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Copper(II) Complex Catalysis of Amino Acid Ester Hydrolysis. A Correlation of Rates with Complex Stability

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Transition-metal ions and complexes have long been known to promote the hydrolysis of amino acid esters.[2-7] Recently, Nakon, Rechani, and Angelici[8] noted a correlation between the formation constant, K_L, of the metal complex (eq 1) and

$$Cu^{2+} + L \overset{K_L}{\rightleftharpoons} CuL^{2+} \quad (1)$$

the catalytic activity of the complex; it was found that large formation constants resulted in reduced Lewis acid character of the metal complex, and, therefore, lower catalytic activities.

In the present paper, we have reexamined catalytic data for Cu(IMDA), where IMDA = $HN(CH_2CO_2^-)_2$, and also extended the correlation by using Cu(II) complexes of 2,2′:6′,2″-terpyridine (terpy) and 2,2′,2″-triaminotriethylamine (tren, $(H_2NCH_2CH_2)_3N$) to promote the hydrolysis of glycine methyl ester. Because all three pyridine rings in terpy are forced to coordinate to the Cu(II) in the same plane (i.e., meridionally), this ligand offered an opportunity also to determine whether or not ligand rigidity was a factor in determining catalyst activity. It seemed possible that more flexible ligands would allow the amino acid ester substrate to coordinate to the metal in a position which was catalytically more active than was available in complexes with a rigid ligand. The results reported below indicate that the rigidity of terpy appears to have no major effect on the catalytic activity of its complex.

Experimental Section

Reagents. Glycine (Mann Research Laboratories), MeGly·HCl (Aldrich Chemical Co.), the trihydrochloride of 2,2′,2″-tris(aminoethyl)amine, tren·3HCl (Strem Chemical Co.), IMDA (J. T. Baker), and terpyridyl (K and K Laboratories, Inc.) were of the highest purity available and were used without further purification. Glycine and IMDA solutions were standardized by potentiometric titration. Solutions of MeGly·HCl and tren·3HCl were standardized by passing aliquots through a Dowex 50W-X8 strongly acidic cation-exchange resin and titrating the effluent solutions with standardized NaOH. Metal ion solutions of $Cu(NO_3)_2.3H_2O$ were standardized similarly. Solutions of terpy were prepared by adding weighed amounts (dried overnight over H_2SO_4 at 50 °C) to standardized $Cu(NO_3)_2$ solutions.

Potentiometric Measurements. The glass electrode was calibrated in terms of hydrogen ion concentration, pH_c, according to the procedure of Rajan and Martell[9] using standard HCl and NaOH solutions. A Corning Digital 112 Research pH meter was used to measure pH_c in all titrations, which were carried out in a double-walled cell of 50-mL capacity. For all equilibrium and kinetic studies, the temperature of the cell was maintained at 25.0 ± 0.1 °C by circulation of thermostated water through the outer jacket of the cell. Solutions were stirred with a magnetic stirrer, and the cell was fitted with Corning glass and calomel electrodes, a nitrogen inlet tube, and a microburet delivery tube.

Protonation constants of MeGly and Gly

$$X + H^+ \rightarrow XH^+ \quad (2)$$

and the hydroxo formation constants (eq 3) of $Cu(tren)^{2+}$ and

$$CuL^{2+} + OH^- \overset{K_{OH}}{\rightleftharpoons} CuLOH^+ \quad (3)$$

$Cu(terpy)^{2+}$ were determined in this cell by titration with NaOH. Also, the mixed ligand formation constants, K_X, where X = Gly^- or MeGly, were determined in this manner.

$$CuL^{2+} + X^{0,-} \overset{K_X}{\rightleftharpoons} CuLX^{2+,+} \quad (4)$$

All titrations were performed in triplicate at an ionic strength of 0.05 M by addition of appropriate amounts of 1 M KNO_3.

The formation constant of $Cu(terpy)^{2+}$ was determined by

$$Cu^{2+} + terpy \overset{K_L}{\rightleftharpoons} Cu(terpy)^{2+} \quad (5)$$

Schwarzenbach's competing ligand[10] method using $trenH_3^{3+}$ in the following reaction in which $trenH_3^{3+}$ represents all possible protonated forms of the ligand. Equimolar Cu^{2+}, $trenH_3^{3+}$, and terpy (1.8×10^{-3} M) and enough 1.0 M KNO_3 to attain an ionic strength of 0.05 were entered into 2-oz bottles (12 bottles per run with 36 total). After purging with N_2, enough NaOH was added to attain the buffer region where reaction 5 occurred, and the bottles were then sealed with Parafilm M (Marathon Products, Neenah, Wis.). The appropriate buffer region was determined by preliminary potentiometric titrations. After 3 h in a 25 °C bath, equilibrium had been reached, and the pH_c of each solution was determined with a Fisher semimicro pH combination electrode.

$$Cu(terpy)^{2+} + trenH_3^{3+} \rightleftharpoons M(tren)^{2+} + terpy + 3H^+ \quad (6)$$

Species necessary to calculate K_L (eq 5) include $Cu(terpy)^{2+}$, $Cu(terpy)OH^+$, $Cu(tren)^{2+}$, $Cu(tren)OH^+$, terpy, and all the protonated and unprotonated forms of tren. Schwarzenbach's stability constants (at 0.1 M (KCl) and 20 °C) for $Cu(tren)^{2+}$ and tren were used in the calculations. All calculations were performed at the West Virginia University Computation Center on an IBM 360–75 digital computer.

Kinetic Measurements. Rates of MeGly hydrolysis in the presence of $Cu(tren)^{2+}$, $Cu(terpy)^{2+}$, and Cu(IMDA) were followed by NaOH addition using pH stat techniques described previously.[6] Ten-milliliter solutions containing 7.5×10^{-4} M MeGly, 7.5×10^{-3} M [$Cu(terpy)^{2+}$] or [$Cu(tren)^{2+}$], and enough KNO_3 to attain an ionic strength of 0.05 M were studied at 25.0 ± 0.1 °C. A 10% excess of terpy and a 1% excess of tren were used to ensure coordination of all Cu^{2+} as $Cu(terpy)^{2+}$ or $Cu(tren)^{2+}$, respectively. A 20% excess of terpy gave the same rates as with a 10% excess indicating free Cu^{2+} was not involved in the hydrolysis. However, solutions containing greater than a 1% excess of tren caused a continual absorption of NaOH extending far past the theoretical end point. Apparently, large concentrations of unprotonated amine groups lead to glass electrode instability at high pH values. Such behavior has also been noted in tetraethylenepentaminenickel(II) catalysis of MeGly.[11] A 30:1 metal chelate [$Cu(terpy)^{2+}$ or $Cu(tren)^{2+}$] to MeGly ratio gave the same rates within experimental error as those with lower ratios indicating that under the conditions used, there is no rate dependence on metal chelate concentration. It was found that a 50:1 ratio of Cu(IMDA) to MeGly (7.5×10^{-4} M) was required to ensure that most of the MeGly was coordinated as Cu(IMDA) MeGly. A 15% excess of IMDA over Cu(II) was used to ensure that free Cu(II) was not involved in the hydrolysis.

After equilibrating CuL^{x+} solutions at 25.0 °C under a N_2 flow, a solution of MeGly·HCl was added, and the pH_c was brought up to the desired value by addition of 0.02 M NaOH. The hydrolysis was then followed by automatic NaOH addition. Pseudo-first-order rate constants, k_{obsd}, were obtained from the slopes of plots of log ($\%_{end} - \%_t$) vs. time, where $\%_{end}$ is the percent of the total syringe volume delivered at the end of the reaction and $\%_t$ is the percent delivered at time t.

Results

Equilibrium Constants. Protonation constants of Gly and MeGly (eq 2) and the hydroxo formation constants of $Cu(terpy)OH^+$ and $Cu(tren)OH^+$ (eq 3) were calculated from potentiometric data using Bjerrum's method.[12] The log values of the protonation constants of Gly and MeGly were 9.57 ± 0.01 and 7.72 ± 0.01, respectively. The $Cu(tren)^{2+}$ and $Cu(terpy)^{2+}$ hydroxo formation constants, K_{OH}, were $10^{4.76\pm0.01}$ M^{-1} and $10^{5.81\pm0.01}$ M^{-1}, respectively.

The value of K_L (eq 4) determined by Schwarzenbach's competing ligand method[10] for $Cu(terpy)^{2+}$ was $10^{13.4\pm0.1}$ M^{-1} in fair agreement with the 10^{13} M^{-1} value reported by James and Williams,[13] in 50% dioxane–H_2O.

In titrations of 1:1 Gly (or MeGly) to $Cu(terpy)^{2+}$ (or $Cu(tren)^{2+}$), values of log K_X (eq 4) were determined at 25.0 °C and an ionic strength of 0.05 M (KNO_3). The log K_X

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Table I. Rate Constants for the Hydrolysis of MeGly as Catalyzed by $Cu(terpy)^{2+}$, $Cu(tren)^{2+}$, and Cu(IMDA)

pH_c[a,b]	$10^4 k_{obsd}$, s^{-1}	$10^{-2} k_{OH}$, $M^{-1} s^{-1}$
7.40	1.02	2.53
7.50	1.23	2.41
7.60	1.03	1.61
7.70	1.81	2.14
7.80	2.40	2.36
7.90	2.96	2.29
8.00	3.74	2.34
8.10	4.42	2.28
8.25	5.50	1.96
pH_c[a,c]	$10^5 k_{obsd}$, s^{-1}	k_{OH}, $M^{-1} s^{-1}$
9.50	6.05	1.17
9.60	9.82	1.33
9.75	12.0	1.30
10.00	21.5	1.32
10.25	29.2	1.02
10.40	70.2	1.72
pH_c[d,e]	k_{obsd}, s^{-1}	$10^{-3} k_{OH}$, $M^{-1} s^{-1}$
7.50	3.83×10^{-3}	7.64
7.40	2.95×10^{-3}	7.24
7.25	2.07×10^{-3}	7.18
7.10	1.44×10^{-3}	7.06
7.00	1.23×10^{-3}	7.58
6.90	9.86×10^{-4}	7.66
6.75	6.84×10^{-4}	7.50

[a] At 25.0 °C and 0.05 M (KNO_3) ionic strength; [MeGly] = 7.5×10^{-4} M. [b] [$Cu(terpy)^{2+}$] = 7.5×10^{-3} M. [c] [$Cu(tren)^{2+}$] = 7.7×10^{-3} M. [d] [Cu(IMDA)] = 3.5×10^{-2} M. [e] I = 0.1 M (KNO_3).

values for addition of Gly and MeGly to $Cu(tren)^{2+}$ were 3.21 ± 0.02 and 2.40 ± 0.01, respectively, while those for $Cu(terpy)^{2+}$ were 4.34 ± 0.01 and 2.89 ± 0.02, respectively.

Kinetics of MeGly Hydrolysis. Pseudo-first-order rate constants, k_{obsd}, for the hydrolysis of MeGly in the presence of $Cu(terpy)^{2+}$, $Cu(tren)^{2+}$, and Cu(IMDA) are given in Table I. The equilibrium constants (log K_X values) indicate that under the conditions used in this study 90% or more of the MeGly is coordinated as $CuLMeGly^{2+}$, where L is tren, terpy, or IMDA. After hydrolysis, these values indicate that Gly remains coordinated to CuL^{2+} as $CuLGly^+$. The predominant reaction in solution can then be written as

$$CuLMeGly^{2+} + OH^- \rightarrow CuLGly^+ + CH_3OH \quad (7)$$

The total amount of NaOH consumed during the kinetic runs was always within 5% of the value predicted by eq 7. The k_{obsd} values determined at different pH_c indicate that reaction 7 follows the rate law

$$\text{rate} = k_{OH}[CuLMeGly^{2+}][OH^-] \quad (8)$$

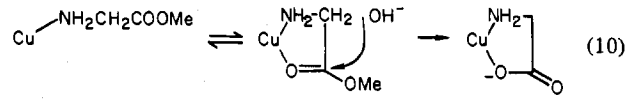
where $k_{OH} = k_{obsd}/[OH^-]$. At 25 °C and an ionic strength of 0.05 M, the average values of k_{OH} for [Cu(tren)$MeGly^{2+}$], [Cu(terpy)$MeGly^{2+}$], and [Cu(IMDA)MeGly] are 1.3, 2.26×10^2, and 7.41×10^3 $M^{-1} s^{-1}$, respectively. The rate of hydrolysis of MeGly in the absence of [$Cu(terpy)^{2+}$] or [Cu(IMDA)] is small in the pH range studied; however, the k_{OH} value for the hydrolysis of Cu(tren)MeGly is virtually the same as that for MeGly in the absence of metal chelates. The value for [Cu(IMDA)MeGly] is significantly different from that (3.2×10^4 $M^{-1} s^{-1}$) reported previously.[14] The reason for the discrepancy is not apparent, but the difference in rates does not affect conclusions given in the Discussion section.

Discussion

The overall Cu^{2+}-catalyzed hydrolysis of MeGly proceeds via the following two steps.

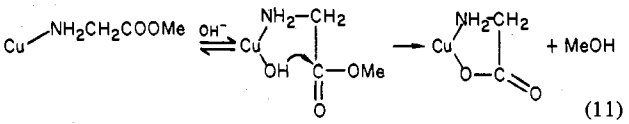
$$CuL^{2+} + MeGly \overset{K_X}{\rightleftharpoons} CuL(MeGly)^{2+} \xrightarrow[OH^-]{k_{OH}} CuL(Gly)^+ + MeOH \quad (9)$$

Under the conditions used in this study almost all of the ester is coordinated to CuL, where L = terpy or tren. Therefore, the observed rate law (eq 8) is the second step (k_{OH}) only. The first-order dependence on OH^- concentration for this step may be accounted for by three general mechanisms. One involves an initial rapidly established equilibrium in which the carbonyl oxygen of the ester group coordinates, followed by a rate-determining attack by OH^-.



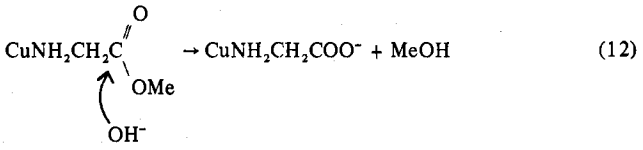
(10)

The second involves rapid, equilibrium formation of a Cu–OH complex, followed by intramolecular OH^- attack.



(11)

The third involves only rate-determining OH^- attack on the uncoordinated carbonyl carbon of the ester group.



(12)

Careful studies by Buckingham et al.[7] showed that both mechanisms (10) and (11) are important in the ester hydrolysis in the inert complex $Co(en)_2Br(NH_2CH_2CO_2\text{-}i\text{-}Pr)^{2+}$; the third mechanism (eq 12) was considered to contribute little if any to the hydrolysis. However, the lability of Cu(II) has prevented the unequivocal determination of the mechanism(s) of ester hydrolysis in Cu-complex-catalyzed systems. Studies of

Table II. Rate (k_{OH}) and Equilibrium Constants Associated with the Cu(II)-Catalyzed Hydrolysis of MeGly at 25 °C

$CuL(MeGly)^n$	k_{OH}, $M^{-1} s^{-1}$	log K_L	log K_X(MeGly)	log K_X(Gly^-)
$Cu(EtGly)^{2+}$	7.6×10^4 [a]		4.04[b]	
Cu(IMDA)(MeGly)	7.6×10^3 [c]	10.63[d]	3.69[e]	6.42[e]
Cu(NTA)$MeGly^-$	4.6×10^2 [f]	13.10[g]	3.06[h]	5.44[h]
Cu(terpy)$MeGly^{2+}$	2.2×10^2	13.4	2.89	4.34
Cu(DPA)$MeGly^{2+}$	1.7×10^2 [i]	14.4[i]	2.81[i]	3.99[i]
Cu(dien)$MeGly^{2+}$	1.4×10^2 [j]	15.91[k]	2.52[k]	4.42[k]
Cu(tren)$MeGly^{2+}$	1.3	18.8[l]	2.40	3.21
MeGly	1.32[m]			

[a] The rate for MeGly would be somewhat faster (~2 times). [b] For EtGly.[4] [c] $k_{OH} = 3.2 \times 10^4$ $M^{-1} s^{-1}$ at I = 0.05 M (KNO_3).[14] [d] G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964). [e] For *n*-BuGly.[14] [f] R. J. Angelici and D. Hopgood, *J. Am. Chem. Soc.*, **70**, 2514 (1968). [g] T. Moeller and R. Ferrus, *Inorg. Chem.*, **1**, 55 (1962). [h] D. Hopgood and R. J. Angelici, *J. Am. Chem. Soc.*, **90**, 2508 (1968). [i] Reference 8. [j] J. W. Allison and R. J. Angelici, *Inorg. Chem.*, **10**, 2338 (1971). [k] R. J. Angelici and J. W. Allison, *ibid.*, **10**, 2233 (1971). [l] Reference 10. [m] R. W. Hay, L. J. Porter, and P. J. Morris, *Aust. J. Chem.*, **19**, 1197 (1966). [n] Ligand L abbreviations: IMDA, $HN(CH_2COO^-)_2$; NTA, $N(CH_2COO^-)_3$; DPA, $(2\text{-}C_5H_4NCH_2)_2NH$; dien, $HN(CH_2CH_2NH_2)_2$; terpy, $(2\text{-}C_5H_4N)_2C_5H_3N$; tren, $N(CH_2CH_2NH_2)_3$.

a related Cu^{2+}-catalyzed ester hydrolysis using various nucleophiles[15] suggested that external OH^- attack (eq 10) was the more likely of the mechanisms.

Correlation of CuL^{2+} Complex Stability with Ester Hydrolysis. Overall rates of the Cu(II)-complex-catalyzed hydrolysis of MeGly are dependent upon both the degree of ester coordination (K_X) and the rate of hydrolysis (k_{OH}) of the coordinated ester (see eq 9). As has been noted previously[8] the degree of ester coordination (K_X) depends upon the coordinating ability of the ligand L on the Cu(II). It was found that ester coordination (i.e., K_X) decreases as the coordination of L (i.e., K_l) increases. This trend can be seen in Table II (columns 3 and 4) which includes results reported earlier[8] as well as those reported herein. From these data, it is clear that CuL^{2+} complexes with the most strongly coordinating L ligands bind the amino acid ester substrate most weakly. This trend is reasonable if one considers that the most strongly binding L groups will most effectively neutralize the Lewis acid character of the Cu(II) making it a less effective Lewis acid toward the ester.

The second step (k_{OH}) in the overall hydrolysis (eq 9) is the rate-determining hydrolysis of the coordinated amino acid ester. Although the mechanism for this step could be one or more of those given in eq 10, 11, or 12, it will be assumed that mechanism 10 is the primary route for the purpose of this discussion. It should be noted, however, that the observed trends can be rationalized in terms of mechanisms 11 and 12 also.

In mechanism 10, the rate of hydrolysis depends on the extent of chelation by the ester group as well as on the subsequent rate of attack of OH^- on the ester carbonyl carbon center. The OH^- attack step, and possibly the rapid equilibrium chelation step, will be favored by CuL^{2+} complexes of high Lewis acidity. As described above, a measure of the Lewis acidity of the CuL^{2+} complexes is K_X. Therefore the rate of the second step (k_{OH}) of eq 9 should decrease as K_X decreases. This trend can be seen in Table II.

Since the Lewis acidities (K_X) of the CuL^{2+} complexes decrease as the formation constant (K_L) for CuL^{2+} increases, k_{OH} should decrease as K_L increases; this trend can be seen in Table II. Since the trend includes data for the two additional complexes, $Cu(terpy)^{2+}$ and $Cu(tren)^{2+}$, reported in this paper, it is evident that the rigidity of the terpy ligand has no major effect on the catalytic activity of its complex.

In summary, it should be noted that the new data reported here follow trends that were observed previously[8] for CuL^{2+} complexes. They indicate that the catalytic activities of the CuL^{2+} complexes in the hydrolysis of amino acid esters depend upon the strength of the binding of L to Cu^{2+}—the more strongly binding the L ligand, the less catalytic the CuL^{2+} complex.

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Registry No. MeGly, 616-34-2; tren, 4097-89-6; terpy, 1148-79-4; IMDA, 28528-43-0; Cu, 7440-50-8.

References and Notes

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Complex Formation in Dilute Aqueous Solutions of Europium Perchlorate Detected through Fluorescence Lifetime Measurements

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The interaction between lanthanide ions (Ln^{3+}) and simple inorganic anions in aqueous solution is generally weak and difficult to quantify.[1] Absorption spectrophotometry is a method commonly used for this purpose, but it has several major disadvantages.[1-3] Of the transitions that exhibit some sensitivity to the environment of Ln^{3+}, charge-transfer and f–d transitions lie at energies too close to or higher than the water cutoff (except cerium(III) complexes and europium(III) complexed by sulfate or thiocyanate).[4] Furthermore, only a few lanthanides have f–f transitions in the near-UV to near-IR spectral regions that are hypersensitive.[5] Europium has a convenient hypersensitive transition at 465 nm, but it is very weak ($\epsilon \sim 0.05\ M^{-1}\ cm^{-1}$) and thus is of limited use in studies at concentrations much less than 0.1 M. Fortunately, Eu^{3+} fluoresces strongly from the $^5D_0$ level to several states within the ground state (^7F) multiplet ($\lambda \sim 600$ nm),[6,7] and changes in the local environment influence relaxation rates by interactions too small to be observable spectroscopically.[8] Thus the local environment can be probed with high sensitivity by an examination of the fluorescence decay characteristics of the aqueous Ln^{3+} solution.

Chelation has been demonstrated to cause dramatic changes in fluorescence lifetimes,[8-10] and in addition, small changes in Eu(III) lifetimes have been observed while varying nitrate concentrations in H_2O and D_2O and were ascribed to complex formation,[11] but calculation of a formation constant was not possible due to the limited range of concentrations used. The same authors saw no change in lifetime upon variations of perchlorate concentrations.

In this note, we show that substantial changes in the lifetime of Eu^{3+} ($^5D_0$) fluorescence can be observed when perchlorate concentration is varied at levels significantly lower than those used in previous work. This effect is hypothesized to be due to a weakly bound complex, and a formation constant (K) for this species is estimated.

Experimental Section

Two sets of solutions were examined containing Eu^{3+} at various concentrations. In the first, Eu^{3+} was dissolved directly as the perchlorate salt, so that $[ClO_4^-] = 3[Eu^{3+}]$. In the second set, excess $NaClO_4$ was added so that $[ClO_4^-] \equiv 0.50$ M. Samples were placed in 1-cm Suprasil fluorescence cells and excited by a pulsed nitrogen pumped dye laser, using the dye α-NPO dissolved in cyclohexane.[12] The dye laser output was grating tuned to the $^7F_0$–$^5L_6$ transition at 393.7 nm. Laser energy was about 100 μJ and pulse length 10 ns. Fluorescence was detected at right angles to the pump beam with a photomultiplier through a cutoff filter, which rejected wavelengths less than 500 nm. No fluorescence was detectable from the $^5D_1$ level. Quantum yields were not measured here but have been observed by

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