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Polyhedron 20 (2001) 75–82

POLYHEDRON

Stability and kinetics of decomposition of binuclear Cu(II) complexes with a symmetrical hexaaza macrocycle: the effect of SCN^- as ancillary ligand

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Received 19 June 2000; accepted 19 September 2000

Abstract

The effect of added KBr and KSCN on the stability constants of the mono and binuclear Cu(II) complexes with a symmetrical hexaazamacrocycle L has been examined in 0.1 M KNO_3. The presence of these salts does not cause any change in the ligand protonation constants, which indicates that, in the presence of 0.1 M KNO_3, there is not preferential interaction of the Br^- and SCN^- anions with the highly protonated forms of the ligand. No ternary Cu–L–Br complexes are detected in the potentiometric study of the equilibrium, but several mono and binuclear Cu–L–SCN complexes are formed at significant amounts and their stabilities are reported. The kinetics of decomposition of the binuclear Cu–L and Cu–L–SCN complexes upon addition of an excess of acid has been also measured. The results obtained for the Cu–L complexes agree well with those previously reported in 1.0 M KNO_3, and they indicate that the release of both Cu(II) ions is statistically controlled. The existence of some differences between the kinetic data corresponding to decomposition of solutions at different starting pH is interpreted in terms of parallel decomposition of the binuclear Cu_2L^{4+}, $Cu_2L(OH)^{3+}$ and $Cu_2L(OH)_2^{2+}$ complexes, the kinetic parameters for the three complexes being slightly different. This interpretation is also supported by the kinetics of decomposition of the Cu–L–SCN^- complexes that also reveals differences between the several complexes in solution. If the present data are interpreted in terms of the classical mechanism for decomposition of Cu(II)-polyamine complexes, they suggest that the nature of the ancillary ligands does not cause large changes in the lability of the Cu–N bonds but it largely affects to the relative rates of attack by H^+ and water. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Stability; Macrocycle; Copper; Dinuclear complexes

1. Introduction

The large symmetrical macrocycle L and its related cryptand L′ (see Scheme 1) form in aqueous solution mono and binuclear Cu(II) complexes according to equilibria 1–2, where the different protonated or hydroxylated forms of the reagents are ignored for simplicity [1–7]. These ligands contain two diethylenetriamine (dien) or tris(2-aminoethyl)amine (tren) subunits linked by rigid *m*-xylyl spacers, and equilibrium data indicate that complexation occurs through coordination of every metal centre to the amine groups in one of the subunits. Thus, the binuclear complexes contain two Cu(II)-dien or Cu(II)-tren moieties whereas the mononuclear complexes contain only one, with the amine groups in the other one being protonated or unprotonated depending on the pH

$$Cu + L \rightleftarrows CuL \tag{1}$$

$$CuL + Cu \rightleftarrows Cu_2L \tag{2}$$

Despite Eqs. (1) and (2) involving several coordination or dissociation steps, we have shown in a recent paper [7] that the coordination and release of both Cu(II) ions from L′ occurs with statistically controlled kinetics; i.e. the rate of the first step is essentially twice

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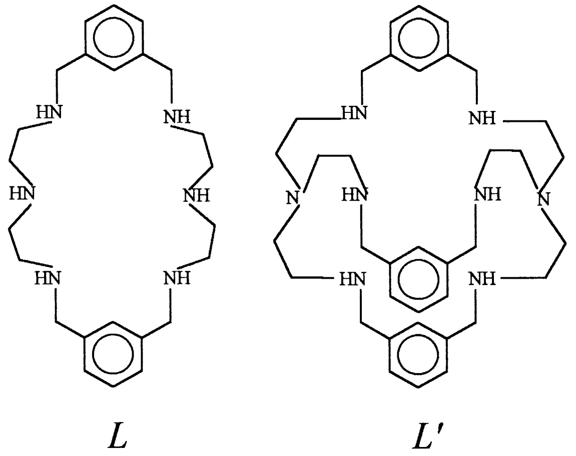
PII: S0277-5387(00)00589-1

the rate of the second one. This indicates that both subunits in the cryptand behave independently and that L′ is flexible enough to undergo rapidly any reorganisation required during the coordination-dissociation processes. We had also reported previously [8] the kinetics of dissociation of Cu–L complexes in acidic media, showing that the mono and binuclear complexes decompose at similar rates, although the possibility of statistical kinetics was unnoticed. The macrocycle L is expected to be more flexible than L′ and so, we decided to re-examine the kinetics of decomposition of Cu–L complexes to look for confirmation of statistical kinetics in the reactions of this kind of complexes. The study has been also extended to binuclear Cu–L–SCN complexes in order to determine the effect of changing the ancillary ligand on the kinetics of the decomposition process. As solutions containing Cu(II), L and SCN^- contain complex mixtures of species, the kinetic studies required a previous determination of the equilibrium constants for the formation of ternary complexes.



Scheme 1.

Table 1
Logarithms of the stability constants for the formation of Cu–L and Cu–L–SCN complexes at 25.0°C in the presence of 0.10 M KNO_3

K	Equilibrium quotient	log K
K_{HL}	$[HL^+]/[L][H^+]$	9.53(5)
K_{H_2L}	$[H_2L^{2+}]/[HL^+][H^+]$	8.73(4)
K_{H_3L}	$[H_3L^{3+}]/[H_2L^{2+}][H^+]$	8.00(5)
K_{H_4L}	$[H_4L^{4+}]/[H_3L^{3+}][H^+]$	7.2(1)
K_{H_5L}	$[H_5L^{5+}]/[H_4L^{4+}][H^+]$	3.6(1)
K_{H_6L}	$[H_6L^{6+}]/[H_5L^{5+}][H^+]$	3.4(1)
K_{CuL}	$[CuL^{2+}]/[Cu^{2+}][L]$	13.7(2)
K_{HCuL}	$[HCuL^{3+}]/[CuL^{2+}][H^+]$	8.4(2)
K_{H_2CuL}	$[H_2CuL^{4+}]/[HCuL^{3+}][H^+]$	7.3(3)
K_{Cu_2L}	$[Cu_2L^{4+}]/[CuL^{2+}][Cu^{2+}]$	10.0(3)
K_{Cu_2LOH}	$[Cu_2L(OH)^{3+}][H^+]/[Cu_2L^{4+}]$	−7.3(1)
$K_{Cu_2L(OH)_2}$	$[Cu_2L(OH)_2^{2+}][H^+]/[Cu_2L(OH)^{3+}]$	−8.5(2)
$K_{H_2CuL(SCN)}$	$[H_2CuL(SCN)^{3+}]/[H_2CuL^{4+}][SCN^-]$	3.45
$K_{H2CuL(SCN)_2}$	$[H_2CuL(SCN)_2^{2+}]/[H_2CuL(SCN)^{3+}]$-$[SCN^-]$	2.34
$K_{Cu_2L(SCN)}$	$[Cu_2L(SCN)^{3+}]/[Cu_2L^{4+}][SCN^-]$	4.13
$K_{Cu_2L(SCN)_2}$	$[Cu_2L(SCN)_2^{2+}]/[Cu_2L(SCN)^{3+}]$-$[SCN^-]$	3.31
$K_{Cu_2L(OH)(SCN)}$	$[Cu_2L(OH)(SCN)^{2+}]/[Cu_2L(OH)^{3+}]$-$[SCN^-]$	3.57

2. Results and discussion

2.1. The protonation of the ligand and the stability of the Cu–L and Cu–L–SCN^- complexes

The stability constants for both the protonation of macrocycle L and the formation of Cu(II) complexes have been previously determined in the presence of 0.10 M KNO_3 [1,2]. The possibility of interaction between anions and the protonated forms of this kind of ligand is now well recognised and, for example, the crystal structure of L·6HBr shows that two bromide ions reside inside the macrocyclic ring [9], whereas $H_6L'^{6+}$ has been shown [10] to encapsulate two nitrate anions. As the ligand samples used in previous works were in the form of L·6HBr, all the titrations were carried out with a Br^- concentration six times higher than $[L]_0$ and there is the possibility of interaction of Br^- with the protonated forms of the ligand and/or the Cu complexes. In order to check this possibility, we prepared a sample of L·$6HNO_3$ and titrated it in solutions containing 0.10 M KNO_3 both in the absence and in the presence of added KBr. The analysis of the titration curves led in all cases to similar values for the equilibrium constants corresponding to ligand protonation. The ligand was also titrated in the presence of added KSCN without any significant difference in the values of the protonation constants. The new sets of values for the formation constants of the H_xL^{x+} species (Section 4) compare well with those previously reported [1,2]; all the values coincide within experimental and computation errors, and the mean values included in Table 1 are the best estimation now available for the log K_{HL} values in 0.10 M KNO_3. Quite similar values have been also reported in the presence of 0.10 M KCl or $NaClO_4$ [4,5,9], although they have not been included in the calculation of the mean values because of the different supporting electrolytes. The lack of differences between results with and without added KBr or KSCN indicates that, in the presence of 0.10 M KNO_3, there is no preferential complexation of Br^- or SCN^- by the highly protonated forms of the ligand. The similarity of the results in KCl and $NaClO_4$ suggests that the same is also true for Cl^- and ClO_4^-, although the smaller values of log K_{H6L} in 0.10 M $NaClO_4$ suggest a weaker H_6L^{6+}–ClO_4^- interaction.

The possibility of bromide and thiocyanate complexation by the mono- and bi-nuclear Cu–L complexes was

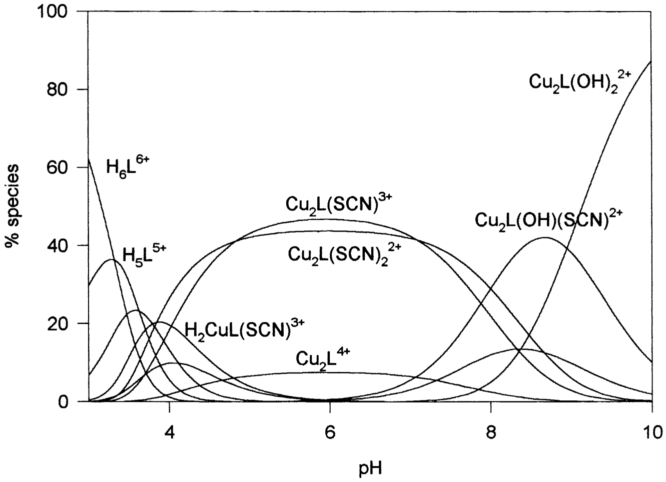


Fig. 1. Species distribution curves for solutions containing Cu, L and SCN^- at 2:1:2 molar ratio ($[L]_0 = 1.0 \times 10^{-3}$ M). The curves not labelled correspond to the species H_4L^{4+} and H_2CuL^{4+} (pH close to 4), and $Cu_2L(OH)^{3+}$ (pH close to 8).

also examined by carrying out titrations of $L{\cdot}6HNO_3$ solutions containing one or two equivalents of Cu, both in the absence and the presence of added KBr or KSCN. The values of the formation constants for the Cu–L complexes derived from titrations in the absence of these salts are again similar to those previously reported (Section 4), and the mean values for the different sets of stability constants are also included in Table 1. The titration curves in the presence of added KBr lead to stability constants very close to those in Table 1, which indicates the absence of stable Cu–L–Br ternary complexes; a conclusion similar to that previously achieved for chloride [3]. In contrast, the analysis of titration curves in the presence of added KSCN requires the inclusion of additional species in the equilibrium model, and the values derived for the formation constants of the new species are also given in Table 1. There are only two mononuclear ternary complexes that correspond to the interaction of one or two SCN^- with H_2CuL^{4+}. The log K values for these species are higher than that corresponding to formation of $Cu(NCS)^+$, which can be interpreted in terms of a certain interaction of the coordinated SCN^- with the protonated amine groups of the macrocycle, as previously proposed for the case of acetate complexes [2]. The absence of stable $H_xCuL(NCS)_y^{(2+x-y)+}$ species ($x = 0,1$; $y = 1,2$) is easily understood because $HCuL^{3+}$ and CuL^{2+} are only formed at pH values where the major species are binuclear complexes. In contrast, H_2CuL^{4+} is formed at pH close to 4, where the formation of binuclear complexes is not very important and allows the formation of detectable amounts of the mononuclear $H_2CuL(NCS)_x^{(4-x)+}$ species.

The values of log K for coordination of SCN^- to the binuclear Cu–L complexes to form $Cu_2L(NCS)_x^{(4-x)+}$ ($x = 1,2$) and $Cu_2L(OH)(NCS)^{2+}$ are also high and suggest a thiocyanate-bridged binuclear structure for these complexes. There are previous literature reports showing the formation of thiocyanate bridges between two metal centres coordinated to large polyaza macrocycles, and the X-ray determined structures usually show a 1,3-μ-NCS bridging [11]. The IR spectra (KBr pellets) of solids obtained from solutions containing Cu, L and SCN^- at 2:1:2 ratios show a band at 2115 cm^{-1} typical of 1,3-μ-NCS bridging [12,13]. In contrast, solids isolated under conditions in which the mononuclear complexes predominate show a band at 2022 cm^{-1} that suggests Cu–NCS coordination in the mononuclear species [12]. The absence of species as $Cu_2L(NCS)_3^+$, $Cu_2L(OH)_3^+$, $Cu_2L(OH)_2(NCS)^+$ or $Cu_2L(OH)(NCS)_2^+$ in the equilibrium model suggests a five-coordinate environment of the Cu centres in the binuclear species, as frequently found for related complexes and demonstrated [3] for the case of $Cu_2L(SO_4)_2$; the coordination of the three amine groups of one N_3-donor sub-unit of the macrocycle leaves only two coordination sites available for other ligands and the high tendency of these complexes to form bridged structures reduces the number of species to those included in Table 1.

As knowledge of the spectral features of the complexes in Table 1 was required before starting the kinetic work, we carried out a spectrophotometric titration of the Cu_2L^{4+} complex with SCN^- that was also used to confirm the validity of the equilibrium model and the stability constants. The species distribution curves in Fig. 1 show that the only species at pH close to 6 in a solution containing Cu, L and SCN^- in 2:1:2 ratio are Cu_2L^{4+}, $Cu_2L(NCS)^{3+}$ and $Cu_2L(NCS)_2^{2+}$. Spectrophotometric titration with KSCN of a MES-buffered solution (pH 6.05) containing Cu and L in 2:1 ratio were used to determine the stability of the thiocyanate-containing binuclear complexes. The data were analysed with program SQUAD [14] and yielded log β values of 4.3 ± 0.1 and 7.0 ± 0.2 for the formation of $Cu_2L(SCN)^{3+}$ and $Cu_2L(SCN)_2^{2+}$ from Cu_2L^{4+}. The value of log $K = 4.3$ for the mono-thiocyanate complex (Eq. (3)) is in excellent agreement with the potentiometric value of Table 1, but the spectrophotometric data indicate a lower stability of $Cu_2L(SCN)_2^{2+}$ (log $K = 2.7$ and 3.3 for Eq. (4) from spectrophotometric and potentiometric data, respectively). This difference can be rationalised by considering the changes in both the experimental conditions and the analysis of the data, although some contribution from the presence of MES is also possible in view of the previously reported effect of this buffer on the kinetics of formation of Cu–L complexes [2].

$$Cu_2L^{4+} + SCN^-L \rightleftarrows Cu_2L(SCN)^{3+} \quad (3)$$

$$Cu_2L(SCN)^{3+} + SCN^- \rightleftarrows Cu_2L(SCN)_2^{2+} \quad (4)$$

The spectra calculated with program SQUAD for the complexes $Cu_2L(SCN)^{3+}$ and $Cu_2L(SCN)_2^{2+}$ indicate that the absorption bands for these compounds are more intense than those corresponding to Cu–L complexes. Both complexes have similar spectra, with bands at 270 and 625 nm ($\varepsilon = 6800$ and 525 for $Cu_2L(SCN)^{3+}$; 7820 and 750 for $Cu_2L(SCN)_2^{2+}$; all the values in M^{-1} cm^{-1}). During the course of the kinetic work we found that the position of these bands is also very similar for all the mono and binuclear species, independently of the number and nature of bridges, which strongly suggests that the coordination environment about Cu is the same in all cases. The complexes always show an intense charge–transfer band in the UV and two medium-intensity d–d bands close to 650 and 1050 nm [15], the number and position of the d–d bands being similar to those found for related Cu(II) complexes with a distorted square-pyramidal coordination [16].

2.2. Kinetics of decomposition of the Cu–L and Cu–L–SCN complexes

According to a recent report [7], the release of the Cu(II) ions from the binuclear $Cu_2L'(OH)^{3+}$ complex is statistically controlled; both metal centres behave independently and dissociate with rate constants $2k$ and k, although kinetic traces for decomposition of the binuclear complex are simplified to a single exponential with observed rate constant k. In contrast, all the mono and binuclear Cu–L complexes had been found to decompose at similar rates, which was interpreted in terms of rapid conversion to the most acidic form of the mononuclear complex followed by rate-determining decomposition of this species [8]. The different conclusions obtained for both related ligands and the existence of some minor differences between the sets of kinetic parameters previously derived for Cu–L complexes prompted us to reexamine the kinetics of decomposition of the binuclear Cu–L complexes. As previous data [8] were obtained in the presence of 1.0 M supporting electrolyte and all the other equilibrium and kinetic data correspond to 0.10 M, we decided to use the latter ionic strength to carry out the kinetic study in this work.

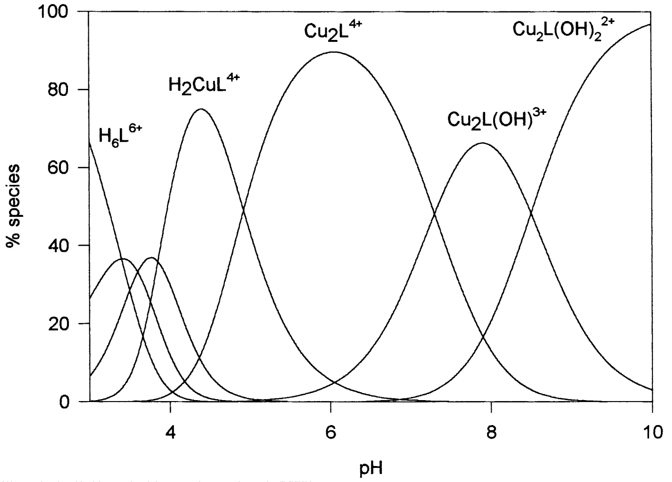


Fig. 2. Species distribution for solutions containing Cu and L at 2:1 molar ratio ($[L]_0 = 1.4 \times 10^{-4}$ M). The curves not labelled with maximum at pH close to 4 correspond to the species H_5L^{5+} and H_4L^{4+}.

The species distribution curves corresponding to solutions containing Cu(II) and L in 2:1 molar ratio are shown in Fig. 2. Depending on pH, the major species in solution are H_2CuL^{4+}, Cu_2L^{4+}, $Cu_2L(OH)^{3+}$ and $Cu_2L(OH)_2^{2+}$. Addition of an excess of acid leads in all cases to complete decomposition, but kinetic experiments must be carried out using several starting pH values of the complex solution in order to detect possible differences in the kinetics of decomposition of the different species. The reaction was monitored at 280 nm because the absorbance changes are larger than those observed at the wavelength used in the previous work (650 nm). In most cases, kinetic traces could be well fitted by a single exponential but for some starting pH values the absorbance-time profiles were not so well behaved and clearly indicated the need for additional exponential terms. However, in those cases the fit by two exponentials lead to observed rate constants that were usually close to each other and difficult to separate, with simplification to a single exponential occurring at some concentrations of acid. For these reasons we have ignored those sets of measurements where a reliable kinetic analysis could not be carried out and only used those experiments where the whole set of kinetic traces can be fitted by a single exponential. The observed rate constants so derived are close to those previously reported in 1.0 M KNO_3. Although the lower concentration of supporting electrolyte precludes the use of high concentrations of added acid, the curvature in the k_{obs} versus $[H^+]$ plots is evident (Fig. 3) and the rate law (Eq. (5)) is the same as previously reported [8].

$$k_{obs} = \frac{a + b\ [H^+]}{1 + c\ [H^+]} \qquad (5)$$

The plots in Fig. 3 show that the k_{obs} values for decomposition of solutions with a starting pH of 4.11 are twice as large as those observed at pH 5.15, and the same is also true for higher pH values. The curves in Fig. 2 indicate that the major Cu(II) complex at pH 4.11 is mononuclear H_2CuL^{4+}, whereas at higher pH there is mainly a mixture of binuclear complexes. Thus, these results suggest that the kinetics of decomposition of the binuclear complexes is statistically controlled, i.e. the rate of dissociation of the first Cu(II) doubles that of the second one. The simplification of a double exponential with rate constants k and $k/2$ to a single

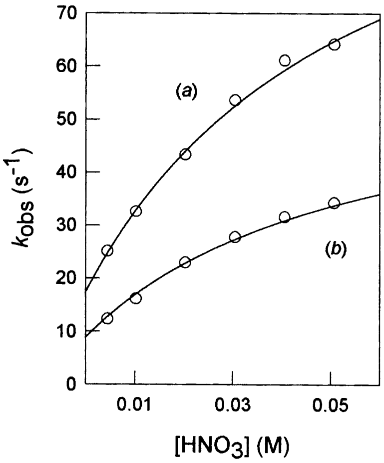


Fig. 3. Plot of k_{obs} vs. the concentration of added acid for the decomposition of complexes in solutions containing Cu and L at 2:1 molar ratio. The starting pH of the complex solution is 4.11 in (a) and 5.15 in (b).

exponential with apparent rate constant $k/2$ has been previously demonstrated for the binuclear Cu complexes of L′ [7].

The kinetic data at pH 5.15, 5.95 and 8.96 are very similar to each other and can be fitted by Eq. (5) with the values of a, b and c given in Table 2. As a consequence of the statistical kinetics, the a, b, c values at pH different from 4.11 correspond to dissociation of the second metal ion; according to Eq. (5) the c values are also valid for the release of the first Cu(II) but a and b must be increased by a factor of 2. The kinetic data at pH 7.08 and 8.23 are significantly different from those obtained at other pH (Section 4), especially at low concentrations of added acid. The fit by Eq. (5) leads in these cases to negligible values of a (Table 2), whereas the b values are similar and the c values are somewhat smaller than those obtained under other conditions in which binuclear complexes exist. These results for the kinetics of decomposition of binuclear Cu–L complexes at pH 7–8 resemble the behaviour of the related Cu–L′ complexes, for which the a values were always zero [7].

The existence of a different kinetic behaviour at intermediate pH values rules out the possibility that all the acid-base equilibria between the three dinuclear Cu–L complexes occur rapidly, which should lead to the overall decomposition being controlled in all cases by decomposition of the most acidic form (Cu_2L^{4+}). The alternative explanation is that the three binuclear complexes decompose in parallel processes with close rate constants. As the major difference between the species distribution at pH 7.08–8.23 and the other pH values is the existence of large concentrations of $Cu_2L(OH)^{3+}$, the experimental data would indicate that the kinetics of decomposition of this complex is different from those corresponding to the other binuclear complexes. This interpretation would also account for the observation of bad defined kinetic traces in some experiments: the need of additional exponential terms would be a consequence of the parallel decomposition of the different species. However, it is surprising the observation of a single exponential even for some pH values at which there are significant amounts of two species; the apparent simplification to a single exponential probably occurs in these cases because of the proximity of the rate constants.

As a summary of kinetic data for decomposition of Cu–L complexes, the present results confirm the previously observed rate law and indicate that the kinetics of dissociation of both metal centres is statistically controlled. Despite the existence of several species in the starting solutions precludes the precise assignment of specific rate constants to the decomposition of every individual complex, there is evidence that the three binuclear species decompose with different kinetics. Whereas the kinetic parameters for decomposition of $Cu_2L(OH)^{3+}$ are quite different from those corresponding to the other complexes, the values for Cu_2L^{4+} and $Cu_2L(OH)_2^{2+}$ are close to each other. This observation indicates that the magnitude of the kinetic changes is not related to the number of coordinated

Table 2
Summary of kinetic data for the decomposition of Cu–L and Cu–L–SCN complexes at 25.0°C in 0.10 M KNO_3 [a]

Cu:L:SCN ratio	Starting pH	a (s^{-1})	10^{-3} b ($M^{-1}s^{-1}$)	c (M^{-1})	b/c (s^{-1})	b/a (M^{-1})	Major species
2:1:0	4.11	17(2)	2.1(4)	18(6)	117	124	H_2CuL^{4+}
	5.15	7.9(6)	1.1(1)	18(3)	61	139	Cu_2L^{4+}
	5.95	9.1(7)	1.5(1)	24(4)	62	165	Cu_2L^{4+}
	7.08		0.8(1)	5(3)	160		Cu_2L^{4+}, $Cu_2L(OH)^{3+}$
	8.23		1.0(1)	8(3)	125		$Cu_2L(OH)^{3+}$, $Cu_2L(OH)_2^{2+}$
	8.96	8(1)	1.1(2)	16(7)	69	138	$Cu_2L(OH)_2^{2+}$
2:1:1	5.18		1.56(3)	20(1)	78		$Cu_2L(SCN)^{3+}$, Cu_2L^{4+}
	6.03		1.31(6)	14(2)	94		$Cu_2L(SCN)^{3+}$, Cu_2L^{4+}
2:1:2	6.09		0.64(1)				$Cu_2L(SCN)^{3+}$, $Cu_2L(SCN)_2^{2+}$
	7.05		0.8(1)	4(3)	200		$Cu_2L(SCN)^{3+}$, $Cu_2L(SCN)_2^{2+}$

[a] See the text for the definition of a, b and c and the meaning of the quotients b/c and b/a.

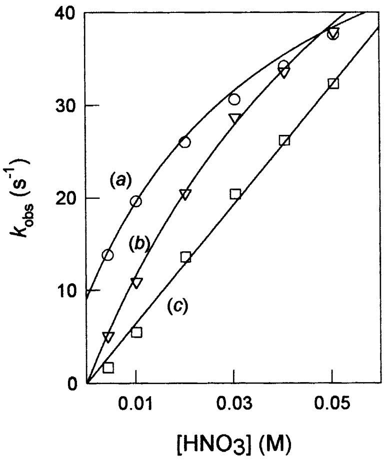


Fig. 4. Plot of k_{obs} vs. the concentration of added acid for the decomposition of complexes in solutions containing Cu, L and SCN$^-$ at different molar ratios and starting pH: (a) 2:1:0 ratio, pH 5.95; (b) 2:1:1 ratio, pH 6.03; (c) 2:1:2 ratio, pH 6.09.

OH$^-$ and it is probably caused simply by the different electronic and steric properties that exist between the three complexes. To gain insight into the kinetic effects caused by these small changes in the nature of the complexes, we decided to look for additional information by studying the kinetics of decomposition of the Cu–L–SCN complexes.

According to equilibrium data, solutions containing Cu, L and SCN$^-$ also contain complex mixtures of species, with Cu_2L^{4+}, $Cu_2L(SCN)^{3+}$ and $Cu_2L(SCN)_2^{2+}$ being the major components at intermediate pH values in solutions containing 2 equiv. of Cu(II), 1 equiv. of L and 1 or 2 equiv. of SCN$^-$ (see Fig. 1). Complete conversion to $Cu_2L(SCN)_2^{2+}$ could not be achieved because addition of larger amounts of thiocyanate causes precipitation. Higher concentrations of added SCN$^-$ could be used without precipitation during the equilibrium measurements in the presence of MES buffer, but the kinetics of decomposition can not be studied under these conditions because the added acid would be neutralised by MES.

Kinetic traces of decomposition in the presence of SCN$^-$ show absorbance changes larger than those observed in the absence of SCN$^-$, which is consistent with the higher absorptivities of the thiocyanate complexes and indicates that the Cu–L–SCN complexes are not converted to Cu–L within the stopped-flow mixing time. Unfortunately, we have not been able to study the kinetics of the reversible reactions between the binuclear Cu–L complexes and SCN$^-$. The kinetics of Eqs. (3) and (4) can not be studied under pseudo-first order conditions of SCN$^-$ excess because of precipitation, and the absorbance changes are too small to obtain accurate kinetic results when the metal complex is used in large excess. Kinetic traces of reactions (3) and (4) under non-pseudo-first order conditions are very difficult to analyse because of the existence of two consecutive reversible equilibria occurring at comparable rates, although they show clearly that these reactions are much slower than decomposition upon addition of acid excess.

Thus, the kinetic traces of decomposition of the complexes in the presence of SCN$^-$ correspond to decomposition of the Cu–L–SCN complexes to yield the free metal ion and ligands. As occurred with the Cu–L complexes, these traces were not well behaved for some starting pH values but for some pH values they could be well fitted by a single exponential with k_{obs} values of the same order than those obtained for the Cu–L complexes (Supplementary data). However, while at the higher concentrations of acid k_{obs} is very close to the values obtained for decomposition of the Cu–L complexes, significant differences are observed at the lowest concentrations (Fig. 4). The dependence of k_{obs} with the concentration of added acid is also given by Eq. (5), although the value of a is negligible in all cases; b and c are also included in Table 2. For solutions containing Cu, L and SCN in 2:1:1 ratio the values of b and c are close to those found for the Cu–L complexes, whereas significantly smaller values of both parameters are observed when the molar ratio is 2:1:2.

As a summary, the kinetic data in this and previous works indicate that the rate law for decomposition of all the mono and binuclear Cu(II) complexes of the binucleating macrocycle L is always the same, although there are small but significant differences between the kinetically relevant parameters a, b and c. Moreover, the values of these parameters are also close to those corresponding to decomposition of the Cu-dien complex ($b = 3.1 \times 10^3$ M^{-1} s^{-1}, $c = 9.0$ M^{-1}, a negligible) [17], which strongly suggests that a common mechanism is operating in all these decomposition processes; the presence of different ancillary ligands coordinated to the Cu(II) ions simply causes small changes in the kinetics of breaking of the Cu-dien subunits. The mechanism that is usually accepted for this process involves incomplete dissociation of the Cu–N bond followed by parallel attacks by H$^+$ and water [7,8,18]. In that case, the quotient b/c measures the lability of the Cu–N bonds, whereas the relative rates of attacks by proton and water can be estimated from the values of b/a. The values of these quotients are also included in Table 2 and indicate that the lability of the Cu–N bonds is not very different for all the Cu–L and Cu–L–SCN complexes. However, there are important differences in the relative rates of decomposition through the two parallel attacks. Although precise values of the kinetic parameters can not be assigned to every species, the largest values of the quotient b/a occur for $Cu_2L(OH)^{3+}$ and the thiocyanate complexes because of the negligible a values for these compounds. Thus, it appears that the nature of the bridging ligand between the metal centres does not affect very much to the lability of the metal-macrocycle bonds but causes important changes in the relative rates of attack by H_2O and H^+.

3. Experimental

The macrocycle 3,6,9,17,20,23-hexaazatricyclo-[23.3.1.1^{11,15}]triaconta-1(29),11(30),12, 14,25,27-hexaene (L) was prepared as $C_{24}H_{38}N_6.6HNO_3$ ($L{\cdot}6HNO_3$) following the literature method [1], except that HBr was replaced by HNO_3 for crystallisation. ^1H and $^{13}C\ \{^1H\}$ NMR spectra confirmed the nature of the ligand and the absence of impurities, and the exact composition was derived from 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 [19].

3.1. Equilibrium determinations

Solutions used during the potentiometric and spectrophotometric equilibrium work were prepared and titrated as previously described [2]. All titrations were carried out in 0.10 M KNO_3 solutions at 25.0°C under N_2, and were analysed with programs BEST [19] (potentiometric titrations) or SQUAD [14] (spectrophotometric titration). The species distribution curves were obtained with programs SPE and SPEPLOT [19].

The protonation constants of the ligand were determined from potentiometric titrations of $L{\cdot}6HNO_3$ in 0.10 M KNO_3 solutions that contained in some cases added KBr or KSCN. The concentration of the ligand was always close to 2×10^{-3} M and the concentration of added salt was $(2–8) \times 10^{-3}$ M. The curves were analysed assuming a fixed value of 13.78 for pK_w. The formation constants of mono- and binuclear Cu–L complexes were determined from titrations of solutions containing Cu and L at 1:1 or 2:1 molar ratios; during the analysis of these curves the ligand protonation constants were fixed at the previously determined values. The formation constants of Cu–L–SCN complexes were derived from titration curves corresponding to solutions that contained 1 or 2 equiv. of KSCN in addition to Cu and L in 1.1 or 2:1 ratio; only the values of the formation constants for thiocyanate-containing species were refined from these curves. Titration of solutions containing a higher concentration of SCN^- could not be used for equilibrium measurements because of precipitation under neutral and basic conditions. The number of data points measured was different for every titration but there were typically 10 points for every neutralisation of a proton, covering a pH range from ca. 3–11.

For the spectrophotometric titration of the binuclear Cu_2L^{4+} complex with KSCN, a 0.10 M KNO_3 solution containing Cu and L (2:1 ratio) was prepared and 0.10 M KOH was added until the pH was close to 6 (formation of ca. 100% Cu_2L^{4+}). MES (0.01 M) was then added followed by KOH addition until a stable pH reading of 6.05. The resulting solution ($[Cu]_0 = 2 \times [L]_0 = 5.11 \times 10^{-4}$ M) was titrated with 2.38×10^{-2} M KSCN without any significant deviation of the initial pH value. The thiocyanate solution was added in 0.04 cm^3 aliquots and the UV–Vis spectrum of the solution was recorded from 250 to 900 nm and digitised at 5 nm intervals. A total of 23 spectra were obtained covering a SCN^-: Cu_2L^{4+} range from 0 to 4.46. The experiment was analysed with program SQUAD [14] assuming that the only species in solution are Cu_2L^{4+}, $Cu_2L(SCN)^{3+}$ and $Cu_2L(SCN)_2^{4+}$, what appears a reasonable simplification in view of the potentiometric results. The agreement of results from both methods and the lack of improvement in the quality of the fit upon inclusion of additional species strongly support the validity of the equilibrium model.

3.2. Kinetic experiments

All the experiments were carried out at 25.0°C with an Applied Photophysics SX17MV stopped-flow instrument. The kinetics of decomposition was always monitored at 280 nm under pseudo-first order conditions of acid excess (HNO_3), with the ionic strength being adjusted to 0.10 M with KNO_3. The solutions of the metal complexes were prepared by mixing the amounts of titrated Cu, L and SCN^- solutions required to achieve a 2:1:x molar ratio ($x = 0,1,2$). After adding the inert electrolyte, the pH of the complex solution was set at the desired value by adding aliquots of titrated HNO_3 and KOH solutions. The analysis of the kinetic traces was carried out using the standard software of the instrument and reported values of the observed rate constants correspond to the mean value for at least five determinations with a standard deviation lower than 5%.

4. Supplementary data

Tables containing the values of the stability constants and the primary kinetic data can be obtained from the authors at the e-mail address manuel.basallote@uca.es.

Acknowledgements

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

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