

$\Lambda-(+)$ ₅₈₉-[Co(en)₂((R(+))-pantoate)]⁺ isomer and a singlet at 3.74 ppm for the $\Delta(-)$ ₅₈₉-[Co(en)₂((R(+))-pantoate)]⁺ isomer. Models indicate that in the Λ isomer the methine proton is forced into a position where it interacts strongly with the nitrogen proton. This causes a steric compression and a shift of the methine resonance to lower field as compared to the Δ isomer where the steric interaction is absent.

For the methylene region of the pantoate ligand, the reaction product gives a six-line resonance pattern. This can be separated into two doublets (separation 21 Hz with a coupling constant of 11 Hz) in the $\Lambda-(+)$ ₅₈₉-[Co(en)₂((R(+))-pantoate)]⁺ isomer, typical of an AB pattern and a split resonance (separation 1 Hz) for the $\Delta(-)$ ₅₈₉-[Co(en)₂((R(+))-pantoate)]⁺ isomer. Again the integrated intensities of the two sets of resonance lines are approximately equal. The CH₂OH tail of the pantoate ligand is possibly oriented so that the OH group could hydrogen bond to the uncoordinated oxygen of the carboxylate group. The

methylene protons would then be oriented so they could be affected greatly by the methyl group and the observed spectra are consistent with the other resonances.

The data discussed for the hydroxy acid complexes and the analogous amino acid complexes suggest that the optically active ligand coordinates in a preferred conformation in the Λ and Δ configurations of the ethylenediamine rings about the cobalt atom. The chemical shift differences may be attributed to the steric interactions of the optically active ligand with the nitrogen protons of the ethylenediamine rings and can therefore be utilized to assign the absolute configurations of bis(ethylenediamine)cobalt(III) complexes of this type. Further studies of related complexes are now in progress.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ITHACA COLLEGE, ITHACA, NEW YORK 14850, AND THE INSTITUTE OF INORGANIC CHEMISTRY, UNIVERSITY OF BASEL, CH-4000 BASEL, SWITZERLAND

Kinetics of Formation of Mixed-Ligand Complexes. II. 2,2'-Bipyridylcopper(II) Reactions with Ethylenediamine, α -Alanine, and β -Alanine¹

By ROBERT F. PASTERNAK,* PETER R. HUBER, U. M. HUBER, AND HELMUT SIGEL

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The temperature-jump technique has been used to determine the rate constants ($\mu = 0.1$, 25°) for the formation and dissociation of the mixed complexes Cu(bipyridyl)(ethylenediamine)²⁺, Cu(bipyridyl)(α -alaninate)⁺, and Cu(bipyridyl)(β -alaninate)⁺. The values found for the forward rate constants for the reaction Cu(bipy) + L \rightleftharpoons Cu(bipy)L are as follows: for ethylenediamine, $(2.0 \pm 0.4) \times 10^9 M^{-1} sec^{-1}$; for the protonated form of ethylenediamine, $(2.2 \pm 0.6) \times 10^4 M^{-1} sec^{-1}$; for α -alaninate, $(1.0 \pm 0.2) \times 10^9 M^{-1} sec^{-1}$; and for β -alaninate, $(3.4 \pm 0.7) \times 10^8 M^{-1} sec^{-1}$. The rate constants for attack by the zwitterion form of these amino acids are zero within experimental error. The reverse rate constants are as follows: for ethylenediamine, $1.4 \pm 0.3 sec^{-1}$; for the protonated form of ethylenediamine, $(1.2 \pm 0.4) \times 10^5 M^{-1} sec^{-1}$; for α -alaninate, $10 \pm 2 sec^{-1}$; for β -alaninate, $110 \pm 20 sec^{-1}$. These values are compared with the rate constants for the formation of the respective binary complexes Cu + L \rightleftharpoons CuL and CuL + L \rightleftharpoons CuL₂. Mechanistic arguments are developed which lead to the conclusion that complexation reactions of copper(II) are likely S_N2 and that sterically controlled substitution can occur for ternary systems as well as binary ones.

Introduction

It has been found²⁻⁴ that ternary Cu(II) complexes often show an extraordinarily high thermodynamic stability compared with the corresponding binary complexes. This is especially true of mixed-ligand Cu(II) complexes containing 2,2'-bipyridyl or another aromatic ligand.⁵ The size of this effect depends upon the kind of coordinating atoms of the second ligand as may be seen from the $\Delta \log K$ values given in Table I^{2,4,6,7} for several mixed-ligand Cu(II) systems. In

$$\Delta \log K = \log K^{Cu(bipy)_{Cu(bipy)L}} - \log K^{Cu_{CuL}} \quad (1)$$
 eq 1, $K^{Cu(bipy)_{Cu(bipy)L}}$ and $K^{Cu_{CuL}}$ are the equilibrium constants for the formation of the ternary and binary complexes, respectively.

* To whom correspondence should be addressed at Ithaca College.
 (1) Part I: R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92**, 6146 (1970).
 (2) R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).
 (3) H. Sigel, *Chimia*, **21**, 389 (1967).
 (4) P. R. Huber, R. Griesser, B. Prijs, and H. Sigel, *Eur. J. Biochem.*, **10**, 238 (1969).
 (5) P. R. Huber, R. Griesser, and H. Sigel, *Inorg. Chem.*, **10**, 945 (1971).
 (6) R. Griesser, B. Prijs, H. Sigel, W. Fory, L. D. Wright, and D. B. McCormick, *Biochemistry*, **9**, 3285 (1970).
 (7) H. Sigel, P. R. Huber, and R. F. Pasternack, *Inorg. Chem.*, **10**, 2226 (1971).

Usually when the equilibrium constants are compared for complexes containing the same kind of ligand in varying numbers, one observes $K^{Cu_{CuL_m}} > K^{Cu_{CuL_{m+n}}}$. However, for the ternary complexes the $\Delta \log K$ values are frequently considerably less negative than expected from the difference $\log K^{Cu_{CuL_2}} - \log K^{Cu_{CuL}}$; in fact, in quite a number of cases these values are even positive.^{2,3} These positive values for $\Delta \log K$ have been found for all systems which contain 2,2'-bipyridyl and a second ligand with oxygen atoms as donors.⁸ By contrast, the 2,2'-bipyridyl-Cu²⁺-ethylenediamine system has a "normal" $\Delta \log K$ of -1.3 . Furthermore, when ethylenediamine is substituted for 2,2'-bipyridyl in the inner coordination sphere of copper(II),
 (8) H. Sigel and D. B. McCormick, *Accounts Chem. Res.*, **3**, 201 (1970), and references therein.

TABLE I
 STABILITIES OF TERNARY COMPLEXES

	$\Delta \log K^a$
2,2'-Bipyridyl-Cu ²⁺ -ethylenediamine ^b	-1.29
2,2'-Bipyridyl-Cu ²⁺ - α -alaninate ^d	-0.26
2,2'-Bipyridyl-Cu ²⁺ - β -alaninate ^e	-0.59
2,2'-Bipyridyl-Cu ²⁺ -glycinate ^b	-0.35
2,2'-Bipyridyl-Cu ²⁺ -pyrocatecholate ^b	+0.43
Ethylenediamine-Cu ²⁺ -pyrocatecholate ^c	-0.76

^a Cf. eq 1. ^b Reference 2. ^c Reference 4. ^d Reference 6. ^e Reference 7.

the respective ternary complexes are considerably less stable (cf. Table I).³ This and the previous work¹ have been undertaken to help determine the factors responsible for the thermodynamic stabilities of ternary systems.

Experimental Section

This study on the kinetics of ternary complexes of copper(II) was carried out by application of the temperature-jump technique.^{9,10} The apparatus has been described elsewhere.¹¹ The ligands used were Nutritional Biochemicals Corp. α - and β -alanine and Eastman Organic Chemicals 2,2'-bipyridyl. Baker reagent grade ethylenediamine was redistilled before use. Baker reagent grade nitrate salts of potassium and copper(II) were used without additional purification. The reaction progress was followed by use of Allied Chemical methyl red as an indicator.

Stock solutions of bipyridyl and ethylenediamine were prepared and stored in the cold and dark. A copper(II) stock solution was prepared and the concentration determined by EDTA titration using murexide as the indicator.

The solutions for the different experiments were made up such that the metal and bipyridyl concentrations were always kept equal while the concentration of the second ligand was varied. The ionic strength was adjusted to 0.1 M with KNO₃ and all solutions were 5.0 \times 10⁻⁵ M in methyl red. The solutions were degassed and the pH was adjusted with small amounts of HNO₃ and/or NaOH to \pm 0.01 pH unit. The equilibrium temperature of these studies was 25°.

All the solutions containing Cu(II), bipyridyl, "second ligand," neutral salt, and indicator showed a single relaxation effect. Blank tests containing either only Cu(II), bipyridyl, indicator, and neutral salt, or only "second ligand," indicator, and neutral salt showed no relaxation effect in the time range of the instrument. Each relaxation time represents an average of at least three photographic determinations, with the relative error of these measurements at \pm 10%. Calculations have been carried out on the Ithaca College RCA 70/35 computer. The equilibrium concentrations of the species in solution were calculated using a Newton-Raphson routine.

The rate constants for attack by the deprotonated forms of the ligands (α -alaninate(1-), β -alaninate(1-), and ethylenediamine) are reported to \pm 20%. The relative errors in rate constants for attack by protonated forms were calculated from $\Delta k_{12}' = (B\tau)^{-1}\Delta\tau/\tau + (A/B)\Delta k_{12}$ (vide infra). It was found that whereas $\Delta k_{12}' \approx 0.25k_{12}'$ for ethylenediamine, $\Delta k_{12}' \geq k_{12}'$ for α -alanine and β -alanine.

Results

Table II includes the equilibrium constants of the reactions involved in the individual complex formations of the particular ligands.

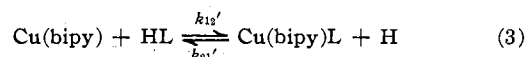
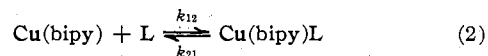
With the help of these constants it was possible to calculate the concentrations of the species participating in the formation of the ternary complexes. A most important assumption has been made. In the pH region studied (pH 4.5-5.5) the reaction of bipyridyl with the free Cu(II) ion has been considered to have gone to completion; that means $[Cu^{2+}]_{tot} = [Cu(bipy)]$.^{1,2} In the pH range chosen hydrolyzed Cu(II)

 TABLE II
 EQUILIBRIUM CONSTANTS AT $\mu = 0.1$ AND 25°

	$pK^H_{H_2L}$	pK^H_{HL}	Log K^{Cu}_{CuL}	Log $K^{Cu}_{CuL_2}$	Log $K^{Cu(bipy)}_{Cu(bipy)L}$
2,2'-Bipyridyl ^a	...	4.49	8.00	5.80	...
Ethylenediamine ^c	7.10	9.87	10.44	9.16	9.15
α -Alanine ^d	2.26	9.83	8.25	7.05	7.99
β -Alanine ^e	3.56	10.22	7.07	5.61	6.48
Methyl red ^b	...	5.00

^a G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963). ^b I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930). ^c Reference 2. ^d Reference 6. ^e Reference 7.

species need not be considered.^{1,2} With this assumption and the experimental restrictions taken, we are left with the equilibria



(The charges are omitted for the sake of convenience.) Reactions 2 and 3 are coupled to the more rapid processes shown in eq 4-6.

The use of standard techniques for deriving expressions for relaxation times led to a variation of an equation published earlier^{1,11,12}

$$1/\tau = Ak_{12} + Bk_{12}' \quad (7)$$

where

$$A = \frac{[Cu(bipy)]}{1 + \alpha} + [L] + \frac{1}{K^{Cu(bipy)}_{Cu(bipy)L}} \quad (8)$$

$$B = \rho \frac{[Cu(bipy)]}{1 + \alpha} + [HL] +$$

$$\frac{1}{K^{Cu(bipy)}_{Cu(bipy)L} K^H_{HL}} \left(\sigma \frac{[Cu(bipy)L]}{1 + \alpha} + [H] \right) \quad (9)$$

$$\beta = \frac{K_{In} + [H]}{K_{In} + [H] + [In]} \quad (10)$$

$$\gamma\alpha = [H]^2 + \beta[OH][H] + \beta[H][HL] + \beta K^H_{H_2L}[OH] + K^H_{H_2L}[H] \quad (11)$$

$$\gamma\sigma = 2\beta[H]^2 + \beta K^H_{H_2L}[H] \quad (12)$$

$$\gamma\rho = K^H_{H_2L}[H] + \beta K^H_{H_2L}[OH] + 2\beta[H][HL] \quad (13)$$

$$\gamma = K^H_{HL}K^H_{H_2L} + \beta K^H_{HL}K^H_{H_2L}[OH]/[H] + \beta K^H_{H_2L}[L] + 4\beta K^H_{HL}[HL]$$

The data of Table III in combination with the eq 8-13 yielded values for $(\tau B)^{-1}$ and (A/B) (cf. eq 7). Plots of these values for the ternary complexes containing ethylenediamine, α -alanine, and β -alanine as ligands other than bipyridyl are shown in Figures 1-3, respectively. The solid lines in Figures 1-3 are calculated by a least-squares calculation. From these plots we learn the following: in the system containing ethylenediamine the protonated form (enH^+)¹³ is an attacking form of the ligand as well as en ; in the systems involving the amino acids rate constants obtained for zwitterion attack are zero within experimental error.¹

(9) M. Eigen and L. DeMaeyer, *Tech. Org. Chem.*, **8**, 895 (1963).

(10) A. F. Pearlmutter and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 858 (1968).

(11) R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *ibid.*, **91**, 4401 (1969).

(12) R. F. Pasternack, E. Gibbs, and J. C. Cassatt, *J. Phys. Chem.*, **78**, 3814 (1969).

(13) L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970).

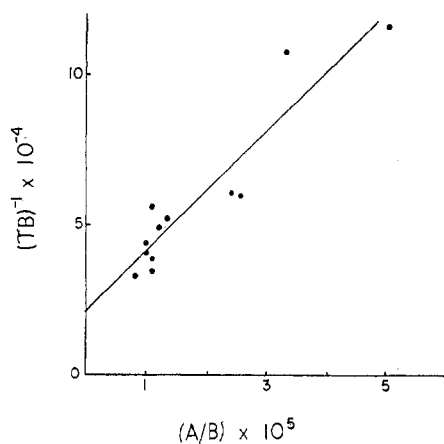


Figure 1.—A plot of $(\tau B)^{-1}$ vs. A/B for the $\text{Cu}(\text{bipy})^{2+}$ -ethylenediamine system. The slope yields a value of $k_{12} = (2.0 \pm 0.4) \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, and the intercept, a value of $k_{12}' = (2.2 \pm 0.6) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ (cf. eq 2, 3, and 7).

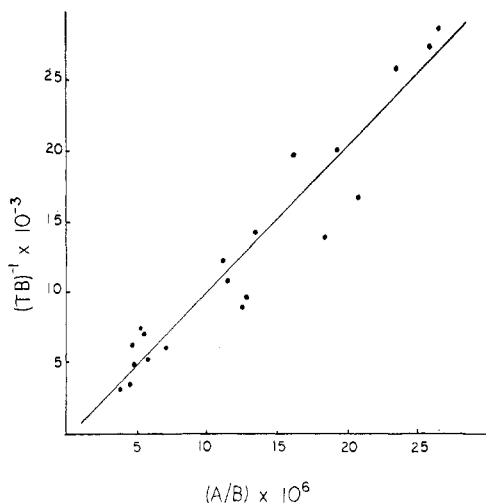


Figure 2.—A plot of $(\tau B)^{-1}$ vs. A/B for the $\text{Cu}(\text{bipy})^{2+}$ - α -alanine system. The slope yields a value of $k_{12} = (1.0 \pm 0.2) \times 10^9 \text{ M}^{-1}$, and the intercept is $k_{12}' = (-0.51 \pm 1) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ which leads to a value of $k_{12}' \approx 0$ (cf. eq 2, 3, and 7).

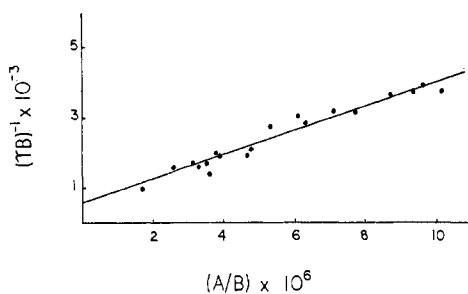


Figure 3.—A plot of $(\tau B)^{-1}$ vs. A/B for the $\text{Cu}(\text{bipy})^{2+}$ - β -alanine system. The slope yields a value of $k_{12} = (3.4 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, and the intercept is $k_{12}' = (0.58 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. We therefore conclude that for this system, as well, $k_{12}' \approx 0$ (cf. eq 2, 3, and 7).

In Table IV^{1,10,13,14} the results of this investigation and of the previous work are summarized.

Discussion

The ternary complexes of bipyridylcopper(II) with the α -amino acid anions glycinate and α -alaninate ex-

(14) W. B. Makinen, A. F. Pearlmitter, and J. E. Stuehr, *J. Amer. Chem. Soc.*, **91**, 4083 (1969).

TABLE III
RESULTS OF THE RELAXATION EXPERIMENTS

$10^4[\text{Cu}^{2+}]_{\text{tot}}$ $= 10^3$	$10^3[\text{L}]_{\text{tot}}$	pH	τ_{obsd} , msec	$10^3[\text{Cu}^{2+}]_{\text{tot}}$ $= 10^3$	$10^3[\text{L}]_{\text{tot}}$	pH	τ_{obsd} , msec
[bipy] _{tot} , M	M			[bipy] _{tot} , M	M		
Ethylenediamine							
2.59	2.50	5.70	3.2	5.18	5.00	5.38	2.5
2.59	5.00	5.07	5.1	5.18	10.0	5.52	3.0
2.59	10.0	4.92	6.9	5.18	10.0	5.00	2.8
5.18	5.00	5.41	2.6	5.18	20.0	5.03	2.7
5.18	5.00	5.04	3.8	10.36	20.0	5.05	1.9
5.18	5.00	5.00	3.2	10.36	20.0	5.11	1.6
α -Alanine							
2.59	2.59	5.15	1.1	2.59	20.7	5.22	1.0
2.59	5.18	4.62	2.4	5.18	5.18	4.80	1.4
2.59	5.18	5.36	0.73	5.18	5.18	5.70	0.74
2.59	10.4	4.69	2.3	5.18	5.18	4.60	2.5
2.59	10.4	5.07	1.3	5.18	5.18	5.00	0.85
2.59	10.4	5.35	0.78	5.18	10.4	4.71	1.6
2.59	20.7	4.63	3.6	5.18	10.4	5.05	0.96
2.59	20.7	4.99	1.6	5.18	10.4	5.26	0.63
2.59	20.7	5.31	0.82	5.18	20.7	4.52	3.4
2.59	20.7	4.62	2.4	5.18	20.7	5.04	1.3
β -Alanine							
2.59	2.59	5.30	2.2	5.18	10.4	5.22	1.6
2.59	10.4	5.05	2.8	5.18	10.4	4.91	2.6
2.59	10.4	5.31	1.9	5.18	20.7	5.01	2.5
2.59	20.7	5.11	2.4	5.18	20.7	5.34	1.2
2.59	20.7	5.30	2.1	10.36	2.59	4.55	3.4
5.18	2.59	4.82	2.2	10.36	5.18	4.74	2.3
5.18	2.59	5.18	1.7	10.36	10.4	4.84	2.2
5.18	5.18	4.92	2.7	10.36	10.4	4.88	2.4
5.18	5.18	5.00	2.7	10.36	10.4	5.13	1.0
5.18	5.18	5.27	1.3	10.36	20.7	4.87	2.1

hibit equal values of $\log K_{\text{Cu}(\text{bipy})\text{Cu}(\text{bipy})\text{L}}$. The forward rate constants, k_{12} , for these two ligands as well as the dissociation rate constants, k_{21} , agree to within a factor of 2. The k_{12} values are about equal to the respective k_1 value; the k_{21} values are about equal to the respective k_{-1} and are considerably smaller than k_{-2} . Therefore, the replacement of two water molecules in the inner coordination sphere by a bipyridyl molecule is of little consequence with respect to the rate constants for reaction with an α -amino acid. Certainly, as may be seen from Table IV, the presence of bipyridyl exerts a still smaller influence on the rate constants than does the presence of the amino acid. For ethylenediamine, $k_{12} \approx k_1$ and $k_{12} = k_2$ as well. Unlike the case of the α -amino acids, k_{21} for this ligand is equal to k_{-2} rather than k_{-1} . Here the presence of bipyridyl in the inner coordination sphere exerts an influence which, within the limits of experimental error, is identical with the presence of ethylenediamine.

The values of 1.2 and 1.4 for

$$\log \frac{K_{\text{Cu}(\alpha\text{-ala})}^{\text{Cu}}}{K_{\text{Cu}(\beta\text{-ala})}^{\text{Cu}}}$$

and

$$\log \frac{K_{\text{Cu}(\alpha\text{-ala})\text{Cu}(\alpha\text{-ala})_2}^{\text{Cu}}}{K_{\text{Cu}(\beta\text{-ala})\text{Cu}(\beta\text{-ala})_2}^{\text{Cu}}}$$

respectively, illustrate the well-known chelate ring size effect¹⁵ that as chelate ring size for closely related ligands increases beyond five members, the stability of the complexes decreases. This effect manifests itself to the same degree for ternary systems (cf. Table II). Kustin, Pasternack, and coworkers^{16,17} have

(15) H. Irving, R. J. P. Williams, D. J. Ferrett, and A. E. Williams, *J. Chem. Soc.*, 3494 (1954).

(16) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966).

(17) A. Kowaluk, K. Kustin, R. F. Pasternack, and S. Petrucci, *ibid.*, **89**, 3126 (1967).

TABLE IV
 RATE CONSTANTS AT 25° AND 0.1 M IONIC STRENGTH

Ligand	k_1^a	k_{-1}^a	k_2^a	k_{-2}^a	k_{12}^b	k_{21}^b
en ^d	3.8×10^9	~ 0.10	1.9×10^9	1.5	2.0×10^9	1.4
enH ^{+,e,d}	1.4×10^6	2.5×10^4	$\sim 3 \times 10^4$	$\sim 2 \times 10^6$	2.2×10^4	1.2×10^6
gly ^{e,f}	4.0×10^9	22	4.0×10^8	48	1.6×10^9	19
α -ala ^g	1.3×10^9	12	1.5×10^8	33	1.0×10^9	10
β -ala ^g	2.0×10^8	11	8.0×10^6	19	3.4×10^8	110

^a $\text{CuL}_{n-1} + \text{L} (k_n) \rightleftharpoons \text{CuL}_n (k_{-n})$; $k_n, M^{-1} \text{sec}^{-1}$; k_{-n}, sec^{-1} . ^b $\text{Cu}(\text{bipy}) + \text{L} (k_{12}) \rightleftharpoons \text{Cu}(\text{bipy})\text{L} (k_{21})$; $k_{12}, M^{-1} \text{sec}^{-1}$; k_{21}, sec^{-1} .
^c For enH⁺, the rate constants refer to the reactions $\text{CuL}_{n-1} + \text{LH}^+ (k_n') \rightleftharpoons \text{CuL}_n + \text{H}^+ (k_{-n}')$; $k_n, M^{-1} \text{sec}^{-1}$; $k_{-n}, M^{-1} \text{sec}^{-1}$;
 $\text{Cu}(\text{bipy}) + \text{LH}^+ (k_{12}') \rightleftharpoons \text{Cu}(\text{bipy})\text{L} + \text{H}^+ (k_{21}')$; $k_{12}, M^{-1} \text{sec}^{-1}$; $k_{21}, M^{-1} \text{sec}^{-1}$. ^d Reference 13. ^e Reference 1. ^f Reference 10.
^g Reference 14.

found that for binary complexes this decrease in stability can be attributed primarily to a decreased forward rate constant for complexation. The forward rate constants for the formation of the ternary complex $\text{Cu}^{\text{II}}(\text{bipy})(\alpha\text{-ala})$ is considerably larger than the one found for $\text{Cu}^{\text{II}}(\text{bipy})(\beta\text{-ala})$, manifesting again the influence of ring size on the rate constants. However, here as well, k_{12} for the β -alanine complex is of comparable size to k_1 therefore demonstrating the relatively small influence bipyridyl is exhibiting on the forward rate constants. The most interesting feature of this particular mixed-ligand system, however, is the fact that k_{21} is considerably larger than k_{-1} and k_{-2} .

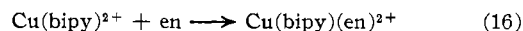
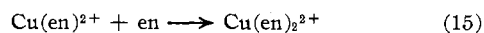
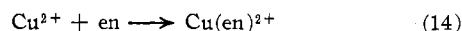
To summarize the results, for each of the ternary complexes studied, the forward rate constant is comparable to the k_1 for the respective binary system. For the α -amino acids, the k_{21} values are similar to the k_{-1} values of the binary systems and, therefore, the $\Delta \log K$ are nearly zero (cf. eq 1). For ethylenediamine the k_{21} value resembles the k_{-2} value and since for this ligand $k_1 \approx k_2 \approx k_{12}$, $\Delta \log K$ has a "normal" value as compared to binary systems. For β -alanine, the k_{12} value shows the influence of complexation with a ligand forming a six-membered chelate ring but the k_{21} does not correlate with either k_{-1} or k_{-2} , exhibiting therefore a special case.

There has been considerable discussion of late on the detailed mechanism of complexation reactions of copper(II).^{1,10,13} An SN1 mechanism is usually favored in analogy to other labile metal ions such as cobalt(II) and nickel(II). The extremely large value for the forward rate constant for the reaction $\text{Cu}(\text{aq})^{2+} + \text{L} \rightleftharpoons \text{CuL}(\text{aq})$ has been taken as a result of the Jahn-Teller distortion of the metal environment from O_h to, in this case, an axially elongated D_{4h} group. Substitution is then considered to take place in the axial position with rapid inversion bringing the ligand into the equatorial plane.¹³ The fact that for copper(II) and α -amino acids, $k_2 < k_1$, unlike the results obtained for nickel(II) and cobalt(II),¹⁹ has proven somewhat puzzling. However, statistical arguments have been proposed as well as arguments involving the inhibition of inversion by the presence of a nonaquo ligand in the inner coordination sphere to account for this effect.^{1,11,20}

If the mechanism is considered to be SN1, then it may be stated that the presence of the bipyridyl in the inner coordination sphere has little effect on the rate of water loss from the axial positions of the copper ion, nor does it influence the rate of inversion and ring closure. On the other hand, once the second ligand is attached, the charge type of the species to be separated

is of great importance in determining the value of the reverse rate constant. Therefore, α -alaninate and glycinate dissociate from the cationic ternary complex with rate constants which are comparable to the dissociation rate constants from the cationic monosubstituted binary complex rather than from the neutral disubstituted binary complex. Furthermore, statistical considerations for the removal of a ligand from the ternary complex are the same as those from the monosubstituted complex.¹ In the case of ethylenediamine, the rate constant for dissociation of the neutral ligand is the same as that obtained for the disubstituted binary complex. Therefore, for these relatively simple ligands, where no additional π -bonding possibilities exist, charge type is of primary importance. For ligands like pyrocatecholate in which $\Delta \log K$ is positive (cf. Table I), we anticipate a normal forward rate constant for the formation of the ternary complex but an extremely small reverse rate constant due in part to the type of electrostatic interaction we observe here and to π -bonding interactions described elsewhere.²

Certain difficulties with this SN1 mechanistic approach have arisen even in the case of binary complexes. First, it is difficult to conceive of a multistep process in which the rate-determining step is a nearly diffusion-controlled bond-breaking process. A formal calculation¹⁰⁻¹² from the kinetic results sets the rate constant for the breaking of a copper(II)-water bond at $\sim 1 \times 10^9 \text{sec}^{-1}$. It is probably as nearly correct to think of the axial position on the copper ion as being free for ligand attack as to propose a mechanism in which an outer-sphere complex is formed between copper ion and ligand and, in a subsequent step, the copper-water bond is broken with insertion of one end of the ligand. Second, Kustin and Kirschenbaum¹³ found that for ethylenediamine $k_2 \approx k_1$, and, therefore, the α -amino acid results in which $k_2 < k_1$ can probably not be accounted for on statistical arguments only. Furthermore our results can be interpreted as providing some evidence for an SN2 mechanism. Let us return to the ethylenediamine system. For this ligand, all three reactions



proceed with almost identical rate constants. Although $\text{Cu}(\text{en})^{2+}$ and $\text{Cu}(\text{bipy})^{2+}$ may appear to be very similar chemical species, it has been shown that they have quite different properties with relation to the stabilities of ternary complexes. Briefly, the mixed-ligand complexes formed with $\text{Cu}(\text{bipy})^{2+}$ are considerably more stable than the analogous complexes of $\text{Cu}(\text{en})^{2+}$. This

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has been interpreted as being due to the relatively low-lying π^* ligand orbitals in bipyridyl which allow for considerable back-donation from the copper ion, the net effect of which is the lowering of the electron density on the copper ion. This delocalization of electron density should manifest itself kinetically but in a manner determined by the mechanism of the reaction. More specifically, lowering of electron density on the copper ion should serve to slow down an S_N1 process but enhance an $S_N2(\text{lim})$ process.²¹ However, we find a value for k_{12} for reaction 16 which is identical with the value of k_2 determined by Kustin and Kirschenbaum for reaction 15. This implies that the rate-determining step involves both bond making and bond breaking and therefore falls into the S_N2 category. Kustin and Kirschenbaum¹³ considered the internal conjugate base (ICB) mechanism suggested by Rorabacher²² for nickel(II) complexation but, to be applicable, this variation of the S_N1 mechanism would necessitate a rate-determining step in which the rate constant is significantly larger than 10^9 sec^{-1} . These authors called attention to the fact that their results are explained at least as well by an S_N2 process. The similarities in k_{12} for ethylenediamine, α -alanine, and glycine can be

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interpreted as reflecting the similar nucleophilicities of these ligands. The reverse rate constants in turn reflect the relative difficulty in breaking bonds between the metal center and the leaving ligand.

We have extended our studies to the investigation of a ternary complex of cobalt(II) where less ambiguity exists concerning the mechanistic details for ligand substitution.²³

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(23) NOTE ADDED IN PROOF.—Other evidence for an S_N2 mechanism for copper complexation reactions has been offered by Sharma and Leussing (D. Leussing, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, and private correspondence). In their study of $\text{Cu}(\text{en})^{2+} + \text{ser}^- \rightleftharpoons \text{Cu}(\text{en})(\text{ser})^+$, these workers obtain a forward rate constant of $6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. The analogous reactions described here of $\text{Cu}(\text{bipy})^{2+}$ with amino acid anions, studied at a temperature 12° below that of the Sharma and Leussing study, yield rate constants two to three times larger. Since, as has been shown, the presence of ethylenediamine in the inner coordination sphere of nickel(II) has a more pronounced labilizing effect on remaining water molecules than does bipyridyl,^{24,25} these kinetic results suggest an associative rather than a dissociative mechanism for copper(II).

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CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Elimination of Solvation Contributions to the Enthalpies of Adduct Formation in Weakly Polar Solvents. II. Adducts of Bis(hexafluoroacetylacetonato)copper(II)

BY M. S. NOZARI AND RUSSELL S. DRAGO*

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An earlier preliminary report on a procedure for eliminating solvent contributions to enthalpies measured in polar solvents has been extended to include the Lewis acid bis(hexafluoroacetylacetonato)copper(II), $\text{Cu}(\text{hfac})_2$. In slightly polar, weakly basic solvents, solvation effects have been shown to cancel (within error limits) for the displacement reaction represented by the equation $\text{AB} + \text{B}' \rightarrow \text{AB}' + \text{B}$, where A is $\text{Cu}(\text{hfac})_2$ and B and B' are Lewis bases. This procedure can be applied to calculate the enthalpy of adduct formation between a Lewis base and $\text{Cu}(\text{hfac})_2$ in the nonpolar solvent for a base which is insoluble in nonpolar solvents.

Introduction

Previous reports from our laboratory¹ have demonstrated that the enthalpies of the interaction of donor-acceptor systems in nonpolar solvents can be accurately estimated (to $\pm 0.2 \text{ kcal mol}^{-1}$) with the double-scale equation²

$$-\Delta H = E_A E_B + C_A C_B \quad (1)$$

where E and C are empirically determined parameters and the subscripts A and B refer to an acid and a base, respectively. The predictive and correlative power of this formula have been successfully tested in a variety

of systems.¹⁻⁷ However, the range of systems which can be investigated is limited by the insolubility of donors, acceptors, or adducts in nonpolar systems. For example, the only transition metal compound which has been incorporated into the E and C scheme is a copper(II)- β -diketone chelate.⁸ It is desirable to examine further the generality of eq 1 and enhance our knowledge of intermolecular interactions. It would be particularly interesting to extend our measurements to other transition metal compounds where π back-bond-

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