

and in ligand bonding.⁸ The gain of an electron by a metal ion is much easier when it is in the high-spin state than when it is in the low-spin state because electron transfer can then occur without change of electron spin state, *i.e.*, without change of multiplicity and also without extensive reorganization of the metal-ligand bonds.⁹

The lowest empty orbitals (t_{2g}) of the high-spin form of a metal have lobes between the ligands which are more accessible to overlap with π or p orbitals of a reducing agent than are the only empty orbitals (e_g) of the low-spin form, which have lobes directed along the metal-ligand bond direction. The result of the overlap of a filled ligand π orbital with a half-filled low-energy t_{2g} orbital is the transfer of an electron from ligand to metal without change of multiplicity.

The effects of π bonding *via* the filled t_{2g} orbitals of a metal need to be considered.¹⁰ These effects will vary depending on the energy of the ligand π orbitals relative to the energy of the metal t_{2g} orbitals and upon whether the ligand π orbitals are filled or empty. Consider the case where there are empty ligand π orbitals of higher energy than the filled metal t_{2g} orbitals. The net result of the π interaction is to stabilize the metal t_{2g} orbitals, which have acquired some ligand orbital character in the process. In effect, the π interaction causes the Dq value for the complex to increase, thus making the complex more stable.

Water is a particularly important ligand in that although the $\text{Co}^{3+}(\text{aq})$ ion is spin paired, it requires very little excitation energy to achieve the high-spin state.¹¹ This energy may be further decreased if the ion is slightly hydrolyzed and one water molecule is replaced by OH^- , which has a smaller ligand field. Cobalt(III), when in the low-spin state, exchanges its ligands slowly.¹² The rapid exchange of water¹³ and of organic hydroxy compounds with cobalt(III) ions requires their excitation to the high-spin state. This ligand-exchange step might conceivably determine the rate of an oxidation.

The cobalt(III)-salicylate system may be considered as a strong-field or low-spin state. This would make it more difficult for electron transfer from ligand to metal, since the lowest t_{2g} orbitals are filled. One of the t_{2g} electrons would have to be excited to the e_g orbitals in order for the cobalt(III) t_{2g} orbitals to be able to accommodate an electron donated from a ligand π orbital, but if the two oxygens of the salicylate ligand have empty π orbitals that can overlap with the filled t_{2g} orbitals of cobalt(III), then the t_{2g} orbitals (which obtain some ligand orbital character in the process) are stabilized. In effect, the π interaction causes the Dq value for the complex to increase, thus making the complex more stable.

We observe spectrophotometrically the formation of intermediate complexes, which are relatively stable,

(8) W. A. Waters and J. L. Liffler, "Oxidation in Organic Chemistry," Vol. 5, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 186-241.

(9) B. R. James, J. R. Lyons, and R. J. P. Williams, *Biochemistry*, **1**, 379 (1962).

(10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1967, pp 707-708.

(11) H. L. Friedman, J. P. Hunt, R. A. Plane, and H. Taube, *J. Amer. Chem. Soc.*, **73**, 4028 (1951).

(12) H. Taube, *Chem. Rev.*, **50**, 69 (1952); H. V. D. Wiesendanger, W. H. Jones, and C. S. Garner, *J. Chem. Phys.*, **27**, 688 (1957).

(13) H. L. Friedman, H. Taube, and J. P. Hunt, *ibid.*, **18**, 759 (1950).

and then after 1 hr or so, the appearance of the pink to colorless solution at 25°, which is due to the formation of cobalt(II). After the appearance of the pink to colorless solution, a sample was run on the Cary 14 spectrophotometer to see if we could observe the oxidized salicylate. We observed a large peak at 260 nm, which is possibly attributable to the formation of the oxidized form of salicylic acid. This oxidized species may be *cis,cis*-muconic acid, which has an absorbance maximum at 260 nm.

Acknowledgment.—This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AFOSR 69-1717.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Fast Kinetics of Formation of Ternary Copper(II)-Ethylenediamine- Histamine Complexes

BY V. S. SHARMA AND D. L. LEUSSING*^{1,2}

Received November 22, 1971

Compared to the abundant literature which is available concerning the rates of formation of binary complexes of labile metal ions, relatively little is yet known about the rates of formation of ternary complexes with these metal ions. Ternary, or mixed-ligand, complexes have particular interest because these often occur as precursor and successor complexes in metal ion mediated reactions between two ligands.

To date several categories of reactions have been uncovered for the formation of mixed-ligand complexes of Cu(II): (I) solvent substitution reactions,³⁻⁶ $(\text{L})\text{Cu}(\text{H}_2\text{O})_2^{2+} + \text{L}' \rightleftharpoons (\text{L})\text{Cu}(\text{L}') + 2\text{H}_2\text{O}$, $k_f \sim 10^8\text{-}10^9 \text{ M}^{-1} \text{ sec}^{-1}$; (II) solvent substitution reactions with release of a proton to solvent,⁶ $(\text{L})\text{Cu}(\text{H}_2\text{O})_2^{2+} + \text{HL}' \rightleftharpoons (\text{L})\text{Cu}(\text{L}') + 2\text{H}_2\text{O} + \text{H}^+$, $k_f \sim 10^4 \text{ M}^{-1} \text{ sec}^{-1}$; and (III) ligand substitution reactions accompanied by transfer of a proton from entering to leaving ligand,⁵ $(\text{L})\text{Cu}(\text{L}) + \text{HL}' \rightleftharpoons (\text{L})\text{Cu}(\text{L}') + \text{HL}$, $k_f \sim 10^3\text{-}10^7 \text{ M}^{-1} \text{ sec}^{-1}$. Another category (IV), direct replacement of one ligand by another, is important at high pH (~ 10) in the presence of excess ligand and has been observed in nmr exchange studies of binary complexes,⁷ $(\text{L})\text{Cu}(\text{L}) + \text{L}^* \rightleftharpoons (\text{L})\text{Cu}(\text{L}^*) + \text{L}$, $k_f \sim 10^4 - 10^6 \text{ M}^{-1} \text{ sec}^{-1}$, for bidentate ligands.

Earlier we have reported⁵ on the rates of formation of $\text{Cu}^{\text{II}}(\text{hm})(\text{ser})^+$ and $\text{Cu}^{\text{II}}(\text{en})(\text{ser})^+$ (hm = histamine, ser = serinate, and en = ethylenediamine), and in this paper we describe the kinetics of formation of $\text{Cu}^{\text{II}}(\text{en})$ -

(1) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) Support of this research by the National Science Foundation is gratefully acknowledged.

(3) R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92**, 6146 (1970).

(4) M. A. Cobb and D. N. Hague, *Chem. Commun.*, 192 (1971).

(5) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138 (1972).

(6) R. F. Pasternack, P. R. Huber, and V. M. Huber, presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(7) R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964).

TABLE I
EXPERIMENTAL CONDITIONS AND RECIPROCAL OF RELAXATION TIMES,
Cu(II)-ETHYLENEDIAMINE-HISTAMINE SYSTEM^a

Expt no.	pH	[Cu] _{tot} , 10 ⁻³ M	[en] _{tot} , 10 ⁻³ M	[hm] _{tot} , 10 ⁻³ M	λ _{obsd} , 10 ² sec ⁻¹	λ _{calcd} , 10 ² sec ⁻¹				
						0.21	0.51	2.2	4.0	7.7
1	5.50	1.0	2.0	1.0	2.5	0.21	0.51	2.2	4.0	7.7
2	5.71	1.0	2.0	1.0	2.3, 11	0.39	0.91	2.3	4.3	11.7
3	6.06	1.0	2.0	1.0	3.1, 23	1.15	2.6	2.7	5.5	22.5
4	5.55	3.0	3.0	2.0	8	0.17	0.47	2.4	7.7	12.4
5	6.03	0.5	2.0	1.0	2.7	1.8	2.8	3.7	5.8	25.8
6	5.83	0.5	2.0	1.0	1.9	0.91	1.9	2.1	4.1	18.0
7	5.84	0.5	0.5	0.5	1.6, 6.0	0.16	0.51	1.8	3.6	5.0
8	6.01	0.5	0.5	0.5	1.7, 7.4	0.23	0.76	1.9	4.4	6.7
9	6.15	0.3	1.0	0.3	1.3	1.2	1.5	2.5	4.2	12.8
10	6.32	0.3	1.0	0.3	1.9	2.1	2.6	3.0	6.3	16.6
11	6.21	0.3	0.3	0.3	1.7, 8.2	0.25	0.83	1.8	3.9	6.6
12	5.51	3.0	3.0	3.0	7.6	0.22	0.82	2.2	7.9	12.4
13	6.48	0.5	0.5	0.5	2.6, 17	0.54	1.9	2.2	7.0	17.0

^a λ = 1/τ, 37°, μ = 0.15 (KNO₃), indicator Bromocresol Purple 0.8 × 10⁻⁵ M.

(hm)²⁺ from the binary complexes which are present in Cu(II)-en-hm mixtures under the acidic conditions that allow useful relaxations to be obtained with the temperature-jump technique.

Experimental Section

The rates of mixed-ligand complex formation were obtained in the same manner as described in the previous paper⁶ using the temperature-jump accessory to a Durrum-Gibson stopped-flow spectrophotometer. Total metal and total ligand concentrations and pH for each of the ternary reaction mixtures were adjusted to give a significant concentration of the mixed complex, Cu(en)(hm)²⁺. Present also in varying amounts, depending on conditions, were the binary species Cu(hm)²⁺, Cu(en)²⁺, Cu(en)₂²⁺, Cu(hm)₂²⁺, and the protonated uncomplexed ligands. Throughout the series of experiments, each of the total concentrations and hydrogen ion concentration were varied by at least a factor of 10. A temperature jump of 10° (27 → 37°) was employed in media at an ionic strength of 0.15 (KNO₃). Details are given in Table I.

To enhance the relaxation effects, Bromocresol Purple was added to the reaction solutions. The spectral changes at 590 nm were recorded both photographically and digitally, the latter using a Nova computer equipped with an Analogic A to D converter (10 bit conversion in 10 μsec). The digital values for ten replicate runs of each experiment were summed to improve the signal-to-noise ratio.

Calculation of Relaxation Times

In the previous study of the ternary Cu(II) complexes of ethylenediamine and histamine with serinate, only one relaxation time was observed in each experiment. However, in the present investigation, two relaxations in a run were sometimes observed. This difference results from the fact that the two diamines in the present mixed systems have thermodynamic and kinetic parameters that are more similar than was the case in the diamine-serinate mixed systems. To resolve the relaxation spectra into their components, the summed digital decay curves were numerically fit in the least-squares sense to the equation

$$A_t = A_\infty + \sum_{i=1}^n C_i e^{-\lambda_i t}$$

where A_t is the absorbance at time t , A_∞ is the absorbance at infinite time, and n is the number of relaxation times. The upper limit of n is fixed by the number of independent near-equilibrium rate equations for the system, which in the present case is five assuming rapid proton exchange between uncomplexed ligands. In practice because some are out of the experimental range while others have low amplitudes, one does not observe all the relaxations. Most of the relaxation

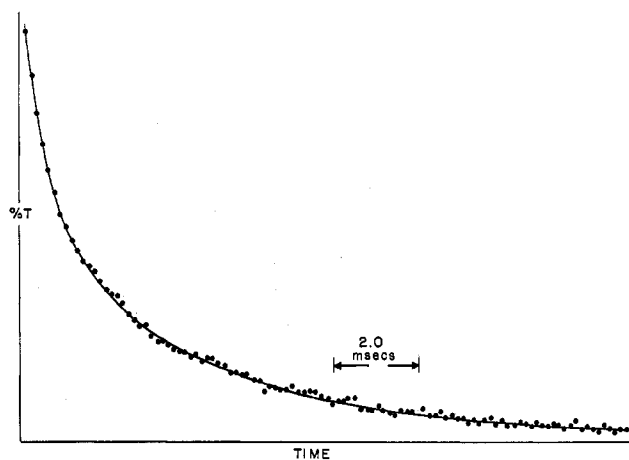


Figure 1.—Relaxation curve for experiment 13 of Table I. The points are the summed digital values for ten replicate runs. The solid curve is the theoretical curve calculated using $\lambda_1 = 257$, $\lambda_2 = 1690$ sec⁻¹. The scale along the % T axis is arbitrary, but the total span of data covers less than two % T units.

TABLE II

(A) STABILITY CONSTANTS OF BINARY AND TERNARY COMPLEXES OF Cu(II) WITH ETHYLENEDIAMINE (en) AND HISTAMINE (hm)^a

Species	Log β	Species	Log β
Hen ⁺	9.696	Cu(en) ₂ ²⁺	18.940
H ₂ en ²⁺	16.628	Cu(hm) ₂ ²⁺	9.278
Hhm ⁺	9.569	Cu(hm) ₂ ²⁺	15.577
H ₂ hm ²⁺	15.581	Cu(en)(hm) ²⁺	18.02
Cu(en) ²⁺	10.175		

(B) FORMATION (k_f) AND DISSOCIATION (k_d) RATE CONSTANTS FOR THE BINARY COMPLEXES OF Cu(II) WITH en AND hm^a

Reaction	k_f , M ⁻¹ sec ⁻¹	k_d , M ⁻¹ sec ⁻¹ or sec ⁻¹
Cu ²⁺ + Hen ⇌ Cu(en) ²⁺ + H ⁺	1.7 × 10 ⁵	5.6 × 10 ⁴
Cu(en) ²⁺ + Hen ⁺ ⇌ Cu(en) ₂ ²⁺ + H ⁺	6.3 × 10 ⁴	5.4 × 10 ⁵
Cu(en) ²⁺ + en ⇌ Cu(en) ₂ ²⁺	3.6 × 10 ⁹	6.1
Cu ²⁺ + Hhm ⁺ ⇌ Cu(hm) ²⁺ + H ⁺	7.1 × 10 ⁴	1.4 × 10 ⁵
Cu ²⁺ + hm ⇌ Cu(hm) ²⁺	2.6 × 10 ⁹	1.4
Cu(hm) ²⁺ + hm ⇌ Cu(hm) ₂ ²⁺	5.6 × 10 ⁵	2.8 × 10 ²

^a At 37°, μ = 0.15 (KNO₃).

curves found here could be accounted for within the experimental error by assuming $n = 1$, but in six cases, $n = 2$ was necessary to give a satisfactory fit. The resolved relaxation times are presented in Table I (as the reciprocals). An example of a fit to a relaxation

TABLE III
 TERNARY RATE CONSTANTS^a

No.	Reaction	$M^{-1} \text{ sec}^{-1}$	
		k_f	k_d
1	$\text{Cu}(\text{hm})^{2+} + \text{en} \rightleftharpoons \text{Cu}(\text{en})(\text{hm})^{2+}$	$(1.2 \pm 0.1) \times 10^{10}$	21 ± 2
1'	$\text{Cu}(\text{hm})(\text{OH})^+ + \text{Hen}^+ \rightleftharpoons \text{Cu}(\text{en})(\text{hm})^{2+} + \text{H}_2\text{O}$	1×10^7	2×10^{-2}
3	$\text{Cu}(\text{en})^{2+} + \text{hm} \rightleftharpoons \text{Cu}(\text{en})(\text{hm})^{2+}$	$(3.6 \pm 2.2) \times 10^8$	50 ± 30
5	$\text{Cu}(\text{hm})_2^{2+} + \text{Hen}^+ \rightleftharpoons \text{Cu}(\text{en})(\text{hm})^{2+} + \text{Hhm}^+$	$(6 \pm 4) \times 10^6$	$(3 \pm 2) \times 10^8$
6	$\text{Cu}(\text{en})_2^{2+} + \text{Hhm}^+ \rightleftharpoons \text{Cu}(\text{en})(\text{hm})^{2+} + \text{Hen}^+$	$(1.63 \pm 0.03) \times 10^6$	$(1.00 \pm 0.02) \times 10^7$

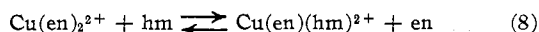
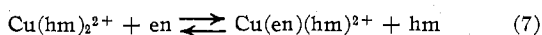
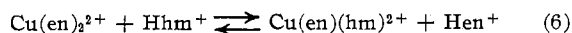
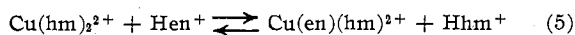
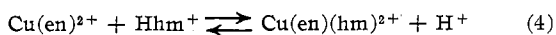
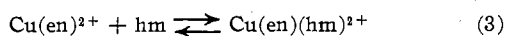
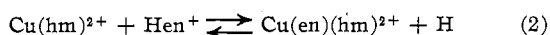
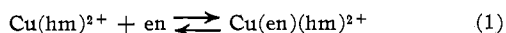
^a At 37°, $\mu = 0.15$ (KNO₃).

curve which exhibits two relaxation times is shown in Figure 1 for experiment 13 of Table I.

The rate constants for trial rate laws were calculated using a least-squares refinement program, ENEK.⁸ The required formation constants for the binary and ternary complexes of Cu(II) with en and hm¹⁰ and the previously determined⁵ rate constants for the binary systems are given in Table II.

Results and Discussion

The reactions of categories I to IV lead to eight paths by which $\text{Cu}(\text{en})(\text{hm})^{2+}$ is likely to be formed.



Owing to the difficulties which are encountered in trying to fit a large number of parameters to a limited amount of data which is subject to experimental uncertainties, initial computations using ENEK had the goal of ultimately reducing the complexity of the problem by identifying the major reaction paths. Various simplified rate laws were tried using as initial estimates of the rate constants values which are typical of the appropriate categories. Trial rate laws which incorporated both a major path and a minor path were observed to lead to convergence on a value with a small standard deviation for the rate constant for the major path. For the minor path, the routine either converged on a value with a large standard deviation or essentially eliminated the path by reducing the rate constant to smaller and smaller values in successive cycles of refinement. Trials in which only minor paths were incorporated gave either poor fits or divergence. After many runs in which various combinations were tried, four major paths (eq 1, 3, 5, 6) were identified. A final simultaneous refinement of the rate constants for these major paths was made using a complete rate law which included all four minor paths. The values for these minor paths were estimated as described above and held constant. The final results with their computed uncertainties are given in Table III. It should

(8) Program ENEK is more powerful version of CORNEK (ref 9) which was employed earlier (ref 5). ENEK uses the data in the form as presented in Tables I and II and calculates the distribution of species as well as performing the other functions of CORNEK.

(9) V. S. Sharma and D. L. Leussing, *Talanta*, **18**, 1137 (1971).

(10) D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc. A*, 1755 (1967).

be noted that convergence to the same values was obtained when the rates for all of the minor paths were set equal to zero, demonstrating their negligible contribution under the present experimental conditions.

The uncertainties given in Table III are seen to be smaller for reactions 1 and 6 than for reactions 3 and 5. This is interpreted to mean that the first pair of reactions are more dominant under the present experimental conditions than the second pair. Judging from their relatively high uncertainties, reactions 3 and 5 are not well defined in the present set of experiments, although they seem to be sufficiently important to cause the overall fit to the data to be significantly poorer if they are completely excluded. The distribution of kinetic activity among the various possible paths seems merely to reflect the distribution of Cu(II) among the various complexes. Owing to the relatively low stability of $\text{Cu}(\text{hm})_2^{2+}$, $\text{Cu}(\text{hm})^{2+}$ is always present at a much higher concentration under the conditions defined in Table I, and the $\text{Cu}(\text{en})_2^{2+}$ concentrations tend to be greater than those of $\text{Cu}(\text{en})^{2+}$.

Reactions 5 and 6 are category III reactions, which involve transfer of a proton from an entering to a leaving ligand. The results found here together with those reported in ref 5 for this type of reaction show that for pairs of reactions which are identical with respect to the entering and leaving ligands, the rates lie in the order $(\text{en})\text{Cu}(\text{L})^{2+} + \text{HL}' \rightarrow (\text{en})\text{Cu}(\text{L}')^{2+} + \text{HL} > (\text{hm})\text{Cu}(\text{L})^{2+} + \text{HL}' \rightarrow (\text{hm})\text{Cu}(\text{L}')^{2+} + \text{HL}$. Thus, the faster rates are observed with the less sterically hindered "inert" ligand.

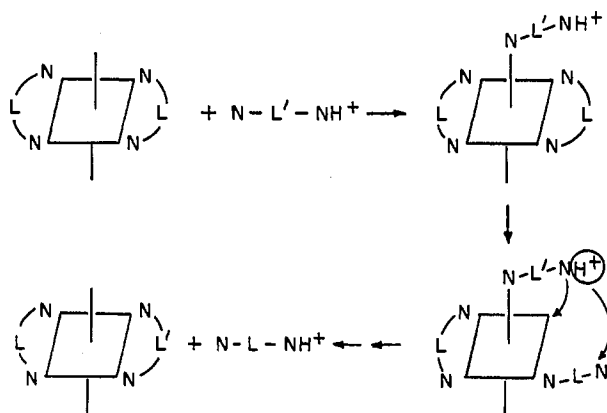
Similarly for a given entering ligand, the rates decrease with the leaving ligand in the order $\text{en} > \text{ser}^- > \text{hm}$. These rates do not follow the order of metal-ligand affinities but once again show the influence of steric effects on the reactions. The observations are contrary to expectations for a dissociative (SN1) mechanism but are highly consistent with an associative (SN2) mechanism.^{11,12}

The reaction sequence probably involves fast coordination of the free amine end of a monoprotonated diamine to an axial position of Cu(II), followed by proton transfer to the leaving ligand, rearrangement, and dissociation according to Scheme I. Because the protonated group of the entering ligand is brought into the proximity of the free amine group of the leaving ligand, and also because the reaction is an intramolecular, first-order process, the proton transfer is likely fast with the subsequent ligand rearrangement steps being rate determining. Since the rate-determining steps are then essentially the same, category III and

(11) D. Benson, "Mechanisms of Inorganic Reactions in Solution," McGraw-Hill, New York, N. Y., 1968, p 21.

(12) The effect of unsaturated ligands on the rates of formation of ternary Cu(II) complexes provides additional evidence for an SN2 mechanism: R. F. Pasternack, private communication.

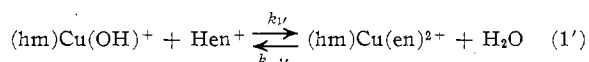
SCHEME I



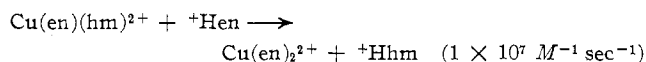
category IV reactions should have similar values for the rate constants, as is observed.

The rate constant calculated for reaction 1 in Table III lies well in the diffusion-controlled region and seems prohibitively high. It should be noted, however, that the value given in Table III is only about two or three times greater than the values for Cu(II)-en reactions given in Table II or reported by Kirschenbaum and Kustin¹³ for 25°.

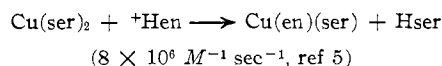
The high rate constants are the direct result of attributing "normal" relaxation times, such as those given in Table I, to paths involving a species (free en) which is present at very low concentration levels owing to its dibasic nature. A kinetically equivalent path involving the rapidly formed conjugate species of reaction 1 can also be written. The product of the concentrations of



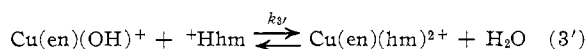
the species on the left-hand side of eq 1' is greater than the corresponding product in eq 1; therefore, $k_{1'}$ will be smaller than k_1 . The $\text{p}K_a$ of $(\text{hm})\text{Cu}(\text{H}_2\text{O})_4^{2+}$ is about 7.0 (25°, $\mu = 0.1$).^{14,15} Assuming this value for 37° and using $\text{p}K_{2a}$ equal to 9.7 for ^+Hen , $k_{1'}$ is calculated to be $2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. Reaction 1' is essentially a category III reaction and is found here to have a rate constant which is consistent with other reactions of this category. Of particular significance is the similarity of the value deduced for $k_{1'}$ to the values found for other category III reactions involving ^+Hen attack



and



The rate constant for reaction 3 shows a "normal" value for water substitution to give a bis Cu(II) complex. However, this fact in itself does not necessarily rule out the existence of a parallel path analogous to (1'). The data only permit qualitative observations to



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

(14) M. A. Doran, S. Chaberek, and A. E. Martell, *J. Amer. Chem. Soc.*, **86**, 2129 (1964).

(15) The $\text{p}K_a$ of $\text{Cu}^{\text{II}}(\text{histidine})^{2+}$ at 37°, $\mu = 0.15$, is 7.3 (ref 16).

(16) D. D. Perrin and V. S. Sharma, *J. Chem. Soc. A*, 724 (1967).

be made regarding $k_{3'}$, however. Category III reactions involving ^+Hhm attack have rate constants that are considerably smaller than are observed for ^+Hen attack: for $\text{Cu}(\text{en})(\text{hm})^{2+} + ^+\text{Hhm} \rightarrow \text{Cu}(\text{hm})_2^{2+} + ^+\text{Hen}$, the rate constant is $3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ and for $\text{Cu}(\text{ser})_2 + ^+\text{Hhm} \rightarrow \text{Cu}(\text{hm})(\text{ser})^+ + \text{Hser}$, a value of $1 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ has been found.⁵ Probably the low value of the former rate constant arises from interference between two bulky histamine molecules, and the latter is closer to being representative of reactions such as (3').

Furthermore, $\text{Cu}(\text{en})_{\text{aq}}^{2+}$ is a more stable complex than $\text{Cu}(\text{hm})_{\text{aq}}^{2+}$. The higher Cu-N interaction should have the effect of lowering the acidity of $\text{Cu}(\text{en})_{\text{aq}}^{2+}$ relative to $\text{Cu}(\text{hm})_{\text{aq}}^{2+}$. This effect also would tend to reduce the rate of (3') compared to (1'). Thus, while the alternate path (3') cannot be definitely ruled out, it may contribute only a fraction of the overall rate which has been ascribed to (3).

The interpretations of the reactions of Cu(II) are complicated by the as yet incompletely understood role of the dynamic Jahn-Teller effect and how it is influenced by coordinated ligands. With respect to this, the suggestion has been made³ that the mechanisms of ligand substitution of $\text{Cu}_{\text{aq}}^{2+}$, $\text{Cu}(\text{gly})^+$, and $\text{Cu}(\text{bipy})^{2+}$ might all be different. The strong Lewis acid character of Cu(II) possibly adds a further complication by providing additional routes to complex formation *via* reaction of hydroxy complexes with protonated ligands. For metal ions with a strong Lewis acid character, such as Cu(II), reaction 1' deserves consideration as a plausible alternate mechanism to the internal conjugate base mechanism which has been proposed¹⁷ to account for similar but slower effects in Ni(II) systems.

(17) D. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA 27514

The Magnetic Properties of the Complex Di- μ -hydroxo-bis[2-(2-ethylaminoethyl)-pyridine]dicopper(II) Perchlorate

BY DAVID Y. JETER,¹ DAVID L. LEWIS, JUDITH C. HEMPEL,
DEREK J. HODGSON, AND WILLIAM E. HATFIELD*

Received November 29, 1971

In recent years much interest has been shown in the magnetic properties of oxygen-bridged, bimetallic copper(II) complexes.²⁻⁶ Many of these complexes have been postulated to exhibit ferromagnetic interactions. Krahrmer, *et al.*,² however, have shown that some of the 1:1 complexes with N-substituted 2-(2-

(1) National Science Foundation Trainee, 1968-1971.

(2) V. R. Krahrmer, M. Maaser, K. Staiger, and E. Uhlig, *Z. Anorg. Allg. Chem.*, **364**, 242 (1967).

(3) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and R. Jones, *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

(4) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

(5) J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *ibid.*, 1593 (1970).

(6) B. J. Cole and W. H. Brumage, *J. Chem. Phys.*, **53**, 4718 (1970).