Kinetic Studies on the Stability Enhancement of Mixed Ligand Copper(II) Complexs with 2,2′-Bipyridyl and Acetylacetonate

Megumu MUNAKATA* and Katsumi YAMADA

Department of Chemistry, Kinki University; Kowakae, Higashi-Osaka-Shi, Osaka 577

(Received March 9, 1978)

The rate constants for the formation and dissociation of the binary Cu^{2+}-acetylacetonate($acac^-$) complex and the ternary 2,2′-bipyridyl(bpy)-Cu^{2+}-$acac^-$ complex have been determined by the temperature-jump method. For the reactions $Cu^{2+}+acac^- \underset{k_{-1b}}{\overset{k_{1b}}{\rightleftharpoons}} Cu(acac)^+$, $Cu(acac)^+ + acac^- \underset{k_{-2b}}{\overset{k_{2b}}{\rightleftharpoons}} Cu(acac)_2$, and $Cu(bpy)^{2+}+acac^- \underset{k_{-1t}}{\overset{k_{1t}}{\rightleftharpoons}} Cu(bpy)(acac)^+$, the rate constants are $k_{1b}=9.0\times10^8\ M^{-1}\ s^{-1}$, $k_{-1b}=3.2\ s^{-1}$, $k_{2b}=7.0\times10^7\ M^{-1}\ s^{-1}$, $k_{-2b}=13\ s^{-1}$, $k_{1t}=1.1\times10^9\ M^{-1}\ s^{-1}$ and $k_{-1t}=1.9\ s^{-1}$. A comparison of the reactions shows that the forward rate for the $Cu(bpy)(acac)^+$ formation is larger than that for $Cu(acac)^+$ and, subsequently, the rate of the complex formation between $Cu(bpy)^{2+}$ and $acac^-$ is enhanced by the coordinating bpy. On the other hand, the reverse rate for the ternary complexation reaction is smaller than for the binary. This illustrates that the dissociation of $acac^-$ of $Cu(bpy)(acac)^+$ becomes more difficult owing to the coordination of the bpy. The above two effects of the bpy may be driving forces producing high stability, *i.e.*, a positive value of $\Delta \log K$ $\left(K=\dfrac{[Cu(bpy)L]}{[Cu(bpy)][L]}\right)$ for the ternary copper(II) complexes with bpy and other ligands containing O as donor atoms.

It has been reported[1-9] that ligands containing O as donor atoms form stabler complexes with 2,2′-bipyridyl copper(II) ion (Eq. A) than with the hydrated Cu^{2+} ion (Eq. B).

$$Cu(bpy) + L \rightleftharpoons Cu(bpy)L$$

$$K^{Cu(bpy)}_{Cu(bpy)L} = \frac{[Cu(bpy)L]}{[Cu(bpy)][L]} \quad (A)$$

$$Cu + L \rightleftharpoons CuL \quad K^{Cu}_{CuL} = \frac{[CuL]}{[Cu][L]} \quad (B)$$

$$\Delta \log K = \log K^{Cu(bpy)}_{Cu(bpy)L} - \log K^{Cu}_{CuL} \quad (C)$$

The value of $\Delta \log K$ is, therefore, positive for ligands containing O donor atoms. This is especially noticeable in view of the fact that the value expected for $\Delta \log K$ is generally negative, since more coordination positions are available for bonding of the first ligand than for the second ligand to a given metal ion. Table 1 shows the $\Delta \log K$ values for some ternary complexes. The most important driving force for stabilization of the ternary complex (*i.e.*, the positive value of $\Delta \log K$) is considered to be the electronic effect due to π bonding formation in the complex.[3] However, little evidence is available which clarifies the electronic effect.

TABLE 1. STABILITIES OF SOME TERNARY Cu^{2+} COMPLEXES (25 °C, $I=0.1$)

Complex	$\Delta \log K$[a]
2,2′-Bipyridyl-Cu^{2+}-acetylacetonate	+0.32 (+0.51[b])
2,2′-Bipyridyl-Cu^{2+}-malonate	+0.27[c]
2,2′-Bipyridyl-Cu^{2+}-glycinate	−0.35[c]
2,2′-Bipyridyl-Cu^{2+}-ethylenediamine	−1.29[c]

a) *Cf.* Eq. 3. b) 60% dioxane (Ref. 9). c) Ref. 3.

One method of elucidating the high stability of ternary bpy-Cu^{2+}-O ligand complexes is a kinetic study of the complexation reaction of the ternary complexes. No kinetics on the complexation reaction of Cu^{2+}-O ligand complexes have however been reported. In this paper the relaxation effects of the complexation of bpy-Cu^{2+}-acetylacetone and Cu^{2+}-acetylacetone (Hacac) have been investigated using temperature-jump techniques. On the basis of the kinetic data the high stability for the ternary bpy-Cu^{2+}-$acac^-$ complex has been discussed.

Experimental

Kinetic experiments were conducted using a Union Giken co-axial cable temperature-jump apparatus RA-1200. A discharge of 30 KV, through two electrodes in 1.0 ml sample solution, from a 0.05 μF condenser, corresponding to an increase in temperature of about 5 °C was used in all experiments. Wako Pure Chemical reagent grade $Cu(NO_3)_2\cdot3H_2O$, KNO_3, 2,2′-bipyridyl, acetylacetone, Chlorophenol Red, and Protein Research Foundation glycine were used without further purification. The concentration of a copper stock solution was determined by an EDTA titration. Experimental solutions containing 1.00×10^{-4} M Chlorophenol Red were maintained at 0.1 ionic strength using KNO_3 and adjusted to the desired pH value with NaOH and/or HNO_3 solution. The temperature of this study was 25 °C. Each relaxation time was estimated from the relaxation graph which was the accumulation of five oscilloscope traces recorded using a Union Giken kinetic data processer RA-450 equipped with an X-Y recorder. The relative error for these measurements was ±5%. The analysis of the temperature-jump data required the appropriate equilibrium constants, which were determined by the titration technique. The titration procedure was essentially the same as in a previous paper.[9] The equilibrium constants obtained are given in Table 2.

TABLE 2. EQUILIBRIUM CONSTANTS (25 °C and $\mu=0.1$)

Symbol	$\log K$
K_a	−9.33
K_{1b}	8.45
K_{2b}	6.73
K_{1t}	8.77
K_{1n}	−6.00[a]

a) HIn=Chlorophenol Red (Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930)).

Results

Ternary Complex. No relaxation effect was observed for solutions containing equal concentrations of Cu^{2+} and bpy under the conditions of these experiments, as had been reported.[10] In the pH range which was studied here, 5.50—5.80, the reaction

$$Cu^{2+} + bpy \rightleftarrows Cu(bpy)^{2+} \quad (1)$$

is effectively complete and a 5 °C temperature-jump does not appreciably perturb it. It the complexation reactions 2—4 of the ternary bpy-Cu-acetylacetone system, no complexation reaction 4 needs to be considered, since the copper(II) ion is square planar and not a distorted octahedron as in the complex with acetylacetone (Hacac).[10]

$$Cu(bpy)^{2+} + acac^- \underset{k_{-1t}}{\overset{k_{1t}}{\rightleftarrows}} Cu(bpy)(acac)^+, \quad (2)$$

where

$$k_{1t}/k_{-1t} = K_{1t} = \frac{[Cu(bpy)(acac)^+]}{[Cu(bpy)^{2+}][acac^-]},$$

$$Cu(bpy)^{2+} + Hacac \underset{k'_{-1t}}{\overset{k'_{1t}}{\rightleftarrows}} Cu(bpy)(acac)^+ + H^+, \quad (3)$$

$$Cu(bpy)(acac)^+ + acac^- \rightleftarrows Cu(bpy)(acac)_2, \quad (4)$$

where K_{1t} is the stability constant of the ternary Cu(bpy)(acac)$^+$ complex. These reactions are coupled to the more rapid protonation processes 5 and 6.

$$Hacac \underset{}{\overset{K_a}{\rightleftarrows}} acac^- + H^+,$$

$$K_a = [acac^-][H^+]/[Hacac], \quad (5)$$

$$HIn \underset{}{\overset{K_{In}}{\rightleftarrows}} In^- + H^+,$$

$$K_{In} = [In^-][H^+]/[HIn], \quad (6)$$

where HIn, K_{1n} and K_a are the acidic form of Chlorophenol Red and the dissociation constants of H_{In} and Hacac, respectively.

By applying the standard techniques[10-12] for deriving relaxation time τ expressions, it can be shown that

$$1/\tau = Ak_{1t} + Bk'_{1t}, \quad (7)$$

where

$$A = \frac{[Cu(bpy)^{2+}]}{1+\alpha} + [acac^-] + \frac{1}{K_{1t}}, \quad (8)$$

$$B = \frac{\alpha[Cu(bpy)^{2+}]}{1+\alpha} + [Hacac] + \frac{1}{K_{1t}K_a}\left([H^+] + \frac{\alpha\beta[Cu(bpy)(acac)^+]}{1+\alpha}\right), \quad (9)$$

$$\alpha = \frac{[H^+]}{K_a + \beta[acac^-]}, \quad (10)$$

$$\beta = \frac{K_{In} + [H^+]}{K_{In} + [In^-] + [H^+]}. \quad (11)$$

The experimental conditions, equilibrium concentrations and observed relaxation times for the bpy-Cu^{2+}-acetylacetone system are shown in Table 3 and $(\tau B)^{-1}$ plotted against A/B is shown in Fig. 1, where the data was handled on the assumption that

$$[Cu^{2+}]_{total} = [bpy]_{total} = [Cu(bpy)^{2+}] \quad (12)$$

The assumption of complete formation of Cu^{2+}-bpy 1 : 1 complex has been demonstrated.[10] The slope of the line in Fig. 1 represents k_{1t} and the intercept k'_{1t} and from the plots, $k_{1t} = 1.1 \times 10^9$ M^{-1} s^{-1} and $k'_{1t} = 0—2 \times 10^{-4}$ M^{-1} s^{-1}. This demonstrates that Hacac is remarkably unreactive towards Cu(bpy)$^{2+}$ and possibly towards Cu^{2+}.

Binary Complex. Two complexation reactions

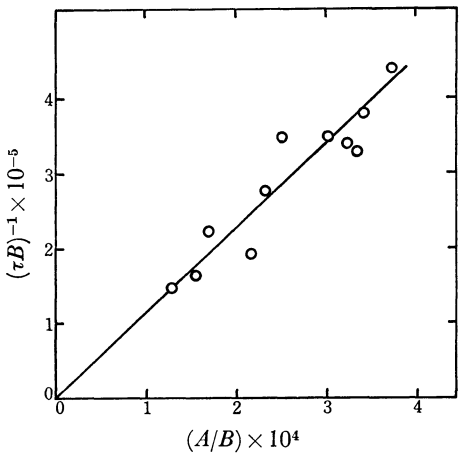


Fig. 1. A plot of $(\tau B)^{-1}$ *vs.* A/B for the 2,2′-bipyridyl-Cu^{2+}-acetylacetone system.
$k_{1t} = 1.1 \times 10^9$ M s^{-1}; $k'_{1t} = 0—2 \times 10^{-4}$ M^{-1} s^{-1},; $k_{-1t} = 1.9$ s^{-1}

Table 3. Equilibrium concentrations and relaxation times for 2,2′-bipyridyl-Cu^{2+}-acetylacetone solutions

$[Cu(bpy)^{2+}]_{tot}$ /10^{-4}	$[Hacac]_{tot}$ /10^{-4}	$[H^+]$ /10^{-6}	[Hacac] /10^{-4}	$[acac^-]$ /10^{-8}	$[Cu(bpy)^{2+}]$ /10^{-6}	[Cu(bpy)(acac)$^+$] /10^{-5}	τ^{-1} /10 s^{-1}
1.00	2.00	1.57	1.05	3.14	5.13	9.49	6.26
3.00	5.00	1.25	2.06	7.72	6.46	29.4	16.3
5.00	5.00	2.15	0.586	1.28	58.7	44.1	13.8
5.00	10.0	3.48	5.12	6.88	12.1	48.8	15.5
8.00	10.0	2.74	2.37	3.98	32.7	76.7	19.7
8.00	8.00	1.40	1.23	4.09	31.9	76.8	17.0
10.0	10.0	1.28	0.659	2.41	65.9	93.4	16.1
30.0	30.0	1.83	1.38	3.53	138	282	13.1
50.0	50.0	1.77	1.76	4.66	176	482	45.0
50.0	100	2.10	50.1	112	7.60	499	117
80.0	80.0	1.39	1.98	6.68	198	780	108

All concentrations are molar. $\mu = 0.1$M(KNO_3). Temperature = 25 °C.

between Cu^{2+} and acetylacetonate have been considered:

$$Cu^{2+} + acac^- \underset{k_{-1b}}{\overset{k_{1b}}{\rightleftharpoons}} Cu(acac)^+,$$

$$K_{1b} = \frac{[Cu(acac)^+]}{[Cu^{2+}][acac^-]}, \quad (13)$$

$$Cu(acac)^+ + acac^- \underset{k_{-2b}}{\overset{k_{2b}}{\rightleftharpoons}} Cu(acac)_2,$$

$$K_{2b} = \frac{[Cu(acac)_2]}{[Cu(acac)^+][acac^-]}. \quad (14)$$

A general treatment for obtaining relaxation time expressions in metal-ligand systems represented by Eqs. 13 and 14 has already been given.[13,14] The reciprocals of the two relaxation time are

$$\frac{1}{\tau_{+,-}} = \frac{1}{2}\{a_{11}+a_{22}\pm\sqrt{(a_{11}+a_{22})^2-4(a_{11}a_{22}-a_{21}a_{12})}\}, \quad (15)$$

where

$$a_{11} = k_{1b}\left([acac^-]+\frac{[Cu^{2+}]}{1+\alpha}+\frac{1}{K_{1b}}\right), \quad (16)$$

$$a_{12} = k_{1b}\left(\frac{1}{K_{1b}}-\frac{[Cu^{2+}]}{1+\alpha}\right), \quad (17)$$

$$a_{21} = k_{2b}\left([acac^-]-\frac{[Cu(acac)^+]}{1+\alpha}\right), \quad (18)$$

$$a_{22} = k_{2b}\left([acac^-]+\frac{[Cu(acac)^+]}{1+\alpha}+\frac{1}{K_{2b}}\right). \quad (19)$$

The plus and minus signs give the short and long relaxation times, respectively. Generally the short relaxation time, τ_+, was observed.[14] Equations 5, 6, and 10—19 were applied to the data of Table 4. The values of τ_{calc}^{-1} were fitted to the best values of k_{1b} and k_{2b} by inserting a large number of combinations for the two unknown constants into a computer program and comparing predicted values for τ_+^{-1} with those (τ_{obsd}^{-1}) observed experimentally. The best fit was determined by minimizing the quantity σ,[15]

$$\sigma = \sum\{(\tau_{calcd}^{-1}-\tau_{obsd}^{-1})/\tau_{obsd}^{-1}\}^2. \quad (20)$$

The best fit forward rate constants are given in Table 4.

Discussion

The kinetics of the complexation reactions of nickel(II), cobalt(II), and copper(II) ions have been extensively studied using a variety of rapid reaction techniques.[16] It has been concluded that the substitution reactions of nickel(II), cobalt(II), and copper(II) ions proceed *via* the rate determining mechanism in which a water molecule dissociates from the inner coordination sphere of a thermodynamically stable species. There have been some reports in which the rate-determining is chelate ring closure, when there is steric hindrance of the ligand to the chelate ring closure.[14] In the case of the fully hydrated copper(II) ion and a normal bidentate ligand, A–B, such as $acac^-$, the complexation reactions may be written as follows:

$$M_{aq} + A\text{–}B_{(aq)} \overset{K_{01}}{\rightleftharpoons} \underset{\text{ion pair}}{W_2MW_1, A\text{–}B}, \quad \text{very rapid,}$$

$$W_2MW_1, A\text{–}B \underset{k_{-01}}{\overset{k_{01}}{\rightleftharpoons}} W_2M\text{–}A\text{–}B + H_2O, \quad \text{slow,}$$

$$W_2M\text{–}A\text{–}B \underset{k'_{-01}}{\overset{k'_{01}}{\rightleftharpoons}} M\begin{matrix}A\\|\\B\end{matrix} + H_2O, \quad \text{fast.}$$

where W_1 and W_2 represent the two water molecules in the inner coordination sphere replaced by A–B. The rate-determining step in the transition from the ion pair to the final complex is the dissociation of a water molecule from the inner coordination sphere of the metal ion. The rate constant for complex formation is then

$$k_{1b} = K_{01}k_{01}, \quad (21)$$

where K_{01} is the ion pair formation constant (Eq. 22) and k_{01} is the rate constant for water dissociation.

$$K_{01} = \frac{[W_2MW_1, A\text{–}B]}{[W_2MW_1][A\text{–}B(aq)]}. \quad (22)$$

Theoretical values of K_{01} can be estimated from Eq. 23,[13] where $U(a)$ is the Debye-Hückel interaction potential and a is the distance between the centers of the ion-pair partners.

TABLE 4. EQUILIBRIUM CONCENTRATIONS AND RELAXATION TIMES FOR Cu^{2+}-ACETYLACETONE SOLUTIONS

$[Cu]_{tot}$ /10^{-4}	$[Hacac]_{tot}$ /10^{-4}	$[H^+]$ /10^{-6}	[Hacac] /10^{-5}	$[acac^-]$ /10^{-8}	$[Cu^{2+}]$ /10^{-5}	$[Cu(acac)^+]$ /10^{-4}	$[Cu(acac)_2]$ /10^{-5}	τ_{obsd}^{-1} /10 s^{-1}	τ_{calcd}^{-1} /10 s^{-1}
1.00	2.00	3.29	8.12	1.16	2.24	0.730	0.453	9.79	8.95
2.00	3.00	1.94	11.1	2.67	2.08	1.57	2.25	9.29	8.83
3.00	4.00	1.69	10.5	2.91	2.87	2.35	3.66	20.2	17.4
4.00	4.00	1.94	5.75	1.39	7.68	3.01	2.25	17.5	18.0
5.00	5.00	2.55	7.43	1.36	9.77	3.75	2.74	20.5	21.5
5.00	4.00	2.22	3.75	0.789	15.1	3.35	1.42	17.3	18.8
5.00	6.00	2.03	9.84	2.27	6.12	3.91	4.77	22.0	25.3
6.00	6.00	3.00	8.80	1.37	11.6	4.50	3.32	27.1	25.2
7.00	7.00	1.98	7.08	1.67	11.4	5.38	4.82	23.6	26.9
$k_{1b}=9.0\times10^8\ M^{-1}\ s^{-1}$					$k_2=7.0\times10^7\ M^{-1}\ s^{-1}$			$\sigma=0.188$	
$k_{-1b}=3.2\ s^{-1}$					$k_{-2b}=13\ s^{-1}$				

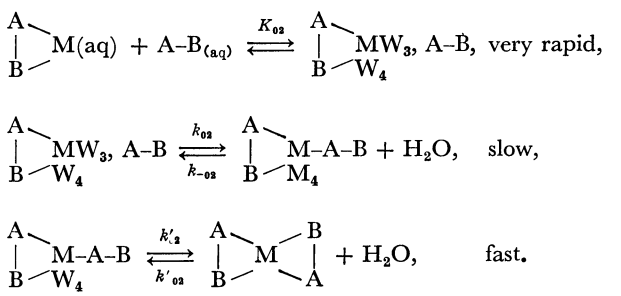
All concentrations are molar. μ=0.1M(KNO_3). Temperature=25 °C.

$$K_{01} = \frac{4\pi Na^3}{3000} \exp\left(-\frac{U(a)}{kT}\right). \quad (23)$$

Choosing $a=5$ Å (under the conditions $\mu=0.1$ and 25 °C) leads to a value of $K_{01}=0.8$ for $+1$, -1 interactions; 2 for $+2$, -1 and $+1$, -2; 0.3 when one of the reactants is uncharged.

The values of the forward rate constant, k_{1b}, for the binary complex formation between Cu^{2+} and acetylacetonate (O, O ligand) is 9.0×10^8 M^{-1} s^{-1} and is smaller than the value for glycinate (N, O ligand)[10] 4.0×10^9 M^{-1} s^{-1} and ethylendiamine (N, N ligand)[17] 3.8×10^9 M^{-1} s^{-1}. This can be interpreted as the easier entrance of the N-donor atom of the ligand in the ion pair into the inner coordination sphere than the O-donor atom.

A similar mechanism may be proposed for the formation of ternary complexes with bpy and higher order complexes.[10]



The observed forward rate constant, k_{1t}, is given by

$$k_{1t} = SK_{02}k_{02}, \quad (24)$$

where S is a statistical factor which can be computed from the number of independent attacking sites available for the ligand. For the first bidentate $acac^-$ substituting on the distorted octahedron of hydrated copper(II) ion there are 12 edges. This is because the rate constant[18] for the internal inversion between the axial water molecules and the equatorial water molecules, 10^{11} s^{-1}, is about two orders of magnitude greater than the rate constant of water dissociation, 4.5×10^8 s^{-1} (calculated for the complexation reaction between Cu^{2+} aq and acac from Eq. 21) and subsequently the six coordinating waters are equally attacked by the ligand. The attacking sites of $Cu(bpy)^{2+}$ for the second bidentate ligand is one, since $Cu(bpy)^{2+}$ is square planar rather than a distorted octahedron. A more satisfactory statistical factor therefore may be 1/12 rather than 1/8 as described in Ref. 10.

It is surprising that the forward rate for the ternary copper complexation reaction 2 is larger than for the binary complexation reaction 13. Furthermore, from a consideration of the statistical factors, the forward rate for the ternary complex formation should be about 15 times that for the binary, where the ion pair formation constants are assumed to be the same in both cases. It has been reported[10] that the forward rate for the $Cu(bpy)(gly)^+$ formation (Eq. 26) is also larger than that for the $Cu(gly)^+$ (Eq. 25) by a factor of about 3 (for $S=1/8$) and by a factor of about 5 if $S=1/12$.

$$Cu^{2+} + gly^- \underset{22\ s^{-1}}{\overset{4\times10^9\ M^{-1}\ s^{-1}}{\rightleftharpoons}} Cu(gly)^+ \quad (25)$$

$$Cu(bpy)^{2+} + gly^- \underset{19\ s^{-1}}{\overset{1.4\times10^9\ M^{-1}\ s^{-1}}{\rightleftharpoons}} Cu(bpy)(gly)^+ \quad (26)$$

These facts suggest that the forward rate for the ternary copper(II) complexation reaction between $Cu(bpy)^{2+}$ and a ligand is increased by the bpy coordinating to the copper(II). The enhancement ratio of the forward rate for the $Cu(bpy)(acac)^+$ formation is larger than that for the $Cu(bpy)(gly)^+$ formation. This corresponds to the increasing order in the $\Delta \log K$ values: $\Delta \log K=-0.35$ for $Cu(bpy)(gly)^+$; 0.32 for $Cu(bpy)(acac)^+$.

The most important factor for the possitive values of $\Delta \log K$ for the ternary copper(II) complexes with bpy and $acac^-$ with O as donor atoms is apparently the remarkable increase in the forward rate for the complexation reaction. The increase indicates that the activation energy of formation of the ternary complex is smaller than that of the binary complex. If the square planar $Cu(bpy)^{2+}$ easily leads to a transition state, *i.e.*, the five coordination state,[19] in which the d-orbitals of the copper(II) ion combine more preferably with O donor atoms than the hydrated copper(II) ions, the forward rate for the reaction between $Cu(bpy)^{2+}$ and a ligand with O donor atoms must be larger than that between hydrated Cu^{2+} and the ligand.

Both reverse rate constants for the ternary $Cu(bpy)L^+$ and binary CuL^+ complexation reactions are statistically the same, since in both cases there is only one way to remove L and the charges are the same. In fact, both the constants for $Cu(bpy)^+$ and $Cu(bpy)(gly)^+$ are the same.[10] On the other hand, the value of the reverse rate constant, 1.9 s^{-1}, for the ternary $Cu(bpy)(acac)^+$ complexation reaction is smaller than 3.2 s^{-1} for the binary $Cu(acac)^+$. The ratio of the former to the latter is 0.6. This illustrates the greater difficulty of dissociation of the Cu-acac bond in the ternary complex than that in the binary complex. The copper-ligand bond may be stabilized by the π-bond interaction between the two ligands through the copper(II).[3,20] The stability constant of the ternary copper(II) complex is slightly enhanced by a small decrease in the dissociation rate. In conclusion, the high stability of the mixed ligand copper(II) complex with 2,2'-bipyridyl and acetylacetonate is largely attributed to the remarkable enhancement of the forward rate for the complexation reaction.

References

1) H. Sigel, K. Becker, and D. B. McCormik, *Biochim. Biophys. Acta*, **148**, 655 (1967)
2) P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **10**, 238 (1969).
3) R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).
4) P. R. Huber, R. Griesser, and H. Sigel, *Inorg. Chem.*, **10**, 945 (1971).
5) H. Sigel, P. R. Huber, and R. F. Pasternack, *Inorg. Chem.*, **10**, 2226 (1971).
6) R. Griesser and H. Sigel, *Inorg. Chem.*, **10**, 2229 (1971).
7) H. Sigel, P. R. Huber, R. Griesser, and B. Prijs, *Inorg. Chem.*, **12**, 1198 (1973).

8) H. Sigel, R. Caraco, and B. Prijs, *Inorg. Chem.*, **13**, 462 (1974).
9) M. Munakata, M. Harada, and S. Niina, *Inorg. Chem.*, **15**, 1727 (1976).
10) R. F. Pasternack and H. Sigel, *J. Am. Chem. Soc.*, **92**, 6146 (1970).
11) R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *J. Am. Chem. Soc.*, **91**, 4401 (1969).
12) R. F. Pasternack, E. Gibbs, and J. C. Cassatt, *J. Phys. Chem.*, **73**, 3814 (1969).
13) G. G. Hammes and J. I. Sternfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).
14) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.*, **88**, 4610 (1966).
15) J. W. Brubaker, A. F. Pearlmutter, J. E. Stuehr, and T. V. Vu, *Inorg. Chem.*, **13**, 559 (1974).
16) M. Eigen and R. G. Wilkins "Mechanism of Inorganic Reactions," Advances in Chemistry Series, No 49, American Chemical Society, Washington, D. C. (1965).
17) L. J. Kirschenbaum and K. Kustin *J. Chem. Soc., A*, **1970** 684.
18) R. Poupko and Z. Luz, *J. Chem. Phys.*, **57**, 3311 (1972).
19) Though a number of the five coordination states for the copper(II) complex are known, few three coordination states have been reported. The transition state on the complex formation may be the former rather than the latter.
20) F. A. Walker, M. Sigel, and D. B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).