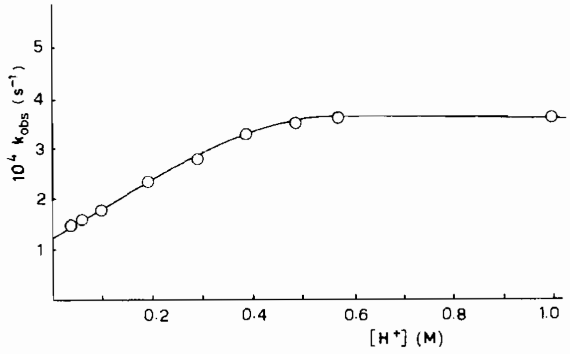


Fig. 2. The dissociation of $[Ni(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ in nitric acid solutions at 25 °C.

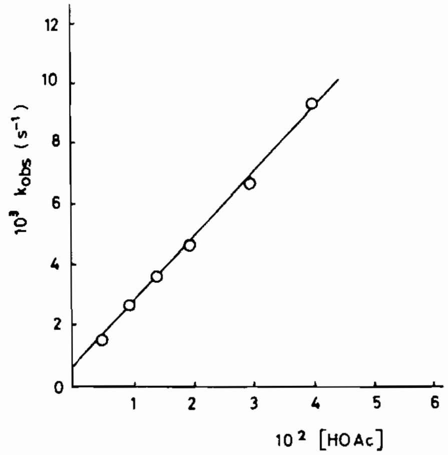


Fig. 3. General acid catalysis by acetic acid in the dissociation of $[Cu(\textit{cis}\text{-}Me_6[18]dieneN_4)]$ at pH 4.60.

Analogous experiments were carried out using the nickel(II) complex. The values of k_{obs} as a function of the hydrogen ion concentration are listed in Table II. A plot of k_{obs} *versus* [H$^+$] shows similar behaviour to that observed with the copper(II) complex. Fig. 2. At low acidities k_H = 6 × 10^{-4} M^{-1} s^{-1} and k_o = 1.25 × 10^{-4} s^{-1} at 25 °C. The value of k is clearly *ca.* 3.6 × 10^{-4} s^{-1}. The use of a double reciprocal plot (eqn. (5)) gives approximate values of k = 5 × 10^{-4} s^{-1} and K = 1.7 M^{-1}. Activation parameters were calculated from the temperature dependence of k and k_o, Table III. For k, $\Delta H^‡$ = 85.3 kJ mol^{-1}, $\Delta S^‡_{298}$ = −29 JK^{-1} mol^{-1}, and for k_o, $\Delta H^‡$ = 51.9 kJ mol^{-1} and $\Delta S^‡_{298}$ = −145 JK^{-1} mol^{-1}.

The acid catalysed dissociation of $[Cu(\textit{cis}\text{-}Me_6[18]dieneN_4)]^{2+}$ is very rapid and in this case the reaction was studied using acetate buffers (0.01 *M* in acetate). Under these conditions, values of k_{obs}/

TABLE IV. The Acid-Catalysed Dissociation of [Cu(*cis*-Me_6[18]dieneN_4)]$^{2+}$ in Acetate Buffers at 25 °C and I = 0.1 *M* ($NaClO_4$).

pH	10^5 [H^+]^a (*M*)	10^3 k_{obs} (s^{-1})	10^{-2} k_H (M^{-1} s^{-1})
4.96	1.42	1.40	0.99
4.76	2.25	2.25	1.00
4.57	3.48	3.35	0.96
4.38	5.39	5.25	0.97
4.24	7.43	7.30	0.98
4.05	11.52	10.95	0.95

[a]Hydrogen ion concentration determined from the pH using an activity coefficient of 0.774 at I = 0.1 *M*. The acetate concentration was 0.01 *M* in each run.

TABLE V. Acetic Acid Catalysis of the Dissociation of [Cu(*cis*-Me_6[18]dieneN_4)]$^{2+}$ at 25 °C, I = 0.1 *M* ($NaClO_4$) and pH 4.60.

10^2 [HOAc] (*M*)^a	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]Reactions carried out using a 1:1 ratio of sodium acetate and acetic acid. The acetic acid concentrations employed are listed.

[H^+] are quite constant at 1.0 × 10^2 M^{-1} s^{-1} at 25 °C and I = 0.1 *M*, Table IV. Separate experiments established that the reaction is also subject to general acid catalysis in addition to specific acid catalysis. As a result k_{obs} = k_H[H^+] + k_{HA}[HA] where [HA] is the concentration of acetic acid. Since K = [H^+][A^-]/[HA] it can be readily shown that

$$k_{obs} = [H^+]\left(k_H + \frac{k_{HA}[A^-]}{K}\right)$$

and

$$k_{obs}/[H^+] = \left(k_H + \frac{k_{HA}[A^-]}{K}\right) \quad (6)$$

Table V lists values of k_{obs} at different acetic acid concentrations at pH 4.60. Clearly there is substantial catalysis by acetic acid. A plot of k_{obs} *versus* [HA] is linear with a positive intercept (*i.e.* k_{obs} = k_H[H^+] + k_{HA}[HA]). The slope of the plot gives the rate constant k_{HA} for general acid catalysis by HA and the intercept k_H[H^+] at pH 4.60. The value of k_{HA} = 2.14 × 10^{-1} M^{-1} s^{-1} with an intercept of 0.8 × 10^{-3} s^{-1}. Since [H^+] = 3.24 × 10^{-5} *M* at pH 4.60 and I = 0.1 *M* the rate constant k_H = 25 M^{-1} s^{-1}. This latter value can be checked using eqn. (6), as k_{HA} = 2.14 × 10^{-1} M^{-1} s^{-1}, [A^-] = 1 × 10^{-2} *M*, K = 2.90 × 10^{-5} (the concentration ionisation constant of acetic acid = $K_T/(0.774)^2$ where K_T is the thermodynamic constant, pK_T = 4.76, and 0.774 is the molar activity coefficient) and k_{obs}/[H^+] = 1.0 × 10^2 M^{-1} s^{-1}. Substituting these values in eqn. (6) gives k_H = 26 M^{-1} s^{-1} at 25 °C and I = 0.1 *M*. Thus dissociation of [Cu(*cis*-Me_6[18]dieneN_4)]$^{2+}$ in acetate buffers at 25 °C can be represented by the eqn.

$$k_{obs} = 25\ M^{-1}\ s^{-1}\ [H^+] + 2.14 \times 10^{-1}\ M^{-1}\ s^{-1}\ [HA]$$

The observation of general acid catalysis with the [Cu(*cis*-Me_6[18]dieneN_4)]$^{2+}$ complex establishes that the proton transfer step is rate determining, rather than dissociation of the protonated complex.

Solvent deuterium isotope effects were studied using Cu(*trans*-Me_6[18]dieneN_4)]$^{2+}$. Reactions were carried out in DCl/D_2O and HCl/H_2O using low acid concentrations. Values of k_{obs} are listed in Table VI. A plot of k_{obs} *versus* [H^+] or [D^+] is linear with a positive intercept due to the solvolytic reaction, and values of k_H and k_D were determined from the slope of these plots. The ratio k_H/k_D is 2.0, a result which can only be interpretated in terms of a slow proton transfer at these acidities. In addition, specific anion effects are observable in these reactions as the dissociation is faster in HCl than in HNO_3. The solvent isotope effect studies provide some evidence for slow proton transfer at low acidities indicating that under these conditions

TABLE VI. Solvent Deuterium Isotope Effects in the Dissociation of [Cu(*trans*-Me_6[18]dieneN_4)]$^{2+}$ at 25 °C.

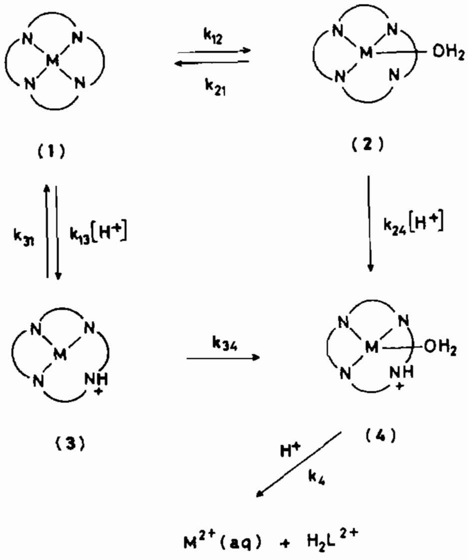
DCl solutions		HCl solutions	
10^3 DCl (*M*)	10^3 k_{obs} (s^{-1})	10^3 HCl (*M*)	10^3 k_{obs} (s^{-1})
19.33	2.14	19.33	2.98
38.66	2.58	38.66	3.73
58.00	3.00	58.00	4.42
k_o = 1.92 × 10^{-3} s^{-1}		k_o = 2.25 × 10^{-3} s^{-1}	
k_D = 1.86 × 10^{-2} M^{-1} s^{-1}		k_H = 3.74 × 10^{-2} M^{-1} s^{-1}	

k_H/k_D = 2.0

protonation of CuL^{2+} is at least partly rate-determining. It is possible that there is a change in rate-determining step from slow proton transfer at low acidities to rate-determining dissociation of $CuLH^{3+}$ at high acidities. Equation (4) of course assumes that dissociation of $CuLH^{3+}$ is rate determining at all acidities.

The Mechanism of Acid Catalysed Dissociation

A general mechanism for the acid catalysed dissociation of polyamine complexes has been proposed [24] and can be adapted for macrocyclic complexes, Scheme 1.



Scheme 1. The acid catalysed dissociation of macrocyclic complexes.

The acid-dependent pathway involves the steps (1) → (3) → (4) → products. The protonation of the bound nitrogen in (1) is difficult, and the difficulty can be reflected both in the slow rates for the protonation reaction k_{13} compared with an unbound nitrogen and the small values of the equilibrium constant K_{MHL}. Thus K_{MHL} is 10.2 M^{-1} for the copper(II) complex of the *trans*[18]diene and 1.7 M^{-1} for the nickel complex at 25 °C. These values for the protonation constants are very similar to those recently reported by Graham and Weatherburn [10] for copper(II) complexes of triazamacrocycles where K_{CuHL} falls in the range 1.8–8.3 M^{-1} at 25 °C. At high acid concentrations the decomposition of the MHL^{3+} species becomes rate determining and the rate constants obtained from plots of $(k_{obs} - k_o)^{-1}$ against $[H^+]^{-1}$ correspond to k_{34}. This step is some five times faster than the corresponding step in the unprotonated complex (k_{12}). For the copper-*trans*-diene complex $k_{34} = 4.8 \times 10^{-3}$ s^{-1} while $k_{12} = k_o = 8 \times 10^{-4}$ s^{-1}. For the nickel-trans-diene complex, $k_{34} = 4 \times 10^{-4}$ s^{-1} and $k_{12} = 1.25 \times 10^{-4}$ s^{-1}.

TABLE VII. Values of k_H at 25 °C.

Complex	k_H (M^{-1} s^{-1})
$[Cu(tet\ a)]^{2+}$ (red)	5.9×10^{-8} [a]
$[Cu(tet\ a)]^{2+}$ (unstable red)	7.0×10^{-7} [a]
$[Cu(tet\ a)]^{2+}$ (blue)	6.2×10^{-4} [a,b]
$[Cu(trans\text{-}Me_6[14]diene)]^{2+}$	2×10^{-4} [a]
$Cu(2,3,2\text{-}tet)]^{2+}$	6.7×10^{-1} [a]
$[Cu(trans\text{-}Me_6[18]diene)]^{2+}$	3.6×10^{-2}
$[Cu(cis\text{-}Me_6[18]diene)]^{2+}$	25
$[Ni(trans\text{-}Me_6[18]diene)]^{2+}$	6×10^{-4}

[a] Calculated from data reported (Ref. 13) for reactions in 6.1 M HCl. Values of $k_H = k_{obs}/[H^+]$. [b] Ref. 21 quotes a $k_H = 2.6 \times 10^{-4}$ M^{-1} s^{-1} at 25 °C and I = 5.0 M. The paper should be consulted for details of the derivation of the k_H term.

The acid catalysed dissociation of the copper complex of the *cis*-diene is particularly interesting since this reaction exhibits both general and specific acid catalysis. The observation of general acid catalysis indicates that rate determining proton transfer occurs, so that in this case the step, k_{13} is rate determining. The activation parameters determined for the copper(II) and nickel(II) complexes of the *trans*-diene are $\Delta H^{\ddagger} = 77.1$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = -32$ JK^{-1} mol^{-1} and $\Delta H^{\ddagger} = 85.3$ kJ mol^{-1}, $\Delta S_{298} = 129$ JK^{-1} mol^{-1} respectively for k_{34}, while for the k_{12} pathways the values are $\Delta H^{\ddagger} = 98.7$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = +18$ JK^{-1} mol^{-1} (copper(II)) and $\Delta H^{\ddagger} = 51.9$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = -145$ JK^{-1} mol^{-1} (nickel (II)). The activation parameters indicate similar transition states for the acid catalysed reactions, but marked differences for the solvolytic reactions. This result may reflect the relative abilities of the two complexes to undergo axial additions with solvent water which may play an important role in the solvolytic reactions.

Table VII lists the values of $k_H = k_{obs}/[H^+]$ for a variety of 14- and 18-membered ring macrocycles and the linear tetraamine 1,9-diamino-3,7-diazanonane (2,3,2-tet). Dissociation of the 14-membered ring macrocycles is very slow which is indicative of the good fit of the metal ion to the 'hole size' of the ligand. The ideal metal–nitrogen bond length for the saturated 14-membered N_4 ring is 2.07 Å [25] and this value corresponds closely to the 'normal' Cu–N bond distance of *ca.* 2.0 Å. The 18-membered diene complexes dissociate quite rapidly, in fact dissociation of $[Cu(cis\text{-}Me_6[18]dieneN_4)]^{2+}$

TABLE VIII. Base-Catalysed Dissociation of $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ and $[Cu(\textit{cis}\text{-}Me_6[18]dieneN_4)]^{2+}$ at I = 0.1 *M* ($NaClO_4$) and 25 °C.

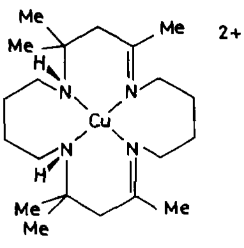
(a) $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$

10^3 $[OH^-]$ (*M*)	10^3 k_{obs} (s^{-1})	$k_{obs}/[OH^-]^2$ (M^{-2} s^{-1})
9.66	0.14	1.5
19.33	0.73	1.9
29.00	1.75	2.0
38.66	2.63	1.8
48.33	4.27	1.8

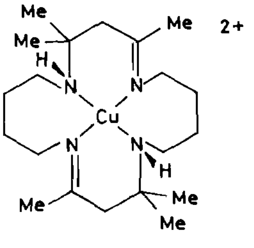
(b) $[Cu(\textit{cis}\text{-}Me_6[18]dieneN_4)]^{2+}$

10^3 $[OH^-]$ (*M*)	10^3 k_{obs} (s^{-1})	$k_{obs}/[OH^-]^2$ (M^{-2} s^{-1})
9.66	0.54	5.8
19.33	2.13	5.7
29.00	5.85	6.9
38.66	7.60	5.1
48.33	14.48	6.2

is faster than that of $[Cu(2,3,2\text{-tet})]^{2+}$. X-ray crystallography [23] has established that $[Cu(\textit{cis}\text{-}Me_6[18]\text{-}dieneN_4)]^{2+}$ has the N-*meso* configuration (III). The *cis* macrocycle adopts a rather contorted conformation in order to minimise angular, torsional and



(III)



(IV)

bond length strain within the molecule and the coordination sphere. The distorted tetrahedral geometry about copper(II) is the most striking feature, but the large variation in the 'bite angles' of the chelate rings is also of significance. The copper–nitrogen bond distance is 1.99–2.02 Å.

The $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ complex has the N-*racemic* stereochemistry (IV) and suffers from fewer steric problems than the *cis*-diene complex. The tetrahedral distortion in this complex is quite small and the six-membered chelate rings adopt half-boat conformations. The strain energies in these two complexes is clearly reflected in their dissociation rates where $[Cu(\textit{cis}\text{-}Me_6[18]dieneN_4)]^{2+}$ dissociates some 700 times more rapidly in acidic solution than $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]$ at 25 °C.

Extrapolation of the available data [25] suggests that the ideal bond length for a saturated 18-membered tetra-aza macrocycle would be *ca.* 2.68 Å which is far removed from the 2.0 Å for normal Cu–N bonds. Rings smaller than those of best fit exert abnormally high Dq values while oversized rings result in markedly low ligand field strengths.

Base-Catalysed Dissociation

Dissociation of the copper(II) complexes also occurs in basic solution. Table VIII lists values of k_{obs} obtained in the range 1–5 × 10^{-2} *M* sodium hydroxide. In this case the reaction shows a second order dependence on the hydroxide ion concentration with values of $k_{obs}/[OH]^2$ being quite constant, Table VIII. For the copper(II) complex of the *trans*-diene, k_{OH} = 1.8 M^{-2} s^{-1} while for the *cis*-diene, $k_{OH} = 5.9\ M^{-2}\ s^{-1}$.

An appropriate reaction scheme would be that shown by eqns. (7) and (8).

$$CuL^{2+} + OH^- \overset{K}{\rightleftharpoons} CuLOH^+ \tag{7}$$

$$CuLOH^+ + OH^- \xrightarrow{k} Cu(OH)_2 + L \tag{8}$$

For such a scheme it can be readily shown that,

$$k_{obs} = \frac{kK[OH^-]^2}{(1 + K[OH^-])} \tag{9}$$

Under the conditions of the present experiments $k[OH] \ll 1$ and $k_{obs} = kK[OH^-]^2$. The k_{OH} rate constants in the final column of Table VIII thus give the product kK. At high base concentrations where $k[OH] \gg 1$ eqn. (9) reduces to $k_{obs} = k[OH]$.

The formation of $CuLOH^{2+}$ complexes with macrocyclic ligands has been studied in a number of cases. For example, Liang and Chung [26] have shown that the conversion of $[Cu(\text{tet }a)(\text{blue})]^{2+}$ to $[Cu(\text{tet }a)(\text{red})]$ (tet *a* = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) is consistent with the reactions

$$[Cu(\text{tet }a)(\text{blue})]^{2+} + OH^- \underset{}{\overset{K_{OH}}{\rightleftharpoons}} [Cu(\text{tet }a)(OH)(\text{blue})]^+$$

$$[Cu(\text{tet }a)(OH)(\text{blue})]^+ \xrightarrow{k_{OH}} [Cu(\text{tet }a)(\text{red})]^{2+} + OH^-$$

In addition they have determined formation constants for adduct formation of $[Cu(\text{tet }a)(\text{blue})]^{2+}$

TABLE IX. Dissociation of $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)^{2+}$ at High Base Concentrations at 25 °C.

NaOH (M)	k_{obs} (s^{-1})	$k_{obs}/[OH^-]$ (M^{-1} s^{-1})	$k_{obs}/[OH^-]^2$ (M^{-2} s^{-1})
0.2	1.21	6.05	30.25
0.3	2.05	6.83	22.78
0.4	2.91	7.28	18.19

[a]Reactions monitored at 380 nm. Ionic strength 0.5 M ($NaClO_4$).

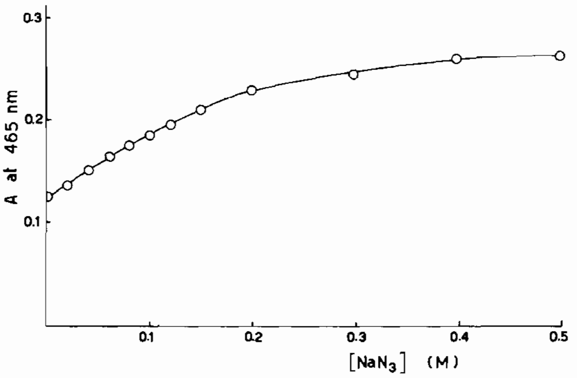


Fig. 4. Interaction of N_3^- with $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ studied at 465 nm. The total concentration of the complex is 1.26×10^{-3} M, temperature = 20 °C.

with a variety of monodentate ligands L. For L = OH^-, K = 50 M^{-1} and similar values were obtained for L = SCN^- and N_3^-.

Studies of the dissociation of $[Cu(\textit{trans}\text{-}Me_6[18]\text{-}dieneN_4]^{2+}$ at high base concentrations were carried out using sodium hydroxide solutions (0.2–0.4 M) adjusted to I = 0.5 M with sodium perchlorate. The reactions were monitored at 380 nm using stopped flow techniques and the values of k_{obs} listed in Table IX are the mean values of six kinetic runs. At these high base concentrations the reaction clearly shows a first order, rather than a second order dependence, on $[OH^-]$ with $k = k_{obs}/[OH^-] = 6.7$ M^{-1} s^{-1}. Since $kK = 1.8$ M^{-2} s^{-1} at low base concentrations, $K = 1.8/6.7 = 0.27$ M^{-1}. The values of the formation constants K for this system are clearly considerably smaller than those observed with $[Cu(\text{tet } a)(\text{blue})]^{2+}$ and such variations will lead to apparently quite different kinetic behaviour (*i.e.* first or second order dependence on $[OH^-]$ at relatively low base concentrations). The conversion of $[Cu(\text{tet } a)(\text{blue})]^{2+} \rightarrow [Cu(\text{tet } a)(\text{red})]^{2+}$ in basic solution involves the intermediacy of the hydroxo-complex which leads to intramolecular specific base catalysis · [26]. The blue species of $[Cu(\text{tet } a)]^{2+}$ differs from the red species only in the configuration of a single chiral nitrogen centre [27]. In the dissociation of a metal ion from a tetra-aza macrocycle it is likely that some change in the chiral nitrogen configurations from the stable R,S,S,R configuration is required and the intermediacy of the metal-hydroxo complex could provide a useful intramolecular catalyst for this process. In order to further confirm the importance of axial interactions in these complexes the reaction of N_3^- with $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ was studied. The complex has λ_{max} = 480 nm in aqueous solution which moves to 465 nm in the presence of azide. Figure 4 shows the absorbance of a 1.26×10^{-3} M solution of the complex at 465 nm as a function of the concentration of N_3^-. In addition to the equilibrium (10)

TABLE X. Complexation of $[Cu(\textit{trans}\text{-}Me_6[18]dieneN_4)]^{2+}$ by Azide Monitored at 465 nm and 20 °C.

$[NaN_3]$ (M)	A[a]	$[NaN_3]$ (M)	A[a]
0.0	0.125	0.20	0.230
0.02	0.135	0.30	0.245
0.04	0.150	0.40	0.262
0.06	0.165	0.50	0.265
0.08	0.175	0.60	0.302
0.10	0.185	0.70	0.320
0.12	0.195	0.80	0.335
0.15	0.210		

[a]Absorbance at 465 nm, using a total concentration of the complex = 1.26×10^{-3} M. For the complex $[CuL]^{2+}$ ϵ = 99 and for $[CuLN_3]^+$ ϵ = 210. The equilibrium constants (azide concentrations in parenthesis) are 6.7 M^{-1} (0.06 M); 6.9 (0.08 M); 7.5 (0.10 M) and 8.3 (0.12 M).

$$CuL^{2+} + N_3^- \xrightleftharpoons{K_1} [CuL(N_3)]^+ \qquad (10)$$

there is also evidence for a further equilibrium (9)

$$[CuL(N_3)]^+ + N_3^- \xrightleftharpoons{K_2} [CuL(N_3)_2] \qquad (11)$$

at high azide concentrations since the absorbance increases markedly beyond 0.5 M NaN_3, Table X. Equilibrium constants were calculated on the basis of equation (10) to give an average value of K_1 = 7.3 M^{-1} at 25 °C. There is a slight upward drift of the equilibrium constants as the azide concentration is increased, Table X, presumably since equilibrium (11) was neglected in the calculations.

Acknowledgement

We thank the SERC for financial support and for the award of a postdoctoral fellowship to one of us (RB).

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