Kinetics and Mechanism of Complex-formation Reactions of Ammonia and Methylamine with Copper(II) Complexes in Aqueous Solution *

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The complex-formation kinetics of copper(II) complexes with ammonia and methylamine was investigated by the temperature-jump relaxation technique. At 2 mol dm^{-3} ionic strength the forward rate constants (dm^3 mol^{-1} s^{-1}) for the studied reactions are: $[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$, $(1.2 \pm 0.1) \times 10^8$ (7 °C); $[Cu(ida)] + NH_3 \rightleftharpoons [Cu(ida)(NH_3)]$, $(3.7 \pm 0.3) \times 10^8$; $[Cu(ida)] + NMeH_2 \rightleftharpoons [Cu(ida)(NMeH_2)]$, $(8.7 \pm 0.3) \times 10^7$; $[Cu(mida)] + NMeH_2 \rightleftharpoons [Cu(mida)(NMeH_2)]$, $(5.4 \pm 0.3) \times 10^7$ (25 °C); ida = iminodiacetate, mida = N-methyliminodiacetate. The results presented and those from previous literature strongly suggest that specific interactions between the co-ordinated groups and the central metal ion do not modify the kinetics and mechanism of the complex formation. The kinetic data are consistent with the Eigen–Wilkins mechanism.

Ligand-substitution reactions of copper(II) are typically rapid. The forward rate constants for the reactions of simple mono- and bi-dentate ligands are close to the diffusion-controlled limit.[1] This unique lability is a consequence of the strongly distorted elongated-octahedral structure of the metal ion which allows rapid co-ordination of an entering ligand at the axial positions.[2,3] Once the ligand is co-ordinated the complex is stabilized through Jahn–Teller inversion. Since this step is much faster than water exchange between the co-ordination sphere and the bulk,[4] it is widely accepted that the rate-determining step is the axial co-ordination of the ligand. In general, the kinetic data appear to be consistent with the Eigen–Wilkins mechanism.[5]

The complex-formation kinetics of binary and ternary copper(II) complexes typically has been interpreted either by taking into account statistical and electrostatic consider-ations,[6–9] steric effects[10–13] and specific interactions between the co-ordinated and entering ligands[14] or by assuming that the reactivity of the metal-ion centre is significantly altered by the co-ordinated ligand(s).[15–17] A subject of interest is how the rate of the Jahn–Teller inversion is affected by the co-ordinated ligands. Recent results from this laboratory indicated that a simple tetradentate ligand, such as the nitrilotriacetate ion (nta), is not able to inhibit this intramolecular process to such an extent that it becomes rate-determining.[18]

The aim of the present study is to provide additional information on the kinetic role of the co-ordinated groups in the ligand-substitution reactions of copper(II) complexes. The formation of the $[Cu(NH_3)_2]^{2+}$ complex and the reactions of ammonia and methylamine with $[Cu(ida)]$ (ida^{2-} = imino-diacetate ion) and $[Cu(mida)]$ (mida^{2-} = N-methylimino-diacetate ion) were investigated by the temperature-jump method.

Experimental

Reagents.—Iminodiacetic acid, methyliminodiacetic acid (Fluka) and NMeH$_2$·HCl (Merck) were recrystallized from

methanol before use. Stock solutions of CuCl$_2$, NH$_4$Cl and chlorophenol red [4,4'-(3H-2,1-benzoxathiol-3-ylidene)bis(2-chlorophenol) S,S-dioxide] were prepared from reagent-grade chemicals (Merck) without further purification. In order to solubilize chlorophenol red, 1% methanol and an equivalent amount of KOH (Baker Chemicals) were added to the stock solution.

All samples were prepared in 2.0 mol dm^{-3} NH$_4$Cl or NMeH$_2$·HCl. The pH was adjusted to the desired value (± 0.01) by dropwise addition of 1.0 mol dm^{-3} HCl or KOH solutions (Baker Chemicals). It was checked both prior and after the kinetic experiments. The equilibrium concentrations of the complexes formed in the studied systems were calculated on the basis of the equilibrium constants listed in Table 1.

Methods.—The pH measurements were done with a Metrohm EA 125 combined electrode connected to a Radiometer PHM 52 digital pH meter. The electrode was

Table 1 Stability constants for the complexes formed in the studied systems at 25 °C[a]

Reaction	log K	Ref.
$H^+ + NH_3 \rightleftharpoons NH_4^+$	10.12[b]	19
$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$	4.46[b]	19
$[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$	3.78[b]	19
$[Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+}$	3.06[b]	19
$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.14[b]	19
$H^+ + NH_3 \rightleftharpoons NH_4^+$	9.53	20
$H^+ + NMeH_2 \rightleftharpoons NMeH_3^+$	10.96	20
$Cu^{2+} + ida^{2-} \rightleftharpoons [Cu(ida)]$	10.57	19
$[Cu(ida)] + ida^{2-} \rightleftharpoons [Cu(ida)_2]^{2-}$	5.97	19
$Cu^{2+} + mida^{2-} \rightleftharpoons [Cu(mida)]$	11.04	19
$[Cu(mida)] + mida^{2-} \rightleftharpoons [Cu(mida)_2]^{2-}$	6.72	19
$[Cu(ida)] + NH_3 \rightleftharpoons [Cu(ida)(NH_3)]$	3.63	21
$[Cu(ida)] + NMeH_2 \rightleftharpoons [Cu(ida)(NMeH_2)]$	3.97	21
$[Cu(mida)] + NMeH_2 \rightleftharpoons [Cu(mida)(NMeH_2)]$	4.03	21

[a] The pK_a values of the tridentate ligands are 1.82, 2.61 and 9.34 for ida and —, 2.12 and 9.65 for mida;[19] log K_{in} = 5.92 at 25 °C[18] and 5.90 $\pm$ 0.01 at 7 °C. [b] Value extrapolated to 7 °C by using stability data from refs. 19 and 22.

calibrated to yield the hydrogen-ion concentration ($-\log[H^+]$) as described elsewhere.[23] At 7 °C the pK_a of the indicator was determined spectrophotometrically.
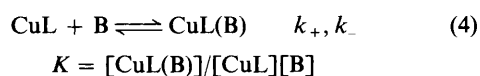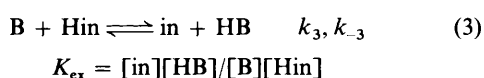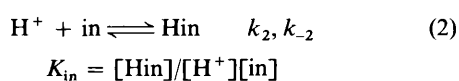
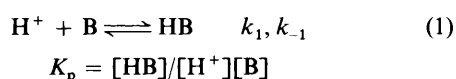The kinetics of the complex-formation reactions was monitored by using a conventional temperature-jump instrument with spectrophotometric detection.[24] The lower limit for the accessible time range was about 2 μs. During the jumps the temperature was raised by 3.0 °C. Other details of the relaxation measurements and the evaluation of the relaxation times (τ) from the experimental relaxation curves were as described elsewhere.[14,18] The experimental conditions are summarized in Table 2.

The complex-formation reactions studied are not associated with significant spectral effects. Therefore, the indicator method was applied and the kinetic curves were monitored at the characteristic absorption band of the indicator, $\lambda = 550$–600 nm. Typically two partially overlapping relaxation effects were observed with opposite amplitudes. The two relaxation times were determined from the average of at least five replicate kinetic runs within an error of 15%. On the basis of experiments in the absence of the copper(II) complexes, the faster relaxation process was assigned to proton-transfer reactions between the indicator and the entering ligand. It was also confirmed that no direct reactions occur between the complexes and the indicator.

The rate constants were estimated with the non-linear least-squares fitting procedure described earlier.[18,25] The reported error limits represent one standard deviation. Except when noted, the kinetic data are given at 25 °C. The concentrations and the experimental and calculated relaxation rates are available as SUP 57005.

Results

The appropriate kinetic model for the studied systems is given in equations (1)–(4) (for simplicity, the charges of the reactants are not given when general symbols are used), where B, in and CuL represent the entering ligand, the indicator and the reacting copper(II) complex, respectively.

$$H^+ + B \rightleftharpoons HB \qquad k_1, k_{-1} \qquad (1)$$

$$K_p = [HB]/[H^+][B]$$

$$H^+ + in \rightleftharpoons Hin \qquad k_2, k_{-2} \qquad (2)$$

$$K_{in} = [Hin]/[H^+][in]$$

$$B + Hin \rightleftharpoons in + HB \qquad k_3, k_{-3} \qquad (3)$$

$$K_{ex} = [in][HB]/[B][Hin]$$

$$CuL + B \rightleftharpoons CuL(B) \qquad k_+, k_- \qquad (4)$$

$$K = [CuL(B)]/[CuL][B]$$

The proton-transfer rate constants for the methylamine–indicator system were determined in separate experiments, as described earlier:[18] $k_1 = (2.7 \pm 0.4) \times 10^{10}$, $k_2 = (5.2 \pm 1.9) \times 10^{10}$ and $k_3 = (5.9 \pm 0.6) \times 10^8$ dm^3 mol^{-1} s^{-1}. The corresponding kinetic data for the ammonia–indicator system are: $k_1 = 4.3 \times 10^{10}$,[26] $k_2 = 4.9 \times 10^{10}$,[18] and $k_3 = 4.9 \times 10^8$ dm^3 mol^{-1} s^{-1}.[18]

In order to obtain measurable relaxation effects reaction (4) needs to be balanced,[27] i.e. $1:10 < [CuL]/[CuL(B)] < 10:1$. In the $[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$ reaction the $[NH_3] = 1/K$ condition was strictly maintained to avoid any interference from the formation of $[Cu(NH_3)]^{2+}$ at lower and $[Cu(NH_3)_3]^{2+}$ at higher free-ligand concentrations. Under the applied conditions more than 90% of the total copper(II) was present as the mono and bis complexes and the effect of additional complex-formation reactions was negligible.

At 25 °C only poorly resolved relaxation effects were observed for this reaction. Thus, the formation of the $[Cu(NH_3)_2]^{2+}$ complex was studied at 7 °C where the two relaxation effects became separated and well defined. Under these conditions the relaxation times could be determined with the usual precision. Since the first relaxation process was at least 5–6 times faster than the second, the proton-transfer reactions (1)–(3) were treated as fast pre-equilibria prior to the complex formation. Expression (5) was derived for the slower

$$r_2 = k_+(\alpha[CuL] + [B]) + k_- \qquad (5)$$

relaxation rate, where α is an equilibrium term given in a previous paper.[18] The forward rate constant, k_+, was calculated by replacing k_- with k_+/K in equation (5).

In the other systems, the proton-transfer reactions are kinetically coupled with the complex formation. On the basis of reactions (1)–(4), standard derivation[27] yields expressions (6)–(10) for the two relaxation rates. For the complex

$$r_{1,2} = \frac{a_{11} + a_{22}}{2} \pm \left[\frac{(a_{11} + a_{22})^2}{4} + a_{12}a_{21} - a_{11}a_{22}\right]^{\frac{1}{2}} \qquad (6)$$

$$a_{11} = \left([Hin] + [B] + \frac{1}{K_{ex}}\right) \times \left(k_3 + \frac{1}{K_{in}} \cdot \frac{k_1k_2}{k_1[B] + k_2[in]}\right) \qquad (7)$$

$$a_{12} = \left(k_3 + \frac{1}{K_{in}} \cdot \frac{k_1k_2}{k_1[B] + k_2[in]}\right)[Hin] \qquad (8)$$

$$a_{21} = k_+[CuL] \qquad (9)$$

$$a_{22} = k_+([CuL] + [B] + K^{-1}) \qquad (10)$$

Table 2 Experimental conditions for the temperature-jump kinetic studies on the CuL + B $\rightleftharpoons$ CuL(B) reaction at 25 °C and $I = 2$ mol dm^{-3}

Reaction	pH	$10^4\,c_{Cu^{2+}}/$ mol dm^{-3}	$10^5\,c_{in}/$ mol dm^{-3}	$10^{-5}\,r_1/$ s^{-1}	$10^{-4}\,r_2/$ s^{-1}	No. of points	Standard deviation (%)
$[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons$ $[Cu(NH_3)_2]^{2+a}$	6.02	4.0–12.1	3.1–10.3	—	5.0–8.6	10	7.4[b]
$[Cu(ida)] + NH_3 \rightleftharpoons$ $[Cu(ida)(NH_3)]$	5.17–5.60	4.0–12.0	11.0	5.3–6.0	19.4–30.3	14	7.1[c]
$[Cu(ida)] + NMeH_2 \rightleftharpoons$ $[Cu(ida)(NMeH_2)]$	6.14–6.91	2.0–10.0	5.5	1.0–1.7	1.9–5.3	12	9.8[c]
$[Cu(mida)] + NMeH_2 \rightleftharpoons$ $[Cu(mida)(NMeH_2)]$	6.28–6.58	2.0–12.0	5.5	0.9–1.3	1.3–4.3	11	6.4[c]

[a] At 7 °C. [b] The relaxation rate was fitted on the basis of equation (5). [c] The two relaxation rates were fitted simultaneously on the basis of equation (6).

Table 3 Rate constants for the ligand-substitution reactions of NH_3 and $NMeH_2$ with copper(II) complexes at 25 °C

Reaction	k/dm^3 mol^{-1} s^{-1}	Ref.
$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$	2.4×10^8	a
$[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$	$(1.2 \pm 0.1) \times 10^8$	b,c
	2.8×10^8	22
$[Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+}$	1.7×10^8	22
$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	3.5×10^8	22
$[Cu(ida)] + NH_3 \rightleftharpoons [Cu(ida)(NH_3)]$	$(3.7 \pm 0.3) \times 10^8$	b
$[Cu(nta)]^- + NH_3 \rightleftharpoons [Cu(nta)(NH_3)]^-$	1.5×10^8	18
$[Cu(ida)] + NMeH_2 \rightleftharpoons [Cu(ida)(NMeH_2)]$	$(8.7 \pm 0.3) \times 10^7$	b
$[Cu(mida)] + NMeH_2 \rightleftharpoons [Cu(mida)(NMeH_2)]$	$(5.4 \pm 0.3) \times 10^7$	b
$[Cu(nta)]^- + NMeH_2 \rightleftharpoons [Cu(nta)(NMeH_2)]^-$	3.4×10^7	18

^{a} Average value from refs. 22, 23 and 28. ^{b} This work. ^{c} At 7 °C.

formation, k_+ was calculated by simultaneously fitting the two relaxation rates. In these calculations k_3, which corresponds to the dominant path in the proton-transfer reaction, was also fitted while k_1, k_2 were included with the predetermined fixed values. The results, together with earlier published rate constants for related reactions of NH_3 and $NMeH_2$, are listed in Table 3.

Discussion
The extreme lability of copper(II) requires the use of special fast kinetic methods to monitor its complex-formation reactions. Even by using these techniques, no direct information is available for the individual steps of the intrinsic mechanism and the dominant kinetic effects cannot be experimentally distinguished. Mechanistic considerations are usually based on the comparison of rate constants for appropriately selected reaction sets.[1] As a consequence, the interpretation of the kinetic data features certain ambiguity and the recommended mechanism often seems to be the subject of personal preference among the equivalent kinetic models.

In order to obtain less biased mechanistic information, the reactions of NH_3 and $NMeH_2$ offer some advantages over previously studied systems. In the case of these simple neutral ligands, electrostatic effects and specific ligand–ligand interactions are unlikely to affect the course of the ligand-substitution reactions. Moreover, in the reactions of NH_3 the sizes of the entering and leaving ligands (H_2O) are very similar and steric effects are expected to be of marginal kinetic importance. Thus, the analysis of the kinetic data obtained here and presented earlier can resolve certain uncertainties regarding the effects of the co-ordinated groups on the reactivity of the metal-ion centre in copper(II) complexes.

Providing that the studied complex-formation reactions proceed through an Eigen–Wilkins type, basically dissociative interchange (I_d) mechanism,[5] k_+ is given by $k_+ = K_{os}k_{ex}$ where K_{os} is the outer-sphere stability constant between the reactants. The co-ordinated group(s) may affect either K_{os} and/or the rate-determining step. In general, the outer-sphere stability constant can be estimated by taking into account electronic interactions and statistical considerations.[1,29] In the reactions listed in Table 3 one of the reactants is neutral and the variation in the electronic contribution to K_{os} is most likely negligible.

Statistically the differences in K_{os} are determined by the number of vacant co-ordination sites, which varies between six for $[Cu(H_2O)_6]^{2+}$ and two for $[Cu(nta)(H_2O)_2]^-$. Alternatively one may consider only the axial positions which are directly involved in the rate-determining step. In this case the number of empty sites is one for $[Cu(nta)]^-$ and two for the other complexes. It follows that a 2–3 times variation in K_{os} and, as a consequence, in the overall rate constants can be justified on the basis of statistical considerations.

As shown in Table 3, the predicted differences in K_{os} may account for the slight variation in the observed rate constants.

This supports the earlier finding[18] that the already co-ordinated groups do not alter the reactivity of the metal ion. It can be also inferred that the axial co-ordination of a ligand remains the rate-determining step in the overall mechanism. Consequently, all reactions considered here proceed through a dissociative interchange mechanism.

The above conclusion also implies that in the case of simple copper(II) complexes the variation in the rate constants should be interpreted by taking into account specific properties of the co-ordinated and entering ligands. In this respect, it should be noted that the corresponding reactions with NH_3 are about 3–4 times faster than those with $NMeH_2$. The same difference was reported in related reactions of glycine and α-alanine.[18] Most likely, the kinetic role of the extra methyl group can be explained in terms of repulsive hydrophobic interactions, which reduce K_{os}. The results clearly demonstrate that, even in the case of closely related ligands, the addition of a simple substituent may noticeably alter the rate of complex-formation reactions. However, the variation of the rate constants does not necessarily reflect a shift in the rate-determining step or a mechanistic changeover in the corresponding reactions.

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