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Copper(II), nickel(II) and zinc(II) complexes of *N,N′,N″,N‴*-tetrakis(2-hydroxypropyl)-1,4,8,11-tetra-azacyclotetradecane. Rates of formation and dissociation of the copper(II) complex

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Abstract—The preparation of the pendant arm macrocycle *N,N′,N″,N‴*-tetrakis(2-hydroxypropyl)-1,4,8,11-tetra-azacyclotetradecane (THPC = L) by reaction of propylene oxide with 1,4,8,11-tetra-azacyclotetradecane (cyclam) is described. Copper(II), nickel(II) and zinc(II) complexes of the ligand have been prepared and characterized. The reaction of L with copper(II) in basic solution has been studied by stopped flow techniques

$$\mathrm{L}+[\mathrm{Cu(OH)_3}]^- \longrightarrow [\mathrm{CuL}]^{2+};\quad k_1$$

$$\mathrm{L}+[\mathrm{Cu(OH)_4}]^{2-} \longrightarrow [\mathrm{CuL}]^{2+};\quad k_2.$$

At 25°C and $I = 1.0$ mol dm^{-3}, $k_1 = 3.7\times10^5$ and $k_2 = 2.1\times10^4$ dm^3 mol^{-1} s^{-1}. These values may be compared with the constants obtained for cyclam, $k_1 = 2.7\times10^6$ and $k_2 = 3.8\times10^4$ dm^3 mol^{-1} s^{-1} at 25°C. The mechanism of the reaction is discussed. The copper(II) complex $[\mathrm{CuL}]^{2+}$ dissociates readily in acidic solution. The kinetics of dissociation have been studied by stopped flow methods in the acidity range 0.05–1.0 mol dm^{-3} $\mathrm{HClO_4}$. Two reactions could be detected, the first reaction was complete within 20–30 ms at 25°C and was attributed to a pre-equilibrium protonation step. The second reaction, associated with an absorbance decrease was assigned to the acid dissociation step and was acid dependent at low acidities and acid independent at high acidities. In the acidity range used the dissociation can be fitted to the kinetic scheme

$$[\mathrm{CuL}]^{2+}+\mathrm{H}^+ \rightleftharpoons [\mathrm{CuLH}]^{3+};\quad K$$

$$[\mathrm{CuLH}]^{3+} \longrightarrow \mathrm{Cu}^{2+}+\mathrm{LH}^+;\quad k$$

and $k_{\mathrm{obs}} = kK[\mathrm{H}^+]/(1+K[\mathrm{H}^+])$, with $k = 7.1\pm0.4$ s^{-1} and $K = 1.3\pm0.1$ dm^3 mol^{-1} at $I = 1.0$ mol dm^{-3} and 25°C. The pK values of THPC determined by potentiometric titration are 9.08, 8.30, <2 and <2 at 25°C. Studies of the solution equilibria of the ligand with copper(II) and nickel(II) by potentiometric methods indicate that with copper(II) the titration data can be fitted to the single equilibrium $\mathrm{Cu}^{2+}+\mathrm{L}\rightleftharpoons\mathrm{CuL}^{2+}$ with $\log\beta_{110} = 15.54(3)$. In the case of nickel(II) deprotonation of the complex occurs with $\log\beta_{110} = 7.32(3)$, $\log\beta_{11\text{-}1} = -1.71(3)$ and $\log\beta_{11\text{-}2} = -12.62(4)$. Deprotonation of the pendant hydroxyl groups in the nickel(II) complex has been confirmed by visible spectral measurements. © 1997 Elsevier Science Ltd

Keywords: macrocycle; metal complexes; formation rates; dissociation rates; formation constants; pendant arm.

The macrocyclic ligand *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,8,11-tetra-azacyclotetradecane (**I** = THEC) was first characterized in 1984 [1,2] and displays many novel properties [3]. For example, the ligand reacts rapidly with metal ions such as copper(II) and nickel(II) and the resulting complexes dissociate readily in acidic solution. The parent ligand 1,4,8,11-tetra-azacyclotetradecane (cyclam) equilibrates very slowly with the labile copper(II) ion and $[\mathrm{Cu(cyclam)}]^{2+}$ is not decomposed in 6 mol dm^{-3} HCl over a period of several weeks [4]. The labile nature

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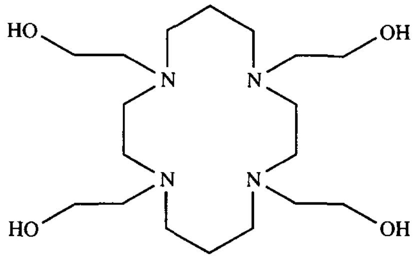
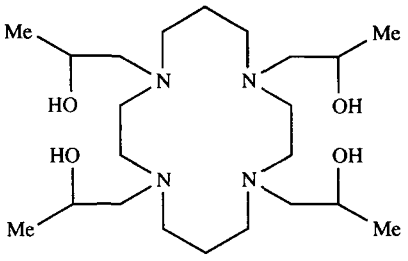


(I) = THEC



(II) = THPC

of the pendent arm complexes may be useful in the development of ligands for metal ion sensor or hydrometallurgical applications. Recently a detailed kinetic study of both the formation and dissociation kinetics of the copper(II), nickel(II) and cobalt(II) complexes of THEC was published [5]. These results confirm the earlier observations [2] that the half-lives of the THEC complexes in 1 mol dm^{-3} HNO_3 are in the millisecond time scale. The origins of these effects are as yet not thoroughly understood and for this reason we have carried out a detailed study of the formation and dissociation kinetics of copper(II) complexes of the associated pendant arm macrocycle *N*,*N*′,*N*″,*N*‴ - tetrakis(2 - hydroxypropyl) - 1,4,8,11 - tetra-azacyclotetradecane (**II** = L = THPC). The present paper reports the results of these measurements and the characterization of the copper(II), nickel(II) and zinc(II) complexes of THPC.

EXPERIMENTAL

Cyclam (1,4,8,11-tetra-azacyclotetradecane) was prepared as previously described [6]. The ligand *N*,*N*′,*N*″,*N*‴-tetrahydroxypropyl-1,4,8,11-tetra-azcyclotetradecane (L) was prepared as follows.

Propylene oxide (5 g) was added dropwise to a stirred solution of cyclam (6 g) in dry ethanol (150 cm^3) at 0°C. After stirring the mixture overnight at room temperature, the solvent was removed on a rotary evaporator to give a white solid. Recrystallization from acetonitrile gave a colourless crystalline solid (2.5 g, 23%) m.p 188–190°C. Found: C, 60.9; H, 11.5; N, 13.1. Calc. for $C_{22}H_{48}N_4O_4$: C, 61.1; H, 11.2; N, 12.9%. The IR spectrum (KBr disc) has ν(OH) at 3405 cm^{-1}. Mass spectrum *m*/*z* 432 [M$^+$].

$[CuL](ClO_4)_2 \cdot H_2O$

The ligand (0.3 g, 0.69 mmol) was dissolved in ethanol (25 cm^3) and copper(II) perchlorate hexahydrate (0.25 g, 0.69 mmol) in ethanol (25 cm^3) added. The solution was heated on a water bath for *ca* 15 min, then concentrated to half volume. On cooling the blue complex crystallized and was filtered off, washed with methanol and dried in *vacuo* over silica gel. Yield 0.3 g (60%). Found: C, 37.3; H, 7.1; N, 7.5. Calc. for $C_{22}H_{50}N_4CuCl_2O_{13}$: C, 37.0; H, 7.1; N. 7.8%.

$[ZnL](ClO_4)_2 \cdot 2H_2O$

The ligand (0.4 g, 0.92 mmol) was dissolved in dry ethanol (25 cm^3) and zinc(II) perchlorate hexahydrate (0.34 g, 0.92 mmol) in ethanol added. The solution was heated on a water bath for 10 min then concentrated to half volume. The precipitated complex was filtered off, washed with methanol and dried *in vacuo* over silica gel. Yield 0.16 g (25%). Found: C, 36.6; H, 7.0; N, 7.2. Calc. for $C_{22}H_{52}N_4ZnCl_2O_{14}$: C, 36.0; H, 7.1; N, 7.6%.

$[NiL](ClO_4)_2 \cdot 2H_2O$

This complex was prepared essentially as described above using nickel(II) perchlorate hexahydrate. Found: C, 36.2; H, 6.8; N, 7.6. Calc. for $C_{22}H_{52}N_4NiCl_2O_{14}$: C, 36.4; H, 7.2; N, 7.7%. The water content of the various complexes appears to depend critically on the degree of drying employed.

Kinetics

The formation kinetics of $[CuL]^{2+}$ were monitored at 290 nm using a Union Giken RA-401 stopped flow spectrophotometer. The ionic strength was adjusted to 1 mol dm^{-3} using $NaClO_4$. Solutions of the ligand were standardized by titration against standard sodium hydroxide solution after addition of 4 equiv. of acid. The stock solution of sodium hydroxide was prepared from ampoules (Titrasol, Merck) and stored in a Nalgene Teflon bottle. Copper(II) perchlorate hexahydrate was recrystallized from water. Solutions were standardized potentiometrically against EDTA using a copper selectrode.

The dissociation kinetics of $[CuL]^+$ were monitored at 636 nm by stopped flow methods. Perchloric acid solutions were employed at two ionic strengths, 1.0 mol dm^{-3} (adjusted with $NaClO_4$) and 2.0 mol dm^{-3} adjusted with NaCl.

Potentiometric measurements

The potentiometric measurements were made with a Radiometer Titralab system interfaced with an Elonex PC. The potentiometric data was processed using the SUPERQUAD program [7]. The pK values of the ligand L were obtained by potentiometric titration of the ligand (after addition of four equivalents of hydrochloric acid) with standard sodium hydroxide solution. Formation constants were determined by methods previously described in detail [8]. The electrode system was standardized prior to each titration in terms of the hydrogen ion concentration and the formation constants are expressed in concentration units. The β values are expressed in terms of l, m and h representing metal, ligand and proton, respectively. Typical concentrations of the ligand and metal (in a 1 : 1 molar ratio) were in the range 0.5×10^{-3}–1.0×10^{-3} mol dm^{-3}.

Physical measurements

Visible spectra were determined using a Perkin–Elmer Lambda 5 or Phillips 8256 spectrophotometer. Conductivity measurements were made using a PTI digital conductivity meter which was standardized using a 1×10^{-3} mol dm^{-3} solution of KCl ($\Lambda_M = 147$ S cm^2 mol^{-1} at 25°C). IR spectra were determined as KBr discs with a Perkin–Elmer FT instrument. ^{1}H NMR spectra were obtained at 300 MHz.

RESULTS AND DISCUSSION

The ligand *N,N′,N″,N‴*-tetrahydroxypropyl-1,4,8,11-tetra-azacyclotetradecane (L) is readily prepared by the reaction of propylene oxide with cyclam. The ligand has ν(OH) at 3405 cm^{-1} and no ν(NH) bands, indicating that alkylation of the four nitrogen centres has occurred. This observation is confirmed by the ^{1}H NMR spectrum in CD_3OCD_3 solvent. There are three multiplet signals at δ1.15(12H) due to the methyl groups, δ2.5 (28H) due to the CH_2 protons and δ3.70 (4H) due to the CH_2—CH_2—CH_2 protons of the cyclam ring.

The copper(II), nickel(II) and zinc(II) complexes were readily prepared as the perchlorate salts by reaction of the ligand with the appropriate metal perchlorate in ethanol solution. The copper(II) complex has λ_{max} 635 nm in aqueous solution and is a 2 : 1 electrolyte in nitromethane ($\Lambda_M = 180$ S cm^2 mol^{-1}) at 20°C. Addition of acid to an aqueous solution leads to rapid dissociation of the complex and the formation of the aquated copper(II) ion.

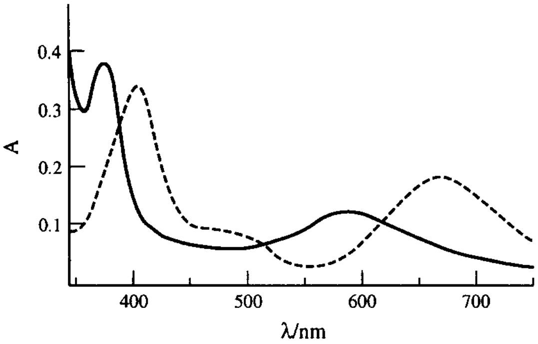


Fig. 1. The visible spectrum of the nickel(II) complex of THPC in aqueous solution (——) and after addition of two drops base (-----) showing deprotonation of the hydroxypropyl side arms.

The blue–turquoise nickel(II) complex has a typical octahedral spectrum with bands at 700 and 595 nm, Fig. 1. Dropwise addition of sodium hydroxide solution gave a bright green solution, indicative of stepwise deprotonation of the 2-hydroxypropyl side arms.

$$[NiL]^{2+} + OH^- \rightleftharpoons [NiLH_{-1}]^+ + H_2O$$

$$[NiLH_{-1}]^+ + OH^- \rightleftharpoons [NiLH_{-2}] + H_2O$$

Similar observations have been made with the $[Ni(THEC)]^{2+}$ complex [1]. Such deprotonations do not occur in the copper(II) complex.

Potentiometric studies

With copper(II) the potentiometric titration results can be fitted to the single equilibrium $Cu^{2+} + L \rightleftharpoons CuL^{2+}$ with $\log\beta_{110} = 15.54(3)$. In the case of nickel(II) deprotonation of the complex occurs

$$Ni^{2+} + L \rightleftharpoons [NiL]^{2+};\quad \log\beta_{110} = 7.32(3)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-1}]^+ + H^+;\quad \log\beta_{11-1} = -1.71(3)$$

$$Ni^{2+} + L \rightleftharpoons [NiLH_{-2}]^+ + H^+;\quad \log\beta_{11-2} = -12.62(4)$$

The $\beta_{l,m,h}$ values are the corresponding formation constants (where l is the stoichiometric coefficient of the ligand, m that of the metal and h that of the hydrogen ion in the complex). The pK_a values for the ionizations

$$[NiL]^{2+} \rightleftharpoons [NiLH_{-1}]^+ + H^+;\quad K'_a$$

$$[NiLH_{-1}]^+ \rightleftharpoons [NiLH_{-2}] + H^+;\quad K''_a$$

can be readily derived as $pK'_a = \log\beta_{110} - \log\beta_{11-1}$ and $pK''_a = \log\beta_{11-1} - \log\beta_{11-2}$, giving $pK'_a = 9.0$ and $pK''_a = 10.9$. These pK values relate to ionization of the two pendant hydroxyl groups in the nickel(II) complex and are consistent with the spectral changes observed on addition of base to an aqueous solution of the complex. It is noteworthy that the the formation constant log β_{110} for copper(II) with THPC is 15.5 compared with a value of *ca* 29 for cyclam. If we consider the equilibrium

$$Cu^{2+} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} CuL^{2+}; \quad \beta_{110}$$

the formation constant $\beta_{110} = k_f/k_d$, where k_f is the formation rate constant and k_d is the rate constant for dissociation of the metal complex. The large formation constant differences observed between cyclam and THPC are likely to arise due to the much faster dissociation rate of the THPC complex and this view is confirmed by the kinetic measurements described below.

Dissociation kinetics

Stopped flow studies of the acid dissociation of $[CuL]^{2+}$ in 0.05–1.0 mol dm^{-3} perchloric acid indicated a biphasic reaction. The first reaction, associated with an absorbance increase, was complete within 20–30 ms at 25°C and was too fast (k_{obs} *ca* 160 s^{-1}) to be studied in detail. This reaction is believed to be due to rapid protonation of the complex. The second reaction, associated with an absorbance decrease was acid dependent at low acidities and acid independent at high acidities. At constant hydrogen ion concentration the reaction is first order in the metal complex concentration. Values of k_{obs} at various acidities at 25°C and $I = 1.0$ mol dm^{-3} are summarized in Table 1.

Plots of k_{obs} *vs* the hydrogen ion concentration are curved, Fig. 2 indicating that the reaction is becoming independent of the hydrogen ion concentration at high acidities, Fig. 2. These observations are consistent with the reaction scheme

$$CuL^{2+} + H^+ \rightleftharpoons CuLH^{3+}; \quad K \qquad (1)$$

$$CuLH^{3+} \longrightarrow Cu^{2+} + LH^+; \quad k \qquad (2)$$

There is a rapid pre-equilibrium protonation, followed by slow rate-determining dissociation of the complex. Using eqs (1) and (2) it can be readily shown that

$$k_{obs} = kK[H^+]/(1 + K[H^+]).$$

Values of kK and K were obtained by curve fitting the data to the expression $k_{obs} = A[H^+]/(1 + B[H^+])$, giving $k = 7.1 \pm 0.4$ s^{-1} and $K = 1.3 \pm 0.1$ dm^3 mol^{-1} at $I = 1.0$ mol dm^{-3}. The equilibrium constant K indicates that the complex is *ca* 58% protonated at a hydrogen ion concentration of 1.0 mol dm^{-3}.

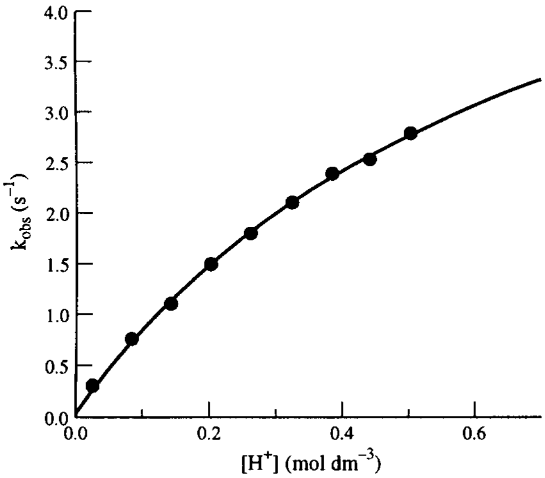


Fig. 2. Plot of k_{obs} *vs* $[H^+]$ for the acid dissociation of $[CuL^{2+}]$ in perchloric acid solution at $I = 1.0$ mol dm^{-3} ($HClO_4$ + NaCl) at 25°C. The solid points are the experimental values and the curve is calculated using the function $k_{obs} = A[H^+]/(1 + B[H^+])$ with $A = 9.5$ dm^3 mol^{-1} s^{-1} and $B = 1.4$ dm^3 mol^{-1}.

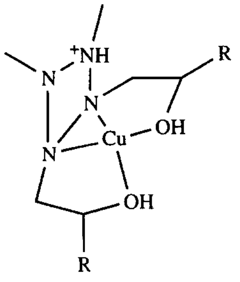
The half-lives of $[Cu(THPC)]^{2+}$ and $[Cu(THEC)]^{2+}$ in 0.05 mol dm^{-3} perchloric acid are 0.5 and 3.5 s at 25°C, respectively. The complex $[Cu(cyclam)]^{2+}$ does not dissociate over a period of weeks in 6 mol dm^{-3} hydrochloric acid [4]. The much more rapid reactions of the pendant arm complexes can possibly be rationalized in terms of stabilization of the intermediate species formed on protonation of a ring nitrogen by a molecular rearrangement in which two nitrogens and two pendant donor atoms bond to copper as shown in **III**.

Formation kinetics

The reaction of L with copper(II) in basic solution in the hydroxide concentration range 0.10–0.40 mol dm^{-3} was studied by stopped flow methods. The reactions were carried out using an excess of the ligand (at least 13 fold) so that first-order conditions applied.

Table 1. Rate constants k_{obs} for the acid dissociation of $[CuL]^{2+}$ as a function of the hydrogen ion concentration at 25°, and $I = 1.0$ mol dm^{-3} ($HClO_4$ + NaCl)

$[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})	$[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})
At $I = 1.0$ mol dm^{-3} ($HClO_4$ + NaCl)			
0.025	0.30	0.322	2.10
0.084	0.75	0.382	2.40
0.144	1.10	0.440	2.55
0.203	1.50	0.500	2.80
0.263	1.80		



(III) R = Me or H

Some measurements were also carried out with the metal ion in excess. The rate constants k_{obs} obtained are summarized in Table 2. Plots of k_{obs} *vs* $[L_T]$, where L_T is the total ligand concentration are linear, Fig. 3, and the second-order rate constants k were obtained from the least squares slope of these plots, Table 3.

The pK values of L were determined by potentiometric titration giving for the equilibria

$$LH_4^{4+} \rightleftharpoons LH_3^{3+} + H^+ \quad pK_1 < 2$$

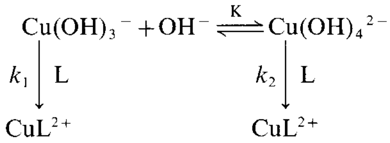
$$LH_3^{3+} \rightleftharpoons LH_2^{2+} + H^+ \quad pK_2 < 2$$

$$LH_2^{2+} \rightleftharpoons LH^+ + H^+ \quad pK_3\ 8.30$$

$$LH^+ \rightleftharpoons L + H^+ \quad pK_4\ 9.08$$

The ligand L is a much weaker base than cyclam, Table 4, and the free base form of the ligand is 100% abundant at pH 12.

Values of the second order rate constant k are dependent upon the hydroxide ion concentration due to the presence of both $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$ in basic solution. The reaction scheme can be summarized.



$$\begin{tikzcd} Cu(OH)_3^- + OH^- \arrow[r, "K", shift left] \arrow[d, "k_1"', "L"] & Cu(OH)_4^{2-} \arrow[l, shift left] \arrow[d, "k_2"', "L"] \\ CuL^{2+} & CuL^{2+} \end{tikzcd}$$

It can be readily shown that:

$$k(1+K[OH^-]) = k_1 + k_2K[OH^-].$$

A plot of $k(1+K[OH^-])$ *vs* $K[OH^-]$ should be linear of slope k_2 and intercept k_1. A typical plot is shown in Fig. 4, giving $k_1 = 3.7 \times 10^5$ and $k_2 = 2.1 \times 10^4$ dm^3 mol^{-1} s^{-1} at 25°C and $I = 1.0$ mol dm^{-3}. Values of K at the various hydroxide ion concentrations were obtained from published data [9]. Comparisons of the rate constants obtained with those available in the literature, Table 5 indicates that L reacts with $[Cu(OH)_3]^-$ some 10 times slower than does cyclam, but at a similar rate with $[Cu(OH)_4]^{2-}$.

The mechanisms of these reactions have been con-

Table 2. Observed first-order rate constants for the reaction of L with hydroxocuprate(II) species in basic solution at $I = 1.0$ mol dm^{-3} and 25°C

$[OH^-]$ (mol dm^{-3})	10^{-6} $[Cu^{2+}]_T$ (mol dm^{-3})	10^{-5} $[L]_T$ (mol dm^{-3})	k_{obs} (s^{-1})
0.10	7.5	10	14.5
0.10	7.5	15	23
0.10	7.5	20	29
0.10	7.5	25	38
0.10	7.5	30	45
0.15	7.5	10	14
0.15	7.5	15	20
0.15	7.5	20	25
0.15	7.5	25	34
0.15	7.5	30	41
0.225	7.5	10	9.5
0.225	7.5	15	15
0.225	7.5	20	20.5
0.225	7.5	25	26
0.225	7.5	30	31
0.30	7.5	10	9
0.30	7.5	15	12
0.30	7.5	20	16
0.30	7.5	25	21
0.30	7.5	30	25
0.40	7.5	10	6
0.40	7.5	15	10
0.40	7.5	20	14.5
0.40	7.5	25	17
0.40	7.5	30	20

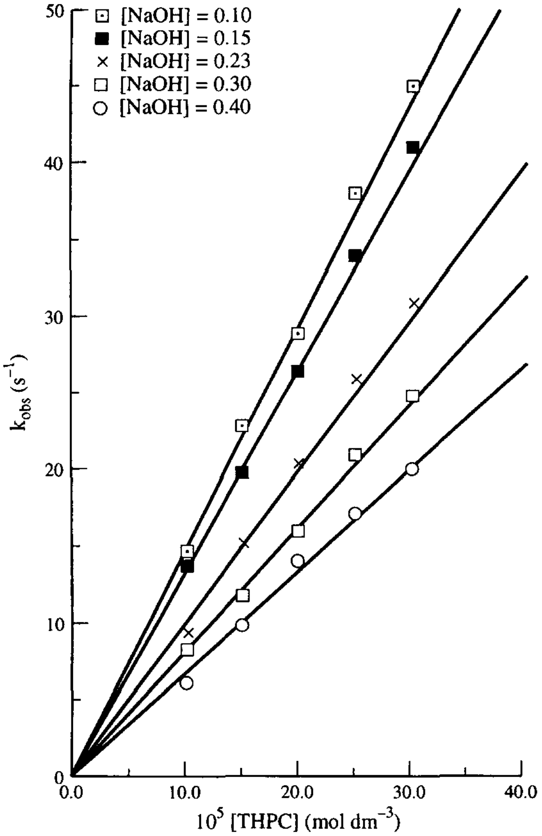


Fig. 3. Plots of k_{obs} *vs* the total ligand concentration [L_T] for the reaction of THPC with hydroxocuprate(II) complexes at various sodium hydroxide concentrations at 25°C and $I = 1.0$ mol dm^{-3} ($NaClO_4 + NaOH$).

sidered in detail by Margerum and co-workers [9]. The position of the rate-determining step is important in comparing the reactivities of closely related multidentate ligands with metal ions. For the ligands cyclam and 5,12-dimethyl cyclam, Jahn–Teller inversion following formation of the first copper–nitrogen bond is proposed as the rate-determining step in the reaction with $[Cu(OH)_3]^-$, while second copper–nitrogen bond formation is proposed as the rate-determining step with $[Cu(OH)_4]^{2-}$. A comparison of the rate constants, Table 5, suggests that a similar situation occurs with THPC.

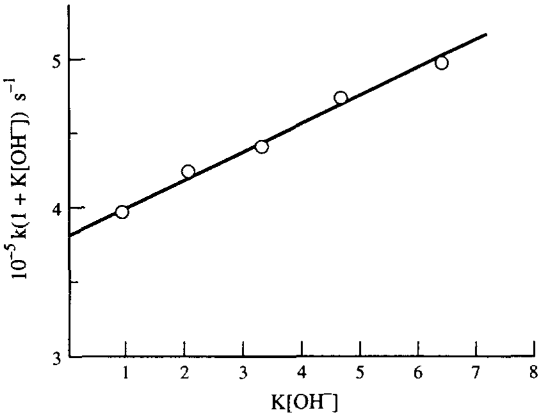


Fig. 4. Plot of $k(1 + K[OH^-])$ *vs* $K[OH^-]$ giving the resolved rate constants k_1 and k_2 at 25°C and $I = 1.0$ mol dm^{-3} for the reaction of THPC with $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$, respectively.

Table 4. The p*K* values of some 14-membered tetra-aza-macrocycles at 25°C

Ligand	pK_4	pK_3	pK_2	pK_1
cyclam	11.06	10.36	2	2
TMC	9.34	8.99	2.58	2.25
THEC	8.83	8.3	2.65	2
THPC	9.08	8.30	2	2

TMC = *N,N′,N″,N‴*-tetramethylcyclam, THEC = *N,N′,N″,N‴*-tetrahydroxyethylcyclam, THPC = *N,N′,N″,N‴*-tetrahydroxypropylcyclam.

Table 5. Resolved rate constants for the reaction of unprotonated macrocyclic tetra-amines with hydroxocuprate(II) species at 25°C

Ligand	$k_1{}^a$ (dm^3 mol^{-1} s^{-1})	$k_2{}^a$ (dm^3 mol^{-1} s^{-1})
Cyclam[b]	2.7×10^6	3.8×10^4
THPC(L)	3.7×10^5	2.1×10^4
Me_2Cyclam[b]	5.6×10^5	0.9×10^4
tet *a*[c]	10^4	10^2
tet *b*[d]	3.2×10^4	5.4×10^2

[a] The rate constant k_1 relates to the reaction of L with $[Cu(OH)_3]^-$ and k_2 to the reaction with $[Cu(OH)_4]^{2-}$.
[b] Reference [10].
[c] Reference [11].
[d] Reference [12].

Table 3. Second-order rate constants as a function of the hydroxide ion concentration for the reaction of L with hydroxocuprate(II) species in basic solution

$[OH^-]$ (mol dm^{-3})	$10^{-5}k$ (dm^3 mol^{-1} s^{-1})	$[OH^-]$ (mol dm^{-3})	$10^{-5}k$ (dm^3 mol^{-1} s^{-1})
0.10	1.69	0.30	0.83
0.15	1.35	0.40	0.68
0.225	1.01		

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