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Stability and kinetics of the acid-promoted decomposition of tertiary binuclear $Cu^{II}{}_2LX^{z+}$ complexes (L = octaaza cryptand, X = SCN^-, N_3^- and 2 NH_3): the ancillary ligand modulates the kinetics of dissociation of the cryptand†

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

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

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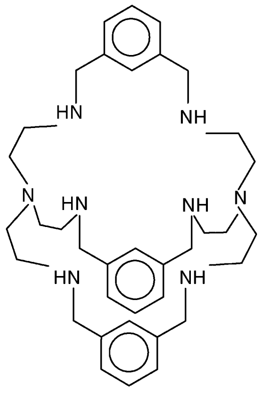
Solution studies indicate that the $Cu_2L(OH)^{3+}$ complex, where L is a large octaaza cryptand, reacts with NH_3, KSCN and NaN_3 to form the binuclear tertiary complexes $Cu_2L(NH_3)_2{}^{4+}$, $Cu_2L(SCN)^{3+}$ and $Cu_2L(N_3)^{3+}$. The equilibrium constants show a special stabilisation of the complexes with ligands able to bridge the Cu^{II} centres, with a maximum stabilisation for azide. Upon addition of an excess of acid, all the complexes decompose with release of Cu^{2+} and the protonated ligands. The kinetics of the acid-promoted decomposition have been studied under pseudo-first order conditions of excess acid. The decomposition of the OH^-, SCN^- and NH_3 complexes is first order with respect to H^+, although with a clear tendency to saturation, and the values of the rate constants depend on the nature of the ancillary ligand. In contrast, $Cu_2L(N_3)^{3+}$ decomposes with a second order dependence on the acid concentration. These results are interpreted in terms of modifications induced by the ancillary ligand in the kinetics of the acid-assisted dissociation of Cu–N(cryptate) bonds. Depending on the steric requirements of the ancillary ligand, the Cu–N(cryptate) bonds are strained at different degrees and the more distorted complexes decompose faster. In the case of azide, there is an optimum fit between the ancillary ligand and the Cu_2L^{4+} site that causes a change in the rate-determining step from dissociation of the first Cu–N bond to the second.

Introduction

Large polyaza macrocycles and cryptands can co-ordinate simultaneously two metal ions and the resulting complexes can be used as models for metalloenzymes that require the close proximity of two metal centers.[1] These ligands and their metal complexes are also of interest in anion sensing because of their ability to selectively recognise anions.[2–5] Thus, for the case of cryptand L, which contains two triethylenetetraamine sub-units linked by *m*-xylyl spacers, the Cu^{II} complexes recognise the bite length of polyatomic anions and form the most stable complex with N_3^-.[2] In contrast, when the cryptand contains furanyl spacers between the tetra-amine sub-units, the Cu^{II} complexes recognise Cl^- preferentially to other halides.[3] Selective complexation of different anions has been described for other complexes[3] and for the highly protonated forms of the ligands.[5] Whereas the structure[6–8] and stability[2,6,9,10] of these binuclear complexes are reasonably well understood, less is known about the kinetics of the reactions in which they participate.

In the last few years, we have studied the kinetics of formation and decomposition of a series of mono- and bi-nuclear Cu^{II} macrocycles and cryptates.[9,11–13] Under conditions in which only the mono- or the bi-nuclear complexes exist, we could demonstrate that the kinetics of release of the metal centres from the binuclear complexes is statistically controlled, *i.e.* the rate of dissociation of the first Cu^{II} doubles the rate corresponding to the second Cu^{II}.[9] In another previous work,[12] we obtained evidence that the presence of co-ordinated SCN^- leads to small changes in the kinetics of decomposition of a Cu^{II}-macrocycle complex, although the macrocycle forms a mixture of species in solution which complicates the analysis of the kinetic results. In this work, we have studied the kinetics of decomposition of tertiary Cu_2LX^{z+} complexes; the cryptand only leaves a vacant co-ordination site on every metal centre and the kinetics of decomposition can be studied under conditions in which only one species exists. When X is SCN^- or N_3^-, one ancillary ligand can act as a bridge between the metal centres, but bridge formation is not possible when X is NH_3 and one ammonia is co-ordinated to each metal centre (see the proposed structures of the complexes in Scheme 1). The results so obtained demonstrate clearly that the ancillary ligands cause important changes in the kinetics of dissociation of the cryptand. The changes are not limited to different values of the rate constants but they also affect the form of the rate law,



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† Electronic supplementary information (ESI) available: kinetic data for the decomposition of binuclear $Cu^{II}{}_2LX^{z+}$ complexes with acid; equations used to calculate the concentration of acid available for complex decomposition. See http://www.rsc.org/suppdata/dt/b1/b111573c/

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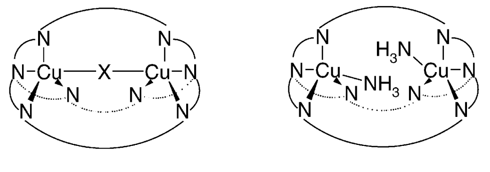
Table 1 Spectrophotometric equilibrium data for the formation of binuclear Cu_2LX^{z+} complexes ($X = SCN^-$, N_3^-, NH_3) from $Cu_2L(OH)^{3+}$ in aqueous solution at 25.0 °C (0.10 mol dm^{-3} ionic strength, pH = 7.05, MOPS buffer)

Species	log K^a	λ_{max}/nm	ε_{max}/$dm^3\ mol^{-1}\ cm^{-1}$
$Cu_2L(SCN)^{3+}$	3.51 ± 0.02	380	$(4.3 \pm 0.2) \times 10^3$
$Cu_2L(N_3)^{3+}$	4.82 ± 0.07	415	$(6.6 \pm 0.1) \times 10^3$
$Cu_2L(NH_3)^{4+}$	2.97 ± 0.08	670	$(2.8 \pm 0.2) \times 10^2$
$Cu_2L(NH_3)_2^{4+}$	6.24 ± 0.15	690	$(5.7 \pm 0.2) \times 10^2$

[a] The values of K correspond to the quotient $[Cu_2LX_n]/[Cu_2L][X]^n$.



Cu_2LX^{3+} (X= SCN^-, N_3^-)

$Cu_2L(NH_3)_2^{4+}$

Scheme 1

which suggests the possibility of mechanistic changes for the decomposition of closely related complexes.

Results

Equilibrium determination

The stability of the $Cu_2L(SCN)^{3+}$ and $Cu_2L(N_3)^{3+}$ complexes with respect to $Cu_2L(OH)^{3+}$ has been previously reported.[2] However, we were interested in comparing the kinetics of decomposition between complexes containing a bridging ligand and compounds without any bridge between the metal centres and so, a determination of the stability of tertiary complexes with NH_3 was necessary. The determination was carried out at pH 7.05 because we observed solubility problems at pH values higher than *ca.* 7.5 in previous potentiometric determinations of the stability of Cu^{II}–L complexes.[9] The added electrolyte (0.10 mol dm^{-3} KNO_3) was selected to make the equilibrium and kinetic data comparable with those previously reported for related complexes.[9,11–13] Because the experimental conditions differ from those previously used,[2] the stability of the SCN^- and N_3^- complexes was re-determined.

The binuclear $Cu_2L(OH)^{3+}$ complex is the only species at pH close to 7 in solutions containing Cu^{II} and L in a 2 : 1 molar ratio,[6,9] and reaction with SCN^- and N_3^- leads to Cu_2LX^{3+} complexes because of the ability of these anions to act as a bridge between the metal centres [eqns. (1)–(2)]. However, NH_3 is unable to act as a bridging ligand and substitution of OH^- must lead to $Cu_2L(NH_3)_2^{4+}$, with one NH_3 co-ordinated to each of the Cu^{II} centres [eqn. (3)]. The data corresponding to titrations of $Cu_2L(OH)^{3+}$ solutions with SCN^-, N_3^- or NH_3 could be easily analysed using an equilibrium model involving the species shown in eqns. (1)–(3) and the mono-substituted $Cu_2L(NH_3)^{4+}$ complex. The values derived for the equilibrium constants are included in Table 1.

$$Cu_2L(OH)^{3+} + SCN^- \rightleftarrows Cu_2L(SCN)^{3+} \qquad (1)$$

$$Cu_2L(OH)^{3+} + N_3^- \rightleftarrows Cu_2L(N_3)^{3+} \qquad (2)$$

$$Cu_2L(OH)^{3+} + 2\,NH_3 \rightleftarrows Cu_2L(NH_3)_2^{4+} \qquad (3)$$

All the complexes show a broad band centred at *ca.* 850 nm similar to that observed for Cu^{II} complexes with tren [tris-(2-aminoethyl)amine] and substituted tren, and typical of Cu^{II} in a trigonal bipyramidal (*TBPY*) co-ordination environment.[14] Additional bands characteristic of each of the Cu_2LX^{z+} complexes are also included in Table 1.

Kinetic experiments

All the binuclear Cu_2LX^{z+} complexes were found to decompose readily upon addition of an excess of acid [eqn. (4)], the process requiring typically less than 1 s for completion. The kinetics of decomposition were monitored under pseudo-first order conditions of excess acid and kinetic traces at different wavelengths could be satisfactorily fitted by a single exponential, the values of the observed rate constants (k_{obs}) being independent of the monitoring wavelength. Some experiments carried out with a diode array detector showed that the initial spectra during the decomposition of the complexes coincide with the spectra of the starting complexes, which indicates that there is no formation of significant amounts of any species during the mixing time of the stopped-flow instrument. The first order dependence with respect to the metal complex was confirmed by the lack of change in k_{obs} when the concentration of the complex was changed. The values of k_{obs} for the tertiary Cu_2LX^{z+} complexes at different concentrations of added acid are included in Table S1 (ESI).

$$Cu_2LX + H^+_{exc} \longrightarrow 2\,Cu^{2+} + H_6L^{6+} + X^- \text{ (or HX)} \qquad (4)$$

As solutions of the metal complexes contained an excess of the ancillary ligand in order to achieve complete formation of the Cu_2LX^{z+} complexes, a fraction of the added acid is used to neutralise the excess of X in the cases of NH_3 and N_3^-. As a consequence, the concentration of acid available for complex decomposition is reduced with respect to the added amount and must be calculated using the reported values of the protonation constants.[15] The equations used are included in Appendix A (ESI) and the corrected concentrations of acid are also shown in Table S1 (ESI).

The dependence of k_{obs} on acid concentration for the decomposition of $Cu_2L(SCN)^{3+}$ and $Cu_2L(NH_3)_2^{4+}$ (Fig. 1) is the same as previously observed for the $Cu_2L(OH)^{3+}$ complex.[9] The data can be fitted by eqn. (5) and the values so derived for parameters *a* and *b* are included in Table 2, which also shows the values corresponding to the OH^- complex for comparative purposes. For a given complex, no significant differences are

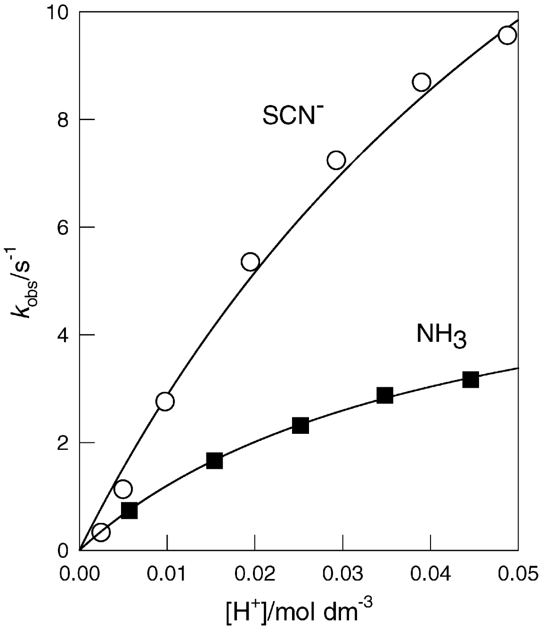


Fig. 1 Plots of k_{obs} *vs.* the concentration of free H^+ for the decomposition of the $Cu_2L(SCN)^{3+}$ and $Cu_2L(NH_3)_2^{4+}$ complexes.

Table 2 Summary of kinetic data for the acid-promoted decomposition of the binuclear Cu_2LX^{z+} complexes (25 °C, 0.10 mol dm^{-3} KNO_3). The values of *a*, *b* and *c* were obtained by fitting the experimental data (ESI) to eqns. (5) and (6) in the text[a]

X	$[X]_0$/mol dm^{-3}	a/s^{-1}	b/dm^3 mol^{-1}	10^{-3} c/dm^6 mol^{-2} s^{-1}
SCN^-	7.5×10^{-3}	25(5)	13(4)	
	4.25×10^{-3}	22(4)	15(4)	
NH_3	4.22×10^{-3}	6.2(3)	24(2)	
	2.70×10^{-3}	6.7(8)	19(4)	
N_3^-	7.50×10^{-4}			1.65(5)
	2.25×10^{-3}			1.36(4)
OH^- [b]		170(60)	5(2)	

[a] The numbers in parentheses represent the standard deviation in the last significant digit. [b] Data from ref. 9.

observed between the values of *a* and *b* derived from two sets of experiments at different concentrations of SCN^- or NH_3.

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

The kinetics of decomposition of the $Cu_2L(N_3)^{3+}$ complex is different from that observed for the OH^-, SCN^- and NH_3 complexes, the values of k_{obs} showing a second order dependence on H^+ [eqn. (6), Fig. 2]. The values of k_{obs} at low concentrations of H^+ indicate that if there is any possibility of a mixed first and second order dependence on $[H^+]$, the contribution of the first order term is negligible. The values of *c* derived from two sets of experiments (Table 2) are somewhat different but the agreement is satisfactory, especially when the complexity of the numerical analysis is considered.

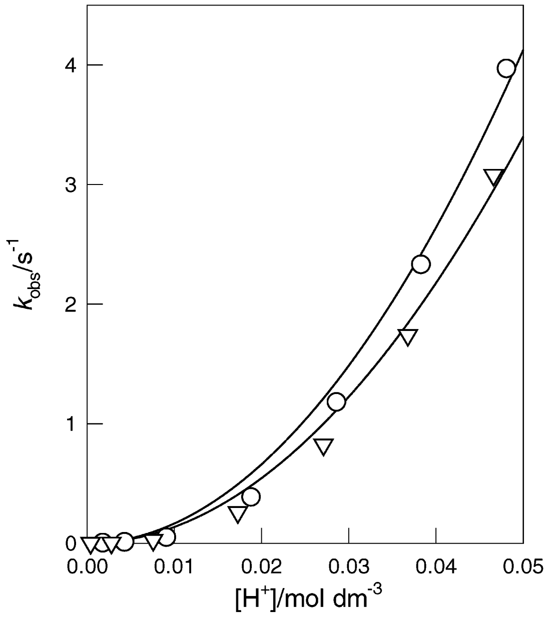


Fig. 2 Plot of k_{obs} *vs.* the concentration of free H^+ for decomposition of the $Cu_2L(N_3)^{3+}$ complex. The curve labels correspond to two sets of experiments at different concentrations of N_3^-: 7.50×10^{-4} mol dm^{-3} (○) and 2.25×10^{-3} mol dm^{-3} (▽).

$$k_{obs} = c\,[H^+]^2 \qquad (6)$$

Table 3 Comparison of the equilibrium constants for the formation of binuclear Cu_2LX^{z+} complexes from Cu_2L^{4+} with the corresponding constants for the formation of Cu^{II}–X complexes from Cu^{2+}

Complex	log K_{Cu_2LX} [a]	log K_{CuX} [b]	Δlog K [c]
$Cu_2L(OH)^{3+}$	8.84	6.10	2.74
$Cu_2L(SCN)^{3+}$	5.62	1.87	3.75
$Cu_2L(N_3)^{3+}$	6.93	2.44	4.49
$Cu_2L(NH_3)^{4+}$	5.08	4.12	0.96
$Cu_2L(NH_3)_2^{4+}$	8.35 [d]	7.58 [e]	0.77

[a] K_{Cu_2LX} = $[Cu_2LX]/[Cu_2L][X]$. [b] K_{CuX} = $[CuX]/[Cu][X]$, data from ref. 15. [c] Δlog K = log K_{Cu_2LX} − log K_{CuX}. [d] $K_{Cu_2L(NH_3)_2}$ = $[Cu_2L(NH_3)_2]/[Cu_2L][NH_3]^2$. [e] $K_{Cu(NH_3)_2}$ = $[Cu(NH_3)_2]/[Cu][NH_3]^2$. (Charges are omitted for simplicity in all the footnotes).

Discussion

Equilibrium constants for the formation of tertiary Cu_2LX^{z+} complexes

The analysis of potentiometric[6,9] and spectrophotometric data for the Cu^{II}–L and Cu_2LX^{z+} complexes indicates that the co-ordination number about Cu^{II} is five in all cases. The band close to 850 nm for all the complexes indicates *TBPY* geometry because the alternative square-pyramidal co-ordination usually leads to a band centred at *ca.* 650 nm.[16] The geometry proposed is supported by the crystal structures of $[Cu_2L(N_3)](ClO_4)_3$, $[Cu_2L(NCO)](ClO_4)_3$ and $[Cu_2L(CO_3)(H)]Br_3$.[6,7] The nature of L, with two tren donor sub-units, favours such a co-ordination environment, which also has been observed in solution studies and crystal structures of Cu^{II} complexes with tren and substituted tren.[14,17]

The values of log *K* in Table 1 for the SCN^- and N_3^- complexes agree reasonably well with those previously determined (2.95 for the thiocyanate complex and 4.78 for the azide complex),[2] the differences being attributable to changes in the experimental conditions (pH, buffer, added electrolyte). The constants in Table 1 are expressed with respect to $Cu_2L(OH)^{3+}$ and so they depend on the strength of interaction of OH^- with the metal centres. However, values relative to Cu_2L^{4+} can be obtained by combining the data in Table 1 with the equilibrium constants previously determined for the Cu^{II}–L complexes.[6,9] The results are included in Table 3 and show that the most stable complex is formed with OH^-, although a more detailed comparison should consider the different basicity, charge and steric requirements of the ancillary ligands. For this reason, we have also included in Table 3 the equilibrium constants for the interaction of the X ligands with $Cu(H_2O)_6^{2+}$.[15] The differences between both sets of values (Δlog *K* in Table 3) are a measure of the stabilisation of the ancillary ligands at the Cu_2L^{4+} site with respect to Cu^{2+}. This new comparison indicates that NH_3 is only slightly more stable in the binuclear complex, whereas the anionic X ligands are highly stabilised in the Cu_2LX^{3+} complexes, in agreement with their ability to act as a bridging ligand. However, the stabilisation depends on the nature of the anion and follows the order $OH^- < SCN^- < N_3^-$. Similar and even larger stabilisation of bridging anions with binuclear metal complexes of bis-tren cryptands can be deduced from previously reported stability data.[2,4] On the basis of theoretical calculations, the preferential complexation of N_3^- at the Cu_2L^{4+} site has been proposed to be caused by a better fit between the Cu–Cu distance and the bite length of the bridging anion,[2] and actually, the crystal structure of $[Cu_2L(N_3)](ClO_4)_3$ reveals the existence of a collinear Cu–N–N–N–Cu assembly.[7]

The kinetics of decomposition of tertiary binuclear Cu_2LX^{z+} complexes

The decomposition of all the binuclear complexes in this work involves the release of two metal ions from the cavity of the cryptand. We have previously shown[9] that the decomposition of the $Cu_2L(OH)^{3+}$ complex occurs with statistically controlled kinetics, *i.e.* the rate of release of the first ion doubles the rate corresponding to the second ion. However, because of mathematical simplifications, the kinetic traces for the binuclear complex are simplified to a single exponential[18] with an apparent rate constant that measures the dissociation of the second metal ion.[9] The observation of a single exponential for all the Cu_2LX^{z+} complexes in this work suggests that their decomposition kinetics are also statistically controlled, and some alternative interpretations can be ruled out. Thus, the possibility of rapid dissociation of the first Cu^{II} followed by rate-determining dissociation of the second can be ruled out because the initial spectra during the decomposition coincide with those of the starting complexes. On the other hand, if the rate-determining step were dissociation of the first ion, the release of Cu^{II} from the mononuclear complexes formed during the decomposition of the binuclear complexes should occur at an anomalously high rate. Thus, the most reasonable interpretation for the observation of a single exponential during decomposition of the Cu_2LX^{z+} complexes is to assume statistically controlled kinetics. In that case, the rate constants in Table S1 (ESI) and the values of *a* and *b* in Table 2 correspond to dissociation of the second Cu^{II}, although the values for the first one can be easily estimated from eqn. (5).

For the acid-promoted decomposition of tertiary Cu_2LX^{z+} complexes, two extreme possibilities can be considered depending on which ligand (L or X) is released first. As monodentate ligands are more weakly bound than polyamines, they are expected to dissociate more rapidly. Actually, the $Cu(tren)(L')^{2+}$ complexes ($L' = NH_2CH_3$, 1-methylimidazole) decompose[19] with dissociation of L′ within the mixing time of the stopped-flow instrument, the observed kinetics being the same as for $Cu(tren)(H_2O)^{2+}$. In contrast, although the co-ordination environment of Cu^{II} ions in the Cu_2LX^{z+} complexes is similar to that of the tren complexes, the data in Table 2 clearly show different decomposition kinetics for every complex. It could be argued that OH^-, N_3^- and SCN^- act as bridging ligands and this inhibits their dissociation, but the NH_3 complex does not contain any bridge and it also decomposes with different kinetics. Thus, the behaviour of the Cu_2LX^{z+} complexes is different from that of the Cu^{II}-tren complexes and their acid-promoted decomposition does not occur with rapid dissociation of the X ligands followed by proton attack at the polyamine cryptate. The decreased lability of the Cu^{II}–X bonds in the complexes of L is probably the result of the steric requirements of the cryptand. Actually, a decrease in the lability of the bonds between Cu^{II} and monodentate ligands has been observed when passing from the complexes of tren to the more sterically demanding Me_3tren and Me_6tren ligands.[14]

Having ruled out the initial rapid dissociation of X, two possibilities can be considered to explain the different kinetics of decomposition of the Cu_2LX^{z+} complexes. One possibility is the participation of ancillary ligands in protonation processes prior to dissociation of the cryptand and the other is that the kinetic differences are caused by changes induced by the X ligands in the kinetics of dissociation of the Cu–N bonds.

Previous attack by H^+ to co-ordinated X requires the existence of basic sites on the ancillary ligand. Although SCN^- and N_3^- have lone pairs of electrons that could be attacked to form species of the type $Cu_2L(HX)^{4+}$, this attack is not possible for $Cu_2L(NH_3)_2^{4+}$ and it decomposes with a kinetics not very different from that of the OH^- and SCN^- complexes. Moreover, the amount of $Cu_2L(HX)^{4+}$ formed would be necessarily very low and there is no reason to think that its formation would favour the dissociation of the cryptand. So, protonation at the ancillary ligand can be reasonably ruled out as a feasible pathway for the decomposition of these complexes. Thus, the effect of the ancillary ligands on the kinetics of decomposition of the Cu_2LX^{z+} complexes appears to consist of a modification of the kinetics of dissociation of the Cu–N bonds.

The mechanism of decomposition of the Cu_2LX^{z+} complexes

According to the mechanism previously proposed for the decomposition of the Cu^{II}–L complexes[9] and related compounds,[11–13] the first step consists of the formation of an activated intermediate in which there is partial dissociation of the Cu–N bond without its replacement by a solvent molecule [eqn. (7)].[19–25] The rate-determining step is attack by protons on the activated intermediate [eqn. (8)], which leads to the complete dissociation of the amino group. The process continues rapidly to achieve complete decomposition of the complex. For simplicity, a mononuclear CuL complex is considered in eqns. (7) and (8), but the statistical kinetics allows similar equations for dissociation of both metal centres.

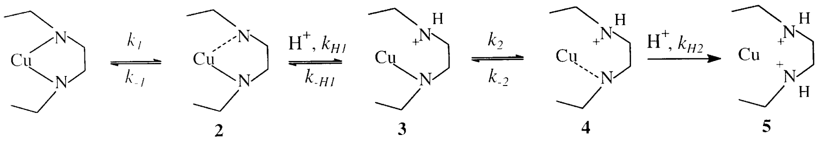
$$\mathrm{CuL} \rightleftarrows (\mathrm{CuL})^* \quad k_1, k_{-1} \qquad (7)$$

$$(\mathrm{CuL})^* + \mathrm{H}^+ \longrightarrow \mathrm{Cu}^{2+} + \mathrm{H_6L}^{6+} \quad k_\mathrm{H} \qquad (8)$$

As the decomposition of metal–polyamine complexes involves the breaking of several M–N bonds, the rate-determining step can be displaced from the breaking of the first bond to the second one, which would lead to a second order dependence on $[H^+]$. Nevertheless, despite the numerous kinetic studies carried out, a second order dependence has only been observed for a limited number of complexes,[22–28] although there are also some cases in which the rate law includes a mixed dependence on $[H^+]$ and $[H^+]^2$.[22,24] The second order dependence is always considered to be the result of a rapid initial protonation step followed by a slower acid-assisted dissociation process. The initial protonation can occur on a co-ordinated amino group[22,28] (and the rate-determining step would be the breaking of the second Cu^{II}–N bond) or at a different atom, as the oxygen of C=O or COO^- groups that may exist in the polyamine ligand.[23,26]

The second order dependence on $[H^+]$ observed for $Cu_2L(N_3)^{3+}$ establishes an initial protonation step that leads to an intermediate of composition "$HCu_2L(N_3)^{4+}$". As pointed out above, protonation at co-ordinated azide appears unlikely and so, the initial protonation step must involve one of the amine groups of the cryptand. In that case, the rate-determining step would be displaced from dissociation of the first Cu^{II}–N bond in the OH^-, SCN^- and NH_3 complexes to the second Cu^{II}–N bond in $Cu_2L(N_3)^{3+}$. To our knowledge, this is the first case in which such displacement of the rate-determining step is observed for complexes with the same polyamine.

The mechanism proposed for the acid-promoted decomposition of the Cu_2LX^{z+} complexes is depicted in Scheme 2, where only a metal centre and two nitrogens are shown for clarity. Following the initial activation of one Cu^{II}–N bond, the resulting intermediate (**2**) is attacked by acid to form **3**, in which the amine group is protonated and completely dissociated. The third step consists of the activation of the second Cu^{II}–N bond and leads to intermediate **4**, which is attacked by H^+ in the rate-determining step (k_{H2}). The following rapid steps leading to dissociation of the remaining co-ordinated amine groups have been omitted for simplicity. If the intermediates are formed under steady-state conditions, the rate law corresponding to this mechanism is given by eqn. (9), although several simplified forms are possible depending on the relative values of the rate constants.



Scheme 2

$$k_{\mathrm{obs}} = \frac{k_1 k_2 k_{\mathrm{H1}} k_{\mathrm{H2}}[\mathrm{H}^+]^2}{k_{-1}k_{-2}k_{-\mathrm{H1}} + k_{-1}k_{\mathrm{H2}}(k_2 + k_{-\mathrm{H1}})[\mathrm{H}^+] + k_2 k_{\mathrm{H1}} k_{\mathrm{H2}}[\mathrm{H}^+]^2} \quad (9)$$

When the product $k_{-1}k_{-2}k_{-\mathrm{H1}}$ is very small, the rate law reduces to eqn. (10) and saturation behaviour is expected. Under these conditions, this mechanism accounts for the results obtained for the OH^-, SCN^- and $\mathrm{NH_3}$ complexes. Eqn. (10) is similar to eqn. (5) with the equivalencies $a = k_1$ and $b = k_2k_{\mathrm{H1}}/[k_{-1}(k_2 + k_{-\mathrm{H1}})]$. Whereas a always measures the lability of the first $\mathrm{Cu^{II}}$–N bond (k_1), b is a complex parameter that includes several of the rate constants in Scheme 2. If the proton attack to the first bond labilises the remaining bonds, $k_2 \gg k_{-\mathrm{H1}}$ and $b = k_{\mathrm{H1}}/k_{-1}$, *i.e.* the kinetics of decomposition only depends on the dissociation of the first $\mathrm{Cu^{II}}$–N bond. However, when $k_{-\mathrm{H1}} \geq k_2$ the value of b includes k_2 and contains some information about the lability of the second Cu–N bond.

$$k_{\mathrm{obs}} = \frac{k_1 k_2 k_{\mathrm{H1}}[\mathrm{H}^+]}{k_{-1}(k_2 + k_{-\mathrm{H1}}) + k_2 k_{\mathrm{H1}}[\mathrm{H}^+]} \quad (10)$$

The values in Table 2 indicate that the order of lability of the $\mathrm{Cu^{II}}$–N bonds (a, k_1) for the complexes of the different X ligands expands for more than an order of magnitude and follows the order $\mathrm{OH}^- > \mathrm{SCN}^- > \mathrm{NH_3}$. In contrast, the b values show smaller changes and follow the inverse trend. It has been pointed out[21] that there is a correlation between the N–Cu–N bond angles and the rate of decomposition of the Cu–polyamine complexes, the most distorted structures decomposing faster. A possible explanation of the results obtained for $\mathrm{Cu_2L(OH)^{3+}}$, $\mathrm{Cu_2L(SCN)^{3+}}$ and $\mathrm{Cu_2L(NH_3)_2^{4+}}$ would be to consider that the different kinetics of decomposition are the result of different degrees of distortion imposed by the ancillary ligands. The absence of a bridge in the $\mathrm{NH_3}$ complex allows a more regular structure and the complex decomposes more slowly (smaller k_1). In contrast, the small size of the OH^- bridge must lead to a more distorted structure and the $\mathrm{Cu_2L(OH)^{3+}}$ complex decomposes more rapidly (larger k_1). The trend in the b values is probably a consequence of larger k_{-1} values for the less distorted complexes.

Simplification of eqn. (9) when the product $k_{-1}k_{-2}k_{-\mathrm{H1}}$ is much larger than the remaining terms in the denominator leads to a second order kinetics [eqn. (11)], equivalent to eqn. (6) with $c = K_1K_2K_{\mathrm{H1}}k_{\mathrm{H2}}$.

$$k_{\mathrm{obs}} = K_1 K_2 K_{\mathrm{H1}} K_{\mathrm{H2}}[\mathrm{H}^+]^2 \quad (11)$$

Thus, the observation of saturation kinetics or of second order dependence on $[\mathrm{H}^+]$ depends on the value of the product $k_{-1}k_{-2}k_{-\mathrm{H1}}$, saturation kinetics being observed when it is small and second orders kinetics when it increases. The OH^-, SCN^- and $\mathrm{NH_3}$ complexes show saturation kinetics, although the values of a and b change with the nature of the ancillary ligand. For the azide complex, Fabbrizzi and co-workers[2] have shown that there is an excellent fit between the size of X and the separation between the metal centres in the cryptand cavity, which leads to a large stability constant and surely also to less strained $\mathrm{Cu^{II}}$–N bonds. In that case, the amine groups would have a high tendency to remain co-ordinated and the value of k_{-1} (and k_{-2}) should increase. If this increase is large enough, the product $k_{-1}k_{-2}k_{-\mathrm{H1}}$ becomes the most important term in the denominator of eqn. (9) and causes a change to second order kinetics.

Conclusion

The kinetic results in this work clearly demonstrate that the ancillary ligands can play an important role in the kinetics of acid-promoted decomposition of polyamine complexes. As any kinetic study of these kinds of processes necessarily involves several sources of potential ancillary ligands (OH^-, anions of the metal salt and the acid, salt used for controlling the ionic strength), caution is necessary when obtaining and comparing kinetic results for these processes. Because the nature of the species in solution depends on the concentrations of the metal, the polyamine and the ancillary ligands in the solutions that are mixed with the acid, a detailed knowledge of the nature and stability of the different species is required.

Experimental

The ligand L was prepared as L·8HBr following the literature procedure[6] and its purity was confirmed by ^{1}H and ^{13}C NMR spectra recorded with a Varian Unity 400 spectrometer. The actual molecular weight and the exact amount of acid in the sample were determined from potentiometric titrations using a Crison 2002 pH-meter provided with an Ingold combined electrode. All the other reagents were obtained from Aldrich and used without further purification.

Equilibrium determinations

The spectrophotometric measurements were carried out with a Perkin-Elmer Lambda 3B instrument. The equilibrium constants for the formation of tertiary $\mathrm{Cu_2LX^{z+}}$ complexes were determined at 25.0 °C under a $\mathrm{N_2}$ atmosphere and in the presence of 0.10 mol dm^{-3} $\mathrm{KNO_3}$. The pH was maintained at 7.05 with a MOPS buffer (3-morpholinopropanesulfonic acid, 0.01 mol dm^{-3}). A stock solution of the starting $\mathrm{Cu_2L(OH)^{3+}}$ complex was prepared by mixing $\mathrm{Cu(NO_3)_2{\cdot}6H_2O}$ and L·6HBr in a 2 : 1 molar ratio and then adjusting the pH. Several samples were then prepared by taking aliquots of the stock solution and adding different amounts of $\mathrm{NH_3}$, KSCN or $\mathrm{NaN_3}$. After addition of the ancillary ligand, the solutions were allowed to stand for two days at 25.0 °C; during this time, the pH was controlled and maintained at 7.05 with titrated $\mathrm{HNO_3}$ and KOH solutions. Typically, 20 solutions were prepared for each ancillary ligand covering concentration ranges of $(1.0\text{–}5.0) \times 10^{-4}$ mol dm^{-3} ($[\mathrm{Cu_2L(OH)^{3+}}]_0$) and 1.0×10^{-5} to 5.6×10^{-3} mol dm^{-3} ($[\mathrm{X}]_0$). The spectra of the solutions were recorded and digitised at 5 nm from 800 to 340 nm. The data were analysed with the program SQUAD,[29] which leads to the values of the equilibrium constants and the spectra of the tertiary complexes.

Kinetic experiments

The kinetic experiments were carried out with an Applied Photophysics SX-17MV instrument. The temperature was controlled at 25.0 °C and the ionic strength was adjusted to 0.10 mol dm^{-3} with $\mathrm{KNO_3}$. Solutions of the $\mathrm{Cu_2LX^{z+}}$ complexes were prepared by mixing $\mathrm{Cu(NO_3)_2{\cdot}6H_2O}$ and L·6HBr in a 2 : 1 molar ratio and then adding an excess of the ancillary ligand as $\mathrm{NH_3}$, KSCN or $\mathrm{NaN_3}$. The pH was finally adjusted to 7.05 with titrated solutions of $\mathrm{HNO_3}$ and KOH. The actual concentrations of the resulting solutions are given in the ESI. All experiments were carried out by mixing these solutions with titrated solutions of HNO_3 under pseudo-first order conditions of excess acid. The wavelength was selected from the previous equilibrium measurements: 690 nm (NH_3 complex), 380 nm (SCN^- complex) or 415 nm (N_3^- complex). All kinetic traces could be fitted by a single exponential using the standard software of the stopped-flow instrument. The reported values of the observed rate constant, k_{obs}, are the mean value of at least six determinations with a standard deviation of less than 5%.

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