peptide nitrogen forces it to be tetrahedral and undoubtedly changes the conformation of the chelate rings and the copper–nitrogen bond distance.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. GM-12152 from the National Institute of General Medical Sciences.

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Received October 16, 1967

Triethylenetetramine-Catalyzed Ligand Exchange between Copper(II)–Triglycine ($CuH_{-2}L^-$) and Ethylenediaminetetraacetate Ion[1]

Sir:

The exchange reaction in eq 1 is catalyzed by small concentrations of trien. Thus, when a 2.6×10^{-4} *M* solution of $CuH_{-2}L^-$ is allowed to react with a 2.5×10^{-3} *M* solution of EDTA in the presence of 1.20×10^{-5} *M* trien at pH 8.5, the reaction velocity is four times larger than when no trien is present. In the absence of trien the reaction is first order in $CuH_{-2}L^-$, while in its presence the reaction approaches zero-order dependence. Spectra of the products indicate that $CuEDTA^{2-}$ is formed in both cases. All reactions are studied by stopped-flow techniques.

$$CuH_{-2}L^- + HEDTA^{3-} + H^+ \xrightarrow{\text{trien}} CuEDTA^{2-} + L^- \quad (1)$$

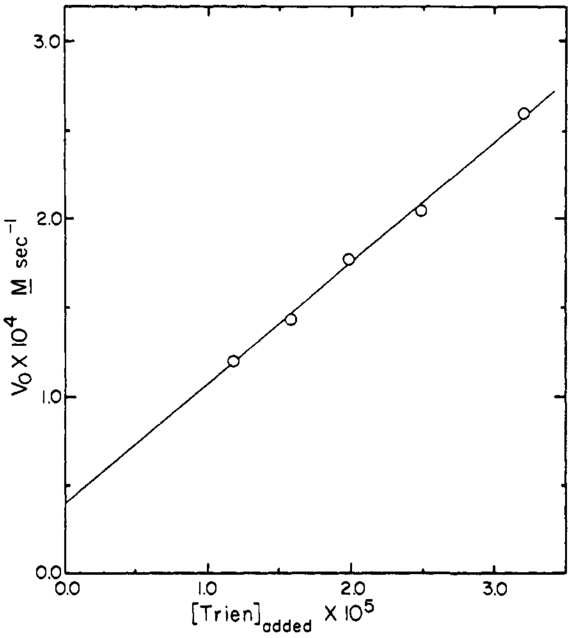

Figure 1. Trien catalysis of the exchange reaction between $CuH_{-2}L^-$ and EDTA. V_0 is the initial velocity of formation of $CuEDTA^{2-}$ with $[CuH_{-2}L^-]_{\text{initial}} = 2.46 \times 10^{-4}$ *M*, [EDTA] = 2.50×10^{-3} *M*, boric acid–borate buffer (0.013 *M*), pH 8.50, 25.0°, 0.10 *M* $NaClO_4$.

Although reaction 1 is subject to general acid catalysis,[2] the effect of trien cannot be attributed to this because of the high pK_a values for $Htrien^+$ and H_2trien^{2+} and the low concentration of added trien in these experiments. The reaction of $CuH_{-2}L^-$ with trien was investigated separately at pH 8.5. It proceeds with a first-order dependence in each reactant ($k_1 = 1.2 \times 10^6$ M^{-1} sec^{-1}) and gives copper–trien and triglycine as products.

The mechanism proposed for reaction 1 is given by

$$CuH_{-2}L^- + \text{trien} \xrightarrow{k_1} Cu(\text{trien})^{2+} + L^- \quad (2)$$

$$Cu(\text{trien})^{2+} + \text{EDTA} \xrightarrow{k_2} CuEDTA^{2-} + \text{trien} \quad (3)$$

where reaction 3 is the rate-determining step. The pH dependence of eq 2 is under study and therefore protons are omitted from the trien. The trien added is converted rapidly to $Cu(\text{trien})^{2+}$, and this concentration is kept constant by the trien released in reaction 3. Therefore when EDTA is in large excess, the rate of formation of $CuEDTA^{2-}$ is a constant (zero-order behavior).

In addition to the trien-catalyzed path, there is a contribution from water and the boric acid buffer to the general acid catalyzed path.[2] Therefore the reaction velocity is

$$\frac{d[CuEDTA^{2-}]}{dt} = V_0 = \left(\sum_{HX} k_{HX}[HX][CuH_{-2}L^-] + k_0[\text{trien}]_{\text{added}}\right) \quad (4)$$

where V_0 is the observed initial velocity, and the first term on the right-hand side is the summation of all species, HX, which contribute to the general acid catalysis. Figure 1 shows the dependence of V_0 on the added trien concentration. The slope gives k_0 which in turn has been shown to depend on the EDTA concentration; $k_0 = k_2[\text{EDTA}]$. The value found for k_2 at pH 8.5 is 2.6×10^3 M^{-1} sec^{-1}, which is in good agreement with the value predicted from the reverse rate constant, $k_{\text{trien}}^{\text{CuEDTA}}$, and the corresponding conditional stability constant at this pH.[3]

This system is an example of one ligand catalyzing the exchange reaction between another ligand and a complex. This could be a general phenomenon, and it complements previous examples of (1) metal ion catalysis of the exchange between a metal ion and a complex[4] and (2) ligand catalysis of complex–complex exchange (coordination chain reactions).[5] The specific reasons for the difference in reactivity of trien and EDTA in this case are under investigation.

Acknowledgments. This investigation was supported by Public Health Service Research Grant No. GM-12152 from the National Institute of General Medical Sciences and by a David Ross Grant (G. K. P.) from Purdue Research Foundation.

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(1) In this paper trien stands for triethylenetetramine, EDTA for ethylenediaminetetraacetate ion, and $CuH_{-2}L^-$ for the copper complex with triglycine(glycylglycylglycine) which has undergone ionization of two peptide protons.

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