Thermodynamic Studies on the Complexation Reaction of Copper(II) Macrocyclic Tetramine Complexes with Hydroxide Ion

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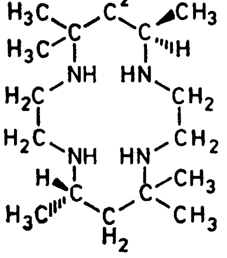
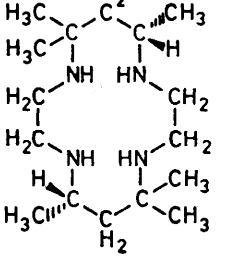
The relative stabilities of the red and blue forms of each of the complexes $[CuL]^{2+}$ and $[CuL(OH)]^+$ (L = *meso*- or *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) have been determined by a spectrophotometric method in basic solution at 25 °C and I = 0.1 mol dm^{-3}. The factors which influence the relative stabilities are discussed.

THE macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane exists as two isomers, tet a and tet b.[1] Each of these isomers forms a blue and a red complex with copper(II),[2] and the crystal structures of these complexes have recently been determined.[3-5] Thus red [Cu(tet a)][ClO$_4$]$_2$ shows a *trans* structure with a square-planar arrangement of the four nitrogens of tet a,[3] while red [Cu(tet b)][ClO$_4$]$_2$ displays a very slightly distorted planar arrangement of the four nitrogens of tet b,[4] the ligand of blue [Cu(tet a)]$^{2+}$ is in a distorted planar configuration,[3] while that of blue [Cu(tet b)]$^{2+}$ is in a folded structure.[5] These complexes therefore provide an opportunity of elaborating the ways in which the structural differences of the co-ordinated macrocyclic tetramines affect the properties of their metal complexes.



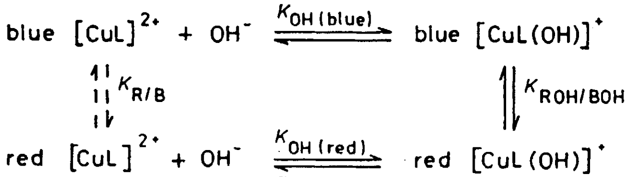
tet a



tet b

The blue-to-red interconversions of these complexes are catalyzed by base through the inversion requirement of the nitrogen atoms. The kinetics of these interconversions and the important contribution of co-ordinated hydroxide ion have been reported recently.[6]

In view of the important role of co-ordinated hydroxide ion in the configurational interconversions of these complexes, it was considered desirable to study the equilibrium behaviour of these complexes in basic solution, as represented by the Scheme. Here L is the macrocyclic ligand, tet a or tet b.

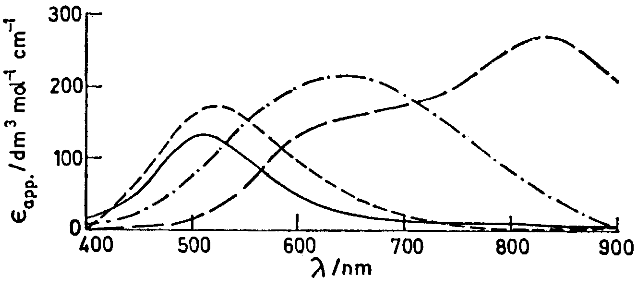


SCHEME

EXPERIMENTAL

Reagents.—The macrocyclic ligands tet a and tet b were prepared by the procedure described by Hay *et al.*[7] The salts blue [Cu(tet a)][ClO$_4$]$_2$[8] (Found: C, 35.35; H, 6.70; Cl, 12.9; N, 10.25. Calc. for $C_{16}H_{36}Cl_2CuN_4O_8$: C, 35.15; H, 6.60; Cl, 13.0; N, 10.25%), red [Cu(tet a)][ClO$_4$]$_2$[9] (Found: C,35.0; H, 6.65; Cl, 13.0; N, 10.35%) [{Cu(tet b)}$_2$Cl][ClO$_4$]$_3$[5] (Found: C, 37.2; H, 7.10; Cl, 13.65. Calc. for $C_{16}H_{36}Cl_4Cu_2O_{12}$: C, 37.3; H, 7.05; Cl, 13.75%), and red [Cu(tet b)][ClO$_4$]$_2$[10] (Found: C, 35.05; H, 6.85; Cl, 13.1%) were prepared as described previously. The electronic spectra of these four complexes in aqueous solution are shown in the Figure. All other chemicals used in this work were of GR grade (Merck).

Instrumentation.—A Cary 17 spectrophotometer with a thermostatted cell compartment was used to record absorption spectra. A Durrum D-115 stopped-flow spectrophotometer was used to measure the absorbance jump after mixing of solutions of base and copper(II) macrocyclic complexes. Equilibrium constants were obtained by this method, using a linear least-squares fit of the data on an IBM 1130 computer.



Molar absorbances of the copper(II) complexes in the visible and near-i.r. region: (——), red [Cu(tet a)]$^{2+}$; (– – – – –), red [Cu(tet b)]$^{2+}$; (— · — · —), blue [Cu(tet a)]$^{2+}$; and (— — —), blue [Cu(tet b)]$^{2+}$

RESULTS

Equilibrium Constants of the Complexation Reactions of Blue [Cu(tet a)]$^{2+}$ *and Blue* [Cu(tet b)]$^{2+}$ *with Hydroxide Ion.*—These blue complexes are unstable, being converted into the red isomers in basic solution. The interconversions are much slower than that of co-ordination of a hydroxide ion. The equilibrium constant for the reaction of blue [Cu(tet b)]$^{2+}$ with hydroxide ion has been reported recently.[6]

The equilibrium constant for the reaction of blue [Cu(tet a)]$^{2+}$ and OH$^-$ was determined by measuring the absorbance jump after stopped-flow mixing of solutions of the base and blue $[Cu(tet\ a)]^{2+}$. The apparent molar absorption coefficients at 650 nm were obtained by using Beer's law.

According to the Rose–Drago equation (1), a plot of $\varepsilon_{app.}$ against $-(\varepsilon_{app.} - \varepsilon_{Cu(tet\ a)})/[OH^-]$, where $[OH^-] = [OH^-]_T - [Cu(tet\ a)(OH)^+\ (blue)]$, gives a straight line of slope $1/K_{OH}$. Values of $[OH^-]$ were calculated by an iterative procedure in which an estimated value of K_{OH} was first used to

$$\varepsilon_{app.} = \frac{-(\varepsilon_{app.} - \varepsilon_{Cu(tet\ a)})}{K_{OH}[OH^-]} + \varepsilon_{Cu(tet\ a)(OH)} \qquad (1)$$

calculate values of $[OH^-]$ which were then used to obtain a new value of K_{OH}, the operation being repeated until the least-squares deviation in the plot of $\varepsilon_{app.}$ *vs.* $-(\varepsilon_{app.} - \varepsilon_{Cu(tet\ a)})/[OH^-]$, was minimized. The final value of K_{OH} thus obtained was 50.3 dm^3 mol^{-1}.

Equilibrium Behaviour of Copper(II)*-tet b Species in Basic Solutions.*—Although the blue-to-red conversion of copper-tet b is essentially quantitative below pH 11, more basic solutions appear to retain (or to reform) some of the blue species. In order to prove that the observed spectral behaviour was not merely due to OH^- addition to the red form or to an additional blue configurational isomer, solutions which had reached equilibrium in 0.03—0.10 mol dm^{-3} Na[OH] were cooled in ice and quickly acidified with cold $HClO_4$. This resulted in the formation of a mixture of the blue and red forms of $[Cu(tet\ b)]^{2+}$. The species were identified by their spectral and kinetic properties.

When the alkaline mixture is treated with cold acid, the protonation rate is much faster than the rate of isomerization, therefore the red and the blue forms are frozen in their configurations. The ratio of the total amount of red forms to the total amount of blue forms in the alkaline solution is thus the same as that in the acidic solution. Since $K_{OH(red)}$ is not large enough to allow the molar absorption coefficient of the adduct red $[Cu(tet\ b)(OH)]^+$ to be determined directly, the above ratio was calculated from the results of quenching a basic solution of $[Cu(tet\ b)]^{2+}$ with acid.

Results of Quenching Basic Solutions of $[Cu(tet\ b)]^{2+}$ *with Acid.*—A solution of sodium hydroxide was added to red $[Cu(tet\ b)]^{2+}$ solution and the mixture was allowed to reach equilibrium (*ca.* 1 h), the temperature being maintained at 25.0 ± 0.1 °C. The colour of the solution changed from red to violet. Cold $HClO_4$ solution was quickly added and the spectra of the acidified solution recorded in order to determine the ratio of the red-to-blue species present. Table 1 gives the apparent molar absorption coefficients found for acidified solutions at 520 {close to $\lambda_{max.}$ for red $[Cu(tet\ b)]^{2+}$}, 700, and 830 nm {wavelengths corresponding to absorption peaks for blue $[Cu(tet\ b)]^{2+}$}. The results can be expressed in terms of equation (2), where ε' is the apparent molar absorption coefficient of the mixture at each wavelength, ε_R the molar absorptivity of the red form, ε_B the molar absorptivity of the blue form, and r the ratio of the total amount of the red forms to the total amount of the

$$\left(\frac{\varepsilon_R r + \varepsilon_B}{\varepsilon'}\right)_{830\ nm} = \left(\frac{\varepsilon_R r + \varepsilon_B}{\varepsilon'}\right)_{700\ nm} = \left(\frac{\varepsilon_R r + \varepsilon_B}{\varepsilon'}\right)_{520\ nm} \qquad (2)$$

blue forms (c_R/c_B). The spectra of the systems of red and blue species were recorded and the values of ε_R and ε_B thus obtained. Various sets of r values [(a)—(c)] were obtained by solving equation (2) at 520 and 700 nm, 520 and 830 nm, and 700 and 830 nm, respectively and were in good agreement (Table 1). The averages of these r values were used to calculate the stability constants $K_{OH(red)}$ and $K_{ROH/BOH}$ from equations (3) and (5), respectively.

$$K_{OH(red)} = \frac{[Cu(tet\ b)(OH)^+(red)]}{[Cu(tet\ b)^{2+}(red)][OH^-]} \qquad (3)$$

$$K_{OH(blue)} = \frac{[Cu(tet\ b)(OH)^+(blue)]}{[Cu(tet\ b)^{2+}(blue)][OH^-]} \qquad (4)$$

$$K_{ROH/BOH} = \frac{[Cu(tet\ b)(OH)^+(red)]}{[Cu(tet\ b)(OH)^+(blue)]} \qquad (5)$$

TABLE 1

Ratios of the amounts of the red to blue forms of copper(II)–tet b species at various hydroxide-ion concentrations, as measured by $HClO_4$ quenching

Initial $[OH^-]$/mol dm^{-3}	Apparent ε' (dm^3 mol^{-1} cm^{-1}) in final solution			Ratio of total red to total blue, r *		
	520 nm	700 nm	830 nm	(a)	(b)	(c)
0.037	147.50	20.30	11.31	33.7	33.8	33.9
0.056	145.23	22.21	14.43	23.3	23.5	23.6
0.079	142.88	24.44	18.50	16.9	16.7	16.4
0.100	141.58	26.90	22.12	13.3	13.2	13.4

* Calculated from data at (a) 520 and 700 nm, (b) 520 and 830 nm, and (c) 700 and 830 nm.

In terms of the individual species present in basic solution, r is defined by equation (6). Substituting equations

$$r = \frac{[Cu(tet\ b)^{2+}(red)] + [Cu(tet\ b)(OH)^+(red)]}{[Cu(tet\ b)^{2+}(blue)] + [Cu(tet\ b)(OH)^+(blue)]} \qquad (6)$$

(3)—(5) into (6) we obtain (7), and therefore a plot of r *vs.* $1/[OH^-]$ should give a straight line with an intercept of

$$r = \left(\frac{1}{K_{OH(blue)}[OH^-]} + 1\right)^{-1} \frac{K_{ROH/BOH}}{K_{OH(red)}[OH^-]} + K_{ROH/BOH} \qquad (7)$$

$K_{ROH/BOH}$ and slope of $\left(\frac{1}{K_{OH(blue)}[OH^-]} + 1\right)^{-1} \frac{K_{ROH/BOH}}{K_{OH(red)}}$. The resulting values of $K_{ROH/BOH}$ and $K_{OH(red)}$ are listed in Table 2, together with the equilibrium constant $K_{R/B}$ obtained from equation (8).

$$K_{R/B} = (K_{OH(blue)}/K_{OH(red)})K_{ROH/BOH} \qquad (8)$$

Equilibrium Behaviour of Copper(II)*-tet a Species in Basic Solutions.*—The equilibrium behaviour of copper(II)–tet a species at high hydroxide-ion concentrations was studied by the procedure described above and no blue isomer was found after the basic solution had been acidified with cold $HClO_4$. This suggests that the red form of $[Cu(tet\ a)(OH)]^+$ is substantially more stable than the blue form.

The apparent molar absorption coefficient at 640 nm of the solution, $\varepsilon_{app.}$, has a linear dependence of $(\varepsilon_{app.} - \varepsilon_{Cu(tet\ a)(red)})/[OH^-]$ in accordance with equation (9), with a

$$\varepsilon_{app.} = \frac{-(\varepsilon_{app.} - \varepsilon_{Cu(tet\ a)(red)})}{K_{OH}[OH^-]} + \varepsilon_{Cu(tet\ a)(OH)(red)} \qquad (9)$$

slope of $-1/K_{OH}$. The value of K_{OH} is given in Table 2.

The stability constants of the red and blue forms of $[Cu(tet\ a)]^{2+}$ reported by Cabbiness and Margerum[2] are 10^{28} and 10^{20} dm^3 mol^{-1} respectively. The values of $K_{R/B}$

and $K_{\mathrm{ROH/BOH}}$ estimated from these stability constants are given in Table 2.

DISCUSSION

The visible spectra of the red forms of $[\mathrm{Cu(tet\ a)}]^{2+}$ and $[\mathrm{Cu(tet\ b)}]^{2+}$ in aqueous solution both have a single absorption peak as shown in the Figure, indicating the same type of square-planar or slightly distorted square-planar structure as those found in the crystalline red complexes.[3,4] The red form of $[\mathrm{Cu(tet\ b)}]^{2+}$ or $[\mathrm{Cu(tet\ a)}]^{2+}$ is more stable than the blue species as shown in Table 2. This is mainly due to the fact that the crystal-field stabilization energies (c.f.s.e.) of the red species are much larger than those of the blue, which have trigonal-bipyramidal [5] and tetrahedrally distorted structures.[11]

TABLE 2

Summary of equilibrium constants for the $[\mathrm{Cu(tet\ b)}]^{2+}$–$\mathrm{OH}^-$ and $[\mathrm{Cu(tet\ a)}]^{2+}$–$\mathrm{OH}^-$ systems at 25.0 ± 0. 1 °C and $I = 0.1$ mol dm^{-3} ($\mathrm{Na[NO_3]} + \mathrm{Na[OH]}$)

Reaction	Equilibrium constant/dm^3 mol^{-1}	
	L = tet b	L = tet a
blue $[\mathrm{CuL}]^{2+} + \mathrm{OH}^- \xrightleftharpoons{K_{\mathrm{OH(blue)}}}$ blue $[\mathrm{CuL(OH)}]^+$	508 [a]	50.3
red $[\mathrm{CuL}]^{2+} + \mathrm{OH}^- \xrightleftharpoons{K_{\mathrm{OH(red)}}}$ red $[\mathrm{CuL(OH)}]^+$	0.96	0.78
blue $[\mathrm{CuL(OH)}]^+ \xrightleftharpoons{K_{\mathrm{ROH/BOH}}}$ red $[\mathrm{CuL(OH)}]^+$	1.3	1.6×10^6
blue $[\mathrm{CuL}]^{2+} \xrightleftharpoons{K_{\mathrm{R/B}}}$ red $[\mathrm{CuL}]^{2+}$	6.9×10^2	10^8 [b]

[a] Ref. 6. [b] Ref. 2.

The value of $K_{\mathrm{R/B}}$ for the copper(II)–tet a system is much larger than that for the copper(II)–tet b system. This difference can be explained in terms of the conformations of the chelate rings of these complexes. The crystal structures of the blue and red forms of $[\mathrm{Cu(tet\ b)}]^{2+}$ have been studied.[4,5] The blue species contains two *gauche* conformations of the five-membered chelate rings and two chair conformations of the six-membered chelate rings,[5] while the red species contains two chair conformations of the six-membered chelate rings and two eclipsed conformations of the five-membered chelate rings.[4] Since the eclipsed five-membered chelate ring is less stable than the *gauche* five-membered chelate ring, the conformational energies of the chelate rings of the red form of $[\mathrm{Cu(tet\ b)}]^{2+}$ are larger than those of the blue.

In the case of the copper(II)–tet a system the situation is different. The structures of both blue and red forms of $[\mathrm{Cu(tet\ a)}]^{2+}$ have been studied [3] and the results indicate that the red species contains four stable chelate rings, two chair forms of the six-membered chelate rings, and two *gauche* forms of the five-membered chelate rings. On the other hand, the blue species contains two unstable chelate rings.[3,12] Since both the c.f.s.e. and the conformational energies of the chelate rings promote the formation of red $[\mathrm{Cu(tet\ a)}]^{2+}$, $K_{\mathrm{R/B}}$ is very large for the copper(II)–tet a system. The value of $K_{\mathrm{R/B}}$ for the copper(II)–tet b system is much smaller than that for the copper(II)–tet a system, in agreement with the opposing effects of the c.f.s.e. {which promotes the formation of red $[\mathrm{Cu(tet\ b)}]^{2+}$} and the conformational energies.[4,6] In this case, the former effect is the more important. The difference between the $K_{\mathrm{ROH/BOH}}$ values for the two systems can be explained similarly.

The tendency for adduct formation between $[\mathrm{CuL}]^{2+}$ and OH^- increases in the order: red $[\mathrm{Cu(tet\ a)}]^{2+}$ < red $[\mathrm{Cu(tet\ b)}]^{2+}$ < blue $[\mathrm{Cu(tet\ a)}]^{2+}$ < blue $[\mathrm{Cu(tet\ b)}]^{2+}$. The red forms of both $[\mathrm{Cu(tet\ a)}]^{2+}$ and $[\mathrm{Cu(tet\ b)}]^{2+}$ are square planar and have very large c.f.s.e. The formation of the adduct of the red species enormously increases the ligand field along the axis containing the copper(II) and hydroxide, *i.e.* the z axis, thus raising the energies of the d_{z^2} and d_{xz}, d_{yz} orbitals,[11] and resulting in a loss of crystal-field stabilization energy. In general, the greater the degree of distortion from a square-planar structure the larger is the tendency to form $[\mathrm{CuL(OH)}]^+$.[12] The above sequence supports this view.

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