On the Differing Acidities of Tri- *vs.* Tetradentate Copper(II) Chelates and its Effects on their Catalytic Properties

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Hydroxo complex formation constants for a series of Cu(II) chelates have been determined, and Bronsted plots of the log of the rate constants of Cu(L)$^{x+}$ promotion of methyl glycinate hydrolysis vs. the log of the hydroxo complex formation constants indicate that the different catalytic activities of tri vs. tetradentate Cu(II) chelates are mainly due to ground state effects, i.e., differences in the Lewis acidities of the two sets of metal chelates.

Previously proposed rate profiles for Cu(L)$^{x+}$ promotion of methyl glycinate hydrolysis are in agreement with these data and are also dicussed in terms of the differing Lewis acidities of the Cu(II) chelates. Correlations of λ_{max} values for tridentate Cu(II) chelates were found with both the log of the rate constant for Cu^{2+} complex-catalysis of methyl glycinate hydrolysis and with the log of the hydroxo-metal-complex formation constants.

Introduction

Over the past few years [1–4], experiments in this laboratory were designed to investigate the effects of auxiliary ligands on the ability of a metal ion to promote a chemical reaction, specifically, the hydrolysis of amino acid esters. Both the Lewis acidities and the total charge of the metal chelates were found to be important in determining the catalytic activities toward ester hydrolysis [1, 4]. Surprisingly, different isokinetic lines were found for a series of tri- and tetradentate-Cu(II) chelate-promoted hydrolysis of methyl glycinate [4]. Therefore, we decided to seek parameters of tri- and tetradentate Cu(II) chelates that are predictive of their differing catalytic behaviors toward methyl glycinate hydrolyses.

Previously, Angelici *et al.* [5] have shown that correlations although not necessarily linear ones exist between the rate constant of amino acid ester hydrolysis and both the log of the formation constant of the Cu(II) chelate (eqn. 1) and the log of

$$Cu^{2+} + L^{x-} \rightleftharpoons CuL^{(2-x)+} \tag{1}$$

the formation constant for the mixed ligand metal chelate (eqn. 2).

$$CuL^{(2-x)+} + MeGly \rightleftharpoons CuL(MeGly)^{(2-x)+} \tag{2}$$

However, neither of these correlations gave any indication of the differing isokinetic temperatures for tri- and tetradentate-Cu(II)-chelate-promoted hydrolyses of MeGly. In this study, hydroxo complex formation constants (eqn. 3) were used as a measure of the Lewis acidities of various Cu(II) chelates. The

$$CuL^{(2-x)+} + OH^- \rightleftharpoons CuL(OH)^{(1-x)+} \tag{3}$$

results indicate that there is a basic difference in the Lewis acid properties of tri- *vs.* tetradentate Cu(II) chelates. This difference in acid properties is used to explain their differing catalytic properties toward MeGly hydrolysis.

Experimental Section

Reagents

Baker Analyzed reagent grade Cu(NO$_3$)$_2$·3H$_2$O was used for all metal solutions, which were standardized *via* standard ion-exchange techniques. Aliquots of the metal ion solution were passed through Dowex 50W-X8 strongly acidic cation-exchange resin, and the effluent solutions were titrated with standard NaOH solutions using phenolphthalein as an indicator [6].

The trihydrochloride salt of 2,2′,2″-triaminotriethylamine (tren·3HCl) was purchased from Strem Chemicals, Inc. Nitrilotriacetic acid (NTA) was purchased from ICN Pharmaceuticals, and terpyridine (terpy) was purchased from K and K Laboratories. The above compounds were of the highest purity available and were used without further purification. Solutions of Cu^{II}terpy were prepared by addition of weighed amounts of ligand, that had been dried overnight in a desiccator (H$_2$SO$_4$) at 50 °C, to metal ion solutions. The trihydrochloride salts of

TABLE I. Formation Constants (K_L) of Cu(L)$^{x+}$ chelates, Hydroxo Formation Constants (K_{OH}) of Cu(L)$^{x+}$ Complexes, Mixed Ligand Formation Constants with Methyl Glycinate (K_x) with Cu(L)$^{x+}$, Second Order Rate Constants for Cu(L)$^{x+}$ Promoted Hydrolyses of MeGly (k_{OH}) at 25 °C and 0.1 M KNO$_3$, and λ_{max} Values for [Cu(L)$^{x+}$] Complexes.

M-Chelate	log K_L	log k_{OH}	log K_x	log K_{OH}[a]	λ_{max} (nm)
Cu(tren)$^{2+}$	18.8[b]	0.05[b]	2.40[b]	4.44 (4.65)[c]	860[d]
Cu(DTMA)$^+$	18.07[e]	0.83[f]	2.48[f]	4.25 (4.57)[e]	710[g]
Cu(PAA)	13.8[f]	2.25[f]	2.79[f]	4.34 (4.39)[h]	670[g]
Cu(NTA)^n	13.05[i]	2.50[j,k]	2.88[j,l]	4.20 (4.39)[j]	775, 880[d]
Cu(DPA)$^{2+}$	14.4[m]	2.06[m]	2.81[m]	5.05 (5.10)[m]	637[m]
Cu(dien)$^{2+}$	15.91[n]	1.39[o]	2.5$2^p$	4.67 (4.6 ± 0.1)[p]	611[d]
Cu(terpy)$^{2+}$	13.4[b]	2.28[b]	3.21[b]	5.71	680[g]
Cu(IMDA)	10.63[q]	4.50[r]	3.1$9^s$	6.26[r]	730[g]

[a]All standard deviations are ±0.01 log units except that for [Cu(terpy)$^{2+}$], ±0.02.   [b]Reference 3.   [c]Reference 13.   [d]Reference 18.   [e]Reference 14.   [f]Reference 4.   [g]Reference 17.   [h]Reference 11.   [i]J. Stary, *Anal. Chim. Acta, 28*, 132 (1963). [j]D. Hopgood and R. J. Angelici, *J. Am. Chem. Soc., 90*, 2508 (1968).   [k]I = 0.073 M (KNO$_3$),   [l]I = 0.077 M (KNO$_3$). [m]Reference 5.   [n]J. W. Allison and R. J. Angelici, *Inorg. Chem., 10*, 2233 (1971).   [o]R. J. Angelici and J. W. Allison, *Inorg. Chem., 10*, 2238 (1971).   [p]Reference 12.   [q]G. Anderegg, *Helv. Chim. Acta, 47*, 1801 (1964).   [r]B. E. Leach and R. J. Angelici, *Inorg. Chem., 8*, 907 (1969).   [s]For n-BuGly.

diethylenetriamine (dien·3HCl) and bis(2,2'-amino-methylpyridyl)amine (DPA) were prepared as described previously [4]. The trihydrobromide salt of N,N-bis(2-aminoethyl)glycine (DTMA·3HBr) was prepared according to Collman [7] as modified by Martell *et al.* [8]. N-methylpyridylaspartic acid (PAA) was a gift from Professor R. J. Angelici.

Solutions of dien·3HCl, MeGly·HCl, tren·3HCl and DPA·3HCl were standardized by standard ion-exchange techniques using Dowex 50W-X8 strongly acidic cation-exchange resin. Solutions of PAA, DTMA·3HBr, and NTA were standardized *via* potentiometric titration using glass and calomel electrodes.

Potentiometric Measurements

A Corning Digital 112 Research Model pH meter was used to determine hydrogen ion concentration for potentiometric titrations. The concentration of all solutions was approximately 2.5×10^{-3} M in Cu^{2+}. All titrations were performed in a double-walled titration cell of 50 ml capacity. The temperatures of all solutions were maintained at ±0.05 °C by circulating thermostatted water through the outer jacket of the cell. The cell was fitted with glass and calomel extention electrodes, a microburet delivery tube, and a nitrogen inlet tube. Ionic strengths of all solutions were maintained at 0.1 M by the addition of an appropriate amount of 1.0 M KNO$_3$. The solutions were stirred with a magnetic stirrer, and all titrations were done in triplicate. The glass electrode was calibrated to read directly $-\log$ [H$^+$] according to the method of Rajan and Martell [9] using standard HCl and NaOH solutions.

Hydroxo (eqn. 3) formation constants were determined *via* Bjerrum's method [10].

Results and Discussion

Monohydroxo complex formation constants (eqn. 3) of Cu(NTA)$^-$, Cu(PAA), Cu(DTMA)$^+$, Cu(tren)$^{2+}$, Cu(terpy)$^{2+}$, Cu(dien)$^{2+}$, and Cu(DPA)$^{2+}$ were determined at 25 °C and an ionic strength of 0.10 M (KNO$_3$) and are listed in Table I. In no case did the titration data indicate that the formation of dihydroxo or polymeric metal species was concomitant with the reaction in eqn. 3 at the pH values studied.

Monohydroxo complex formation constants for [Cu(DPA)$^{2+}$] [5], [Cu(PAA)] [11], and [Cu(dien)$^{2+}$] [12] are in agreement with published values; however, the values for [Cu(NTA)$^-$] [13], [Cu(tren)$^{2+}$] [15], and [Cu(DTMA)$^+$] [14] are all somewhat lower than literature values, with the largest difference, a factor of 2, occurring for [Cu-(DTMA)$^+$]. Literature values for [Cu(tren)$^{2+}$] and [Cu(DTMA)$^+$] are $10^{4.65}$ and $10^{4.57}$ M^{-1}. On the basis of metal–ligand formation constants (Table I) which indicate that both [Cu(tren)$^{2+}$] and [Cu-(DTMA)$^+$] are >100 times as stable as [Cu(dien)$^{2+}$], ($10^{4.6}$ M^{-1}) it would seem that the least stable metal complex would have the highest Lewis acidity and should therefore most easily form a hydroxo complex. Furthermore [Cu(DTMA)$^+$] has a +1 charge while [Cu(dien)$^{2+}$] has one of +2, which again suggests the latter complex would more easily undergo reaction with OH$^-$. [Cu(tren)$^{2+}$] has four amine donors as compared to three for [Cu(dien)$^{2+}$] sug-
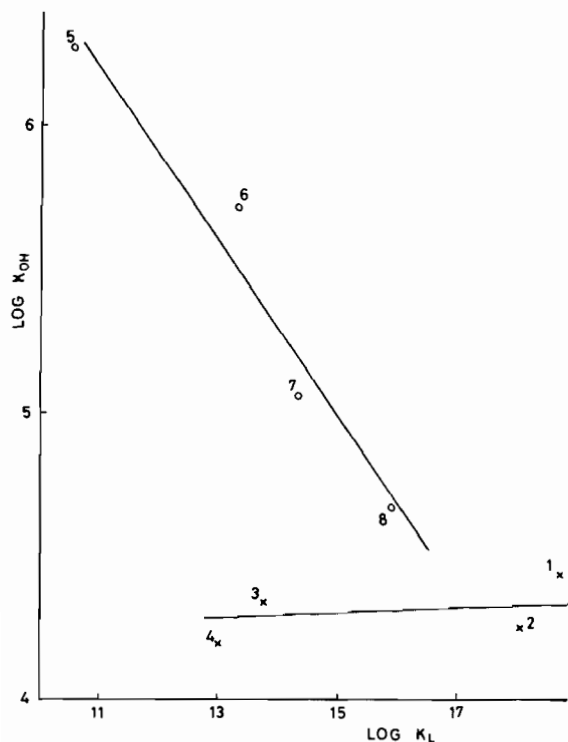
Fig. 1. Plot of log of the hydroxo complex formation constant of a series of $Cu(L)(OH)^{(x-1)+}$ chelates *vs.* log of the formation constants of $Cu(L)^{x+}$: 1, $Cu(tren)^{2+}$; 2, $Cu(DTMA)^+$; 3, $Cu(PAA)$; 4, $Cu(NTA)^-$; 5, $Cu(IMDA)$; 6, $Cu(terpy)^{2+}$; 7, $Cu(DPA)^{2+}$; 8, $Cu(dien)^{2+}$.

Fig. 2. Plots of log of the rate constant (log k_{OH}) of MeGly hydrolysis, log of the hydroxo complex formation constant, and log of the formation constant *vs.* λ_{max} for a series of tridentate Cu(II) chelates: 1, $Cu(dien)^{2+}$; 2, $Cu(DPA)^{2+}$; 3, $Cu(terpy)^{2+}$; 4, $Cu(IMDA)$. O'_3, represents log k_{OH} *vs.* λ_{max} for $Cu(terpy)^{2+}$.

gesting that the latter complex would be a better acid than the former one. Based on these reasons, we believe our values to be more correct; however, the arguments which follow are independent of the set of monohydroxo complex formation constants one chooses to use (Table I).

In Fig. 1, the log K_{OH} (eqn. 3) is plotted *vs.* the log of the formation constant (K_L, eqn. 1). From this plot it is evident that for tridentate Cu(II) chelates log K_{OH} values decrease as those for log K_L increase. This trend is readily explained in that the strongest binding ligands, *i.e.*, with the greater σ-donor strengths, will be most effective at reducing the Lewis acidities of the Cu(II) chelates. Thus, $[Cu(L)-OH^{(x-1)+}]$ complex formation is promoted by weakly donating L ligands and is inhibited by strong donors, *i.e.*, $-NH_2$.

However, in Fig. 1, log K_{OH} for tetradentate Cu(II) chelates appears to be independent of log K_L, the formation constant of the metal chelates, which is in contrast to the tridentate Cu(II) chelates. Apparently the donor strengths of the ligand are more important than charge effects in tridentate Cu(II) chelates but not in the tetradentate series, which could account for the differing slopes in Fig. 1. At first this is surprising, but the tetradentate com-
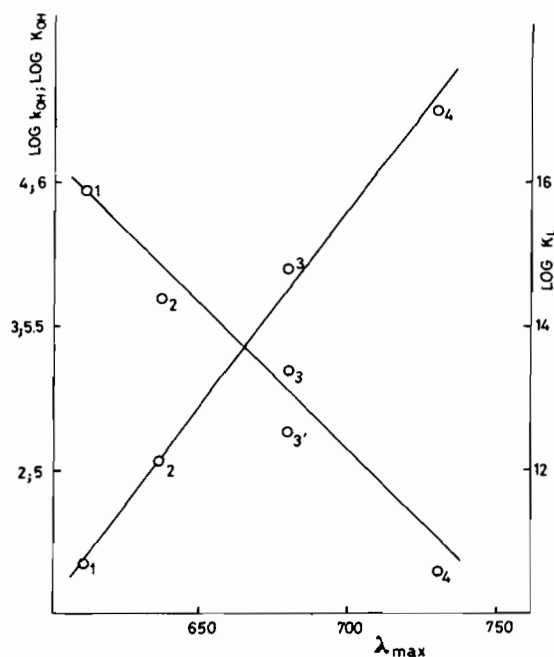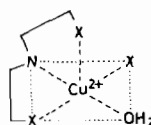
plexing agents are all tripodal in nature and probably involve the coordination of an arm of the chelating agent to an axial site of Cu(II)(I). It has long been known that such coordination results in a red shift of the Cu(II) band in the visible spectra and has been

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dubbed the 'pentaammine effect'. Dramatic evidence of the 'red shift' has been reported by Bjerrum [15] and Hall, *et al.* [16]. The visible data in Table I demonstrates that the 'pentaammine effect' is operative in the tetradentate Cu(II) chelates in this study. $[Cu(IMDA)]$ absorbs at 730 nm [17], while $[Cu(NTA)^-]$ with almost identical groups coordinated in the square plane of Cu(II) but a carboxylate group coordinated to an axial site absorbs at 775 and 880 nm [18]. $[Cu(dien)^{2+}]$ absorbs at 611 nm [18] but $[Cu(DTMA)^+]$, and $[Cu(tren)^{2+}]$ having almost identical donors in the square plane but a carboxylate and amino group, respectively, coordinated to an axial site absorb at 710 [17] and 860 nm [18], respectively. It is interesting to note that the $\Delta\lambda_{max}$ value for coordination of a strong σ-donor (NH_2) to an axial Cu(II) site is ~250 nm as compared to

only ~100 nm for the weak σ-donor, COO$^-$. These shifts must be due to a reordering of the d orbitals of Cu(II), which probably results in a less strongly bound water molecule in the equatorial plane of Cu(II).

This would explain the fact that tridentate Cu(II) chelates have higher K_{OH} values than those of the tetradentate complexes even though some of the tridentate Cu(II) chelates have higher formation constants (K_L values, eqn. 1) than those of tetradentate Cu(II) complexes. The latter point is important in that apparently coordination of an arm of the chelating agent to an axial site of Cu(II) has a more pronounced effect on the acid properties (eqn. 3) of Cu(II) chelates than the replacement of weak σ-donors, e.g., $-COO^-$, by stronger ones, e.g., $-NH_2$.

Further evidence can be seen in Fig. 2, where relationships between visible λ_{max} values of tridentate Cu(II) chelates exhibit good correlations with log K_L (eqn. 1) and log K_{OH} (eqn. 3) values, while tetradentate Cu(II) chelates (not shown for reasons of clarity) do not. Since shifts in λ_{max} are very sensitive to changes in σ-donor strengths and not to changes in total charge [19], this suggests that K_L and K_{OH} values for tridentate Cu(II) chelates are primarily dependent on donor strengths of coordinated atoms and to a much lesser degree on charge effects. Since the above two correlations do not hold for tetradentate-tripod Cu(II) chelates, one must assume that in these systems charge effects must be at least more comparable in magnitude to that of σ-donor effects. Otherwise, the tetradentate Cu(II) complexes would be expected to exhibit correlations similar to the tridentate series. As mentioned previously, the coordination of a chelate arm to an axial Cu(II) site results in weakening of the $Cu-OH_2$ equatorial bond as shown by K_{OH} values listed in Table I. Therefore, the other equatorial donor$-Cu(II)$ bonds probably are also weakened by axial coordination, resulting in a decreased dependence of K_L values on σ-donor strengths and necessarily an increased dependence on charge effects. This would explain the relative independence of K_{OH} values (Table I) of tripod-tetradentate Cu(II) chelates to σ-donor strengths i.e., a factor of only 2 considering 4 amine donors in tren vs. 1 amine and three oxygen ones in NTA. Therefore, charge effects (found in the $\Delta S°$ term) and σ-donor effects (found in the $\Delta H°$ term) essentially cancel each other out, resulting in fairly constant values for a series in which nitrogen and oxygen donors are varied from 1 to 4.

### Correlation of log K_{OH} and log k_{OH} for MeGly Hydrolysis

Overall rates of Cu(II)-chelate-catalyzed hydrolyses of MeGly have been shown [20] to be dependent upon both the degree of coordination of ester coordination (K_x) (eqn. 2) and the rate cons-

tant (k_{OH}) for hydrolysis of the coordinated ester eqn. 4. As has been noticed previously the degree

$$Rate = k_{OH}[Cu(L)MeGly][OH^-] \qquad (4)$$
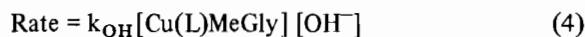
of ester coordination (K_x) (eqn. 2) depends on the coordinating ability of the ligand L bound to Cu(II). It was shown [5] that ester coordination (i.e., K_x) decreased as the coordination of L (i.e., K_L (eqn. 1)) increased. From the data in Table I it seems clear that CuL^{x+} complexes with the most strongly coordinating L ligand 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 in the overall hydrolysis is the loss of H_2O from the coordination sphere of Cu(II) and subsequent binding of the ester carbonyl oxygen
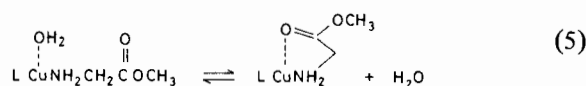
(eqn. 5). The loss of H_2O from a binding site on Cu(II) should be dependent on the Lewis acid character of the metal complex. The lower the Lewis acidity of the metal complex, the greater the rate of H_2O loss. Therefore, metal complexes with the most strongly coordinating L ligands should have the highest rate of H_2O loss.

The third step in the overall hydrolysis is the external attack by OH$^-$ on the coordinated ester carbonyl carbon (eqn. 6).

$$LCuMeGly + OH^- \rightarrow LCuGly^- + MeOH \qquad (6)$$
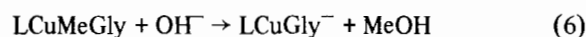
The more strongly the ester carbonyl oxygen is bound to the Cu(II), the greater the degree of polarization of the ester carbonyl group and therefore, the greater the rate of OH$^-$ attack. Therefore, the most strongly coordinated L ligands should result in the weakest binding of the ester carbonyl oxygen. This is a result of the reduced Lewis acidity of the metal chelates with the strongest σ-donor groups.

Therefore, all three steps in the Cu(II)-complex-promoted hydrolysis of MeGly have a dependency on the Lewis acidity of the metal chelate. Previously, we have noticed [4] that a series of Cu(II)-complex-promoted hydrolyses of MeGly yielded two isokinetic lines, one for tridentate Cu(II) and one for tetradentate Cu(II) complexes. Although all of the hydrolyses follow the same rate law, we proposed [4] two different rate profiles to explain the two isokinetic lines. The tridentate Cu(II) chelates fall on the same isokinetic line as do the metal complexes of ethyl
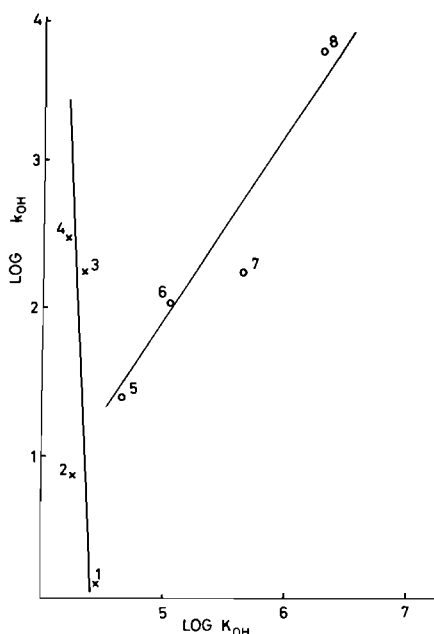
Fig. 3. Bronsted plots of the log of the rate constant (log k_{OH}) of MeGly hydrolysis for a series of $Cu(L)^{x+}$ *vs.* log of the hydroxo complex formation: 1, $Cu(tren)^{2+}$; 2, Cu-$(DTMA)^+$; 3, Cu(PAA); 4, $Cu(NTA)^-$; 5, $Cu(dien)^{2+}$; 6, $Cu(DPA)^{2+}$; 7, $Cu(terpy)^{2+}$; 8, Cu(IMDA).

N,N-diacetoxyglycinate whose hydrolyses have been shown to correlate directly with the rates of H_2O exchange, *i.e.*, $Cu(II) > Zn(II) > Co(II) > Ni(II)$ [2]. Therefore, the second step in the overall mechanism (*i.e.*, loss of H_2O and the ester carbonyl binding) is considered to be most important.

On the other hand, the tetradentate Cu(II)-chelate-promoted hydrolyses of MeGly fall on the same isokinetic line as those of methylglycinate complexes of M-nitrilotriacetates. In this case the rates of the hydrolyses do not correlate with the rates of H_2O exchange, *i.e.*, $Cu(II) > Ni(II) > Zn(II) > Co(II)$ [1]. Therefore, it was proposed that the third step (attack by OH^-) is predominant in these metal-chelate-catalyzed systems. This explanation also is in agreement with the observed isokinetic temperatures for the tri- and tetradentate Cu(II)-complex-catalyzed hydrolyses: 392 K (electronic effects are dominant) and 274 K (solvent effects are dominant) respectively.

Since the two series of Cu(II) complexes, tridentate and tetradentate, yield two different isokinetic lines for the hydrolysis of MeGly, there ought to exist thermodynamic and/or spectral parameters that would be predictive of the two differing behaviours. As has been discussed previously, Fig. 1 indicates that the tridentate Cu(II) chelates yield a different slope than do those containing tetradentate donors. Hydroxo complex formation is clearly a measure of

the acidities of the metal complexes and Fig. 1 indicates the differing acid character of the two sets of metal chelates. Therefore, it is not surprising that the metal complexes yield differing isokinetic temperatures for the promotion of MeGly hydrolysis since catalysis is clearly dependent on the Lewis acidities of the metal chelates.

The above is confirmed in Fig. 3, where Bronsted plots clearly indicate the log k_{OH} values for MeGly hydrolyses appear to be independent of log K_{OH} values for the tetradentate Cu(II) chelates, but the tridentate Cu(II) chelates exhibit a good correlation. This can also be seen in Fig. 2 in that there appears to be a good correlation between λ_{max} for tridentate Cu(II) chelates and log k_{OH} for MeGly catalyzed hydrolysis. Only the point for [Cu-$(terpy)^{2+}$] appears off the line, and we offer no explanation for this. These correlations can be explained, as others above, in that K_{OH}, k_{OH} and λ_{max} values for tridentate Cu(II) chelates are mostly dependent on σ-donor strengths (ΔH°, ΔH^*) of the ligands, whereas K_{OH} and k_{OH} values for tetradentate tripod Cu(II) complexes are dependent on both σ-donor strengths (ΔH°, ΔH^*) and charge effects (ΔS°, ΔS^*).

These data are in agreement with our previous hypothesis of differing rate profiles for tri- and tetradentate Cu(II)-chelate-catalyzed hydrolysis of MeGly [4]. The tridentate Cu(II) complexes are proposed to have a rate profile in which H_2O loss is responsible for most of ΔG^*. The breaking of a $Cu-OH_2$ bond should be mostly enthalpic in nature and not dependent on the total charge of the metal complex. Therefore, one would expect a direct correlation between log K_{OH} and log K_L and log K_{OH} and log k_{OH} as is observed. However, tetradentate Cu(II)-chelate-catalyzed hydrolyses are proposed to have a rate profile in which OH^- attack on the metal-bound ester is responsible for most of ΔG^*. Attack by OH^- should therefore, be enthalpic and entropic dependent, *i.e.*, affected by both the strength of the metal-binding ester of carbonyl oxygen and by the total charge on the metal complex. As expected, there is no correlation for log k_{OH} with log K_{OH} for the tetradentate Cu(II) chelates.

In summary, we have shown that tri- and tetradentate Cu(II) chelates have differing Lewis acid properties, that they result in differing catalytic properties toward MeGly hydrolysis, and that previous arguments concerning differing rate profiles for Cu(II)-catalyzed-hydrolyses of MeGly can be understood in terms of the acid properties of the metal complexes.

Acknowledgements

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19 R. Nakon, E. M. Beadle, Jr., and R. J. Angelici, *J. Am. Chem. Soc., 96,* 719 (1974). The donor groups (2 amino and 2 carboxylate) of bisprolinato-Cu(II) (neutral), bis-(3-[(carboxymethyl)thio]-*L*-alaninato Cu(II) and di-, mono-, and unprotonated derivatives of bis(3-[2-amino-ethyl)thio]-*L*-alaninato Cu(II) are all identical. The λ_{max} values of the various metal chelates, despite a total charge variance of +2 to −2 are all identical.