DALTON
FULL PAPER

Statistically controlled kinetics for the formation and decomposition of binuclear complexes of Cu^{II} with a large octaaza cryptand†

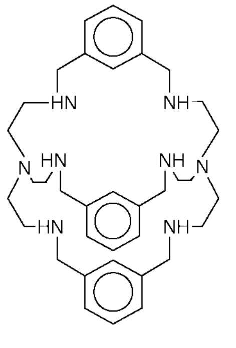
Manuel G. Basallote,* Joaquín Durán, M. Jesús Fernández-Trujillo and M. Angeles Máñez

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 Cádiz, Spain

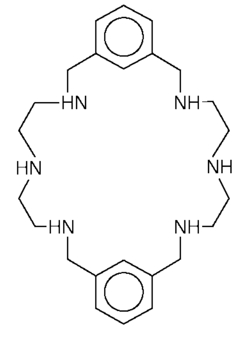
Received 26th July 1999, Accepted 21st September 1999

Kinetic studies have been made on the formation and decomposition of mono- and bi-nuclear copper(II) complexes with a symmetrical binucleating octaaza cryptand L containing two tris(2-aminoethyl)amine (tren) moieties bridged by three *m*-xylyl groups. The decomposition of binuclear Cu^{II}–L complexes upon addition of acid excess occurs with two separate kinetic steps; the rate constant for the faster step shows saturation behaviour, whereas a simple linear dependence on $[H^+]$ is observed for the slower step. Under similar conditions, the mononuclear complex also decomposes in two steps, with rate constants very close to those found for the binuclear species. The whole of the kinetic data for the acid-promoted decomposition of the mono- and bi-nuclear complexes indicates that the rate constants for the successive dissociation of both metal centres are statistically controlled, the value for the first Cu^{II} being twice as large as that corresponding to the second one. The second order rate constants for the formation of the mono- and bi-nuclear complexes have been determined in very basic solutions, and the rate of co-ordination of the first metal ion is also found to be double that of the second one, showing again statistically controlled kinetics. These results clearly indicate that both tren sub-units of L behave independently during complex formation and decomposition, *i.e.* there is no significant kinetic effect caused by the proximity of the metal centres and the cryptand is flexible enough to undergo rapidly any reorganisation required to accommodate them. The kinetic data for the formation and decomposition of these compounds are also compared with literature data for related complexes, and possible reaction mechanisms are discussed.

The chemistry of binuclear metal complexes is a continuously growing field because of their relevance to the function of many metalloenzymes[1] and the interest in determining the modifications in the properties of the complexes caused by the close proximity of two metal centres.[2] Binucleating polyaza macrocycles and cryptands, such as L and L′,[3,4] have cavities large enough to accommodate two metal ions, forcing them to be placed close to each other. The distance between the metal centres and the co-ordination environment about them can be changed by varying the nature of the macrocycle or by introducing exogenous bridging ligands. Metal complexes with this kind of ligands have been used in recent years to study molecular recognition,[5] catalytic processes[6] and the formation of dioxygen complexes.[7] Although there is a great amount of information available about the stability of the mono- and bi-nuclear complexes formed by this kind of ligands,[8] relatively little is known about their kinetics of formation and decomposition. We have previously shown that mono- and bi-nuclear copper(II) complexes of L′ are formed and decompose at very similar rates,[9,10] which suggests that L′ is flexible enough to make rapid any reorganisation of the macrocycle and that there is no significant effect of the first metal ion on the rate of co-ordination of the second one. It is expected that an increase in the steric requirements of the ligand, such as that caused by changing from macrocycle L′ to the cryptand L, could lead to a difference in the kinetics of co-ordination of both metal ions. For this reason we decided to study the kinetics of formation and decomposition of Cu^{II}–L cryptates. The results presented in this paper show that both tetraamine sub-units of L appear to behave independently and, as a consequence, the relative rates of co-ordination and release of both metal ions are statistically controlled.



L



L′

Experimental

The cryptand L was prepared as $C_{36}H_{54}N_8$·8HBr (L·8HBr) following the literature method,[3] and its purity checked by ^1H and ^{13}C-{^1H} NMR. The actual molecular weight of the sample was derived from the analysis of potentiometric curves. All other reagents were obtained from Aldrich and used without further purification. The UV-Vis and NMR spectra were recorded with a Perkin-Elmer Lambda 3B spectrophotometer and a Varian Unity 400 spectrometer, respectively. The pH readings were obtained with a Crison 2002 instrument provided with an Ingold combined electrode and calibrated according to the procedure recommended by Martell and Motekaitis.[11]

---

† *Supplementary data available*: stability constants and observed rate constants. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3817/, otherwise available from BLDSC (No. SUP 57648, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

This journal is © The Royal Society of Chemistry 1999

Equilibrium determinations

All the potentiometric titrations were carried out in 0.10 mol dm^{-3} KNO_3 solutions at 25.0 °C under N_2, and were analysed with the program BEST;[11] the species distribution curves were obtained with programs SPE and SPEPLOT.[11] The protonation constants of the ligand were determined from potentiometric titration of L·8HBr (*ca.* 2×10^{-3} mol dm^{-3}) in 0.10 mol dm^{-3} KNO_3. The analysis of the ligand titration data also yielded a molecular weight of 1330 for our sample. This value suggests a composition similar to that previously found[3] and was used to determine the ligand concentration in the solutions required for the kinetic work. The formation constants of the mono- and bi-nuclear copper(II) complexes were determined from titrations of solutions containing Cu^{II} and L at 1 : 1 and 2 : 1 molar ratios; during the analysis of these curves the ligand protonation constants were fixed at the previously determined values. All the curves were analysed assuming a fixed value of 13.78 for pK_w. The number of data points measured was different for each titration but there were typically 10 points for each neutralisation of a proton, covering a pH range from *ca.* 3 to 11.

Kinetic experiments

All the experiments were carried out at 25.0 °C with an Applied Photophysics SX-17MV stopped-flow instrument; the ionic strength of the solution was adjusted to the desired value (0.1 or 1.0 mol dm^{-3}) by adding the amount of KNO_3 required. All experiments were carried out under pseudo-first order conditions, and the actual concentrations of the reagents are given in SUP 57648. The wavelength was selected in each case from preliminary spectral scanning experiments using a diode-array detector; this procedure was also used in some cases to obtain the kinetic data for the acid-promoted decomposition of the complexes. Single-wavelength curves were fitted using the standard software of the instrument, and the diode-array data were analysed with the program GLINT.[12] Reported values of the rate constants correspond to the mean values for at least five determinations. The kinetics of the acid-promoted decomposition of the complexes was studied by mixing a solution of the complex at a given pH with another solution containing a large excess of HNO_3. The kinetics of complex formation in basic solutions was studied by mixing solutions of Cu^{II} and L containing in both cases the required amounts of KOH and KNO_3.

Results

The structure of cryptand L allows the simultaneous co-ordination of two metal ions to yield stable binuclear complexes in which every metal centre is co-ordinated to the four nitrogens of one tren sub-unit, the co-ordination sphere being completed with exogenous ligands such as H_2O or OH^-.[3] The values of the stability constants for the protonation of L and the formation of L–Cu^{II} complexes are very similar to those previously found by Martell and co-workers,[3] and both sets of data are given in SUP 57648. The species distribution curves in Fig. 1 show the high stability of $Cu_2L(OH)^{3+}$ that is the only species present in solutions containing Cu^{II} and L in 2 : 1 molar ratio when the pH is higher than *ca.* 6.5. Significant amounts of Cu_2L^{4+} and H_3CuL^{5+} are also formed within a narrow pH range (4–6), whereas the only species present in more acidic solutions are Cu^{2+} and the highly protonated forms of the ligand.

Kinetics of decomposition of Cu^{II}–L complexes in acid solutions

The equilibrium curves in Fig. 1 show that addition of a large excess of acid to solutions containing Cu^{II}–L complexes will cause complete dissociation of the ligand to form Cu^{2+} and H_6L^{6+}. If the pH of the starting solution is higher than 6.5 the net reaction will be decomposition of $Cu_2L(OH)^{3+}$, eqn. (1),

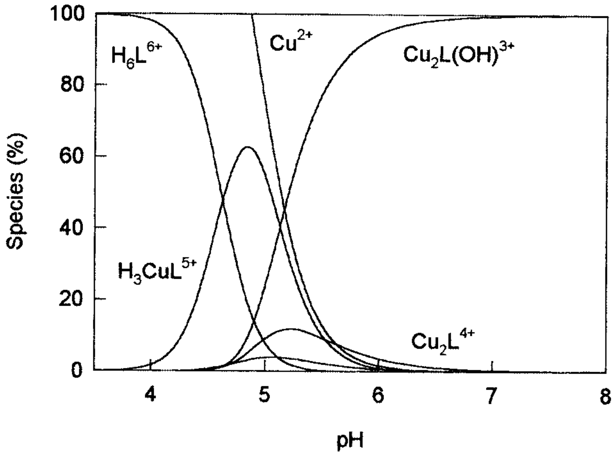


Fig. 1 Species distribution curves for solutions containing L and Cu^{II} in 1 : 2 molar ratio ($[L]_0 = 2 \times 10^{-3}$ mol dm^{-3}, 0.10 mol dm^{-3} KNO_3, 25.0 °C).

$$Cu_2L(OH)^{3+} + H^+_{exc} \longrightarrow Cu^{2+} + H_xL^{x+} \qquad (1)$$

but when the initial pH is close to 4.5 the process corresponds to the decomposition of H_3CuL^{5+}, eqn. (2), that is the only

$$H_3CuL^{5+} + H^+_{exc} \longrightarrow Cu^{2+} + H_xL^{x+} \qquad (2)$$

complex in solution under those conditions. Thus, a simple change in the pH of the starting solution allows a comparative kinetic study of the processes represented by eqns. (1) and (2) and should provide valuable information about the similarities or differences in the kinetics of decomposition of the mono- and bi-nuclear complexes of cryptand L.

We initially tried kinetic experiments in solutions containing a concentration of supporting electrolyte of 1.0 mol dm^{-3} (KNO_3 + HNO_3), but had to decrease it to 0.10 mol dm^{-3} because of precipitation in the stock solutions at pH higher than 6. Although the concentrations of acid are limited by the reduced ionic strength, subsequent kinetic experiments showed that reactions (1) and (2) occur to completion even at the lowest $[H^+]$ used. The electronic spectra of stock solutions containing 2 equivalents of Cu^{II} and 1 equivalent of L ($[L]_0 = 3.4 \times 10^{-4}$ mol dm^{-3}) are featureless at pH lower than 4, but two bands centred at 310 and 820 nm appear when the pH is increased to values corresponding to complex formation, showing that Cu^{II}–L complexes have molar absorptivities much higher than those of Cu^{2+}. Both bands have essentially the same shape at all pH values higher than 4.5, but the absorbance is higher in basic solutions, consistent with formation of a binuclear complex containing two chromophores. The decomposition of Cu^{II}–L complexes upon addition of acid in excess occurs on the stopped-flow timescale under all the conditions studied. Nevertheless, although both bands disappear at similar rates, a careful analysis of the data indicates that complex decomposition occurs with biphasic kinetics, the absorbance decrease being faster at 820 than at 310 nm. The values of the rate constants corresponding to both steps can be obtained by fitting the traces at 820 nm by a single exponential (k_{1obs}) and the traces at 310 nm by two consecutive exponentials (k_{1obs} and k_{2obs}). In those cases where the two constants are close to each other, a better estimation of k_{2obs} is obtained from the fit of traces at 310 nm by two exponentials with k_{1obs} fixed at the value derived from the corresponding trace at 820 nm. Alternatively, the values of k_{1obs} and k_{2obs} can be obtained from the fit of the diode-array data using the program GLINT; in this case the kinetic model consists of two consecutive irreversible reactions and the program also calculates the spectra of the absorbing species in the reaction mixture. In most cases we carried out fixed wavelength and diode-array experiments, and the results

Table 1 Summary of kinetic data for the acid-promoted decomposition of mono- and bi-nuclear copper(II) complexes of L at 25.0 °C. The values of the parameters a and b were obtained by fitting k_{1obs} and k_{2obs} data in SUP 57648 using eqn. (3) in the text[a]

	k_{1obs}		k_{2obs}		
Starting conditions[b]	$10^{-2}\,a_1$/s^{-1}	b_1/dm^3 mol^{-1}	$10^{-2}\,a_2$/s^{-1}	b_2/dm^3 mol^{-1}	$10^{-2}\,a_2b_2$/dm^3 mol^{-1} s^{-1}
1.0, 4.88	3.8(2)	18(2)	0.30(1)	28(5)	
0.1, 4.71	3.6(1)	43(2)	0.26(1)	37(4)	
0.1, 4.27	3.7(1)	37(3)	0.29(1)	35(3)	
0.1, 8.73	2(1)	6(4)			1.2(1)
0.1, 8.26	2(1)	4(3)			0.80(4)
0.1, 7.10	1.7(6)	5(2)			1.6(2)

[a] The numbers in parentheses represent the standard deviations in the last significant digit. [b] Concentration of supporting electrolyte (in mol dm^{-3}) followed by the pH of the complex solution before addition of the acid excess.

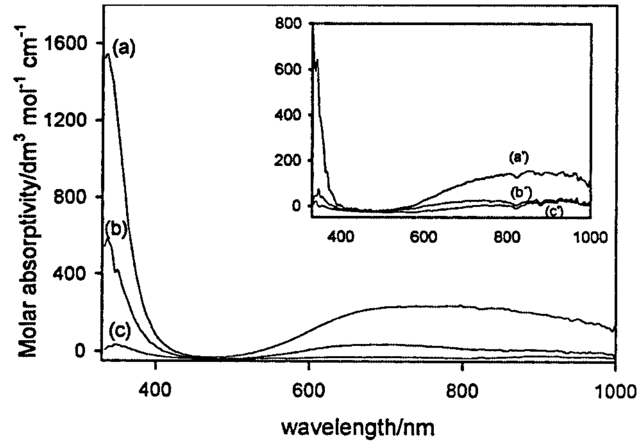


Fig. 2 Calculated absorption spectra for the starting complex (a), the reaction intermediate (b), and the final product (c) in the acid-promoted decomposition of the binuclear $Cu_2L(OH)^{3+}$ complex. The inset shows the corresponding spectra (a′, b′, c′) for the decomposition of the mononuclear complex.

obtained with the two procedures are in good agreement except for those cases in which k_{1obs} is so high that the number of spectra recorded during the first step is too small. In the latter cases diode-array data do not lead to reliable values of k_{1obs} and the results were derived exclusively from fixed wavelength experiments; otherwise both methods were indistinctly used to obtain the values of the rate constants included in SUP 57648.

The spectra calculated for $Cu_2L(OH)^{3+}$, the reaction intermediate and the final decomposition product are included in Fig. 2, and the inset shows the corresponding spectra for the mononuclear species H_3CuL^{5+}. As the formation of the mononuclear complex is never complete, the absolute values of the molar absorptivity were obtained using the concentration calculated with the program SPE and so they are only approximate. The spectra in Fig. 2 show that the absorbance changes during the decomposition of the mono- and the bi-nuclear complexes are very similar, the absolute values being approximately twice as large for the binuclear species. The spectra also suggest that the chromophores in the binuclear complex behave almost independently and that structural changes during the decomposition process are similar for both the mono- and the bi-nuclear species. On the other hand, the values of k_{1obs} and k_{2obs} in SUP 57648 indicate that the rates of decomposition of the mono- and the bi-nuclear complexes are very close, as previously found for the closely related Cu^{II}–L′ complexes.[9] In that case the diode-array instrumentation was not available and the kinetics was monitored by following the exponential decay of a band at 650 nm. The similar values of k_{obs} under all conditions were interpreted assuming rapid conversion (within the stopped-flow mixing time) of the binuclear complex to the mononuclear species followed by rate-determining decomposition of the mononuclear complex.[9] The results now

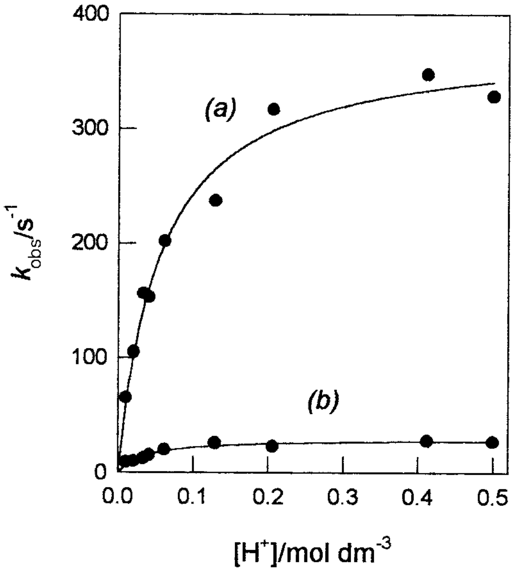


Fig. 3 Plots of the observed rate constant *vs.* the concentration of acid for the acid-promoted decomposition of the mononuclear Cu^{II}–L complex ($[Cu]_0 = [L]_0 = 3.38 \times 10^{-4}$ mol dm^{-3}, pH 4.88, 25.0 °C, 1.0 mol dm^{-3} KNO_3). Curves (*a*) and (*b*) correspond to k_{1obs} and k_{2obs}, respectively.

available clearly demonstrate that this interpretation is not valid, at least for the Cu^{II}–L complexes, and we are currently re-examining the kinetics of the previously reported system.

The dependence of the observed rate constants on the acid concentration is illustrated in Fig. 3. There is in general a tendency of k_{1obs} and k_{2obs} to saturation that is especially evident for the decomposition of the mononuclear complex using 1.0 mol dm^{-3} ionic strength. In other cases the observed rate constants do not approach the limiting value but there is a clear curvature in the plot and the data can be fitted by eqn. (3) to

$$k_{obs} = \frac{ab[H^+]}{1 + b[H^+]} \qquad (3)$$

obtain the values of parameters a and b in Table 1. The values of both parameters agree within error for experiments corresponding to the decomposition of the same complex (pH close to 4.5 and 7.5 for the mono- and the bi-nuclear complexes, respectively). The a_1 values are always within the range $(1\text{–}4) \times 10^2$ s^{-1}, an order of magnitude faster than for the second step, and there are no large differences between the values corresponding to the mono- and the bi-nuclear complexes. On the contrary, b_1 values for the decomposition of the binuclear complex are significantly smaller than for the mononuclear species. For the case of k_{2obs} values corresponding to decomposition of the binuclear complex (starting pH higher than 6), the value of b is not well defined and the data were fitted by a straight line, the slope being presented in Table 1 as $a \times b$. In any case, the values of this product are compatible with a values similar to those derived for the second step of the mononuclear species (25–30 s^{-1}) and values of b close to those found for the first step of the mononuclear complex (*ca.* 5 $dm^3\ mol^{-1}$).

Kinetics of formation of the mono- and bi-nuclear Cu^{II}–L complexes

The major problem for studying the kinetics of complex formation with this kind of ligand is the large number of species involved, although the analysis of kinetic data is facilitated by the use of appropriate pH ranges. The major simplification occurs at very high pH, where L is completely deprotonated and Cu^{II} exists as a mixture of $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$; kinetic data at varying concentrations of OH^- usually allow one to separate the contributions from both hydroxo-complexes to the rate of complex formation. For the case of copper(II) complexes with the cryptand L there is an additional complication caused by the formation of mono- and bi-nuclear complexes, eqns. (4) and (5), although this can easily be solved by carrying out

$$Cu(OH)_x^{(x-2)-} + L \rightleftharpoons CuL(OH)^+ + (x-1)\,OH^- \quad (4)$$

$$Cu(OH)_x^{(x-2)-} + CuL(OH)^+ \rightleftharpoons Cu_2L(OH)^{3+} + x\,OH^- \quad (5)$$

kinetic experiments in the presence of both an excess and deficit of Cu^{II}. If there is an excess of metal, reactions (4) and (5) are displaced towards formation of the binuclear complex and kinetic traces include contributions from the co-ordination of both metal centres. On the contrary, only mononuclear complexes are formed if there is a deficit of Cu^{II}, and kinetic traces under these conditions correspond exclusively to the formation of the mononuclear complex.

Although we tried kinetic experiments on complex formation in basic solutions using the diode-array detector for monitoring the reaction under conditions of both an excess and a deficit of Cu^{II}, the process had to be studied at 260 nm using low concentrations of the reagents to avoid precipitation. Kinetic traces obtained at fixed OH^- concentration under pseudo-first order conditions of ligand or metal excess could always be fitted well by a single exponential, and the values of the observed rate constant are given in SUP 57648.

In the presence of ligand excess only the mononuclear complex is formed and the values of k_{obs} correspond to reaction (4). The dependence of k_{obs} on the ligand concentration is linear (see Fig. 4), and the values derived for the second order rate constant (k_{fm}) at several concentrations of OH^- are included in Table 2. There is a decrease of k_{fm} when the OH^- concentration is increased, and the data can be fitted by eqn. (6) with $c = 1.4 \pm 0.3 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ and $d = 4 \pm 2\ dm^3\ mol^{-1}$.

$$k_{fm} = \frac{c}{1 + d[OH^-]} \quad (6)$$

Although experiments using an excess of Cu^{II} lead to formation of the binuclear complex according to eqns. (4) and (5), kinetic traces show a single step with k_{obs} values close to those corresponding to the formation of the mononuclear complex. However, k_{obs} for the binuclear complex is slightly smaller than for the mononuclear complex, which indicates that formation of both complexes occurs on the same timescale and kinetic traces under conditions of metal excess must include the effect of co-ordination of both metal ions. Another important difference is that the dependence of k_{obs} on the copper(II) concentration is given now by eqn. (7) (see Fig. 4). The values of k_{fb}

$$k_{obs} = k_{fb}[Cu]_0 + k_{db} \quad (7)$$

and k_{db} are also included in Table 2, k_{fm} being approximately twice as large as k_{fb} for a given OH^- concentration.

Table 2 Summary of kinetic data for the formation of mono- and bi-nuclear copper(II) complexes of L in basic solutions at 25.0 °C. The values of k_{fm} correspond to the second order rate constant for the irreversible formation of the mononuclear complex, whereas k_{fb} and k_{db} correspond to the rate constants for the formation and decomposition of the binuclear complex[a]

$[OH^-]$/ $mol\ dm^{-3}$	$10^{-3}\ k_{fm}$/ $dm^3\ mol^{-1}\ s^{-1}$	$10^{-3}\ k_{fb}$/ $dm^3\ mol^{-1}\ s^{-1}$	k_{db}/s^{-1}
0.15	8.5(2)		
0.22	8.3(2)	3.1(2)	0.54(6)
0.25	8.0(1)		
0.35	6.5(2)	2.8(1)	0.44(2)
0.44	4.6(2)	2.2(2)	0.25(7)

[a] The numbers in parentheses represent the standard deviations in the last significant digit.

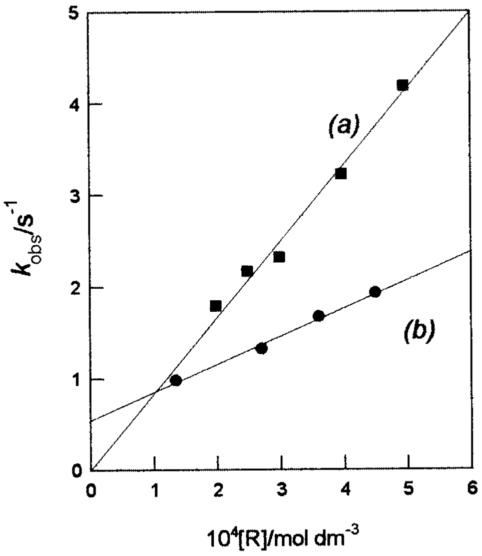


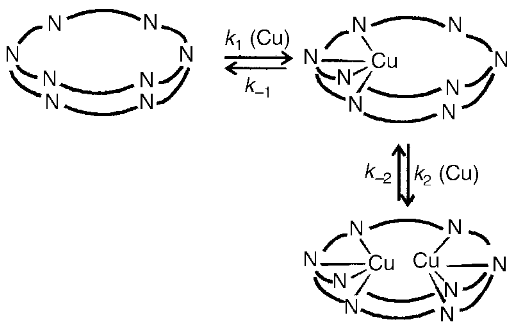
Fig. 4 Plots of the observed rate constant *vs.* the concentration of the reagent in excess for the formation of Cu^{II}–L complexes in 0.44 mol dm^{-3} KOH solution at 25.0 °C. The data in (*a*) correspond to ligand excess (R = L, $[Cu]_0 = 2.2 \times 10^{-5}\ mol\ dm^{-3}$), whereas data in (*b*) correspond to metal excess (R = Cu, $[L]_0 = 1.0 \times 10^{-5}\ mol\ dm^{-3}$).

The non-zero intercept in eqn. (7) suggests that formation of the binuclear complex is reversible under the experimental conditions used. We were initially surprised to find that conversion into the binuclear complex is incomplete in the presence of metal excess and so carried out approximate equilibrium calculations with the program SPE. These calculations confirmed that conversion into the mononuclear complex is complete in the presence of ligand excess, but an equilibrium mixture of L and the mono- and bi-nuclear complexes is formed at the concentrations of the kinetic experiments using metal excess. Thus, eqns. (4) and (5) are displaced to the left at very high concentrations of OH^- and k_{obs} includes contributions from both the formation (k_{fb}) and decomposition (k_{db}) of the binuclear complex.

Discussion

Statistical considerations

The reversible formation of binuclear copper(II) complexes with cryptand L is represented in a very simplified way in Scheme 1. It shows clearly that the relative values of the rate constants for complex formation (k_1 and k_2) or decomposition (k_{-1} and k_{-2}) will depend on the degree of interaction between both metal centres. It is expected from statistical considerations that



Scheme 1

$k_1 = 2\ k_2$ and $k_{-2} = 2\ k_{-1}$ if both N_4-donor sub-units behave independently and the cryptand is flexible enough to reorganise rapidly. Nevertheless, slow reorganisation of the ligand or a certain interaction between the metal centres (steric or electronic, direct or facilitated by the presence or the absence of a bridging ligand) can lead to relative values of the rate constants that differ from the statistical prediction.

The results in the present work indicate that both the formation of the binuclear complex in very basic media and its decomposition in strongly acidic solution occur with a kinetics similar to that of the mononuclear complex, the values of the rate constants being always close to each other. The absence of separate kinetic steps for the co-ordination or release of both metal centres suggests that formation and decomposition of the binuclear complex occurs in an apparent single process because of a simplification of the rate law caused by a certain correlation between rate constants and molar absorptivities. This simplification of the kinetics can be theoretically predicted and has been previously observed for other systems containing several isolated and independently reacting centres.[13–16] The decomposition of the binuclear complex upon addition of a large excess of acid is irreversible and must involve the formation of a mononuclear intermediate. The process should then occur with biphasic kinetics, that reduces to a single step with $k_{\mathrm{obs}} = k_{-1}$ when the rate constants and molar absorptivities obey eqn. (8).[13,14] Actually, the spectra of the species derived

$$\frac{k_{-2}}{k_{-1}} = \frac{\varepsilon_{\mathrm{Cu_2L}} - \varepsilon_{\mathrm{Cu}}}{\varepsilon_{\mathrm{Cu_2L}} - \varepsilon_{\mathrm{CuL}}} \qquad (8)$$

from the mononuclear complex (Fig. 2, inset) are intermediate between those of $\mathrm{Cu^{II}}$ and the binuclear complex, which means that $\varepsilon_{\mathrm{CuL}} \approx (\varepsilon_{\mathrm{Cu}} + \varepsilon_{\mathrm{Cu_2L}})/2$ for both steps in the decomposition. Substitution into eqn. (8) leads to $k_{-2}/k_{-1} \approx 2$; *i.e.* the decomposition of the binuclear complex occurs with rate constants close to the statistical prediction.

On the other hand, the data in Table 2 indicate that the quotient $k_{\mathrm{fm}}/k_{\mathrm{fb}}$ is only slightly higher than 2, which suggests that complex formation is also statistically controlled. However, eqn. (8) cannot be invoked to explain the appearance of a single kinetic step in the formation of the binuclear complex because this equation is derived for two irreversible consecutive reactions,[13,14] and complex formation in basic media occurs under reversible conditions. Nevertheless, statistically controlled kinetics has previously been observed for other reversible reactions,[15] and it can easily be demonstrated that kinetic traces for a reaction sequence of the type $\mathrm{A} \underset{k_{-1}}{\overset{2k_2}{\rightleftharpoons}} \mathrm{B} \underset{2k_{-1}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}$ are biphasic with rate constants $k_{-1} + k_2$ and $2(k_{-1} + k_2)$ but simplify to a single exponential with $k_{\mathrm{obs}} = k_{-1} + k_2$ when $\varepsilon_{\mathrm{B}} = (\varepsilon_{\mathrm{A}} + \varepsilon_{\mathrm{C}})/2$. If some of the steps are second order processes, the corresponding pseudo-first order rate constants must be used and, for the case of the $\mathrm{Cu^{II}}$–L complexes, the condition for the observation of a single kinetic step is also $\varepsilon_{\mathrm{CuL}} \approx (\varepsilon_{\mathrm{Cu}} + \varepsilon_{\mathrm{Cu_2L}})/2$.

Thus, comments in previous paragraphs indicate that, despite the fact that the co-ordination and release of each metal centre are not simple processes, the reactions in Scheme 1 occur with relative values of the rate constants close to the statistical prediction. Each step in Scheme 1 involves reorganisation of the cryptand and the formation (or breaking) of four Cu–N bonds; for the case of the binuclear complex there is an additional step corresponding to the formation or rupture of a hydroxo bridge. It appears that the cryptand is large and flexible enough to allow the independent accommodation of both metal centres into the N_4 sub-units and that formation of a hydroxo bridge between them does not change the statistical ratio of rate constants for complex formation or dissociation.

Mechanistic considerations and comparison with related complexes

Acid-promoted decomposition of the mono- and bi-nuclear $\mathrm{Cu^{II}}$–L complexes. The literature includes a large variety of rate laws for the acid-promoted decomposition of metal complexes containing polydentate ligands in which the dependence on the acid concentration goes from simple linear to polynomial passing by the saturation kinetics represented by eqn. (3) and related equations. Although there are alternative interpretations,[17] the observation of saturation kinetics for the decomposition of linear and macrocyclic polyamine complexes is usually interpreted in terms of rate-limiting acid attack on an activated form of the metal complex: $\mathrm{ML} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{ML})^* \xrightarrow[k_2]{\mathrm{H}^+} \mathrm{M} + \mathrm{HL}^+$. The activated intermediate is considered to form through the partial breaking of the Cu–N bond, with proton attack at the amine nitrogen occurring prior to or during solvent replacement of the donor.[18] The rate equation for this mechanism coincides with eqn. (3) when the intermediate $(\mathrm{ML})^*$ is assumed to be formed under steady state conditions; the limiting rate constant a then corresponds to k_1 and b is equivalent to the quotient k_2/k_{-1}. The values of a_1 and b_1 in Table 1 for the decomposition of the mono- and the bi-nuclear $\mathrm{Cu^{II}}$–L complexes are close to each other and also close to those found previously for copper(II) complexes of the macrocycle L′.[9] Although the different rate laws prevent comparison with other complexes, the rate of decomposition appears to be little affected by the co-ordination environment about the metal centre; on the contrary, it is strongly dependent on the type of chelate rings formed. For example, $\mathrm{Cu(en)^{2+}}$ decomposes with saturation kinetics and values of $a = 1.3 \times 10^2\ \mathrm{s^{-1}}$ and $b = 33\ \mathrm{dm^3\ mol^{-1}}$; the complexes $\mathrm{Cu(dien)^{2+}}$, $\mathrm{Cu(trien)^{2+}}$ and $\mathrm{Cu(tren)^{2+}}$,‡ that only contain en-type chelate rings, show a similar kinetic behaviour with relatively small changes in the values of a and b.[19] Nevertheless, a substantial decrease in the rate of decomposition is observed when the complex contains some chelate rings of larger size and, for example, the product ab decreases to $0.08\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for $\mathrm{Cu(2,3,2\text{-}tet)^{2+}}$ and to $0.49\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for $\mathrm{Cu(3,3,3\text{-}tet)^{2+}}$.[20] A decrease of the decomposition rate is also observed for the complexes of mono-nucleating polyaza macrocyclic ligands, although the effect is less pronounced than that caused by the change in the type of chelate rings. Thus, macrocyclic complexes such as $\mathrm{Cu([9]aneN_3)^{2+}}$ and $\mathrm{Cu([18]aneN_6)^{2+}}$, that only contain ethylene bridges between the N donors, show a modest decrease

---

‡ Ligand abbreviations: en = ethylenediamine; dien = diethylenetriamine; trien = triethylenetetraamine; tren = tris(2-aminoethyl)amine; 2,3,2-tet = 3,7-diazanonane-1,11-diamine; 3,3,3-tet = 4,8-diazaundecane-1,11-diamine; [9]aneN$_3$ = 1,4,7-triazacyclononane; [18]aneN$_6$ = 1,4,7,10,13,16-hexaazacyclooctadecane; [13]aneN$_4$ = 1,4,7,10-tetraazacyclotridecane; cyclam = 1,4,8,11-tetraazacyclotetradecane; Me$_4$trien = *N,N,N‴,N‴*-tetramethyl-3,6-diazaoctane-1,8-diamine; Et$_2$-2,3,2-tet = 3,6,10,13-tetraazapentadecane; tet-b = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $2_{\mathrm{N}}.1_{\mathrm{O}}.1_{\mathrm{O}}$ = 13,18-dioxa-1,4,7,10-tetraazabicyclo[8.5.5]eicosane.

in the rate of decomposition, with $a = 40$ s^{-1} and $b = 1.3$ dm^3 mol^{-1} for the former complex[19] and $ab = 70$ dm^3 mol^{-1} s^{-1} for the latter.[21] On the contrary, macrocyclic complexes in which not all the amine nitrogens are linked by ethylene bridges tend to decompose more slowly; for example, $ab = 8 \times 10^{-4}$ and 3×10^{-4} dm^3 mol^{-1} s^{-1} for Cu([13]aneN$_4$)$^{2+}$ and Cu(cyclam)$^{2+}$ respectively.[22,23] It is important to note that the values of a_1 and b_1 found in this work for both the mono- and the bi-nuclear copper(II) complexes of L are very close to those reported for Cu(tren)$^{2+}$ ($a = 4.9 \times 10^2$ s^{-1} and $b = 4.6$ dm^3 mol^{-1}),[19] which suggests again an independent behaviour of the N$_4$-donor sub-units of the binucleating cryptand.

Despite the existence of several metal–ligand bonds susceptible to proton attack, polyphasic kinetics has only been observed for the decomposition of a relatively small number of complexes with polydentate ligands,[19,23] although it is possible that polyphasic kinetics has inadvertently been ignored in some cases because of the good fit of single wavelength traces by a single exponential. Interestingly, two different kinetic steps are also observed in the decomposition of Cu(tren)$^{2+}$,[19] the rate constant for the slow step being close to the values found in this work for the Cu^{II}–L complexes. Although the data for Cu(tren)$^{2+}$ were interpreted in terms of two different reaction pathways leading to decomposition,[19] our global analysis of the time dependence of the spectral data for Cu^{II}–L complexes suggests that complete decomposition of these compounds occurs in two consecutive steps. The first step occurs at a rate similar to that of complexes with other polyamines and leads to an intermediate in which the co-ordination environment about Cu^{II} appears to be drastically changed. Actually, while the spectra in Fig. 2 for both the mono- and the bi-nuclear complexes are similar to those of Cu(tren)(H$_2$O)$^{2+}$ and related complexes with trigonal bipyramidal (*TBPY*) co-ordination,[24] the spectra of the intermediates have much lower molar absorptivities in the visible and they are closer to the spectrum of Cu(H$_2$O)$_6$$^{2+}$. It is possible that the first kinetic step corresponds to the dissociation of the co-ordinated NH groups of L at a rate similar to that observed for other complexes with Cu^{II}–NH (polyamine) bonds; in the absence of a co-ordinated tren sub-unit, there is no reason for a *TBPY* co-ordination in the intermediate formed in the first step and the complex reorganises to a new co-ordination environment.

The formation of mono- and bi-nuclear copper(II) complexes of L in basic media. It has been pointed out above that Cu^{II} exists at very high pH as a mixture of Cu(OH)$_3$$^-$ and Cu(OH)$_4$$^{2-}$, whereas the ligand is completely deprotonated. The formation of the mononuclear complex under these conditions can be considered to occur through the mechanism in eqns. (9)–(11),

$$\mathrm{Cu(OH)_3^-} + \mathrm{OH^-} \overset{K_{\mathrm{OH}}}{\rightleftharpoons} \mathrm{Cu(OH)_4^{2-}} \qquad (9)$$

$$\mathrm{Cu(OH)_3^-} + \mathrm{L} \xrightarrow{k_3} \mathrm{CuL(OH)^+} + 2\,\mathrm{OH^-} \qquad (10)$$

$$\mathrm{Cu(OH)_4^{2-}} + \mathrm{L} \xrightarrow{k_4} \mathrm{CuL(OH)^+} + 3\,\mathrm{OH^-} \qquad (11)$$

that has been previously proposed for other copper complexes.[9,25–28] The formation of the binuclear complex will go through the same mechanism, although with different rate constants for statistical reasons (see above).

The rate equation (12) for this mechanism is similar to the

$$k_{\mathrm{f}} = \frac{k_3 + k_4 K_{\mathrm{OH}}[\mathrm{OH^-}]}{1 + K_{\mathrm{OH}}[\mathrm{OH^-}]} \qquad (12)$$

experimental one, eqn. (6), with the equivalencies: $k_3 = c = (1.4 \pm 0.3) \times 10^4$ dm^3 mol^{-1} s^{-1} and $K_{\mathrm{OH}} = d = 4 \pm 2$ dm^3 mol^{-1}, k_4 being negligible. These results indicate that formation of Cu^{II}–L complexes occurs almost exclusively through reaction of Cu(OH)$_3$$^-$, in agreement with previous findings for the related macrocycle L′, for which complex formation from Cu(OH)$_4$$^{2-}$ is more than two orders of magnitude slower;[9] a very different reactivity of both hydroxo-complexes is considered evidence of a change in the rate-determining step for complex formation from both species.[25,26] The value derived for K_{OH} in the present work is also in good agreement with those previously reported.[9,27]

Although copper(II) complexes with the ligands L and L′ decompose at similar rates upon addition of acid excess, the rate constants for complex formation in basic solutions are quite different, k_3 for the formation of the cryptate CuL(OH)$^+$ being two orders of magnitude smaller than for the related macrocycle L′ ($k_3 = 2.2 \times 10^6$ dm^3 mol^{-1} s^{-1}).[9] The intimate mechanism of complex formation is very difficult to determine because of the existence of several N-co-ordination and Jahn–Teller inversion steps.[25] It has been previously proposed that if Jahn–Teller inversion following first-bond formation is the rate-determining step in the formation of open-chain and macrocyclic polyamine complexes, a certain difference between the values of k_3 may be attributed to steric effects of nitrogen substitution. However, if the experimental value of k_3 is much lower than expected on the basis of this substitution, it may indicate a shift in the rate-determining step to second-bond formation or the subsequent inversion process.[26] The value of k_3 for the complex of macrocycle L′ is very close to the values for complexes with other polyamines of similar steric requirements, such as Me$_4$trien or Et$_2$-2,3,2-tet,[26,27] which suggests rate-determining Jahn–Teller inversion following the formation of the first Cu–N bond.[25–27] On the contrary, the value for CuL(OH)$^+$ is significantly smaller and closer to the values found for the complexes with tet-b and $2_{\mathrm{N}}.1_{\mathrm{O}}.1_{\mathrm{O}}$,[26,29] for which the rate-determining step has been proposed to be the formation of the second Cu–N bond.[26] Thus, it appears that the lower basicity of the central nitrogens of L and the increased steric requirements of the tren sub-units is enough to cause a shift in the rate-determining step for complex formation.

Acknowledgements

Financial support from the Spanish Dirección General de Enseñanza Superior (Proyecto PB96-1516) and Junta de Andalucía (FQM-0137) is gratefully acknowledged.

References

1 J. M. Brown, L. Powers, B. Kincaid, J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 4210; J. A. Tanier, E. D. Getzoff, K. M. Beem, J. S. Richardson and D. C. Richardson, *J. Mol. Biol.*, 1982, **106**, 181; G. L. Woolery, L. Powers, M. Winkler, E. J. Solomon and T. G. Spiro, *J. Am. Chem. Soc.*, 1984, **106**, 86; R. M. Fronko, J. F. Penner-Hahn and C. J. Bender, *J. Am. Chem. Soc.*, 1988, **110**, 7554; C. R. Andrew, P. Lappalainen, M. Saraste, M. T. Hay, Y. Lu, C. Dennison, G. W. Canters, J. A. Fee, C. E. Slutter, N. Nakamura and J. Sanders-Loehr, *J. Am. Chem. Soc.*, 1995, **117**, 10759; I. Michaud-Soret, L. Jacquamet, N. Debaecker-Petit, L. Le Pape, V. V. Barynin and J. M. Latour, *Inorg. Chem.*, 1998, **37**, 3874; H. Sakiyama, R. Mochizuki, A. Sugawara, M. Sakamoto, Y. Nishida and M. Yamasaki, *J. Chem. Soc., Dalton Trans.*, 1999, 997; T. D. Ju, R. A. Ghiladi, D. H. Lee, G. P. F. van Strijdonck, A. S. Woods, R. J. Cotter, V. G. Young and K. D. Karlin, *Inorg. Chem.*, 1999, **38**, 2244.

2 J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quirós and E. R. T. Tiekink, *Inorg. Chem.*, 1997, **36**, 4988; M. P. Donzello, C. Ercolani, K. M. Kadish, Z. Ou and U. Russo, *Inorg. Chem.*, 1998, **37**, 3682; P. Amudha, M. Kandaswamy, L. Govindasamy and D. Velmurugan, *Inorg. Chem.*, 1998, **37**, 4486; A. Escuer, C. I. Harding, Y. Dussart, J. Nelson, V. McKee and R. Vicente, *J. Chem. Soc., Dalton Trans.*, 1999, 223; V. M. Miskowski, S. Franzen, A. P. Shreve, M. R. Ondrias, S. E. Wallace-Williams, M. E. Barr and W. H. Woodruff, *Inorg. Chem.*, 1999, **38**, 2546; B. Bosnich, *Inorg. Chem.*, 1999, **38**, 2554.

3 R. Menif, J. Reibenspies and A. E. Martell, *Inorg. Chem.*, 1991, **30**, 3446.

4 R. Menif, A. E. Martell, P. Squattrito and A. Clearfield, *Inorg. Chem.*, 1990, **29**, 4723.

5 Q. Lu, J. Reibenspies, A. E. Martell and R. J. Motekaitis, *Inorg. Chem.*, 1996, **35**, 2636; M. T. B. Luiz, B. Szpoganicz, M. Rizzotto, A. E. Martell and M. G. Basallote, *Inorg. Chim. Acta*, 1997, **254**, 345; T. F. Pauwels, W. Lippens, G. G. Herman and A. M. Goeminne, *Polyhedron*, 1998, **17**, 1715; T. F. Pauwels, W. Lippens, P. W. Smet, G. G. Herman and A. M. Goeminne, *Polyhedron*, 1999, **18**, 1029.

6 R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1991, **30**, 694; D. A. Rockcliffe and A. E. Martell, *Inorg. Chem.*, 1993, **32**, 3143; K. P. McCue, D. A. Voss, Jr., C. Marks and J. R. Morrow, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2961; M. T. B. Luiz, B. Szpoganicz, M. Rizzotto, M. G. Basallote and A. E. Martell, *Inorg. Chim. Acta*, 1999, **287**, 134.

7 M. G. Basallote and A. E. Martell, *Inorg. Chem.*, 1988, **27**, 4219; M. P. Ngwenya, D. Chen, A. E. Martell and J. Reibenspies, *Inorg. Chem.*, 1991, **30**, 2732; M. Becker, S. Schindler and R. van Eldik, *Inorg. Chem.*, 1994, **33**, 5370; S. Mahapatra, S. Kaderli, A. Llobet, Y. Neuhold, T. Palanché, J. A. Halfen, V. G. Young, Jr., T. A. Kaden, L. Que, Jr., A. D. Zuberbüller and W. B. Tolman, *Inorg. Chem.*, 1997, **36**, 6343.

8 R. M. Smith, A. E. Martell and R. J. Motekaitis, *NIST Critical Stability Constants of Metal Complexes Database*, U.S. Dept. of Commerce, Gaithesbourgh, 1993.

9 M. J. Fernández-Trujillo, B. Szpoganicz, M. A. Máñez, L. T. Kist and M. G. Basallote, *Polyhedron*, 1996, **15**, 3511.

10 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, M. A. Máñez and B. Szpoganicz, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1093.

11 A. E. Martell and R. J. Motekaitis, *Determination and use of stability constants*, VCH, New York, 1992.

12 GLINT Software, Applied Photophysics Ltd., Leatherhead, 1995.

13 R. G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd edn., VCH, Weinheim, 1991, p. 22.

14 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 1981, pp. 70 and 71.

15 P. Kathirgamanathan, A. B. Soares, D. T. Richens and A. G. Sykes, *Inorg. Chem.*, 1985, **24**, 2950; B. L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 310.

16 W. Marty and J. H. Espenson, *Inorg. Chem.*, 1979, **18**, 1246; J. P. Bourke, E. Karu and R. D. Cannon, *Inorg. Chem.*, 1996, **35**, 1577; M. C. Pohl and J. H. Espenson, *Inorg. Chem.*, 1980, **19**, 235; F. A. Armstrong, R. A. Henderson and A. G. Sykes, *J. Am. Chem. Soc.*, 1980, **102**, 6545.

17 Ref. 13, p. 227.

18 R. A. Read and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 3143.

19 S. Siddiqui and R. E. Shepherd, *Inorg. Chem.*, 1983, **22**, 3726.

20 L. H. Chen and C. S. Chung, *Inorg. Chem.*, 1989, **28**, 1402.

21 R. W. Hay, M. T. H. Tarafder and M. M. Hassan, *Polyhedron*, 1996, **15**, 725.

22 W. J. Lan and C. S. Chung, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 191.

23 L. H. Chen and C. S. Chung, *Inorg. Chem.*, 1988, **27**, 1880.

24 A. M. Dittler-Klingemann, C. Orvig, F. E. Hahn, F. Thaler, C. D. Hubbard, R. van Eldik, S. Schindler and I. Fábián, *Inorg. Chem.*, 1996, **35**, 7798; F. Thaler, C. D. Hubbard, F. W. Heinemann, R. van Eldik, S. Schindler, I. Fábián, A. M. Dittler-Klingemann, F. E. Hahn and C. Orvig, *Inorg. Chem.*, 1998, **37**, 4022.

25 Ref. 13, pp. 224–226.

26 J. A. Drumhiller, F. Montavon, J. M. Lehn and R. W. Taylor, *Inorg. Chem.*, 1986, **25**, 3751.

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

28 B. F. Liang, D. W. Margerum and C. S. Chung, *Inorg. Chem.*, 1979, **18**, 2001; B. F. Liang and C. S. Chung, *Inorg. Chem.*, 1980, **19**, 1867.

29 F. T. Chen, C. S. Lee and C. S. Chung, *Polyhedron*, 1983, **2**, 1301.

Paper 9/06029D