Thermodynamic and Kinetic Effects of 12-Membered Macrocycles. Polarographic Studies of 1,4,7,10-Tetra-azacyclododecanecopper(II) [1]

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Thermodynamic parameters and reaction rates for complex formation between Cu^{2+} and 1,4,7,10-tetra-azacyclododecane (tcdd) have been determined polarographically. The stability constant (log K 24.8 at 25 °C) for the 1 : 1 complex is more than 10^4-fold greater than that for the corresponding open-chain tetra-amine, 3,6-diazaoctane-1,8-diamine (3,6NH-od). The enhanced stability with tcdd is entirely due to a more favourable entropy change, which is in sharp contrast to the 14-membered macrocyclic effect attributed to a more favourable enthalpy change by Hinz and Margerum. The rate constants are 1.84×10^6 and 1.80×10^{-1} dm^3 mol^{-1} s^{-1} for the reaction of $[Cu(O_2CMe)]^+$ with $Htcdd^+$ and H_2tccd^{2+}, respectively. The sluggishness with which the diprotonated species reacts suggests that the rate-determining step is an associative process, probably proton loss preceding second-bond formation. The increased stability constant of the 12-membered macrocyclic complex is reflected most in the dissociation rate constants.

THE effect of increased stability of a metal complex containing a macrocyclic tetra-amine ligand over that containing similar acyclic tetra-amine ligands has long been recognized as the macrocyclic effect or juxtapositional fixedness.[2] However, regarding the thermodynamic parameters contributing to the macrocyclic effect, little evidence had been presented which could confirm Margerum's proposition based on the special configuration and solvation of macrocyclic ligands.[3] The inherent difficulties were partly ascribed to the fact that complexes of macrocyclic ligands are too stable and the rates of formation and dissociation are too slow. Recently Hinz and Margerum [4] determined thermodynamic parameters for complex formation of Ni^{II} with 1,4,8,11-tetra-azacyclotetradecane (tctd, cyclam) by way of the exchange reactions with CN^-. A surprising result was that a 10^6-fold increase in the stability constant of $[Ni(tctd)]^{2+}$ relative to the corresponding open-chain 3,7-diazanonane-1,9-diamine (3,7NH-nd, 2,3,2-tet) complex was accounted for by a more favourable change in ΔH. It was reasoned that the free macrocycle is less solvated due to steric hindrance and hence less energy must be expended for desolvation before complex formation.

Meanwhile, in a separate kinetic study on the reaction of $[Ni(OH_2)_6]^{2+}$ with tctd, Kaden [5] reported that the mono- and di-protonated ligand species exhibited formation rate constants which were *ca.* 30 000 times smaller than those of the open-chain ligand 3,6-diazaoctane-1,8-diamine (3,6NH-od, trien). Kaden suggested that the kinetic effect of the rigid cyclic structure is in the rate-limiting step which shifts to formation of the second co-ordination bond.

In the current series of investigations of the macrocyclic effect, we have attempted to determine stability constants and formation and dissociation rate constants at the same time for several cyclic complexes. Our study originated from interest in the competition between the macrocyclic effect and the destabilizing effect of severe steric constraints anticipated for cyclic tetra-amines with less than 14-membered rings.[6] For our purpose the polarographic method was suitable. We report the results on the reaction of Cu^{II} with 1,4,7,10-tetra-azacyclododecane (tcdd, cyclen).

EXPERIMENTAL

Reagents.—1,4,7,10-Tetra-azacyclododecane (tcdd) was prepared according to the methods of Stetter and Mayer [7] and Collman and Schneider [8] (m.p. of tcdd·4HCl, 255—260 °C). Copper(II) nitrate solution was prepared by dissolving a known amount of metallic copper (99.999% pure) in dilute nitric acid and removing the excess of nitric acid by distillation under reduced pressure. All other chemicals were of analytical reagent grade and were used without further purification.

Apparatus and Procedure.—All the polarograms and the current–time curves were obtained with a Yanagimoto p-8 pen-recording polarograph or a manual polarograph similar to that of Kolthoff and Lingane.[9] The characteristic features of the dropping mercury electrode (d.m.e.) and all other apparatus and experimental procedures were described elsewhere.[10] The pK_a values of tcdd were determined by potentiometric titration of tcdd·4HCl with carbonate-free NaOH solution.

RESULTS

Equilibrium Studies.—Since tcdd is highly protonated in the pH region studied, the protonation constants were

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[1] Preliminary report, *J.C.S. Chem. Comm.*, 1975, 326.

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[3] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540.

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determined. These values are listed in Table 1 together with those of other cyclic and linear tetra-amines.

The tcdd complex of Cu^{II} in an acetate buffer solution ($4.30 < pH < 5.80$) gave a well defined single wave of the diffusion-controlled nature at the d.m.e. The acetate ion had no effect on the limiting current or half-wave potential, which is interpreted in that no mixed-ligand complex was formed under the experimental conditions. Plots of $\log [i/(i_d - i)]$ against the d.c. potential, E, were invariably linear with reciprocal gradients falling in the range -36 to -40 mV, corresponding to a reversible two-electron reduction (calc. -29.6 mV).[10,11]

TABLE 1

Comparison of protonation constants for cyclic and linear tetra-amines

	tcdd	tctd [a]	ttctd [b]	3,6NH-od [c]
$\log K_1$	10.7	11.5	12.6	10.1
$\log K_2$	9.7	10.2	10.4	9.3
$\log K_3$	1.5—2	1.6	0.8	6.8
$\log K_4$		0.9		3.4

[a] Ref. 4. [b] Ref. 3. [c] Ref. 19.

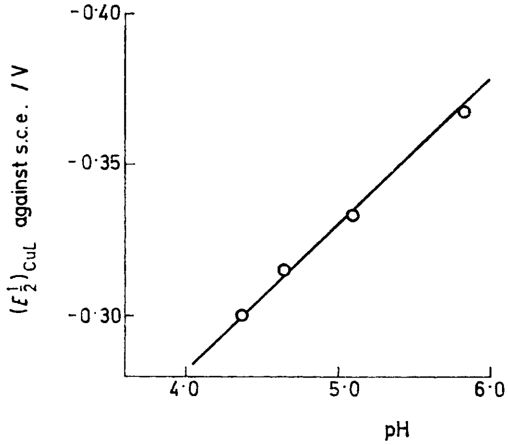

FIGURE 1 Effect of pH on $(E_{\frac{1}{2}})_{CuL}$ at $I = 0.20$ mol dm^{-3}, 25 °C, 10^3[tcdd] = 4.0 mol dm^{-3}, $[MeCO_2^-]$ = 0.10 mol dm^{-3}, and $10^3[Cu^{2+}]$ = 0.30 mol dm^{-3}

The effects of pH and concentration of the free tcdd ligand on the half-wave potentials were studied. At a given concentration of free tcdd $(E_{\frac{1}{2}})_{CuL}$ shifted linearly to more negative potentials with increasing pH (Figure 1), obeying relation (1). Similarly, at a given pH, $(E_{\frac{1}{2}})_{CuL}$

$$\Delta(E_{\frac{1}{2}})_{CuL}/\Delta pH = -50 \text{ mV} \qquad (1)$$

shifted to more negative potentials with an increase in the concentration of free tcdd, $[L]_f$, which gives relation (2) (Table 2). These findings led us to conclude that Cu^{2+} forms only a 1 : 1 complex with tcdd and that the electrode reaction mechanism for the reduction of the complex is given by equation (3), with a corresponding half-wave

$$[Cu(tcdd)]^{2+} + 2e^- + Hg \rightleftharpoons Cu(Hg) + tcdd \qquad (3)$$
$$tcdd + 2H^+ \rightleftharpoons H_2tcdd^{2+} \text{ (rapid)}$$

potential given by equation (4).[10e] Therefore, the shift of the half-wave potential due to complex formation, $\Delta(E_{\frac{1}{2}})_{CuL}$, may be expressed as in equation (5) [10e] where k denotes a diffusion-current constant and $(\alpha_H)_L$ is defined as $1 + ([H^+]/K_1) + ([H^+]^2/K_1K_2) + ([H^+]^3/K_1K_2K_3) + ([H^+]^4/K_1K_2K_3K_4) \approx ([H^+]^2/K_1K_2)$ (K_1 is the ith protonation constant of tcdd) under the experimental conditions.

$$(E_{\frac{1}{2}})_{CuL} = E_{Cu(Hg)}^{\ominus} + 0.0296 \left\{\log f_{Cu^{2+}} + \log \frac{k_{Cu(Hg)}}{k_{CuL}} + \log \frac{K_{CuZ}[L]_f}{(\alpha_H)_L}\right\} \qquad (4)$$

From equation (5), the formation constant of the 1 : 1 copper(II)–tcdd complex, K_{CuL}, was determined. The thermodynamic functions for the formation of the complex

$$\Delta(E_{\frac{1}{2}})_{CuL} = 0.0296\left\{\log \frac{K_{CuL}[L]_f}{(\alpha_H)_L} + \log \frac{k_{CuL}}{k_{Cu^{2+}}}\right\} \qquad (5)$$

were calculated from the temperature dependence of K_{CuL} (Figure 2). The results are compared with the corresponding values for various tetra-amines in Table 3.

TABLE 2

Effect of the concentration of free tcdd on the half-wave potential [a]

10^3(tcdd)$_f$ / mol dm^{-3}	$(E_{\frac{1}{2}})_{CuL}$ / V against s.c.e.	$\Delta(E_{\frac{1}{2}})_{Cu}$/mV	
		calc.[b]	obs.
2.0	-0.358_0	+9.0	+9.0
4.0	-0.367_1	0	0
8.0	-0.377_0	-9.0	-10.0
16.0	-0.397_1	-17.9	-20.0

[a] $[MeCO_2]^-$ = 0.10 mol dm^{-3}, $10^3[Cu^{2+}]$ = 0.30 mol dm^{-3}, pH 5.82, I = 0.20 mol dm^{-3}, and 25 °C. [b] From equation (2).

$$\Delta(E_{\frac{1}{2}})_{CuL}/\Delta \log [L]_f = -30 \text{ mV} \qquad (2)$$

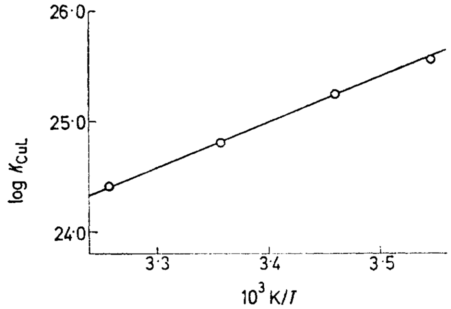

FIGURE 2 Determination of thermodynamic functions for the formation of the complex of Cu^{2+} with tcdd at I = 0.20 mol dm^{-3}

Kinetic Studies.—The formation of the tcdd complex proceeded at a measurable rate in acetate buffer solution ($pH < 4.0$). In experiments to determine the apparent initial rates of complex formation, $-\Delta[Cu^{2+}]_{0,app.}/\Delta t$, the following relations were found: (*i*) at given concentrations of hydrogen and acetate ions, the apparent initial rate was proportional to the initial concentration of copper(II) ion, $[Cu^{2+}]_{0,app.}$ and of tcdd, $[L]_f$ (Table 4); (*ii*) at given concentrations of H^+, Cu^{2+}, and tcdd, a plot of $(-\Delta[Cu^{2+}]_{0,app.}/\Delta t)\beta_{O_2CMe}$ against the concentration of free acetate ion gave a straight line passing through the origin, where β_{O_2CMe} is defined as $1 + K_{Cu(O_2CMe)}[MeCO_2^-] + K_{Cu(O_2CMe)}K_{Cu(O_2CMe)_2}[MeCO_2^-]^2$ (Figure 3); and (*iii*) at given concentrations of

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[11] Ref. 9, p. 193.

Cu^{2+}, $MeCO_2^-$, and tcdd, a plot of $(-\Delta[Cu^{2+}]_{0,app.}/\Delta t)\{(\alpha_H)_L/[H^+]\}$ against pH was linear with a finite intercept (Figure 4).

These findings establish that the complex formation is first order with respect to the concentrations of Cu^{2+} and tcdd and that a 1 : 1 copper(II)–acetate complex, $[Cu(O_2CMe)]^+$, and mono- ($[HL]^+$) and di-protonated tcdd ($[H_2L]^{2+}$) are involved in the slow step. Thus, the reaction mechanism in equations (6) and (7) is suggested and the corresponding rate equation is (8). The formation rate constants at 25 °C, k_6 and k_7, were determined as 1.84×10^6 and 1.80×10^{-1} $dm^3\ mol^{-1}\ s^{-1}$ from the intercept and gradient of the linear relation in Figure 4.

TABLE 3

Comparison of stability constants and enthalpies and entropies of formation of tetra-amine complexes at 25 °C

Complex	log K	ΔH / kcal mol^{-1}	ΔS / cal K^{-1} mol^{-1}
$[Cu(tcdd)]^{2+}$ [a]	24.8	−18.3	51.4
$[Cu(3,6NH\text{-}od)]^{2+}$ [b]	20.0	−21.6	19.5
$[Cu(3,7NH\text{-}nd)]^{2+}$ [b]	23.9	−27.7	16.5
$[Cu(en)_2]^{2+}$ [b]	19.7	−25.2	5.8
$[Ni(tctd)]^{2+}$ [c]	22.2	−31.0	−2
$[Ni(3,6NH\text{-}od)]^{2+}$ [c]	13.8	−14.0	16.0
$[Ni(3,7NH\text{-}nd)]^{2+}$ [c]	15.8	−19.4	7.2

[a] This work. [b] Ref. 16; en = ethylenediamine. [c] Ref. 4.

TABLE 4

Determination of the initial rate constant

(*i*) Variation of $[tcdd]_f$; $10^3[Cu^{2+}]_{0,app.} = 0.47$ mol dm^{-3}, $[MeCO_2^-] = 0.10$ mol dm^{-3}, pH 3.90, $I = 0.20$ mol dm^{-3}, and 25 °C

$10^3[tcdd]_f$ / mol dm^{-3}	10^6 Initial rate / mol dm^{-3} s^{-1}	10^3 (Initial rate/$[tcdd]_f$) / s^{-1}
0.313	0.75_0	2.40
0.626	1.53	2.44
1.252	3.10	2.48

(*ii*) Variation of $[Cu^{2+}]_{0,app.}$; $10^3[tcdd]_f = 0.626$ mol dm^{-3}, $[MeCO_2] = 0.10$ mol dm^{-3}, pH 3.50, $I = 0.20$ mol dm^{-3}, and 25 °C

$10^3[Cu^{2+}]_{0,app.}$ / mol dm^{-3}	10^6 Initial rate / mol dm^{-3} s^{-1}	10^3 (Initial rate/$[Cu^{2+}]_{0,app.}$) / s^{-1}
0.313	0.491	1.57
0.469	0.748	1.59
0.940	1.47_2	1.56

$$\begin{array}{l} \mathrm{Cu(O_2CMe)_2} \searrow\!\!\!\nwarrow^{\text{rapid}} \\ \qquad\qquad [\mathrm{Cu(O_2CMe)}]^+ + \\ \qquad \mathrm{Cu^{2+}} \swarrow\!\!\!\nearrow^{\text{rapid}} \end{array}$$

$$\left\{\begin{array}{ll} [\mathrm{HL}]^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [\mathrm{CuL}]^{2+} + \mathrm{MeCO_2H}, \text{ slow} & (6) \\ [\mathrm{H_2L}]^{2+} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [\mathrm{CuL}]^{2+} + \mathrm{MeCO_2H} + \mathrm{H^+}, \text{ slow} & (7) \end{array}\right.$$

$$\frac{-d[Cu^{2+}]_{0,app.}}{dt} = \frac{K_{Cu(O_2Me)}[MeCO_2^-][Cu^{2+}]_{0,app.}}{\beta_{O_2CMe}} \cdot \frac{[L]_f}{(\alpha_H)_L} \cdot \left(\frac{k_6[H^+]}{K_1} + \frac{k_7[H^+]^2}{K_1K_2}\right) \quad (8)$$

DISCUSSION

The Cyclic Effect on Protonation Constants.—The effect of the proximity of the N donors and the rigid conformation of tcdd is well demonstrated in the protonation constants (Table 1). In analogy to 14-membered cyclic ligands,[12] the first and second protonation constants for tcdd are higher than for the linear 3,6NH-od. The lower pK_1 and pK_2 of tcdd compared to those of 14-membered tetra-amines may reflect the more severe steric constraint of the 12-membered ring conformation. The big gap between the second and third protonation constants found in the 14-membered ligands [13] is also observed for tcdd.

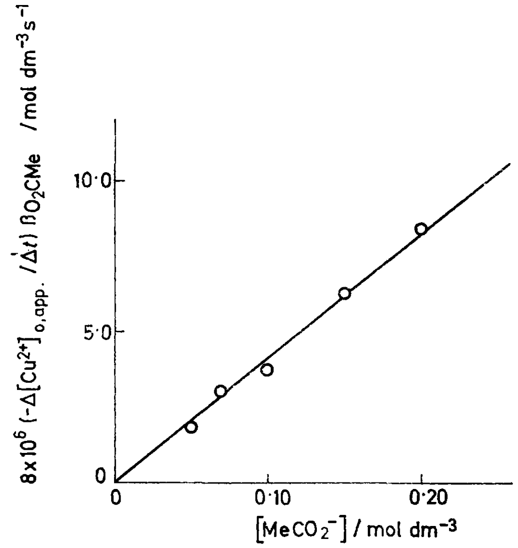

FIGURE 3 Plot of $(-\Delta[Cu^{2+}]_{0,app.}/\Delta t)\beta_{O_2CMe}$ against $[MeCO_2^-]$ at pH 4.00, $I = 0.20$ mol dm^{-3}, 25 °C, $10^3[tcdd] = 0.323$ mol dm^{-3}, and $10^3[Cu^{2+}] = 0.387$ mol dm^{-3}

The Cyclic Effect on Stability Constants.—Table 3 clearly shows that the macrocyclic effect of the 12-membered ring is evident despite the unfavourable enthalpy term. The enhanced stability of $[Cu(tcdd)]^{2+}$ arises entirely from the favourable change in ΔS.

In complex formation with tetra-amine ligands the difficulty in occupying the co-ordination sites becomes greater with more fused five-membered chelate rings.[14,15] Such steric constraints are reflected in the enthalpy of complex formation,[16] and hence it is not surprising that the complex $[Cu(tcdd)]^{2+}$ has a lower heat of formation than $[Cu(3,6NH\text{-}od)]^{2+}$. Another endothermic contribution may come from the lower co-ordinate bond energy due to the change from two primary and two secondary (3,6NH-od) to four secondary nitrogen atoms (tcdd).[17]

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[12] D. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

[13] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.

[14] Y. Itaka, M. Shina, and E. Kimura, *Inorg. Chem.*, 1974, **13**, 2886.

[15] Y. Kushi and E. Kimura, paper presented at the 24th Co-ordination Chem. Symp., Kanazawa, Japan, October 1974.

[16] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Co-ordination Chem. Rev.*, 1972, 8.

[17] For example, R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1972, 745.

The smaller extent of ligand solvation expected for cyclic tetra-amines [4] should have the opposite contribution. All these factors add up to the observed ΔH.

The very favourable entropy contribution for the tcdd compared with the 3,6NH-od complex can be explained by reorientation before chelation due to steric requirements, and the decreased solvation in the inner co-ordination sphere of the complex due to distorted geometry together with that in the outer sphere due to the hydrophobic exterior. However, the contrast in the entropy contributions for formation of the complexes $[Cu(tcdd)]^{2+}$ and $[Ni(tctd)]^{2+}$ does not seem to be fully accounted by the difference in the metal ion or the ligand ring size, and we are investigating this further.

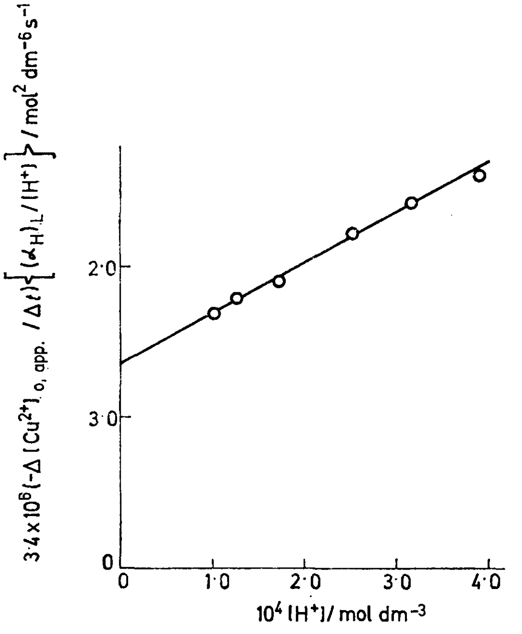

FIGURE 4 Plot of $(-\Delta[Cu^{2+}]_{0,app.}/\Delta t):(\alpha_H)_L/[H^+]$; against $[H^+]$ at $I = 0.20$ mol dm^{-3}, 25 °C, 10^3[tcdd] = 0.625 mol dm^{-3}, $10^3[Cu^{2+}]$ = 0.47 mol dm^{-3}, and $[MeCO_2^-]$ = 0.10 mol dm^{-3}

The Cyclic Effect on the Kinetics.—The cyclic effect on the formation and dissociation rate constants was studied by comparing with those of the tcdd and 3,6NH-od complexes. For the reaction of non-cyclic polyamine ligands, the kinetics are well explained by a dissociative mechanism in which the rate-determining step is the first co-ordinate bond formation.[18] However, for a macrocyclic ligand it will be very difficult to follow a similar stepwise desolvation and metal–ligand bond formation process because of the restricted geometry and the proximity of the N donors.

In the reaction of Cu^{2+} with tcdd the kinetics measured in acetate buffer showed an involvement of $[Cu(O_2CMe)]^+$. The co-ordination of acetate to the copper will reduce the electrostatic repulsion between Cu^{2+} and protonated tcdd species, and enhance the rate of the dissociation of co-ordinated water. A similar case is the complex formation of Ni^{2+} with ethylenediaminetetra-acetic acid in acetate buffer.[19] Since the rate constants for the reaction of $[Cu(O_2CMe)]^+$ with 3,6NH-od are not available, we estimated them on the basis of the *ICB* mechanism.[20] A value of 2×10^9 dm^3 mol^{-1} s^{-1} was obtained for reaction (6) (L = 3,6NH-od), by using the following parameters: $10^{8.3}$ s^{-1} for the rate constant of inner-sphere exchange of a water molecule ($k_{Cu}^{-H_2O}$); [21] 0.20 dm^3 mol^{-1} for the outer-sphere association constant ($K_{o.s.}$); [22] 50 for the *ICB* rate enhancement (K_{ICB}); [23] and 5 for the acetate-ion rate enhancement (K_{O_2CMe}).[19,23] Thus, the reaction of $Htcdd^+$ with $[Cu(O_2CMe)]^+$ is estimated to be slower by an order of 10^3 than that of protonated 3,6NH-od which proceeds by the usual *ICB* mechanism. The rate constant for the reaction of diprotonated 3,6NH-od was similarly calculated to be $10^{6.6}$ dm^3 mol^{-1} s^{-1}, *ca.* 10^8 times faster than the reaction of H_2tcdd^{2+}. The rate of the complex formation is thus dramatically changed by the cyclic structure.

For protonated non-cyclic polyamine ligands, deprotonation, which is an essential prior step for co-ordination, could be easily achieved by internal transfer to other unprotonated N atoms of relatively high basicity. Hence, in the reaction of diprotonated 3,6NH-od this step may be neglected in dissociative mechanism.[18] One could argue that the sluggishness with which H_2tcdd^{2+} co-ordinates is due to the proximity of the N donor atoms, resulting in a shift of the rate-determining step to the proton transfer. In this regard, it is of interest that unprotonated tctd reacts as fast as non-cyclic tetra-amines.[24]

TABLE 5

Rate constants for the tcdd and 3,6NH-od systems at I = 0.20 mol dm^{-3} and 25 °C

(*a*) $[Cu(O_2CMe)]^+ + [HL] \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [CuL]^{2+} + MeCO_2H$

System	log K_{ML}	log k_6	Relative k_6	log k_{-6}	Relative k_{-6} [a]
3,6NH-od [b]	20.4	9.30	1.0	−1.8	1.0
tcdd	24.8	6.30	$10^{-3.0}$	−10.9	$10^{-4.7}$

(*b*) $[Cu(O_2CMe)]^+ + [H_2L]^{2+} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [CuL]^{2+} + MeCO_2H + H^+$

System	log K_{ML}	log k_7	Relative k_7	log k_{-7}	Relative k_{-7} [a]
3,6NH-od [b]	20.4	6.6	1.0	5.5	1.0
tcdd	24.8	−0.74	$10^{-8.3}$	−8.2	$10^{-9.3}$

[a] Relative $k_{-i} = \dfrac{k_{-i}\text{ (for tcdd) } K_{ML}\text{ (for 3,6NH-od)}}{k_{-i}\text{ (for 3,6NH-od) } K_{ML}\text{ (for tcdd)}}$.

[b] Estimated assuming an *ICB* mechanism.

The dissociation rate constants, $k_{-6} = 10^{-10.9}$ dm^3 mol^{-1} s^{-1} and $k_7 = 10^{-8.2}$ dm^6 mol^{-2} s^{-1}, for the reverse

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[23] R. E. Shephered, G. M. Hodgson, and D. W. Margerum, *Inorg. Chem.*, 1971, **10**, 989.

[24] C. T. Lin, D. B. Rorabacher, G. R. Cayley, and D. W. Margerum, *Inorg. Chem.*, 1975, **14**, 919.

reactions in (6) and (7) were calculated from the forward reaction rates and the formation constants. They are compared with those of the 3,6NH-od reactions in Table 5. It is concluded that the thermodynamic macrocyclic effect reflects more the dissociation rather than the formation process and that diprotonation dramatically retards the dissociation as does the formation rate. Dissociation rate constants for the copper complex of 7,7,14,14-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (ttctd, tet *a*) may be similarly calculated from the data given in ref. 13 (Table 6). In the cyclic structure it is impossible to extend the metal–ligand distance sufficiently to cause bond rupture without extensive rearrangement of the ligand within the coordination sphere.[2a]

TABLE 6

Calculated dissociation rate constants for ttctd and 3,7NH-nd systems

Reactions: $Cu^{2+} + [HL]^+ \underset{k_d^{H}}{\rightleftharpoons} [CuL]^{2+} + H^+$;

$Cu^{2+} + [H_2L]^{2+} \underset{k_d^{2H}}{\rightleftharpoons} [CuL]^{2+} + 2H^+$

System	log K_d^{H}	log k_d^{H}	Relative k_d^{H}	log k_d^{2H}	Relative k_d^{2H}
ttctd	20.0	−3.5	$10^{-2.4}$	−2.0	$10^{-8.3}$
3,7NH-nd *	23.9	−5.0	1.0	2.4	1.0

* k_d^{iH} Was estimated as for 3,6NH-od. For the pK_a values of 3,7NH-od, see D. C. Weatherbern, E. J. Bills, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557.

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