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Kinetics and mechanism of the acid dissociation of copper(II) complex of novel *C*-functionalized macrocyclic dioxotetraamines

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Abstract—The kinetics of the acid dissociation of copper(II) complex of a novel *C*-functionalized macrocyclic dioxotetraamine has been studied using a stopped-flow spectrophotometer. It was proven that substituents decrease the acid dissociation rates. The dissociation rate follows the law $v_d = C_{com}kK_1K_2H^2/(1 + K_1H + K_1K_2H^2)$. On the intermediates we have obtained, the dissociation kinetics are interpreted by a mechanism involving the negatively charged carbonyl oxygen of the complex being rapidly protonated in a pre-equilibrium step, the rate-determining step being intramolecular hydrogen(enolic tautomer) migration(to imine nitrogen). The dissociation rate reached a plateau in strongly acidic solution. By means of temperatures coefficient method, K_1, K_2 of the pre-equilibrium step and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the rate-determining step were obtained and the results discussed. It is the strong in-plane ligand field that increased ΔH of the rate-determining step and thus decreases the dissociation rate constant. The Brönsted type linear free energy relationships do exist in this *C*-functionalized dioxotetraamine copper(II) complex. The results clarify insights into acid dissociation mechanisms for the 14-membered macrocyclic dioxotetraamine copper(II) complex.

Keywords: macrocyclic dioxotetraamine; acid dissociation; kinetics; mechanism; copper(II) complex.

Acid-assisted dissociation kinetics of open-chain polyamine complexes has been extensively studied,[1–10] and many of these works have been reviewed [9]. Recently, there has been considerable interest in the kinetics and mechanism of the acid dissociation of macrocyclic polyamine complexes [11–14]. Most of the previous work concerns mainly the macrocyclic complex without substituents. In general, due to the thermodynamic macrocyclic effect and the kinetic macrocyclic effect, macrocyclic complexes are thermodynamically stable and kinetically inert, the rates of dissociation of metal complexes with tetraazacycloalkanes being relatively slow. In some instances they are so slow that one can study them even under extreme conditions, such as in 10 M $HClO_4$ [11].

Dioxotetraamine macrocycles are unique metal chelators, their structures bear the dual feature of macrocyclic polyamine and oligopeptides [15–20]. Macrocyclic dioxotetraamine complexes display interesting properties from the point of view of the redox activity and stability. Most interesting is the observation that the replacement of the amino group by an amide function greatly affects the dissociation rate of metal complexes with tetraaza macrocycles. Hay [21] described the kinetics of the dissociation of the copper(II) and nickel(II) complexes with 1,4,8,11-tetraaza-cyclotetradecane-12,14-dione(dioxocyclam) in the pH region 4–5, in which the analogous complexes with 14-aneN4(cyclam) give no sign of dissociation. In the study of the complex formation of dioxotetraamine, it was considered that existence of non-deprotonated or singly deprotonated copper(II) complex is unlikely [20]. That is, the dioxotetraamine

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dissociates both its amide hydrogen simultaneously when coordinated to a 3*d* metal ion. However, non-deprotonated copper(II) complexes of dioxotetraamine macrocycles have been prepared in this laboratory [16]. More recently, we proved that singly deprotonated copper(II) complexes do exist both in the solid state and in aqueous solution [18]. The existence of the two types of complex we have found so far provides us with critical evidence for discussion of the details of acid dissociation or formation of macrocyclic dioxo-tetraamine copper(II) complexes. Also, in a study of the acid dissociation of macrocyclic copper(II) complex, Siegfried [21] and Hay [22] gave a different acid dissociation tendency, but there is no evidence to support their mechanism. There is no acid dissociation study on substituted macrocyclic dioxotetraamine copper(II) complex. Whether substituents have significant influence on the dissociation rate can provide some information on the acid dissociation mechanism and this is still unclear. This stimulated us to further investigate the acid dissociation kinetics and mechanism and clarify insights into the dissociation process.

In this paper, we report the results of our systematic studies on the acid dissociation reaction of our new series *C*-functionalized macrocyclic dioxotetraamine copper(II) complexes in order to determine the "kinetic macrocyclic effect" and some important kinetic parameters to clarify insights into the reaction mechanism and the influence of the substituent.

EXPERIMENTAL

Reagents

All the reagents used were of reagent grade. KNO_3 and chloroacetic acid were recrystallized before use. Redistilled water was used for all the solutions. The *C*-functionalized macrocyclic dioxotetraamine were prepared according to our novel synthesis methods [17].

Instruments

Electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer. Stability of macrocyclic dioxotetraamine copper(II) complexes were determined in the same way as reported previously [17]. pHs were measured on a Beckman Φ71 pH meter.

Kinetic measurements

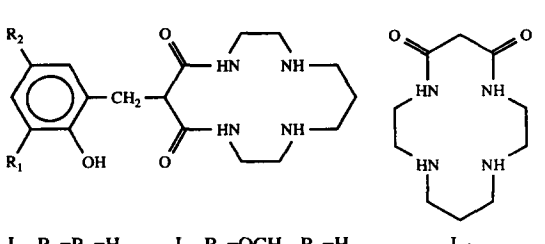
The dissociation kinetics was followed on a Union Giken RA-410 stopped-flow spectrophotometer. The complex and buffer solution were prepared by using 0.5 mol dm^{-3} KNO_3 solution. Experimental conditions were [complex] = 3.0×10^{-3} mol dm^{-3} (I = 0.5 mol dm^{-3} KNO_3), [buffer] = 0.10 mol dm^{-3} chloroacetic acid (I = 0.5 mol dm^{-3} KNO_3), pH was adjusted with 1 mol dm^{-3} KOH. Complex solutions were prepared by mixing equimolar quantities of the ligand and standard $Cu(NO_3)_2$, followed by adjustment of pH to 7 with NaOH, at which the complex is fully formed in the form $[Cu(H_{-2}L)]$. The dissociation was followed at their absorption maxima, i.e., 500 nm (L1), 505 nm (L2), 495 nm (L3), 490 nm (L4), 515 nm (dioxocyclam). Reaction time ranges from 5 s to 2 min. In our experiments, the reaction has excellent reproducibility.

RESULTS AND DISCUSSION

All these complexes have a *d–d* absorption band at ~500 nm, but the free ligands have no absorption in this region. In acid dissociation experiments, the absorption at 500 nm disappeared without any interference.

Under the experimental conditions of constant hydrogen concentration, a first-order reaction with respect to the concentration of complex was observed, that is, the kinetics of the acid dissociation of the copper(II) complexes follows the rate law $v_d = k_{obs} C_{com}$, where C_{com} is the total concentration of the complex and k_{obs} is the pseudo-first-order rate constant. It should be noted that k_{obs} is a function of pH and temperature of the solution.

Figures 1 and 2 show k_{obs} values at different pH and temperature.



Scheme 1. Structure of the ligands.

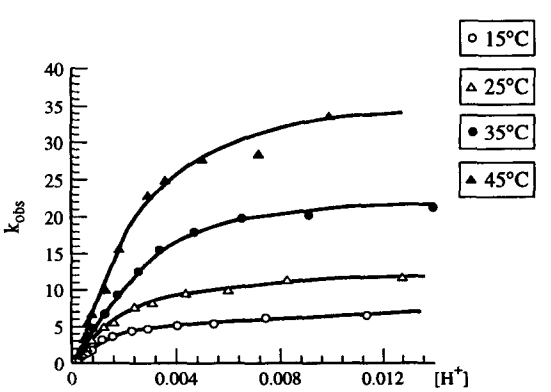


Fig. 1. The plot of k_{obs} *vs* $[H^+]$ for $CuH_{-2}L_1$.

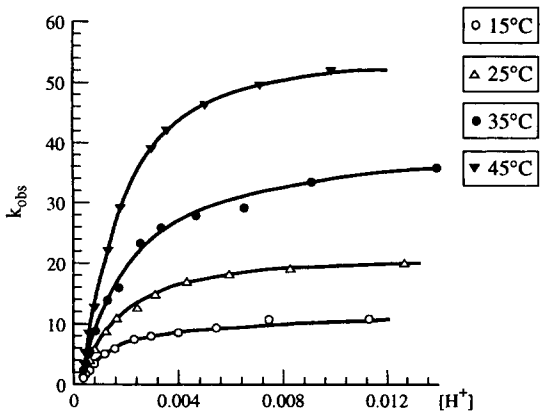
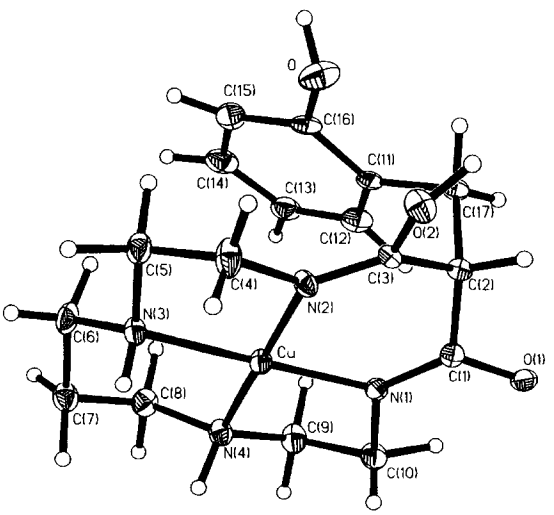


Fig. 2. The plot of k_{obs} *vs* $[H^+]$ for $CuH_{-2}L_5$.

We can see that k_{obs} increased rapidly with the increase of $[H^+]$ at low hydrogen concentration, further increase of $[H^+]$, k_{obs} increases slowly, up to a plateau, k_{obs} keeps constant with the increase of $[H^+]$. This phenomenon is similar to those reported by Siegfried [21], but quite different from those reported by Hay [22] who studied the similar reaction in a narrow pH region and found that k_{obs} linearly increases with $[H^+]^2$. Reference to Figs 1 and 2 suggests an order for $[H^+]$ varying from 1 to 0. From a mathematical view, the tendency coincides with the following equation [23]:

$$k_{obs} = a[H^+]/(1 + b[H^+]) \quad (1)$$

where a and b are constants. The above equation is just the experimental rate law. From the above experimental rate law, plots of $1/k_{obs}$ *vs* $1/[H^+]$ should give a straight line. The slope and intercept are $1/a$ and b/a values respectively. a and a/b values and regression coefficient r obtained are summarized in Table 1.



Scheme 2. Crystal structure of singly-deprotonated L_1 copper(II) complex.

Previously we prepared a singly deprotonated 14-membered dioxotetraamine copper(II) complex [18] and a non-deprotonated 13-membered macrocyclic dioxotetraamine copper(II) complex [16]. The singly-deprotonated copper(II) complex of L_1 has the following structure:

In the singly-deprotonated 14-membered macrocyclic dioxotetraamine copper(II) complex, the amido hydrogen binds to amido oxygen instead of nitrogen. Considering that undeprotonated 13-membered macrocyclic dioxotetraamine copper(II) complex can exist in the solid state and the mechanism proposed by Siegfried [21], we propose the following acid-dissociation mechanism.

Under the conditions investigated, the initial form of the complex is entirely $[Cu(H_{-2}L)]$. The first and the second step are the protonation of the negatively charged carbonyl oxygens. The protonation of the negatively charged carbonyl oxygens leads to the enolic tautomer structure, these two intermediates have been isolated and characterized both in solid state and in aqueous solution previously [16,18]. The two protonation processes are actually the neutralization reaction of an acid and a base, their rates are very fast, therefore they are pre-equilibrium processes. The third step is the protonation of the amido nitrogen with simultaneous deprotonation of the amido oxygen. This process is most probably, in our opinion, intramolecular hydrogen migration (as shown in the mechanism) because it is more accessible than other protonation modes. This is the rate-determining step, the products being solvated copper(II) ion and free ligand. The free ligand is quickly protonated in the acid solution (neutralization reaction).

The observed reaction rate is first-order with respect to complex concentration C_{com}. However, k_{obs} shows a first-order dependence on $[H^+]$ at low $[H^+]$ and zero-order at high $[H^+]$ as shown in Figs 1 and 2.

From the following stoichiometric relation:

$$C_{com} = [ML] + [MH_{-1}L] + [MH_{-2}L], \quad (2)$$

we have

$$C_{com} = [ML](1 + K_1[H] + K_1K_2[H]^2)/K_1K_2[H]^2. \quad (3)$$

According to the mechanism,

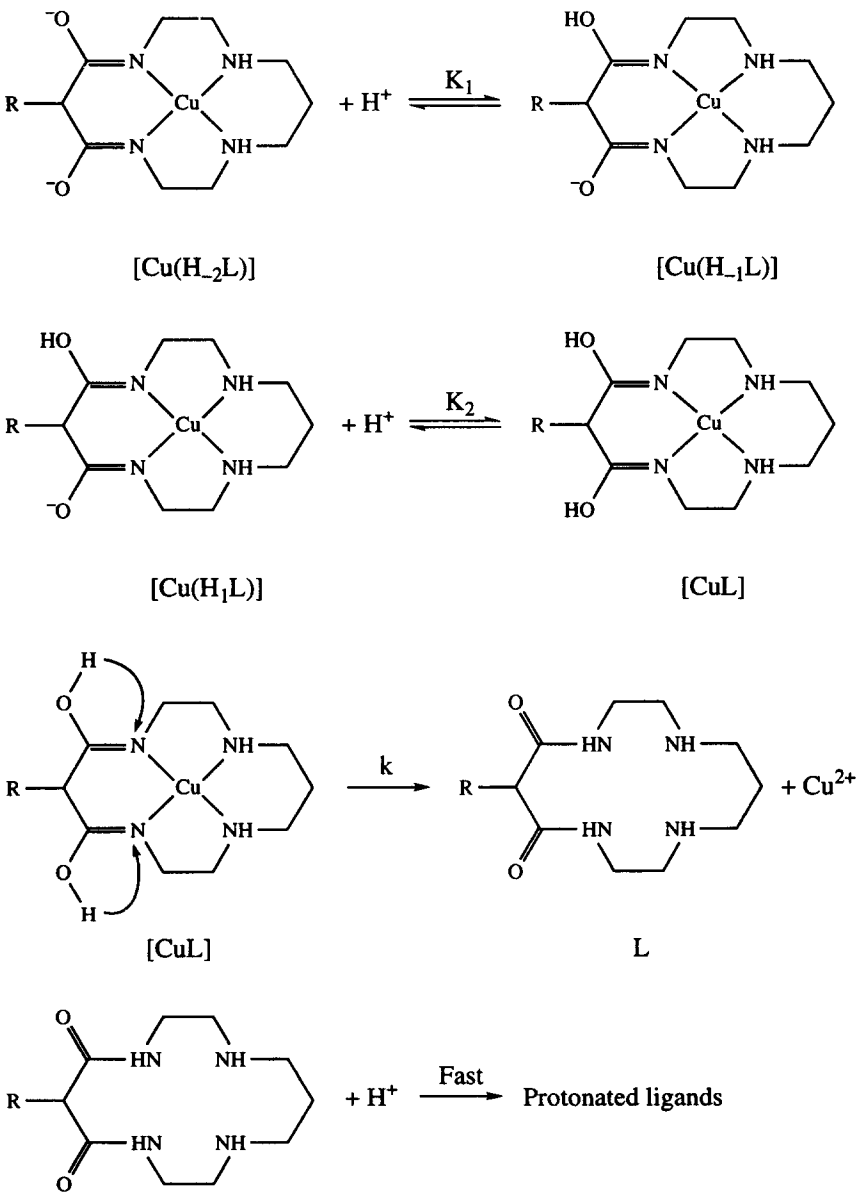
$$v_d = k[ML] = C_{com}kK_1K_2[H]^2/(1 + K_1[H] + K_1K_2[H]^2), \quad (4)$$

therefore,

$$k_{obs} = kK_1K_2[H]^2/(1 + K_1[H] + K_1K_2[H]^2). \quad (5)$$

Table 1. *a*, *b* parameters in the experimental rate law and regression coefficients at different temperatures ($I = 0.5$ mol dm^{-3} KNO_3)

Complex		$CuH_{-2}L_1$	$CuH_{-2}L_2$	$CuH_{-2}L_3$	$CuH_{-2}L_4$	$CuH_{-2}L_5$
288 K	*a*/*b*	7.29	12.1	5.15	6.63	12.6
	a	0.00437	0.00194	0.00218	0.00123	0.00683
	r	0.997	0.987	0.985	0.991	0.996
298 K	*a*/*b*	14.1	14.8	11.3	11.2	24.6
	a	0.00606	0.00399	0.00322	0.00200	0.000107
	r	0.991	0.980	0.979	0.999	0.995
308 K	*a*/*b*	30.1	27.4	20.7	20.76	39.4
	a	0.00804	0.00650	0.00527	0.00335	0.000213
	r	0.986	0.986	0.989	0.998	0.988
318 K	*a*/*b*	46.8	40.6	32.3	39.7	60.4
	a	0.000130	0.000112	0.00906	0.00468	0.000380
	r	0.987	0.995	0.999	0.997	0.996



Scheme 3. Proposed acid-dissociation mechanism.

From the above equations, we stress that k_{obs} is not simply two power to hydrogen ion. At high $[H^+]$, $1 + K_1[H] + K_1K_2[H]^2 = K_1K_2[H]^2$, $k_{obs} = k$, that is, the k_{obs} becomes a constant at high $[H^+]$(zero-order dependence). At low $[H^+]$ (pH > 5.5), $1 + K_1[H] + K_1K_2[H]^2 = 1$, $k_{obs} = kK_1K_2[H]^2$, that is a second-order dependance on $[H^+]$ should be observed. However, at this $[H^+]$ concentration, because of the fast equilibrium of step 1 and 2 in the mechanism, we cannot observe acid dissociation of the copper(II) complex, i.e., the complex does not dissociate at all, therefore, we cannot investigate the dissociation kinetics at pH higher than 5.5 because of the strong coordination tendency of the macrocyclic ligands. Looking at the data in Fig. 2, we assumed that, even at the lowest concentrations of acid used ($[H^+] = 0.0003$ mol dm^{-3}, $K_1 = 20{,}000$), therefore $K_1[H^+] \gg 1$ appears to be correct. Consequently, under the conditions used in this study the limiting rate law that operates is:

$$k_{obs} = kK_2[H^+]/(1 + K_2[H^+]). \quad (6)$$

The above equation is exactly the same as the experimental rate law (1). Therefore, the mechanism proposed by us is reasonable. Comparing (6) with (1), we have:

$$a = kK_2 \quad (7)$$

$$b = K_2, \quad (8)$$

$$a/b = k. \quad (9)$$

According to (7) and (8), using the values of Table 1, K_2 values of the complex can be obtained and listed in Table 2.

It should be noted that the values of K_2 in Table 2 are not precise because of several calculations and approximations, but we still can conclude that the K_2 values decrease with the increase of temperature. From non-linear least-square fitting of the experimental points using the formula (5), plateau values of k_{obs} (initial value of k) and the equilibrium constant K_1, we can obtain the real values of k, K_1 and K_1K_2. Figure 3 and 4 represent experimental point and fitted curves. Table 3 and 4 are the $1/K_1K_2$ and k values. Regression of $\ln(1/K_1K_2)$ *vs* $1/T$, the values of ΔH^{ϕ}(kJ mol) and ΔS^{ϕ} (kJ/mol) were obtained, they are also listed in Table 3.

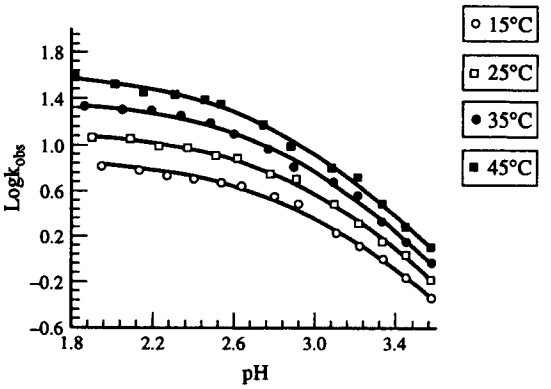


Fig. 3. Plot of Log k_{obs} *vs* pH for $CuH_{-2}L_1$.

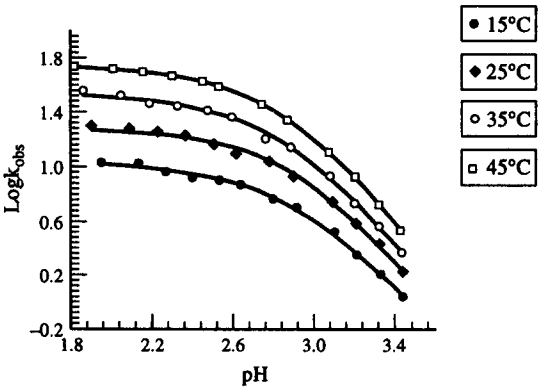


Fig. 4. Plot of Log k_{obs} *vs* pH for $CuH_{-2}L_5$.

From Eyring's equation

$$\ln(k/T) = -\Delta H_m^{\neq}/RT + \Delta S_m^{\neq}/R + \ln(R/N_A h), \quad (7)$$

where $R = 8.3144$ J mol K, $N_A = 6.023 \times 10^{23}$ mol^{-1}, $h = 6.636 \times 10^{-34}$ J s. Regression of k/T *vs* $1/T$, activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of the rate-determining step can be obtained. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and correlation coefficient r were summarized in Table 4. In fact, $1/K_1K_2$ values are the equilibrium constants of the following reaction:

$$ML = MH_{-2}L + 2H^+, \quad (8)$$

values of $1/K_1K_2$ represent the stability of the complex

Table 2. $K_2 \times 10^4$ values of the complexes ($I = 0.5$ mol dm^{-3} KNO_3)

Complex	$CuH_{-2}L_1$	$CuH_{-2}L_2$	$CuH_{-2}L_3$	$CuH_{-2}L_4$	$CuH_{-2}L_5$
288 K	5.99	1.60	4.23	1.86	5.42
298 K	4.30	2.69	2.85	1.78	0.14
308 K	2.67	2.37	2.55	1.61	0.05
318 K	0.03	2.80	2.80	1.18	0.06

Table 3. Pre-equilibrium constant $1/(K_1K_2) \times 10^7$ at different temperatures ($I = 0.5$ mol dm^{-3} KNO_3)

Complex	288 K	298 K	308 K	318 K	ΔH^ϕ (kJ mol)	ΔS^ϕ (J mol K)
$CuH_{-2}L_1$	6.75	9.34	14.02	17.81	25.3	−30.3
$CuH_{-2}L_2$	18.24	19.31	20.30	22.47	5.12	−92.2
$CuH_{-2}L_3$	7.78	10.00	13.53	17.75	21.2	−43.7
$CuH_{-2}L_4$	9.45	10.92	12.98	15.40	12.5	−72.2
$CuH_{-2}L_5$	9.13	11.52	15.67	17.94	17.8	−53.8

Table 4. Rate constants k at different temperatures ($I = 0.5$ mol dm^{-3} KNO_3)

Complex	288 K	298 K	308 K	318 K	$\Delta H^\neq$ (kJ mol)	$\Delta S^\neq$ (J mol K)	r
$CuH_{-2}L_1$	8.05	13.83	25.06	43.89	40.77	−86.02	0.9991
$CuH_{-2}L_2$	9.45	16.75	29.54	49.15	39.51	−88.88	0.9912
$CuH_{-2}L_3$	6.49	11.74	21.34	37.05	41.86	−83.90	0.9998
$CuH_{-2}L_2$	9.45	16.75	29.54	49.15	39.51	−88.88	0.9912
$CuH_{-2}L_4$	5.08	9.47	17.42	32.37	44.50	−76.86	0.9996
$CuH_{-2}L_5$	11.32	19.54	35.24	56.99	38.94	−89.38	0.9995

$CuH_{-2}L$. This process has an endothermic effect with an increase of entropy. This means it will consume some energy to deprotonate the non-deprotonated copper(II) complex. The sequence of K_1K_2 values are exactly the same as determined by pH potentiometric titration. $CuH_{-2}L_2$ has the greatest $1/K_1K_2$ value, this indicates that there are some interactions of the phenol substituent and the hydrogen ions bound to the carbonyl oxygens. The value of K_1 for $CuH_{-2}L_1$ at 25 °C, $I = 0.1$ mol dm^{-3} $NaClO_4$ is 1.99×10^4 [24]. Using this value, we get $K_2 = 4.69 \times 10^3$ which agrees well with the values obtained in this study. All this indicates that the first protonation constant of $CuH_{-2}L_1$ is larger than that of the second protonation constant of the complexes. This means that the hydrogen ion bound to negatively charged carbonyl oxygen repels the proton of the second carbonyl oxygen. This result agrees well with the results reported earlier [18].

The a/b values (k) in Table 1 and k values of the rate-determining step in Table 4 are nearly the same. They regularly change with the ligands. Electron-withdrawing substituents decrease k of their complexes. For all the C-functionalized complexes in this study, the k values are obviously smaller than that of the complexes without substituents. In fact, the d–d transition wavelengths of all the functionalized complexes are shorter than similar complexes without substituents, the great d–d transition energies provide the evidence that they have great in-plane ligand field strength and strong Cu—N bonds. More energy is needed to break the Cu—N bond in the former (large enthalpy). Therefore, shorter wavelength in d–d transition leads to larger positive $\Delta H^\neq$ and smaller k of the rate-determining step, i.e., large activation enthalpy leads to small k.

The rate-determining step is an endothermic process. Comparing with $CuH_{-2}L_5$, substituents increase the endothermic effect of the rate-determining step because of the strong in-plane ligand field. The kK_1K_2 value in our study is 1.70×10^7dm^2 mol^2 s^{-1} for $CuH_{-2}L_5$ at pH 1.9–3.7. This value agrees well with the result of Hay [22] who obtained 1.17×10^7 dm^2 mol^2 s^{-1} for the same ligand in $I = 0.1$ mol dm^{-3} $NaClO_4$. However, Siegfried [21] obtained the value 6.3×10^7 dm^2 mol^2 s^{-1}, the agreement is not very good, the difference may, in our opinion, arise from the different buffers used in the two studies. We found that k_{obs} values in the same pH are different in different buffers. The k_{obs} do not change smoothly with the change of buffers, this change of k_{obs} greatly influences the values (in orders of magnitude) of K_1 and K_2. This phenomenon shows that buffers affect the dissociation rate of the complex, therefore, we use only one buffer (chloroacetic acid) to ensure the continuity of the data. Although K_1 and K_2 are very sensitive to experimental conditions, especially to the change of buffer, k value of the rate-determining step is relatively insensitive to k_{obs}, because k is simply the plateau value of k_{obs}. As shown in eq. (5), in the investigated pH range, $1 < K_1[H] < K_1K_2[H]^2$, that is $K_1K_2[H]^2$ has a greater contribution than the other two terms, the contribution of $K_1[H^+]$ is negligible, especially in a strong acid solutions, therefore, K_1K_2 values are more reliable than K_1 values.

The k of the rate-determining step also varies with the stability of the $MH_{-2}L$ [24]. Large stability of the complex increased their k of the rate-determining step. This implies that large stability increases the rate of intramolecular hydrogen migration. The reason is that the stability constant not only depends on in-plane interaction of metal ion with ligands, but also depends on axial interaction. In these *C*-functionalized macrocyclic complexes, strong in-plane interaction greatly reduced axial interaction, thus decreasing the stability of the complexes. The activation $\Delta H^{\neq}$ is only related to the in-plane interaction, therefore, strong in-plane interaction has different influence on stability of the complexes and k values of the acid dissociation. The Bronsted type linear free energy relationships do exist in this *C*-functionalized dioxotetraamine copper(II) complex (Fig. 5).

From all the above results, we can further clarify the mechanism. Steps 1 and 2 were firmly proved by the characteristic of the intermediates, the K_1K_2 values determined kinetically agree well with those obtained by pH titration. In the acid dissociation mechanism, only step 3 is to be identified. There are two pathways to dissociate the complex, the first, as shown in the mechanism, is by intramolecular hydrogen migration; the second, through the intermolecular protonation in the following equation:

$$H^+ + CuL \rightarrow \text{products}.$$

In this case, we have:

$$k_{obs} = k[H^+][CuL] = kK_1K_2[H]^3/$$
$$(1 + K_1[H] + K_1K_2[H]^2). \quad (10)$$

From (10) we may conclude that it would be first order dependence on $[H^+]$ in low pH (high H^+ concentration). Of course this is not true, therefore, intermolecular hydrogen migration or competitive protonation at another site should be firmly excluded. From Figs 2 and 3 we can see there are no significant differences (in order) of the dissociation rate between L_1 and L_5 complexes, so do the k values. This indicates that substituents do not decrease the dissociation rate considerably, therefore, intermolecular hydrogen migration in the rate-determing step is unlikely.

From the above results, we can see that although the macrocyclic dioxotetraamine has a strong in-plane ligand field, its copper(II) complex is still sensitive toward acidity. The low kinetic stability (kinetic macrocyclic effect) is attributed to the negatively charged carbonyl oxygen, this is an easily accessible basic site so that the proton can successfully attack the dioxotetraamine complex and induce the acid dissociation. While in the saturated analogs, there are no free electron pairs on the nitrogens or other atoms (basic site), therefore, it is very difficult to undergo protonation.

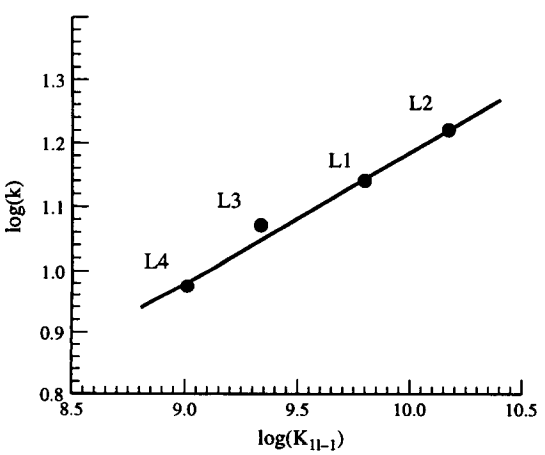


Fig. 5. Plot of log$k$ *vs* log$K(11-1)$.

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