each of the n-butenes.[5] If it is assumed that no geometric or statistical factors are involved, the product ratios corresponding to the energy barrier height differences should be 1-butene:*cis*-2-butene:*trans*-2-butene = 15:18:67 at 36.5°; the observed ratios were 26:24:50. When this treatment was applied to ECP (Figure 10), the predicted product ratios at room temperature were 1-pentene:*cis*-2-pentene:*trans*-2-pentene = 8:46:46; the observed ratios were 6:47:47. It is quite clear, therefore, that the selectivities in these reactions, as in the isomerization of butenes[4,5] over the same catalyst, are largely controlled by the relative heights of the activation energy barriers.

In conclusion, there is reason to suppose that the reaction of MCP does not pass through the same intermediate species present in the isomerization of the n-butenes over silica–alumina. From our earlier studies[5] of butene isomerization over the same catalyst in the same temperature range, it was concluded that the product selectivities were controlled by a statistical factor and the relative barrier heights between the intermediate *sec*-butylcarbonium ion and the several products. From these data it can be estimated that if the same metastable state were present along the reaction coordinate, the product ratios should be 1-butene:*cis*-2-butene:*trans*-2-butene = 1:1.2:1.2. The observed product ratios (*ca.* 1:1:2) differed significantly from these, even though they too resulted mainly from differences in activation energy. The (c-$C_4H_9^+$) ion suggested in Figure 11 must be located at much higher energy than is the *sec*-butyl ion because of the thermodynamic instability of MCP relative to the butenes.[18]

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(18) Estimated from the data of O. N. Kachinaskaya, *Vestn. Mosk. Univ., Ser. II: Khim.*, **16**, 69 (1961); *Chem. Abstr.*, **56**, 9506 (1962).

Kinetics of Copper(II)–Glycine Interactions in Aqueous Solution

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Abstract: Rate constants for the formation of copper(II) complexes with the glycine anion have been measured by a combination of temperature-jump and close-to-equilibrium stopped-flow techniques. Measurements were carried out in moderately acid solutions to avoid complications due to copper–hydroxy species. Relaxation times, in the millisecond time region, could be interpreted only as reactions between metal ion and free anion, even though the zwitterion predominated at the pH's used. The forward rate constants for the mono and bis complexes with glycine were found to be 4×10^9 and 4×10^8 M^{-1} sec^{-1}, respectively, at 25° and $I = 0.1$. These constants, although large, were consistent with the Eigen–Tamm mechanism for the formation of metal complexes wherein the release of a water molecule from the inner hydration sphere of the metal ion is the rate-determining step. The unimolecular rate constants for ligand penetration into the inner hydration sphere of the copper ion were estimated to be 2×10^9 and 5×10^8 sec^{-1} for the first and second steps, respectively.

The development of relaxation techniques[2] has resulted in the characterization of many fast reactions which were previously inaccessible using classical techniques. The study of metal–ligand interactions should provide some necessary information which could be used by chemists involved in examining more complex biochemical systems. To date, particular emphasis has been placed upon Mg^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} because these metals react with ligands under particularly favorable conditions: the rate constants are easily accessible, hydroxy species do not interfere (except for Fe^{3+}) at normal pH's, and often large changes in light transmission occur upon reaction. A compilation of rate data by many techniques for metal–ligand reactions was recently given by Eigen and Wilkins.[3] The measured forward rate constants for complex formation were interpreted as favoring SN1 mechanisms since these constants depended primarily on the metal ion and did not vary greatly with the ligand.

This study was undertaken to help clarify the nature of metal–ligand reactions involving copper. Copper has not been so extensively studied as many of the other transition elements, presumably because of its rapid water exchange rate,[4] $>10^8$ sec^{-1}, and ease of formation of hydroxy species even at relatively low pH's. The results of this study show that even when the ligand is almost completely in the zwitterion form, the rate for copper recombination with the anion can be directly determined.

Experimental Section

Materials. Matheson Coleman and Bell reagent grade $Cu(NO_3)_2 \cdot 3H_2O$, Fisher reagent grade KNO_3, and Nutritional Biochemicals glycine were used without further purification. All solutions were prepared with degassed Stokes distilled water.

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(1) To whom all correspondence should be addressed.

(2) *E.g.*, M. Eigen and L. De Maeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter XVIII, and references contained therein.

(3) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

(4) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

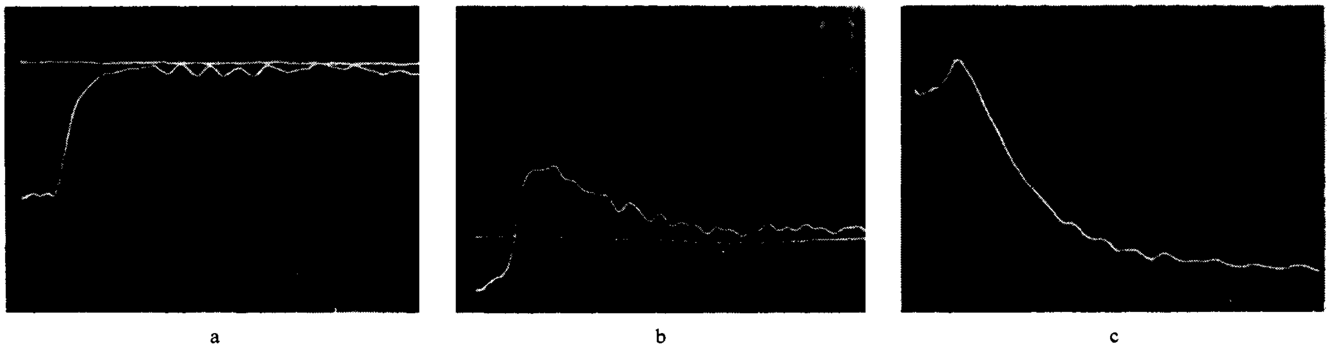

Figure 1. Stopped-flow reaction traces at different wavelengths for $[Cu]^0 = 0.01$ *M*, $[H(gly)]^0 = 0.30$ *M*, and pH 3.63. Time scale is 2 msec per horizontal division, and vertical scale is 1.25% transmittance per division. (a) 475 mμ, showing τ_1; (b) 525 mμ, τ_1 and τ_2 visible; (c) 600 mμ, showing τ_2.

The solutions studied were made by pipetting the appropriate amounts of stock solution into volumetric flasks and diluting. The ionic strength of the solutions studied was maintained at 0.1 using KNO_3.

Instrumentation. The pH of the solutions was adjusted by the dropwise addition of KOH and/or HNO_3 in conjunction with a pH meter (Beckman Expandomatic). Spectra of reactant and product solutions were examined in a Cary 14 spectrophotometer to determine optimum wavelengths for the kinetic study. Kinetic runs were made on a commercially available Gibson-Durrum[5] stopped-flow spectrophotometer, thermostated to 25.0 ± 0.1°, and a temperature-jump apparatus obtained from Messanlagen Studiengesellschaft, Göttingen, West Germany. The enthalpy changes associated with the complexing reactions were sufficiently large that the use of indicators was not necessary. Concentration changes following the temperature jump were monitored by transmittance at 550 mμ. Although both instruments measure changes in transmittance, for small changes in transmittance (generally 5% or less), it may be shown that there is a linear relationship between transmittance and absorbance.[2] As a result, the observed transmittances were used directly.

Kinetic Runs. The stopped-flow apparatus was used as a concentration perturbation technique. Relaxation theory applies to systems which are close to equilibrium. When a perturbation is applied to the system, it must be small enough so that the rate equations may be linearized. In a mixing experiment, such as that involved with the stopped-flow apparatus, such is the case only near the end of the reaction. In most cases the systems were sufficiently close to equilibrium shortly after mixing; in some of the more concentrated solutions (*e.g.*, Table II, no. 12–18), only the last 10% of the full stopped-flow traces were relaxational. In fact, owing to the "dead time"[6] of the stopped-flow (~2 msec), the reaction for the more concentrated (*i.e.*, rapidly reacting) solutions may not be observed until two to three half-times have elapsed. Thus, one is examining only approximately the last 10% of the reaction under the experimental conditions chosen. (Swinehart and Castellan[7] have previously used this principle for studying the chromate–dichromate reaction using conventional mixing.) The relaxation times were computed from at least two (generally three) oscilloscope traces, photographed with a Polaroid camera. All traces were enlarged on graph paper and then plotted on semilog paper to determine the relaxation times. For the more concentrated solutions, only the latter part of the trace was used. Any curves which were found to be nonexponential were discarded.

An advantage of the stopped-flow method is that it often allows unequivocal assignment of a sequence of steps which may occur during the course of a reaction. On the stopped flow, a fast reaction followed by a slow reaction appears as shown in Figure 1b (a slow reaction followed by a fast reaction would, of course, appear as one step). For the more concentrated solutions, two distinct steps could be detected and thus assigned unambiguously, *i.e.*, the first step is associated with the formation of the mono complex; the second, with the bis complex. By varying the wavelength, one could adjust conditions such that only one or the other of the observed steps was visible (Figure 1). However, on the temperature-jump apparatus, two separate relaxation times generally can be correlated with the possible reactions occurring only through a detailed concentration analysis of the relaxation times seen.

Some controversy exists in the literature concerning the nature and existence of the species $Cu(gly)H^{2+}$, wherein the glycine zwitterion presumably acts as a monodentate ligand. Some thermodynamic studies have indicated the presence of this species,[8] some not.[9] For this reason all calculations have been performed both with and without $Cu(gly)H^{2+}$ as a significant species. Table I lists the equilibrium constants used for the metal complex and ligand ionization equilibria.

Table I. Equilibrium Constants for the Copper–Glycine System[a]

Symbol	Reaction			Log K^b
K_{a1}	$H^+(gly)^-$	$+ H^+$	$= H^+(gly)H$	2.34
K_{a2}	gly^-	$+ H^+$	$= H^+(gly)^-$	9.60
K_1	Cu^{2+}	$+ gly^-$	$= Cu(gly)^-$	8.07
K_3	$Cu(gly)^+$	$+ gly^-$	$= Cu(gly)_2$	6.90
K_2	Cu^{2+}	$+ H^+(gly)^-$	$= Cu(gly)H^{2+}$	1.59[c]

[a] At 25° and $I = 0.1$. [b] All constants, unless otherwise noted, are from L. Sillen and A. Martell, Ed., "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, pp 377–381. [c] R. M. Keefer, *J. Am. Chem. Soc.*, **70**, 476 (1948). Since Keefer's values for the other equilibrium constants differ substantially from the more recent values used in this investigation, only K_2 was taken from his paper. The results, however, are quite insensitive to the value of K_2 chosen.

Results

A tabulation of concentration data and the relaxation times for the two steps are given in Table II. Computations were done on a Univac 1107 computer. The symbols τ_1 and τ_2 refer to the relaxation times associated with the formation of the complexes $Cu(gly)^+$ and $Cu(gly)_2$, respectively. The measured relaxation times are estimated to be reliable to ±15%. This uncertainty is due principally to the fact that the two relaxation times were not sufficiently separated to be treated as distinct steps. In addition, only the last portions of the stopped-flow traces were used, in order to ensure close-to-equilibrium conditions.

In evaluating the data, several mechanisms were considered in detail. Among these were schemes which in-

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(5) Durrum Corp., Palo Alto, Calif.

(6) It is important to distinguish "mixing time" from "dead time." The latter is usually defined as the time between mixing and observation. If the stopping is sufficiently rapid, one can still study reactions of half-times less than the dead time. The effect must be quite large if it is still to be seen after several half-times have elapsed. Such is the case with several of the solutions under study.

(7) J. Swinehart and G. Castellan, *Inorg. Chem.*, **3**, 278 (1964); J. Swinehart, *J. Chem. Educ.*, **44**, 524 (1967).

(8) R. M. Keefer, *J. Am. Chem. Soc.*, **70**, 476 (1948).

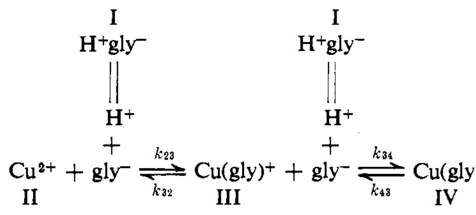
(9) R. M. Izatt, J. J. Christensen, and V. Kothari, *Inorg. Chem.*, **3**, 1565 (1964).

Table II. Tabulation of Equilibrium Concentrations and Results[a]

No.	$[\mathrm{Cu}]^0$, M[b]	$[\mathrm{H(gly)}]^0$, M[b]	pH[c]	$[\overline{\mathrm{Cu}}]$, M	$[\overline{\mathrm{H(gly)}}]$, M	$[\overline{\mathrm{Cu(gly)}}]$, M	$[\overline{\mathrm{Cu(gly)_2}}]$, M	$[\overline{\mathrm{gly}}]$, M	τ_1^{-1}, sec^{-1} [d]	τ_2^{-1} sec^{-1} [d]
1	0.00175	0.000175	4.19	1.68×10^{-3}	1.07×10^{-4}	6.59×10^{-5}	1.74×10^{-7}	3.33×10^{-10}	(84)	56 (51)
2	0.00175	0.00035	4.02	1.65×10^{-3}	2.44×10^{-4}	9.86×10^{-5}	3.97×10^{-7}	5.07×10^{-10}	(77)	47 (51)
3	0.0035	0.0007	3.75	3.30×10^{-3}	4.72×10^{-4}	2.03×10^{-4}	8.51×10^{-7}	5.25×10^{-10}	(81)	47 (51)
4	0.007	0.0007	3.62	6.74×10^{-3}	4.11×10^{-4}	2.59×10^{-4}	6.68×10^{-7}	3.26×10^{-10}	(84)	39 (51)
5	0.01	0.0015	3.37	9.52×10^{-3}	9.14×10^{-3}	4.76×10^{-4}	1.61×10^{-6}	4.25×10^{-10}	(83)	53 (51)
6	0.01	0.002	3.58	9.14×10^{-3}	1.06×10^{-3}	8.56×10^{-4}	5.46×10^{-6}	7.99×10^{-10}	(152)	41 (53)
7	0.01	0.002	3.31	9.43×10^{-3}	1.26×10^{-3}	5.67×10^{-4}	2.31×10^{-6}	5.11×10^{-10}	(82)	56 (51)
8	0.015	0.001	4.80	1.46×10^{-2}	5.01×10^{-4}	4.45×10^{-4}	9.27×10^{-7}	2.60×10^{-10}	(97)	46 (51)
9	0.015	0.0015	3.31	1.44×10^{-2}	8.19×10^{-4}	5.67×10^{-4}	1.50×10^{-6}	3.34×10^{-10}	(90)	43 (51)
10	0.015	0.002	3.26	1.43×10^{-2}	1.14×10^{-3}	6.89×10^{-4}	2.25×10^{-6}	4.09×10^{-10}	(90)	53 (51)
11	0.01	0.004	3.28	8.96×10^{-3}	2.58×10^{-3}	1.03×10^{-3}	7.99×10^{-6}	9.77×10^{-10}	(103)	49 (51)
12	0.01	0.02	3.21	6.46×10^{-3}	1.40×10^{-2}	3.42×10^{-3}	1.22×10^{-4}	4.49×10^{-9}	(214)	58 (55)
13	0.01	0.03	3.23	5.25×10^{-3}	2.15×10^{-2}	4.49×10^{-3}	2.59×10^{-4}	7.24×10^{-9}	(287)	62 (59)
14	0.01	0.04	3.25	4.31×10^{-3}	2.93×10^{-2}	5.26×10^{-3}	4.34×10^{-4}	1.04×10^{-8}	(355)	71 (63)
15	0.01	0.20	3.54	3.55×10^{-4}	1.72×10^{-1}	4.96×10^{-3}	4.69×10^{-3}	1.19×10^{-7}	1540 (1380)	376 (388)
16	0.01	0.30	3.63	1.38×10^{-4}	2.66×10^{-1}	3.58×10^{-3}	6.29×10^{-3}	2.21×10^{-7}	1820 (1840)	420 (653)
17	0.01	0.40	3.50	1.37×10^{-4}	3.53×10^{-1}	3.57×10^{-3}	6.29×10^{-3}	2.21×10^{-7}	1260 (1530)	462 (617)
18	0.01	0.50	3.58	6.70×10^{-5}	4.50×10^{-3}	2.68×10^{-3}	7.25×10^{-3}	3.39×10^{-7}	2100 (1990)	924[e] (956)
19	0.04	0.075	3.11	1.70×10^{-2}	4.14×10^{-2}	2.12×10^{-2}	1.78×10^{-3}	1.06×10^{-8}	833[e] (909)	(64)
20	0.04	0.075	2.65	2.82×10^{-2}	3.88×10^{-2}	1.14×10^{-2}	3.13×10^{-4}	3.44×10^{-9}	160[e] (198)	(54)
21	0.01	0.50	3.72	3.70×10^{-5}	4.58×10^{-1}	2.08×10^{-3}	7.88×10^{-3}	4.76×10^{-7}	(2690)	990[e] (1420)
22	0.005	0.25	3.65	7.95×10^{-5}	2.28×10^{-1}	1.89×10^{-3}	3.03×10^{-3}	2.01×10^{-7}	935[e] (1220)	(510)

[a] Not all species are listed. The species $\mathrm{Cu(gly)H^{2+}}$ was not included in the calculation. All measurements are from stopped-flow data unless otherwise indicated. [b] Initial concentrations of Cu(II) and glycine. [c] [H] was calculated by dividing the measured hydrogen ion activity by $\gamma_\pm$ ($\cong 0.79$). [d] Experimental values given first. Values calculated from eq 4 are in parentheses with k_{23} and k_{34} as in text. [e] Measurements are from the temperature-jump apparatus.

volved $\mathrm{CuOH^+}$ reacting with $\mathrm{gly^-}$ or which proceeded through intermediates such as $\mathrm{Cu(gly)H^{2+}}$. It was found to be impossible to even roughly correlate the data with such mechanisms. On the other hand, a mechanism involving the reaction of $\mathrm{Cu^{2+}}$ with the free unprotonated ligand ($\mathrm{gly^-}$) was found to quantitatively account for all the data. This mechanism can be written as shown in mechanism a, where $\mathrm{H^+gly^-}$ represents



$$\begin{array}{ccccc} \mathrm{I} & & & \mathrm{I} & \\ \mathrm{H^+gly^-} & & & \mathrm{H^+gly^-} & \\ \| & & & \| & \\ \mathrm{H^+} & & & \mathrm{H^+} & \\ + & & & + & \\ \mathrm{Cu^{2+}} + \mathrm{gly^-} & \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} & \mathrm{Cu(gly)^+} & + \ \mathrm{gly^-} & \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \ \mathrm{Cu(gly)_2} \\ \mathrm{II} & & \mathrm{III} & & \mathrm{IV} \end{array} \qquad \text{(a)}$$

the zwitterion form of glycine which predominates at the pH's used and where the very rapid steps are indicated by = signs and the slower complexing steps by arrows. This assignment is based upon the now well-known results[10] that proton-transfer reactions are normally diffusion controlled.[11] The proton-transfer reaction in (a) would then be characterized by a relaxation time of about 10^{-7} sec under the conditions of this work.

The rate equations for restoration of equilibrium, near equilibrium, may be written[12] (charges omitted)

$$\frac{\mathrm{d}\delta[\mathrm{Cu(gly)}]}{\mathrm{d}t} = a_{11}\delta[\mathrm{Cu(gly)}] + a_{12}\delta[\mathrm{Cu(gly)_2}] = \lambda\delta[\mathrm{Cu(gly)}] \quad (1)$$

$$\frac{\mathrm{d}\delta[\mathrm{Cu(gly)_2}]}{\mathrm{d}t} = a_{21}\delta[\mathrm{Cu(gly)}] + a_{21}\delta[\mathrm{Cu(gly)_2}] = \lambda\delta[\mathrm{Cu(gly)_2}] \quad (2)$$

where $\lambda \equiv -\tau^{-1}$ and

$$a_{11} = -k_{23}[\overline{\mathrm{Cu}}]/(1 + \alpha) - k_{32} - k_{23}[\overline{\mathrm{gly}}] + k_{34}([\overline{\mathrm{Cu(gly)}}]/(1 + \alpha) - [\overline{\mathrm{gly}}]) \quad \text{(3a)}$$

$$a_{12} = -k_{23}(2[\overline{\mathrm{Cu}}]/(1 + \alpha) + [\overline{\mathrm{gly}}]) + 2k_{34}[\overline{\mathrm{Cu(gly)}}]/(1 + \alpha) + k_{43} \quad \text{(3b)}$$

$$a_{21} = k_{34}([\overline{\mathrm{gly}}] - [\overline{\mathrm{Cu(gly)}}]/(1 + \alpha)) \quad \text{(3c)}$$

$$a_{22} = -2k_{34}[\overline{\mathrm{Cu(gly)}}]/(1 + \alpha) - k_{43} \quad \text{(3d)}$$

and $\alpha = [\overline{\mathrm{H}}]/(K_{a2} + [\overline{\mathrm{gly}}])$. The two relaxation times for mechanism a may be obtained by solving the resulting determinant[13] for the two roots of λ

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

where the plus and minus signs will give the short and long relaxation times, respectively. The data in Table II were fitted to eq 4 by generating a set of τ_1 and τ_2 values. This was done by inserting a large number of combinations for k_{23} and k_{34} into the computer program and comparing the results with the experimental values. The best fit to the data[14] (to about 15%, the estimated reliability of the measured relaxation times) are given[15] by

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[10] (a) M. Eigen, *Angew. Chem.*, **75**, 489 (1963); *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964); (b) M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Progr. Reaction Kinetics*, **2**, 285 (1964).

[11] The exceptions are some pseudo-acids and internally hydrogen-bonded systems.

[12] (a) Reference 2, pp 907–911; (b) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[13] *Cf.* ref 2, p 908.

[14] Since the completion of this manuscript, it has been found that Simandi and Margerum have independently confirmed k_{23} assuming the same mechanism. L. I. Simandi and D. W. Margerum, Purdue University, private communication.

[15] Evaluation using $\mathrm{Cu(gly)H^{2+}}$ as a significant species (Table I) leaves the rate constants virtually unchanged.

$k_{23} = 4.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ and $k_{34} = 4.0 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. A check on the internal consistency is provided by the limit of τ_2^{-1} in very dilute solutions, which should tend toward k_{43}. This can be calculated from k_{34} and the stability constant K_3 to be 50 sec^{-1}. The observed limiting value of τ_2^{-1} (Table II, no. 1-11) is (51 ± 9) sec^{-1}.

Discussion

Eigen and coworkers[16] have proposed a mechanism, now generally accepted, for metal-ligand formation based largely on the results of ultrasonic absorption studies in 2:2 electrolytes. It may be schematically shown as mechanism b, where step I-II represents the

$$\underset{\text{I}}{\text{Me}^{z+}(\text{aq}) + (\text{aq})\text{L}^{z-}} \overset{K_{\text{os}}}{=\!=\!=} \underset{\text{II}}{\text{Me}^{z+}\cdot\text{OH}_2\cdot\text{L}^{z-}} \underset{k_r}{\overset{k_{\text{H}_2\text{O}}}{\rightleftharpoons}} \underset{\text{III}}{(\text{MeL})_{\text{aq}}{}^{(z_+ + z_-)}} + \text{H}_2\text{O} \quad (\text{b})$$

diffusion of the ions together to form the outer-sphere complex[17] (metal ion and ligand still separated by one water molecule). The stability constant for this step is represented by K_{os}. The next, and rate-determining, step is the formation of the contact (inner-sphere) complex. The unimolecular rate constant $k_{\text{H}_2\text{O}}$ in mechanism b usually is the same as, or slightly less than, the rate constants for water exchange, k_{ex}, in the primary hydration sheath of the metal ion, when such data are available.[18] Stationary-state treatment of the intermediate (II) allows one to relate the observed second-order rate constants k_f (*i.e.*, k_{23} or k_{34} in mechanism a) to the unimolecular rate constants $k_{\text{H}_2\text{O}}$ in mechanism b. The result is

$$k_f = K_{\text{os}} \frac{\gamma_+ \gamma_-}{\gamma^{\ddagger}} k_{\text{H}_2\text{O}}$$

where γ_+, γ_-, and $\gamma^{\ddagger}$ are the activity coefficients of the reacting partners and the transition state. The electrostatic stability constant, K_{os}, may be estimated using the equation,[19] $K_{\text{os}} = 4\pi N a^3/[3000 \exp(Z)]$, where $Z = z_a z_b e_0^2/(\epsilon a k T)$, N is Avogadro's number, a is the distance of closest approach of the two ions, z_i is the charge, ϵ is the solvent dielectric constant (78.30), and T is the temperature. Activity coefficients may be estimated for the conditions of the study ($I = 0.1$) by means of the Davies equation,[20] which is fairly reliable up to ionic strength 0.1. The results for the formation of the first complex are $\gamma_+ \simeq 0.38$, $\gamma_- = \gamma^{\ddagger}$, and $K_{\text{os}} \simeq 6$; $k_{\text{H}_2\text{O}} = 2 \times 10^9\ \text{sec}^{-1}$. For the second complex we have $\gamma^{\ddagger} = 1$ (uncharged), $\gamma_+ = \gamma_- \simeq 0.79$, and $K_{\text{os}} \simeq 2$. The latter includes a statistical factor of $^4/_6$ to account for the occupied positions on the complex Cu(gly)$^+$. For the second step then, $k_{\text{H}_2\text{O}} = 5 \times 10^8\ \text{sec}^{-1}$. A summary of the rate constants is given in Table III.

Table III. Rate Constants for $\text{Cu(gly)}_{n-1} + \text{gly} \rightleftharpoons \text{Cu(gly)}_n$

n	k_f, $M^{-1}\ \text{sec}^{-1}$	$k_{\text{H}_2\text{O}}$, sec^{-1}	k_r, sec^{-1}
1	4.0×10^9	2×10^9	34
2	4.0×10^8	5×10^8	50

The numerical values of the calculated water exchange rate constants warrant some comment. It is well known that the d^9 Cu(II) ion is subject to Jahn-Teller distortion,[21] such that two of the ligands (axial) are more distant from the metal ion than the four planar (equatorial) ligands.[22] This results in a greater lability of the axial water molecules.[4] In addition there may be a rapid inversion of this structure such that water at all six positions exchanges very rapidly at rates comparable to, or less than, the inversion process. Recent nmr oxygen-17 exchange studies of the hexaaquocopper(II) ion[23] indicate that the value of $k_{\text{ex}} \geq 3 \times 10^9\ \text{sec}^{-1}$. The result estimated in Table III from the rate constant for the formation of Cu(gly)$^+$ is in agreement with the nmr data. Another study is directly comparable with the present. From the results of ultrasonic absorption in aqueous copper(II) acetate,[24] one may estimate that $k_{\text{H}_2\text{O}} \cong 1 \times 10^9\ \text{sec}^{-1}$, for the formation of the first complex, in quite good agreement with the value estimated in the present work. If some of the positions of the copper(II) ion were occupied relatively tightly by a ligand, one would expect that the inversion of axial and equatorial positions would be impeded. This would be reflected in a lower rate of water displacement from the remaining water-occupied positions. This, in fact, is exactly what the present results indicate; the value of $k_{\text{H}_2\text{O}}$ for the addition of the second glycine is estimated to be $5 \times 10^8\ \text{sec}^{-1}$. These results are opposite in direction to the trend found by Hammes and Steinfeld[12b] for Ni^{2+} and Co^{2+}, where such considerations do not apply. Recent nmr measurements[25] indicate the exchange rate for Cu(gly)$_3^-$ to be $5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, from which one may estimate the value of $k_{\text{H}_2\text{O}}$ to be about the same as, or even slower than, that for the bis complex.

Our results are somewhat surprising in showing the preference of Cu^{2+} for the glycine anion, even though the zwitterion is present in much larger concentrations. This phenomenon is directly related to the role of copper in some biological systems. When, for example, the copper-activated enzyme, ascorbate oxidase, is titrated with hydrogen ion, deactivation occurs.[26] This

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(16) (a) H. Diebler and M. Eigen, *Z. Physik. Chem.* (Frankfurt), **20**, 299 (1959); (b) M. Eigen and K. Tamm, *Z. Elektrochem.*, **60**, 93, 107 (1962).

(17) If the ligand is strongly solvated, the encounter complex (state II) may have the ligand and metal ion separated by two hydration layers. In such cases, an additional (fast) step would be observed in the relaxation spectrum; see ref 2.

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is postulated to be due to protonation of the amino acid groups on the enzyme causing decomposition of the metal–enzyme complex.

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The Preparation and Characterization of the (3)-1,2- and (3)-1,7-Dicarbadodecahydroundecaborate(−1) Ions

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Abstract: Treatment of the 1,2- or 1,7-dicarbaclovododecaborane(12) isomers and their carbon-substituted derivatives with alcoholic base leads to the selective removal of a single boron atom to give (3)-1,2- or (3)-1,7-dicarbadodecahydroundecaborate(−1) isomers in quantitative yield. These anions have the gross heavy atom structure of an icosahedron with one missing vertex. The resolution of the enantiomers of a representative 1-substituted (3)-1,2- and 1-substituted (3)-1,7-dicarbadodecahydroundecaborate(−1) ion are reported.

In 1963 it was reported[1–9] that decaborane(14) reacted with acetylenic compounds in the presence of Lewis bases to produce members of a new class of organoboranes. The parent compound 1,2-dicarbaclovododecaborane(12), $B_{10}C_2H_{12}$, and various carbon-substituted derivatives were reported.[10] The structure of this compound was shown to have the geometry of a regular icosahedron with two carbon atoms at adjacent vertices[11] as depicted in Figure 1.

Grafstein and Dvorak[12] reported the thermal rearrangement of 1,2-dicarbaclovododecaborane(12) at 400–500° to give a new isomer of $B_{10}C_2H_{12}$ with the carbon atoms located at the 1,7 position of the icosahedron. More recently Papetti and Heying[13] described the preparation of a third isomer of $B_{10}C_2H_{12}$ with the carbon atoms occupying the 1,12 positions of the icosahedron. The 1,12 isomer was prepared by thermal rearrangement of the 1,2 isomer at temperatures near 600°. Weisboeck and Hawthorne[14] have reported the selective degradation of 1,2-dicarbaclovododecaborane(12) and its derivatives by methanolic potassium hydroxide in accord with the equation

$$B_{10}C_2H_{12} + CH_3O^- + 2CH_3OH \longrightarrow B_9C_2H_{12}^- + B(OCH_3)_3 + H_2$$

The resulting (3)-1,2-dicarbadodecahydroundecaborate(−1) ion, (3)-1,2-$B_9C_2H_{12}^-$, and several of its carbon-substituted derivatives have been isolated as heavy cation salts.[15] Acidification of (3)-1,2-$B_9C_2H_{12}^-$ produced the neutral dicarbaundecaborane(13), $B_9C_2H_{13}$.[14] The (3)-1,2-$B_9C_2H_{12}^-$ anion is formally generated by removal of B^+ from $B_{10}C_2H_{12}$. Evidence was presented by Wiesboeck and Hawthorne[14] that the (3)-1,2-$B_9C_2H_{12}$ anion and the $B_9C_2H_{13}$ molecule are icosahedral fragments, isoelectronic with the hypothetical $B_{11}H_{12}^{-3}$ and the known $B_{11}H_{13}^{-2}$ anions,[16] respectively. The proposed structure of the (3)-1,2-$B_9C_2H_{12}^-$ ion is shown in Figure 2.

In this paper the details of the preparation and characterization of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions and their carbon-substituted derivatives are described along with the results of the investigation of the structure and chemistry of these unusual ions.

Results and Discussion

The ethanolic base degradations of 1,2- and 1,7-dicarbaclovododecaborane(12) and their carbon-substituted derivatives produce, in very high yield, two isomeric series of anions having the general formula $B_9C_2H_{10}R,R'^-$ where R and R′ are substituents on the carbon atoms. The stoichiometry of these reactions is

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