oxymercuration of olefinic compounds.[16,17] This particular feature of the behavior of these systems is significant in the light of the demonstrated formation of $Hg(CH_3)_2$ through the methylation of mercury(II) by methylcobalamin.[2,8] The circumstances which favor the dialkylation of mercury(II) in this and certain other cases are still unclear and warrant further attention.

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Copper(II)-Catalyzed Hydrolysis of the Methyl Esters of Glycylglycine and Glycylsarcosine

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Abstract: The ester hydrolysis of glycylglycine methyl ester (GGOMe) is catalyzed by Cu(II) in the 6.5–8.0 pH range. Under these conditions the ester is bound in $Cu(H_{-1}GGOMe)^+$ *via* the terminal amino group, the deprotonated amide nitrogen, and possibly the ester group. Coordination by the deprotonated amide nitrogen moves the ester group in position to bind to the metal ion, which promotes the hydrolysis of the ester. The first-order dependence on $[OH^-]$ suggests a mechanism in which rate-determining OH^- attack occurs at the coordinated ester carbon atom. This rate is approximately 10^3 times faster than the hydrolysis in the absence of the Cu(II). To illustrate the importance of amide deprotonation to the catalysis, the effect of Cu(II) on the hydrolysis of glycylsarcosine methyl ester (GSOMe) in which the amide proton is replaced by a CH_3 group was studied. In this case, there is no evidence for Cu(II) catalysis. Also, the hydrolysis of GGOMe in the presence of Zn(II) was examined. While Zn(II) is known to be an effective catalyst for amino acid ester hydrolysis, it does not facilitate amide proton dissociation in dipeptides and therefore shows no significant catalysis of GGOMe hydrolysis. Kinetic studies of the ester hydrolysis of $Cu(H_{-1}GGOMe)_2$ and the glycylglycine (GG) complex $Cu(H_{-1}GG)(GGOMe)$ are also discussed and contrasted with the above results.

Transition metals have long been known to promote the hydrolysis of α-amino acid esters and their derivatives.[2] We have now extended these investigations to dipeptide esters. The present paper reports kinetic studies on the Cu(II)-promoted hydrolysis of glycylglycine methyl ester (GGOMe) and glycylsarcosine methyl ester (GSOMe) to give the corresponding dipeptides, GG and GS, and methanol. The results indicate that ionization of the amide hydrogen in GGOMe is of major importance to the Cu(II)-catalyzed hydrolysis of this ester. In contrast, there is no evidence for Cu(II) catalysis of the hydrolysis of GSOMe which has no amide hydrogen. In addition to catalyzing GGOMe hydrolysis, Cu(II) constrains the reaction to give GG as the only product, in contrast to the uncatalyzed reaction which yields the cyclized product 2,5-piperazinedione as well.[3] Thus, the presence of Cu(II) brings about some major changes in the hydrolysis of dipeptide esters.

Experimental Section

Reagents. Baker Analyzed Reagent Grade $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were used for all metal solutions, which were standardized *via* standard ion exchange techniques. Aliquots of the metal ion solutions were passed through Dowex 50W-X8 strongly acidic cation exchange resin, and the effluent solutions were titrated with standard NaOH solution using phenolphthalein as an indicator.

Glycylglycine (GG) and the hydrochloride salt of glycylglycine methyl ester were purchased from Mann Research Laboratories and were of the highest purity available. They were used without further purification. Glycylglycine solutions were standardized by pH titration. Solutions of the hydrochloride salt of glycylglycine methyl ester and glycylsarcosine methyl ester were standardized *via* ion exchange methods using Dowex 50W-X8 strongly acidic cation exchange resin. The calculated amount of hydrochloride salt based on weight and the amount obtained *via* the ion exchange technique were the same within 2%, indicating no hydrolysis of the ester occurred on the column.

Preparation of Glycylsarcosine Methyl Ester (GSOMe). Glycylsarcosine was purchased from Sigma Chemical Co. and was recrystallized three times from water–ethanol prior to use. Two grams of the dipeptide was then mixed with 25 ml of methanol, and HCl gas was bubbled into the mixture. After the glycylsarcosine dissolved, HCl addition was continued for 0.5 hr. Attempts to crystallize the hydrochloride salt of the dipeptide ester result in the formation of an oil.[4] The oil was dried under vacuum, and the solidified product was dissolved in ethanol. Crystals were obtained by adding ethyl acetate until the solution became cloudy and then cooling to −40°. The product was then recrystallized from ethanol by the addition of dioxane or ethyl acetate. The melting point of the purified dipeptide ester hydrochloride was 144.5–146°.

The infrared spectrum of the product in D_2O at pD 2.45 contained two strong carbonyl absorption maxima at 1740 and 1686 cm^{-1} corresponding to ester and amide carbonyl absorptions, respectively.[5] The proton nmr spectrum was obtained with a Varian Associates Model A-60 spectrometer on GSOMe at pD 2.45 in

(1) Fellow of the Alfred P. Sloan Foundation, 1970–1972.
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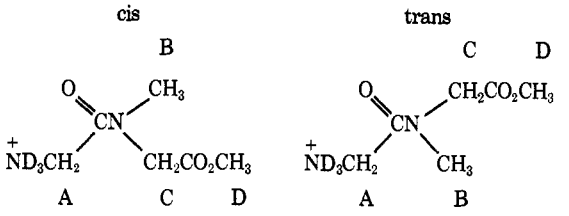
Table I. Proton Nmr Spectrum of Glycylsarcosine Methyl Ester



Assignment	cis τ	cis Rel intensity	trans τ	trans Rel intensity
B	6.88	3	6.79	12
D	6.04	3	6.10	12
C	5.92	2	5.77	8
A	5.63	*a*	5.63	*a*

[a] Peaks of cis and trans isomers are unresolved; total relative intensity is 10.

D_2O solvent using HDO (τ 5.20 to TMS) as an internal standard. Peak assignments (Table I) were based on intensities and by comparison with the known spectrum of *N*-acetylsarcosine methyl ester.[6] The large number of peaks observed is due to restricted rotation around the amide C–N bond giving rise to cis and trans isomers.

Kinetic Measurements. Rates of hydrolysis of GGOMe and GSOMe in the presence of Cu(II) and glycylglycinatocopper(II), $Cu(H_{-1}GG)$, were determined by pH-stat techniques described previously.[7] Ten milliliter solutions containing 1:1 and 2:1 ratios of ester to metal ion and enough KNO_3 to give an ionic strength of 0.05 *M* were studied in the pH range 6.5–9.0 at 25.0°. The pH meter was calibrated in terms of H^+ concentration (pH_c) as reported previously.[5]

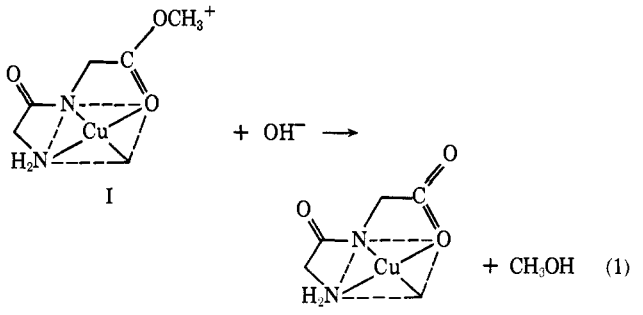
In all cases the solutions were equilibrated at 25.0° under a constant nitrogen flow. The ester solution was then added, and the pH was brought up to the desired value by addition of 0.02 *M* sodium hydroxide. The hydrolysis was then followed by automatic addition of 0.02 *M* NaOH. Pseudo-first-order rate constants were obtained by plotting log ($\%_{end} - \%_t$) *vs.* time, where $\%_{end}$ is the per cent of the total volume of NaOH delivered at the end point and $\%_t$ is the per cent delivered at any time, *t*.

Formation Constant Determinations. The procedure used to determine the formation constants of $Zn(GGOMe)^{2+}$ and $Zn(GGOMe)_2^{2+}$ is described in the previous paper.[5]

Results

1:1 GGOMe–Cu(II). Rates of ester hydrolysis in solutions containing equimolar GGOMe and Cu(II) were measured in the pH range 6.5–8.0. Infrared and pH titration studies of these solutions[5] indicated that at least 90% of the ester is coordinated to the Cu(II) in the amide deprotonated form, $Cu(H_{-1}GGOMe)^+$ (structure I), in this pH range. Although the planar deprotonated amide nitrogen moves the ester group in I into an excellent position for coordinating to the metal ion, infrared studies[5] were inconclusive as to whether the ester did or did not coordinate.

After hydrolysis the glycylglycine product is coordinated also in the deprotonated form, $Cu(H_{-1}GG)$ (structure II), as shown by Kim and Martell.[8] That this was the form of the product was confirmed by measuring the concentrations of $Cu(H_{-1}GG)$ using Kim and Martell's[8] extinction coefficient at 645 nm. The spectrally determined concentrations were always within 10% of the expected values. Thus the overall reaction is that given in eq 1. The amount



I II (1)

of NaOH consumed during the reaction was always within 6% of the theoretical value calculated from eq 1. Values of k_{obsd} (Table II) measured at various pH

Table II. Metal Ion Catalyzed Rates of GGOMe Hydrolysis at 25.0° and 0.05 *M* Ionic Strength (KNO_3)

pH_c	$10^4[Cu^{2+}]$, *M*	10^4k_{obsd}, sec^{-1}	pH_c	10^4[Cu-($H_{-1}GG$)], *M*	10^4k_{obsd}, sec^{-1}
1:1 GGOMe–Cu(II)[a]			GGOMe–Cu($H_{-1}GG$)][d]		
8.00	8.00	15.2	9.00	12.0	2.49
7.70	8.00	11.2	8.80	12.0	2.08
7.50	8.00	8.59	8.60	12.0	1.89
7.30	8.00	4.49	8.30	12.0	1.50
7.00	8.00	1.96	8.00	12.0	1.39
6.50	8.00	0.714			
6.50	8.00[b]	0.713	9.00	16.0	2.57
			8.50	16.0	1.80
			8.00	16.0	1.35
1:1 GGOMe–Zn(II)[a]			7.80	16.0	1.28
7.50	8.00[c]	0.00565			
7.30	8.00[c]	0.00321	9.00	20.0	2.61
7.20	8.00[c]	0.00268	8.50	20.0	1.84
7.00	8.00[c]	0.00182	8.00	20.0	1.44
			7.80	20.0	1.30
2:1 GGOMe–Cu(II)[a]					
9.00	4.00	2.99			
8.80	4.00	1.59			
8.60	4.00	0.957			
8.00	4.00	0.289			
7.80	4.00	0.174			

[a] [GGOMe] = 8.00×10^{-4} *M* except as noted. [b] [GGOMe] = 5.40×10^{-4} *M*. [c] Metal ion is Zn(II). [d] [GGOMe] = 4.00×10^{-4} *M*.

values and Cu(II) concentrations indicate that the reaction follows the rate law

$$\text{rate} = k_{OH}[Cu(H_{-1}GGOMe)][OH^-] \quad (2)$$

where $k_{OH} = k_{obsd}/[OH^-]$. At 25.0° and 0.05 *M* ionic strength, k_{OH} is 1.33×10^3 M^{-1} sec^{-1}. Excess Cu(II), *i.e.*, 50% more moles of Cu(II) than GGOMe, did not change k_{obsd} from that obtained with equimolar ester and metal ion.

1:1 GGOMe–Zn(II). The rates of ester hydrolysis were measured in the pH range 7.0–7.5. Potentiometric studies indicated that all of the GGOMe is complexed, but both 1:1 and 2:1 ester to Zn(II) chelates were present in this pH range. The following equilibrium constants were determined potentiometrically. Due to the number of Zn(II) complexes in

$$Zn^{2+} + GGOMe \rightleftharpoons Zn(GGOMe)^{2+} \quad \log K_1 = 2.77 \pm 0.03 \quad (3)$$

$$Zn(GGOMe)^{2+} + GGOMe \rightleftharpoons Zn(GGOMe)_2^{2+} \quad \log K_2 = 2.33 \pm 0.05 \quad (4)$$

(6) F. A. Bovey, J. J. Ryan, and F. P. Hood, *Macromolecules*, **1**, 305 (1968).
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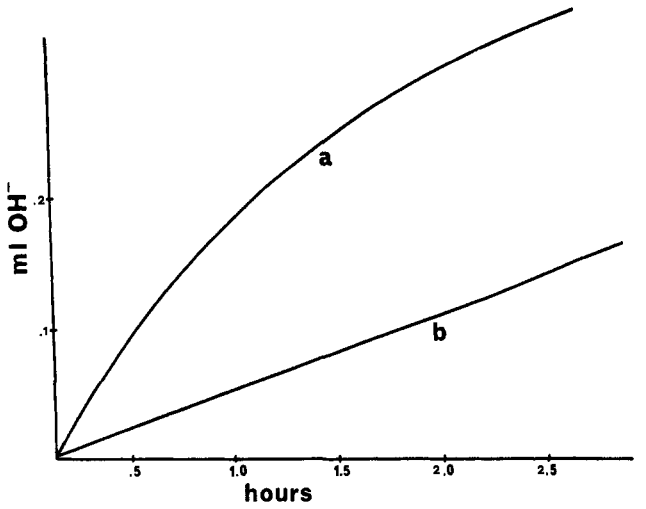


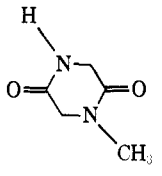
Figure 1. Hydrolysis of GSOMe in the absence and in the presence of Cu(II) at 25.0°: (a) 8.0×10^{-3} *M* GSOMe at pH 6.80, and (b) 8.0×10^{-3} *M* GSOMe, 8.0×10^{-3} *M* Cu(II) at pH 6.80.

solution, we did not establish which species are (is) catalytically active.

The pseudo-first-order rate constants (k_{obsd}) (Table II) indicate that the rate of hydrolysis is first order in total ester concentration and first order in [OH^-]. Due to the slowness of the hydrolysis, no attempt was made to follow the reaction to completion. The pseudo-first-order rate constants were obtained by using a calculated (theoretical) end point. Above pH 7.5, zinc hydroxide precipitated from the 1:1 GGOMe–Zn(II) solutions.

1:1 GSOMe–Cu(II). Since the hydrolysis of GSOMe in the presence of Cu(II) was slow and 1:1 GSOMe–Cu(II) solutions precipitated copper hydroxide above pH 6.8, no attempt was made to fully analyze the kinetic data for this system. However, in Figure 1, the observed uptake of OH^- at pH 6.80 and 25.0° is plotted *vs.* time for the hydrolysis of GSOMe both in the presence and in the absence of Cu(II). It is readily apparent that the uptake of base is slower in the presence of Cu(II) than in its absence.

Several factors, however, make it impossible to say that Cu(II) inhibits the reaction. First, the reactions probably give different products. In the absence of Cu(II), both hydrolysis to GS and cyclization to *N*-methyl-2,5-piperazinedione (III) occur as indicated

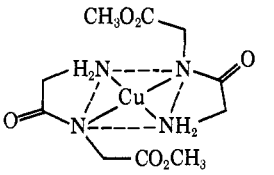


III

by an infrared study.[5] These products were also observed in similar reactions of GGOMe.[3] Since the amino group of GSOMe is protonated in the pH range studied, both hydrolysis and cyclization release one H^+ per mole of GSOMe reacting.

In the presence of Cu(II), little cyclization occurs[5] presumably because the terminal amino group is bound to the metal ion and, therefore, cannot intramolecularly attack the ester to form III. Thus Cu(II) would decrease the rate of H^+ release (and OH^- consumption) by inhibiting the cyclization reaction. In order to determine whether Cu(II) actually inhibits or catalyzes the ester hydrolysis reaction, a complete product analysis would be required.

2:1 GGOMe–Cu(II). The rates of ester hydrolysis in solutions containing 2:1 GGOMe–Cu(II) were determined in the 7.5–9.0 pH range. At these conditions of pH and concentration, the predominant form of the ester is as the amide-deprotonated ligand in the complex $Cu(H_{-1}GGOMe)_2$ (structure IV).



IV

Complete hydrolysis of the ester gave a solution containing glycylglycine in the form $Cu(H_{-1}GG)(GG)^-$, in which one ligand has lost an amide proton and the other has not. This has been shown[8] to be the predominant form of 2:1 GG–Cu(II) solutions in this pH range. Thus the reaction studied is as follows

$$Cu(H_{-1}GGOMe)_2 + OH^- \longrightarrow Cu(H_{-1}GG)(GG)^- + H_2O + 2CH_3OH \quad (5)$$

The amount of OH^- consumed during the reaction was always within 9% of the theoretical value based on this equation.

Values of k_{obsd} were evaluated from data taken during the first 50% of the reaction, since a small but noticeable rate increase occurred after 60% completion. This increase could be due to cyclization of the small amount of GGOMe present in solution resulting from equilibrium 7; it is known to cyclize rapidly at these pH conditions,[3] or it could be due to the hydrolysis of $Cu(H_{-1}GG)(GGOMe)$ which at lower pH (Table II) occurs faster than that of $Cu(H_{-1}GGOMe)_2$. The hydrolysis of $Cu(H_{-1}GGOMe)_2$ followed (Table II) the rate law

$$\text{rate} = k_{OH}[Cu(H_{-1}GGOMe)_2][OH^-] \quad (6)$$

where $k_{OH} = k_{obsd}/[OH^-]$. The value of k_{OH} at 25.0° and 0.05 *M* ionic strength is 0.0169×10^3 M^{-1} sec^{-1}.

GGOMe–Cu(H_{-1}GG). Since the hydrolysis of $Cu(H_{-1}GGOMe)_2$ (eq 3) presumably involved hydrolysis of first one ester group and then the second, a solution containing GG, GGOMe, and Cu(II) would exist when half of the ester groups had hydrolyzed. Thus to study the latter stage of this reaction, GGOMe was studied in the presence of GG and Cu(II) in the 7.8–9.0 pH range. Under these conditions, GG is coordinated to Cu(II) in the form $Cu(H_{-1}GG)$, structure II. This complex binds GGOMe as established by pH titration and infrared studies,[5] according to the equilibirium

$$Cu(H_{-1}GG) + GGOMe \rightleftharpoons Cu(H_{-1}GG)(GGOMe) \quad (7)$$
$$\log K_2' = 2.4 \pm 0.1$$

Because of ester hydrolysis during the pH titrations, the value of K_2' is less accurate than desired; it nevertheless indicates that significant amounts of GGOMe are bound to the $Cu(H_{-1}GG)$ complex.

The product of the hydrolysis was $Cu(H_{-1}GG)(GG)^-$, as noted above. The rate of hydrolysis (Table II) of 4.0×10^{-4} *M* GGOMe in the presence of 12.0×10^{-4} *M* to 20.0×10^{-4} *M* $Cu(H_{-1}GG)$ was independent of the $Cu(H_{-1}GG)$ concentration suggesting that under these conditions, equilibrium 7 lies far to the right. This is qualitatively supported by the approximate equilibrium constant for that reaction. Thus the net hydrolysis reaction is

$$Cu(H_{-1}GG)(GGOMe) + OH^- \longrightarrow Cu(H_{-1}GG)(GG)^- + H_2O + CH_3OH \quad (8)$$

The amount of OH^- consumed during the kinetic studies corresponded within 10% to that calculated on the basis of this equation.

Values of k_{obsd} for reaction 8 follow a two-term rate expression

$$\text{rate} = (k_1 + k_{OH}[OH^-])[Cu(H_{-1}GG)(GGOMe)] \quad (9)$$

where $k_1 + k_{OH}[OH^-] = k_{obsd}$. From a plot of k_{obsd} *vs.* $[OH^-]$, the intercept and slope gave values for k_1 (1.23×10^{-4} sec^{-1}) and k_{OH} (9.8 M^{-1} sec^{-1}) at 25.0° and 0.05 *M* ionic strength.

Discussion

The rate of hydrolysis of $Cu(H_{-1}GGOMe)$ to form $Cu(H_{-1}GG)$ according to eq 1 is first order in the ester complex and first order in OH^-. A logical mechanism for the reaction is initial coordination of the ester group to the Cu(II) (if it is not already coordinated) followed by rate-determining OH^- attack at the ester carbon. It is not possible to distinguish experimentally between this mechanism and one in which the Cu(II) first binds OH^-, which then attacks the ester intramolecularly. To simplify the discussion, it will be assumed that the reaction occurs by external OH^- attack. In terms of this mechanism, the experimental rate constant, k_{OH}, is the product of the equilibrium constant for ester coordination and the rate constant for OH^- attack. This value is given in Table III and compared with other base hydrolysis rate constants for related ester derivatives.

Table III. Comparison of Ester Hydrolysis Rates at 25.0°

Ester	k_{OH}, M^{-1} sec^{-1}	Ref
$NH_2CH_2CO_2Et$	0.63	13
$NH_2CH_2CONHCH_2CO_2Et$	0.63	3
$Cu(NH_2CH_2CO_2Et)^{2+}$	7.6×10^4	9
$Zn(NH_2CH_2CO_2Et)^{2+}$	2.3×10^4	10
$Cu(H_{-1}GGOMe)^+$	1.3×10^{3} [a]	
$Cu(H_{-1}GGOMe)_2$	17[a]	
$Cu(H_{-1}GG)(GGOMe)$	9.8[a]	

[a] Since methyl esters hydrolyze about two times faster than their ethyl analogs, these values should be divided by two for comparison with the Et derivatives.

It is obvious that coordination of GGOMe to Cu(II) as $Cu(H_{-1}GGOMe)^+$ has enhanced the rate of hydrolysis as compared to the free ester by a factor of approximately 1000.

Essential to this catalysis is the deprotonation and coordination of the amide nitrogen atom which positions the ester group adjacent to the metal ion. To further confirm the importance of amide deprotonation, a metal ion (Zn(II)) which does not assist proton ionization[9] from the amide group was studied. If proton dissociation were unnecessary for catalysis, Zn(II) should be nearly as good a catalyst as Cu(II), as it is in other ester hydrolyses. Thus the rates of hydrolysis of glycine ethyl ester with Zn(II)[10] are only about one-third those with Cu(II),[11] Table III. Similarly *N,N*-di(carboxymethyl)glycine ethyl ester hydrolyzes about one-third as fast when coordinated to Zn(II) as compared to that with Cu(II).[12]

Because 1:1 GGOMe–Zn(II) solutions contained both $Zn(GGOMe)^{2+}$ and $Zn(GGOMe)_2^{2+}$, the observed first-order dependence on ester and OH^- cannot be readily assigned to a mechanism. On the other hand, a comparison of observed rate constants at a given pH for the hydrolysis in the absence and presence of Zn(II) shows that the metal ion has little effect on the hydrolysis rate. For example, at pH 7.0, k_{obsd} in the absence of metal ion for GGOEt hydrolysis[3] is 6.3×10^{-8} sec^{-1}; this compares with 18×10^{-8} sec^{-1} for GGOMe in the presence of equimolar Zn(II). Since Me esters hydrolyze twice as fast[13] as their Et analogs, Zn(II) has increased the rate by a factor of only 1.5. In these comparisons, we have assumed that the ester undergoes no cyclization since it is all coordinated to the Zn(II) *via* the amino group and amide carbonyl oxygen atom. If some cyclization were occurring, this would reduce the effect of Zn(II) still further. Regardless of the precise magnitude of the Zn(II) effect, it is extremely small as compared to the 1000-fold rate enhancement caused by Cu(II). This evidence strongly supports the necessity for amide proton ionization for metal ion catalysis to occur.

One further test was to use a very similar dipeptide ester which had no amide proton as in glycylsarcosine methyl ester (GSOMe). Unfortunately, this ester undergoes hydrolysis and cyclization more rapidly than GGOMe, and it forms a mixture of $Cu(GSOMe)^{2+}$ and $Cu(GSOMe)_2^{2+}$ in solutions containing Cu(II). However, kinetic runs in the absence and presence of Cu(II) at the same pH clearly show (Figure 1) that the rate of OH^- uptake is *slower* in the presence of Cu(II) than in its absence. Because the ratio of hydrolysis to cyclization is probably different (see Results section) with and without Cu(II), it is not possible to say that Cu(II) inhibits the reaction, but if there is any catalysis, it must be small indeed.

Finally, little ester catalysis should be observed when access to the Cu(II) is blocked by other ligands. Therefore, in $Cu(H_{-1}GGOMe)_2$ (structure IV) where all four square-planar sites are occupied, the only possible sites for ester–copper(II) binding are in the weak axial positions. As expected, the value of k_{OH} (Table III) is substantially smaller. The value of k_{OH} (Table III) is still smaller for $Cu(H_{-1}GG)(GGOMe)$ where the ester amide is not deprotonated[5] and coordination of GGOMe presumably occurs through the amino group and amide carbonyl oxygen. The small acceleration (*ca.* eight times faster than the free ester) here cannot

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(10) J. E. Hix, Jr., and M. M. Jones, *Inorg. Chem.*, **5**, 1863 (1966).
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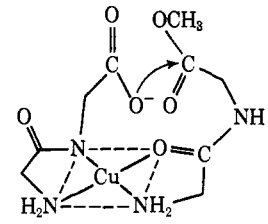
(12) B. E. Leach and R. J. Angelici, *J. Amer. Chem. Soc.*, **90**, 2504 (1968).
(13) R. J. Angelici and D. Hopgood, *J. Amer. Chem. Soc.*, **90**, 2514 (1968).

result from coordination of the ester group to the Cu(II). This may be due to electron withdrawal from the ester *via* the two coordinating atoms.

Unlike the hydrolysis of GGOMe in the other Cu(II) complexes, a fairly large fraction of its hydrolysis in Cu(H_{-1}GG)(GGOMe) proceeds *via* a OH^- independent pathway (k_1, see Results). This could be ascribed to H_2O rather than OH^- attack in the mechanism described earlier. By dividing k_1 by 55 *M* for water and comparing this constant with k_{OH}, one finds that the ratio of rates for OH^- to H_2O attack is approximately 5×10^6. This is significantly lower than is usually observed (10^9–10^{11}) for these two nucleophiles in the hydrolysis of carboxylic acid esters.[13] Hence the unusually high value of k_1 implies that another hydroxide-independent mechanism may be occurring. One speculative possibility is an intramolecular attack of the H_{-1}GG carboxylate group on the ester group as shown in structure V. If Cu(H_{-1}GG)(GGOMe) has the cis geometry as shown in V, the $-CO_2^-$ and $-CO_2CH_3$



V

groups are in an ideal position for such an attack to occur as shown by molecular models. The anhydride intermediate formed as a result of the intramolecular attack would then rapidly hydrolyze to give the observed product, Cu(H_{-1}GG)(GG)$^-$.

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Chemical and Structural Studies of the $B_{10}C_2H_{12}^{2-}$ Ions Produced from Icosahedral $B_{10}C_2H_{12}$ Carboranes

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Abstract: The isomeric 1,2-, 1,7-, and 1,12-$B_{10}C_2H_{12}$ carboranes and some of their derivatives can be reduced with sodium to form $B_{10}C_2H_{12}^{2-}$ ions which can be subsequently protonated to yield (13)-9,11-$B_{10}C_2H_{13}^-$ ion, (13)-7,10-$B_{10}C_2H_{13}^-$ ion, and derivatives of the (13)-7,10-$B_{10}C_2H_{13}^-$ ion. The (13)-9,11-$B_{10}C_2H_{13}^-$ ion can be thermally rearranged to the (13)-7,10-$B_{10}C_2H_{13}^-$ ion. Pyrolysis of $(CH_3)_4N^+$(13)-7,10-$B_{10}C_2H_{13}^-$ produced $(CH_3)_3N \cdot BH_2$-1,2-$B_{10}C_2H_{11}$ and $(CH_3)_4N^+$(12)-7,9-$B_9C_2H_{12}^-$.

The reduction of the icosahedral $B_{10}C_2H_{12}$ carboranes with sodium to produce $B_{10}C_2H_{12}^{2-}$ ions has been reported by several workers.[1-4] Even though the $B_{10}C_2H_{12}^{2-}$ ions have not been isolated in pure form they have been shown to undergo, *in situ*, three general types of reactions. First, in accord with the prediction of Hoffmann and Lipscomb[5] that anionic *m*- and *p*-carborane species should be comparable in stability to the ortho ion and a reversal in the ortho → meta transformation may become possible, it is known that such rearrangements occur in the $B_{10}C_2H_{12}^{2-}$ series. For example, the resultant $B_{10}C_2H_{12}^{2-}$ ion from the reduction of 1,12-$B_{10}C_2H_{12}$ can be oxidized to produce 1,7-$B_{10}C_2H_{12}$.[3,4]

$$1,12\text{-}B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{[O]} 1,7\text{-}B_{10}C_2H_{12}$$

Similarly the oxidation of the $B_{10}C_2H_{12}^{2-}$ ion produced from 1,7-$B_{10}C_2H_{12}$ yields 1,2-$B_{10}C_2H_{12}$.[2]

$$1,7\text{-}B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{[O]} 1,2\text{-}B_{10}C_2H_{12}$$

Finally the oxidation of the $B_{10}C_2H_{12}^{2-}$ ion produced from 1,2-$B_{10}C_2H_{12}$ yields 1,2-$B_{10}C_2H_{12}$.[2]

$$1,2\text{-}B_{10}C_2H_{12} \underset{[O]}{\overset{+2e^-}{\rightleftharpoons}} B_{10}C_2H_{12}^{2-}$$

Thus the 1,2 → 1,7 → 1,12 order of thermal rearrangement[1] observed for the neutral $B_{10}C_2H_{12}$ carboranes is reversed in order, 1,12 → 1,7 → 1,2, in the dianion series.[2-4] A second general reaction of the $B_{10}C_2H_{12}^{2-}$ ions involves their complexation by transition metal ions to form a series of unique 13-vertex polyhedral

$$4B_{10}C_2H_{12}^{2-} + 3Co^{2+} \longrightarrow 2[(B_{10}C_2H_{12})_2Co^{III}]^- + Co^0$$

metallocarboranes[6,7] in which the transition metal atom occupies a vertex position. A third general

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