pound, the ring flip would, therefore, require still more energy than for either **1** or **2** and this is evidenced in the fact that the ring flip of the dihydrobis(pyrazolyl)borate is not observed by pmr.

One of the major goals of this investigation was to obtain some estimate of the strength of the $C-H\cdots Mo$ interaction. Using the results presented in Table II, we proceed as follows. From the low-temperature process, with $E_a \approx \Delta H^{\pm} \approx 14$ kcal mol^{-1}, we do not believe that much can be learned. The breaking of one $C-H\cdots Mo$ bond is probably compensated by the formation of the new one as the rotation about the B–C bond proceeds. There is probably some partial loss of bond energy in the transition state, but the shift of the other ligands probably also contributes significantly to the total activation energy. There does not appear to be any way to sort out the two contributions nor to determine the degree of $C-H\cdots Mo$ bond breaking which has occurred in the transition state.

The high-temperature process does, however, provide some estimate of the $C-H\cdots Mo$ interaction energy. The activation energy for this process, which is about 19 kcal mol^{-1} for **1** and about 17 kcal mol^{-1} for **2**, has three main components: (1) the energy of breaking the $C-H\cdots Mo$ bond, A, (2) the energy of relaxing the very puckered boat conformation of the chelate ring to a flatter boat, like that found in [Et$_2$B(pz)$_2$]Mo(CO)$_2$-(η^3-C$_3$H$_5$)(pyrazole),[6] B, (3) the activation energy for the ring flip (and associated ligand rearrangements), C. The quantities A, B, and C are +, − and +, respectively. The magnitude of C is probably similar to that for the ring inversion in cyclohexane, viz., about 6 kcal/mol. If it is assumed that B also has a magnitude of about 6 kcal mol^{-1}, C and B cancel each other, leaving A equal to the measured $\Delta H^{\pm}$, namely 17–19 kcal mol^{-1}. This is admittedly a very rough estimate, but it seems a reasonable one.

Kinetics of Reaction of Copper(II) Ion with a Variety of Ligands

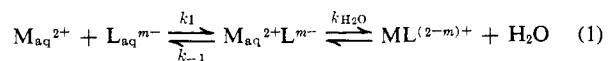**Thomas S. Roche and Ralph G. Wilkins*[1]**

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received November 17, 1973

Abstract: The activation parameters for the formation of the monocomplex of copper(II) with ten different ligands have been determined. The ligands studied included 2-substituted pyridyl derivatives, tri- and tetraamines, and aminodicarboxylates. The results are compared with complexing of these ligands by nickel(II), and conclusions are drawn as to the mechanisms of complex formation.

There has been an increasing number of studies of the kinetics of complexing of copper(II). Recent work has centered on the ligands ammonia,[2] ethylenediamine,[3,4] and tetraethylenepentaamine,[5] amino acids and derivatives,[6–12] β-diketones,[13,14] and the dye pyridine-2-azo-p-dimethylaniline[15,16] in their reactivity toward the aquated copper ion, as well as toward complexed copper(II), forming ternary complexes.[17]

Disagreement exists as to the detailed mechanism of complex formation, particularly in the formation of ternary complexes. Toward Cu^{2+}, the reactions of a large number of ligands can be interpreted in terms of the generally accepted mechanism for complexation by bivalent metal ions in aqueous solution. In this, ligand–water interchange occurs within the outer-sphere complex, leading to the inner-sphere complex

$$M_{aq}{}^{2+} + L_{aq}{}^{m-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_{aq}{}^{2+}L^{m-} \overset{k_{H_2O}}{\rightleftharpoons} ML^{(2-m)+} + H_2O \quad (1)$$

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On the basis of this mechanism, k_{H_2O} is several orders of magnitude larger than for other metal ions of comparable radius and is ascribed to operation of the Jahn–Teller effect.[18] Rate-determining substitution occurs at the labile apical positions of the tetragonally distorted copper(II) ion, and this is followed by a rapid apical–equatorial inversion. The net result of this is to place the ligand in an equatorial position. Even more rapid ring closure can follow the formation of the first copper(II)–donor atom bond in the case of multidentate ligands.

We have examined the kinetics of formation of the monocopper(II) complex by a number of different types of ligands including pyridyl derivatives, di- and polyamines, and iminodiacetates. This includes the determination of activation parameters for a number of systems; there has been virtually no investigation of the temperature coefficient of rate constants for copper complexing. The mechanism indicated in eq 1 is established for a wide number of nickel(II) reactions.[19] The comparison of the present results with those for nickel(II) with similar ligands,[20,21] might be expected then to be helpful in deciding the applicability of eq 1 to copper(II) also.[5,22,23]

Experimental Section

Materials. All of the ligands used were highest quality commercial products. 2,2'-Bipyridine was purified by sublimation. TPTZ (G. F. Smith) was purified by recrystallization from petroleum ether. dien·3HCl, trien·4HCl, and tren·3HCl were used as recrystallized salts; we thank Dr. Frances M. Bogdansky for a gift of these salts. Copper(II) solutions were prepared from a stock solution of $Cu(NO_3)_2$, standardized by titration with EDTA using murexide as indicator.

Kinetic Experiments. All the reactions were followed in a stopped-flow apparatus using the general approach outlined in previous papers.[20,21] Reactions were run under pseudo-first-order conditions with copper(II) ion in excess, typically 10^{-3} to 10^{-4} M, and ligand usually about 10^{-4} to 10^{-5} M. The formation of the copper(II) complex was followed directly: bipy (280 nm), phen (305 nm), terpy (320 nm), TPTZ (320–330 nm), and the remaining ligands (250–260 nm). An increase in absorbance was observed as complex formed. An ionic strength of 0.3 M was maintained by the addition of $NaNO_3$ or, occasionally, $NaClO_4$. No buffers were required for reactions at pH less than 3; acetate–acetic acid and formate–formic acid were used for studies at higher pH. A small change (0.1–0.2) in pH units accompanied some reactions. The latter portion of the traces was then used. Temperature control of the reaction solutions was provided by thermostated water circulated in the glass jackets surrounding the driving syringes and in the blocks containing the mixing chamber and the observation tube. The system was thermostated for at least 30 min before measurements were made. The accuracies for the temperatures reported are considered to be 25.0 ± 0.1, 15.0 ± 0.3, and 0.5 ± 0.5°. Excellent first-order plots were usually obtained, although the fastest reactions studied with $t_{1/2} \sim 5$ msec sometimes gave pronounced plot scatter. The observed first-order rate constants (k_1) are the average of at least three determinations, and the error in k_1 is ±10%. The second-order rate constants k ($= k_1[Cu(II)]^{-1}$) were calculated and found to be independent of the copper ion concentration. In all cases studied, ≥95% of the mono complex was formed, so that treatment for reversibility was unnecessary.[24]

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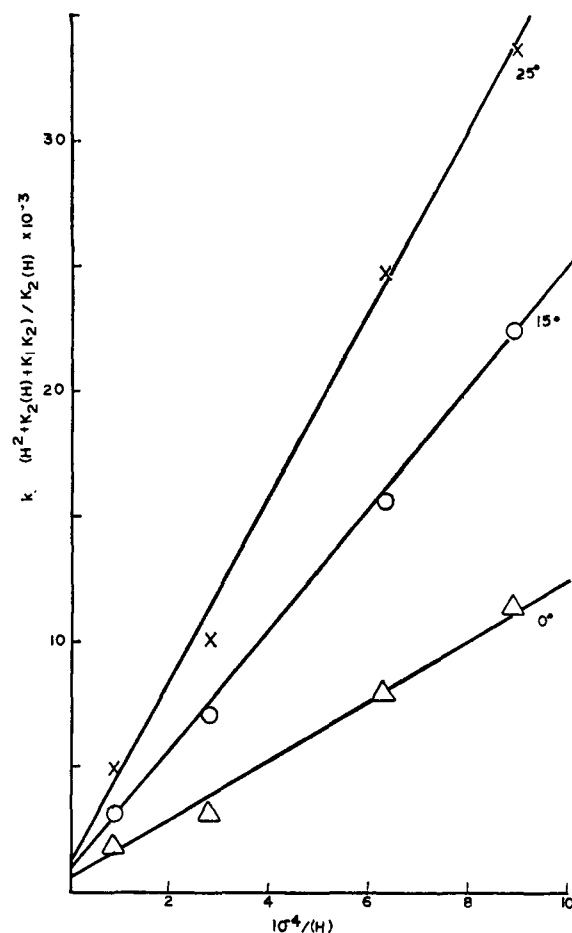(24) See paragraph at end of paper regarding supplementary material.

Figure 1. Plot of $k([H^+]^2 + K_2[H^+] + K_1K_2)(K_2[H^+])^{-1} \times 10^{-3}$ vs. $10^{-4}[H^+]^{-1}$ for reaction of Cu^{2+} with dien.

Results and Discussion

All the formation reactions were second order. By examining the variation of the second-order rate constant with pH, it is possible to assess, with the aid of the appropriate plot,[20,21] the contributions of the various forms of the ligand toward the rate. From the variation of the rate constants with temperature, the activation parameters can be determined. As an example, we can use the data for the reaction of Cu^{2+} with dien (present as protonated forms) from pH 4 to 5.[24] For this (eq 4 of ref 21)

$$k\frac{[H^+]^2 + K_2[H^+] + K_1K_2}{K_2[H^+]} = k_2 + k_1\frac{K_1}{[H^+]} \quad (2)$$

where k is the observed second-order rate constant, k_1 and k_2 are the rate constants for reaction of dienH$^+$ and dienH$_2^{2+}$, and K_1 and K_2 are the ionization constants of dienH$^+$ and dienH$_2^{2+}$. The appropriate plots at 25.0, 15.0, and 0.5° are shown in Figure 1. The values of pK_2 used at these temperatures are 4.25, 4.43 and 4.74, respectively, and of pK_1 are 8.98, 9.28, and 9.8. These were calculated from the heats of ionization of -12.0 and -7.2 kcal mol^{-1} for dienH$^+$ and dienH$_2^{2+}$, respectively.[25] The values of the slope and K_1 lead to k_1 values of 3.7×10^8, 5.4×10^8, and 8.6×10^8 M^{-1} sec^{-1} at 25.0, 15.0, and 0.5°, respectively.

(25) R. M. Izatt and J. J. Christensen in "Handbook of Biochemistry and Selected Data for Molecular Biology," 2nd ed, H. Sober, Ed., The Chemical Rubber Publishing Company, Cleveland, Ohio, 1921, J.58.

Table I. Kinetic Data for the Formation of Copper(II) Monocomplexes at 25° and Ionic Strength 0.30 M^a

Reacting form of ligand	Ligand abbrev	k, M^{-1} sec^{-1}	$\Delta H^{\pm}$, kcal mol^{-1}	$\Delta S^{\pm}$, eu
2-Aminomethylpyridine	amp			
ampH+		8.6×10^3	4.6	-25
2,2'-Bipyridine	bipy	5.0×10^7 ($\sim4 \times 10^7$)^b		
bipyH+		2.6×10^5 (2.9×10^5)^b	4.3	-19
1,10-Phenanthroline	phen	6.4×10^7	5.1	-6
phenH+		$<5 \times 10^2$		
2,2',2''-Terpyridine	terpy			
terpyH+		8.0×10^5	4.9	-15
terpyH$_2$$^{2+}$		$<5 \times 10^2$		
Terpyridyl-s-triazine	TPTZ			
TPTZH+		2.4×10^7	6.0	-5
TPTZH$_2$$^{2+}$		$<1 \times 10^3$		
NH(CH$_2$CH$_2$NH$_2$)$_2$	dien			
dienH+		3.7×10^8	-6	-41
dienH$_2$$^{2+}$		$\sim1 \times 10^3$		
(NH$_2$CH$_2$CH$_2$NHCH$_2$)$_2$	trien			
trienH$_2$$^{2+}$		7.0×10^6 (7.5×10^6)^c	~3	~-16
trienH$_3$$^{3+}$		$\sim2 \times 10^3$ (1.6×10^4)^c		
N(CH$_2$CH$_2$NH$_2$)$_3$	tren			
trenH$_2$$^{2+}$		3.8×10^6	~0	
trenH$_3$$^{3+}$		$\sim1 \times 10^2$		
NH(CH$_2$COO$^-$)$_2$	IDA	3.0×10^9	3.2	-4
IDAH$^-$		1.2×10^4	9.9	-7
CH$_3$N(CH$_2$COO$^-$)$_2$	MIDA	7.4×10^9	3.3	-2
MIDAH$^-$		1.1×10^4	10.9	-3

^{a} Experiments with bipy, phen, and terpy were carried out at $I = 1.0\ M$. ^{b} Reference 27. ^{c} Reference 23.

Table II. Comparison of Rate Constants for Substitution of Ni(II) and Cu(II) at 25° and Variable Ionic Strength

Ligand	k_{Ni}, M^{-1} sec^{-1}	k_{Cu}, M^{-1} sec^{-1}	$k_{\mathrm{Cu}}/k_{\mathrm{Ni}}$	Ref
		"Normal"		
NH$_3$	4.6×10^3	2.0×10^8	4.3×10^4	a, 2
imid	6.4×10^3	5.7×10^8	8.9×10^4	21, 2
phen	3.5×10^3	6.4×10^7	1.8×10^4	21, b
bipy	2.0×10^3	5.0×10^7	2.5×10^4	21, b
TPTZH+	1.7×10^3	2.4×10^7	1.4×10^4	b, f
trienH$_2$$^{2+}$	9.7×10	7.0×10^6	7.0×10^4	c, b
tetrenH$_2$$^{2+}$	3.2×10^2	4.2×10^7	1.3×10^5	c, 5
tetrenH$_3$$^{3+}$	3.5	1.6×10^5	4.6×10^4	c, d
IDA^{2-}	8.8×10^4	3.0×10^9	3.4×10^4	20, b
IDAH$^-$	7.7×10^{-2}	1.2×10^4	1.6×10^5	20, b
		"Abnormal"		
enH+	5.9×10^2	1.4×10^5	2.4×10^2	3, 4, 20
ampH+	3.5×10	8.6×10^3	2.5×10^2	20, b
teMeenH+	0.2	1.0×10^3	5.0×10^3	e, d
bipyH+	2.5×10	2.6×10^5	1.0×10^4	21, b
terpyH+	9.0×10	8.0×10^5	0.9×10^3	21, b
phenH+	3	$<5 \times 10^2$	$<2 \times 10^2$	21, b
TPTZH$_2$$^{2+}$	~10	$<1 \times 10^3$	$<10^2$	b, f
terpyH$_2$$^{2+}$	~0.5	$<5 \times 10^2$	$<10^3$	21, b

^{a} D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966). ^{b} This work. ^{c} D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963). ^{d} Reference 23. ^{e} T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, **11**, 288 (1972). ^{f} T. S. Roche, Ph.D. Thesis, State University of New York at Buffalo, 1972.

The other data collected in Table I were obtained similarly using the raw kinetic data[24] in conjunction with literature values[25] for the ionization constant of the acid form of the ligand and the heats of ionization.

The ratio of rate constants for reaction of Cu_{aq}^{2+} and Ni_{aq}^{2+} with a common ligand lies between about 5×10^4 and 2×10^5 for a large number of unidentate and multidentate ligands.[22,23] A representative selection is contained in Table II, which also lists a number for which this behavior is not observed. It is our working premise that when the ratio $k_{\mathrm{Cu}}/k_{\mathrm{Ni}}$ is far removed from 10^5, that the first-bond formation is not rate determining for one of the two metal ions or that alternatively the mechanisms for the two metal ions differ radically. Otherwise, we assume that eq 1 represents complexing by both metals.

Substituted Pyridines. Data for the reactions of bipy, phen, and terpy have been previously given and discussed.[26] These reactions in addition to those of amp and TPTZ with Cu(II), could be studied directly, thus avoiding the complications of added indicator to follow the change. Additionally the studies could be made in relatively strong acid media (because of the weak basicity of the ligand and the strength of the complex) so that buffers were unnecessary. There are problems in the use of these (see below).[5] The negligible contribution of ampH$_2$$^{2+}$ and amp, phenH+, terpyH$_2$$^{2+}$ and terpy, TPTZ$_2$$^{2+}$, and TPTZ to the rates of the reactions under the experimental conditions allowed accurate data to be obtained for ampH+, phen, terpyH+, and TPT-

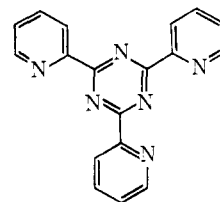(26) T. S. Roche and R. G. Wilkins, *Chem. Commun.*, 1681 (1970).

ZH+, respectively. Activation parameters could be obtained for bipyH+ from the appropriate plot intercepts but not for bipy because of plot scatter. Our results for bipy and bipyH+ at 25° are in very good agreement with temperature-jump measurements[27] (Table I).

The reactions of phen and bipy with a number of bivalent metal ions can be understood on the basis of eq 1 but with a variable value of K_0 which may range from 0.02 to 0.15.[19,28] If the value for k_0 of 2×10^9 sec^{-1} is accepted for the reactions of Cu_{aq}^{2+},[2,6,23,29] then since $k \sim K_0k_0$ from eq 1, the value of K_0 is 0.032. The slightly lower value of k for the reaction of bipy is consistently found,[19] and may reflect a degree of steric control in this more flexible ligand.[30] The ratio $k_{\mathrm{Cu}}/k_{\mathrm{Ni}}$ as well as the actual values for the rate constant for reaction of TPTZH+ (I), bearing in mind the positive

I = TPTZ

charge of the ligand, indicates an almost "normal" behavior, showing the relative unimportance of the

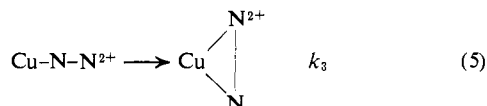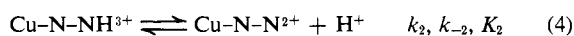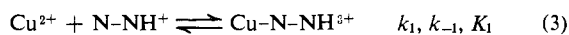(27) H. Diebler, *Ber. Bunsenges. Phys. Chem.*, **74**, 268 (1970).
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(29) G. Maass, *Z. Phys. Chem. (Frankfurt am Main)*, **60**, 138 (1968).
(30) One of the referees suggests that steric control should be even more important for phen than bipy. The referee suggests that these types of ligands may react anomalously rapidly in water and that this view is strengthened by recent studies in acetonitrile (P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, **12**, 113 (1973)) and methanol (D. J. Benton and P. Moore, *J. Chem. Soc., Chem. Commun.*, 717 (1972)). Conclusions based on the relative reaction rates shown by these heterocyclic ligands may therefore be invalid.

proton with so many active donor centers available. The ratio of rate constants for Cu^{2+} reacting with NH_3 compared with $TPTZH^+$ is 8.5, quite close to the expected ratio for K_0 of 8 at $I = 0.3$ M and separation distance of 4.0 Å for outer-sphere complexing by these ligands.

The low value for the k_{Cu}/k_{Ni} ratio for reaction of ampH$^+$ indicates that proton loss may be a rate-limiting step in the reaction with Cu^{2+} but not Ni^{2+}, an explanation which has been advanced for reaction of enH$^+$ and supported by some reasonably accurate estimations.[4] If we represent the protonated form as N–NH$^+$, then the suggested mechanism would be
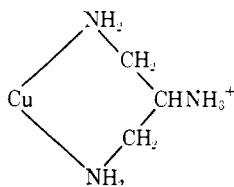
$$Cu^{2+} + N\text{--}NH^+ \rightleftharpoons Cu\text{--}N\text{--}NH^{3+} \qquad k_1, k_{-1}, K_1 \qquad (3)$$

$$Cu\text{--}N\text{--}NH^{3+} \rightleftharpoons Cu\text{--}N\text{--}N^{2+} + H^+ \qquad k_2, k_{-2}, K_2 \qquad (4)$$

$$Cu\text{--}N\text{--}N^{2+} \longrightarrow Cu \underset{N}{\overset{N^{2+}}{\big\langle}} \qquad k_3 \qquad (5)$$

The pK_2 for Cu–N–NH^{3+} would be about 2 units less than that of the free amine,[31] i.e., 6.6. Since k_{-2} can be estimated as 5×10^9 M^{-1} sec^{-1},[34] then $k_2 = 10^{9.7}/10^{6.6}$ or 10^3 sec^{-1}. It is clear then that $k_{-1} \gg k_2$ and $k_3 > k_{-2}[H^+]$, so that $k = K_1 k_2 \sim 10 \times 10^3$–$10^4$ M^{-1} sec^{-1} which is quite close to the observed value. Similarly

$$\Delta H^{\ddagger} = \Delta H_1 + \Delta H_2^{\ddagger} \qquad (6)$$

which with $\Delta H_1 \sim -4$ kcal mol^{-1}, leads to $\Delta H_2^{\ddagger} = 8.6$ kcal mol^{-1}, a reasonable if somewhat low value. It appears that the lower value for the rate constant for reaction of ampH$^+$ compared with enH$^+$ resides mainly in a lowered value for K_1.[4] Considerations of the strong acidity of coordinated bipyH$^+$ and terpyH$^+$, and therefore large values for k_2 in eq 4, indicate that rate-determining proton loss is probably not the explanation for the much lowered values of k_{Cu} (and k_{Ni}) than expected. These may reside in low K_0 values.[21] The striking effect of monoprotonation of phen and diprotonation of TPTZ and terpy in blocking first-bond formation is shown in the remarkably low values for k_{Cu} and low k_{Cu}/k_{Ni} ratios. The reactivity sequence phen > bipy > TPTZH$^+$ > terpyH$^+$ > bipyH$^+$ > TPTZH$_2^{2+}$ $\sim$ phenH$^+$ $\sim$ terpyH$_2^{2+}$ is observed for complexing toward Cu^{2+} and Ni^{2+} (Table II).

Polyamines. With the acid conditions of the experiments, only dienH$^+$, trienH$_2^{2+}$, and trenH$_2^{2+}$ contributed substantially to the rate of the various reactions with copper(II). Their activation parameters could therefore be accurately assessed. It was difficult to estimate

the rate constant for dienH$_2^{2+}$, trienH$_3^{3+}$, and trenH$_3^{3+}$ from the intercepts of plots, but these did not exceed 10^3, 10^3, or 10^2 M^{-1} sec^{-1}, respectively. Changing the buffer (formate replacing acetate) as well as its concentration showed[24] that there was only a slight variation of rate constant with buffer concentration, provided the latter was maintained low (see ref 5).

The reactions of Cu(II) complexes, including Cu_{aq}^{2+}, with tetraethylenepentaamine (tetren) have been studied.[5,23] The rate constants for reaction of tetren-H$_2^{2+}$, tetrenH$_3^{3+}$ (Table II), and tetrenH$_4^{4+}$ (1.4×10^4 M^{-1} sec^{-1} at 25°) have been determined. A scheme similar to eq 3–5 has been considered for these reactions and the conclusion reached that proton removal is probably not a rate-limiting step.[5,22,23] One could come to the same conclusion in considering the reactions of dienH$^+$, trienH$_2^{2+}$, and trenH$_2^{2+}$ with Cu^{2+}. The rate constants for the diprotonated ligands are markedly lower than those for en (4×10^9 M^{-1} sec^{-1})^3 and NH_3 (2×10^8 M^{-1} sec^{-1})^2 but this could reside in the bipositive charge repulsion as well as a marked degree of steric hindrance, which itself can introduce a decelerating factor of as much as ten with N-alkylamines and ethylenediamines.[32,33] In all these cases, two unprotonated adjacent nitrogens are available for strong and facile attachment before a proton has to be lost, unlike the situation with the protonated bidentate ligands. If Cu–N bond formation is rate limiting, however, it is difficult to understand the negative value for the enthalpy of activation of reaction of dienH$^+$. The rate plots were not particularly good, and the ΔH values used for the ionization of the protonated ligand[25] may be in error, but neither would lead to such a marked negative value for $\Delta H^{\ddagger}$. For at least dienH$^+$, of the three protonated amines examined in this study, deprotonation may have an important influence on the rate characteristics. The scheme would be (representing dien as N–N–N)

$$Cu^{2+} + N\text{--}N\text{--}NH^+ \rightleftharpoons Cu \underset{N\text{--}NH^+}{\overset{N}{\big\langle}} \qquad k_1, k_{-1}, K_1 \qquad (7)$$

$$Cu \underset{N\text{--}NH^+}{\overset{N}{\big\langle}} \rightleftharpoons Cu \underset{N\text{--}N}{\overset{N}{\big\langle}} + H^+ \qquad k_2, k_{-2} \qquad (8)$$

$$Cu \underset{N\text{--}N}{\overset{N}{\big\langle}} \longrightarrow Cu \underset{N}{\overset{N}{\big\langle}}N \qquad k_3 \qquad (9)$$

The value for K_1 can be estimated as 10^7.[31] If $k_2 < k_{-1}$ and $k_2[H^+] < k_3$, the observed rate constant is given by $K_1 k_2$. The value for k_2 can be estimated as $\lesssim 10^2$ sec^{-1}, and so the calculated ($\sim 10^9$ M^{-1} sec^{-1}) and observed (4×10^8 M^{-1} sec^{-1}) rate constants are in good agreement on the basis of this scheme. Similarly from eq 6, $\Delta H^{\ddagger}_{obsd}$ will be made up of a large negative value for ΔH_1 (possibly as high as -12 kcal mol^{-1}) offset by a positive enthalpy of activation for proton loss in reaction 8. This is likely to be lower than 12[35] and lead to an overall negative enthalpy of activation as observed. The "normal" ratio for k_{Cu}/k_{Ni} for trienH$_2^{2+}$ and the positive $\Delta H^{\ddagger}$ for its reaction with Cu^{2+} may suggest that first metal–ligand bond formation is rate limiting

(31) J. E. Prue and G. Schwarzenbach, Helv. Chim. Acta, 33, 995 (1950), measured the pK of

$$Cu \underset{NH_2}{\overset{NH_2}{\big\langle}} \underset{CH_2}{\overset{CH_2}{\big\langle}} \underset{CH_2}{\big\langle} CHNH_3^+$$

as 7.3 compared with pK_1 for the free amine as 9.6. The stability constant is 10^9. The value of K_1 might be expected to be less than 10^9 because of the positively charged, propyl-type NH substituted group.[32,33]
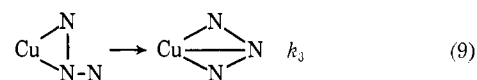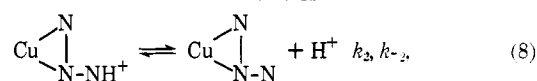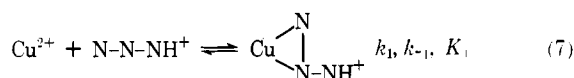
(32) D. B. Rorabacher and C. A. Melendez-Cepeda, J. Amer. Chem. Soc., 93, 6071 (1971).

(33) T. S. Turan and D. B. Rorabacher, Inorg. Chem., 11, 288 (1972).

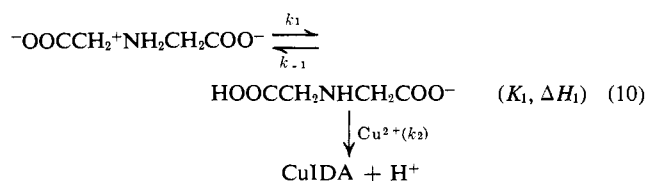(34) M. Eigen, Angew. Chem., Int. Ed., Engl., 3, 1 (1964).

(35) The heat of reaction (eq 7) in kcal mol^{-1} will lie between 10 (that for deprotonation of monoprotonated amines) and 6 (that for deprotonation of multiprotonated or multicharged amines).[25] The heat of activation for step k_{-2} is 2–4 kcal mol^{-1}, and so that for the forward direction will be 8–14 kcal mol^{-1}.

here as has been concluded also by Rorabacher and coworkers.[23] The situation with trenH$_2^{2+}$ is unclear.

The low values for the rate constants for reaction of dienH$_2^{2+}$, trienH$_3^{3+}$, and trenH$_3^{3+}$ probably reside in a combination of small values for K_1 and k_2 (and later deprotonation rate constants) in schemes such as eq 3–5.

Iminodiacetates. The rate constants for IDA^{2-} and MIDA^{2-} reacting with Cu^{2+} are similar to and slightly higher, respectively, than that for glycinate ion.[6] The additional negative charge over gly$^-$ confers a three–four times greater reactivity toward Ni^{2+} [20] so that the k_{Cu}/k_{Ni} ratios for IDA^{2-} and MIDA^{2-} are near normal. The values of $\Delta H^{\ddagger}$ of the order 3–5 kcal mol^{-1} for these and other reactions in Table I are anticipated for near diffusion-controlled reactions.

The low values for the rate constants for reaction of IDAH$^-$ and MIDAH$^-$ may arise from the fact that only the nonzwitterionic form of the ligand is reactive, and this is present in very low concentration, e.g.

$$^-OOCCH_2{}^+NH_2CH_2COO^- \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}}$$

$$HOOCCH_2NHCH_2COO^- \quad (K_1, \Delta H_1) \quad (10)$$

$$\downarrow Cu^{2+}(k_2)$$

$$CuIDA + H^+$$

Since k_{-1} is likely to be much larger than $k_2[\text{Cu}^{2+}]$,[36] the observed rate constants and activation enthalpies are composite, given by K_1k_2 and $(\Delta H_1 + \Delta H_2{}^{\ddagger})$, respectively. If values for reaction of IDA^{2-} are used for k_2 and $\Delta H_2{}^{\ddagger}$, then K_1 and ΔH_1 are estimated to be 4 $\times$ 10^{-6} and 6.7 kcal mol^{-1}, respectively. For glycine these values are 4.5 $\times$ 10^{-6} and about 9 kcal mol^{-1}, so that the estimations for the thermodynamic parameters of

the tautomerization, from our kinetic data, are reasonable.

Although the data for IDAH$^-$ and MIDAH$^-$ can also be rationalized in terms of a rate-determining proton loss, this is unlikely to be the correct explanation since the k_{Cu}/k_{Ni} ratio is "normal" $\sim$10^5. This suggests a common mechanism for the two metals, and a proton-loss cannot be rate-limiting for the much slower reacting Ni^{2+} ion. As might be anticipated the doubly protonated forms are unreactive ($k < 10^3 M^{-1}$ sec^{-1}).

For a number of the systems studied involving the polyamines and the iminodicarboxylates, some of the rate terms can be formulated in terms of different reactants. Thus the rate term involving Cu$_{aq}^{2+}$ and IDA^{2-} or dienH$^+$ can also be expressed as one in which CuOH$^+$ reacts with IDAH or dienH$_2^{2+}$. Since the pK of the Cu(II) ion is known only approximately as 8.0, and because a dimeric hydroxy species dominates in alkaline solution,[37] we can only estimate approximate rate constants for the CuOH$^+$, IDAH^{2-} (1.6 $\times$ 10$^8 M^{-1}$ sec^{-1}) pairs. These values appear improbably high and these, and some other possible combinations, are considered very unlikely.

Supplementary Material Available. A listing of full kinetic data factor will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 $\times$ 148 mm, 24$\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-5082.

(36) M. Sheinblatt and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **86**, 4814 (1964), have measured the value for k_1 for the intramolecular proton transfer in glycine as $\sim$200 sec^{-1}. The value of k_{-1} is therefore 5 $\times$ 10^7 sec^{-1} for glycine, and presumably of this magnitude for that in eq 9.

(37) A. Arnek and C. C. Patel, *Acta Chem. Scand.*, **22**, 1097 (1968).