Formation and Scission of the Imidazolate-bridge Linkage in Binuclear Copper(II) Complex with Glycylglycine as a Function of pH in Aqueous Solution

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Abstract

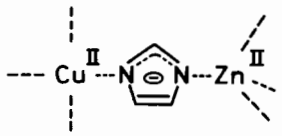
The formation and scission of the imidazolate-bridge linkage in the binuclear copper(II) complex with glycylglycine ($[GlyGlyCu^{II}Im^{-}Cu^{II}GlyGly]^{-}$, GlyGly = glycylglycinate(2–), Im^{-} = imidazolate-(1–)) were studied in aqueous solutions as a function of pH. Potentiometric titration and electron spin resonance spectroscopy showed that the binuclear complex was formed in the range $9.8 < pH < 11.5$. The bridge was broken by protonation at lower pH to give rise to two kinds of mononuclear complexes, $[GlyGlyCu^{II}H_2O]$ and $[GlyGlyCu^{II}ImH]$ (ImH = imidazole). The equilibrium constant was 7.46×10^{-5} mol dm^{-3}. Above pH 11.5, the bridge in the binuclear complex was broken by hydroxide ion to give rise to $[GlyGlyCu^{II}OH^{-}]^{-}$ and $[GlyGlyCu^{II}\text{-}Im^{-}]^{-}$. The coordinated imidazolate of the latter complex was not displaced by hydroxide ion even under conditions of high pH.

Introduction

Imidazolate-bridged binuclear copper(II) complexes have received much attention as models for the active site of bovine erythrocyte superoxide dismutase in which the imidazolate of the histidyl residue bridges Cu^{2+} and Zn^{2+} ions [1]. The enzyme catalyzes the dismutation of O_2^{-} [2], the function of the bridging imidazolate is not clear. Studies with such complexes have shown that electronic [3–5] and magnetic exchange interactions [6–9] between the two metal centers are mediated by the imidazolate bridge, and that therefore, the bridge breaking may change the redox properties of the Cu^{II} site [4].

The pH dependence of the enzyme is also of interest, since the structure of the active center changes with the pH of the solution. At low pH, the imidazolate bridge has been reported to be broken, probably at the side facing the Zn^{II} [10], a contradiction of the proposed mechanism for the reduced Cu^{I} enzyme in which the bridge is broken at the side facing the Cu^{I} [11]. At high pH, the Cu^{2+} ion migrates intermolecularly to another Zn^{II} binding site to form a stable imidazolate-bridged Cu^{II}–Cu^{II} couple if the Zn^{II} site is vacant [12]. Therefore, we are interested in the effects of pH on the imidazolate-bridge linkage.

For this study, we chose a simple model, a symmetrical binuclear copper(II) complex in which two Cu^{II}–glycylglycine complexes were linked by an imidazolate bridge. Complex species present in the



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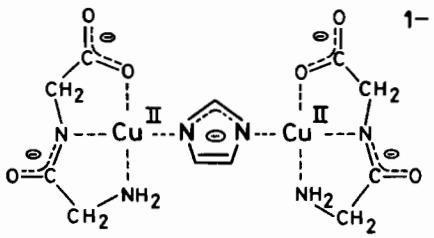

$[GlyGlyCu^{II}Im^{-}Cu^{II}GlyGly]^{-}$

solution at various pH conditions were identified by the use of electron spin resonance (ESR) spectra, and equilibrium constants between these complexes were calculated by potentiometric titration. Lippard *et al.* studied some binuclear complexes, but they could not identify all of the complex species in solution because of their complexity [3, 8]. In this study, the use of the Cu^{II}–glycylglycine complex, which has been well characterized [13], enabled us to identify the complexes in solution. In addition, the crystal

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structure of this binuclear complex with glycylglycine is known [14]. This is the first report of this kind of imidazolate-bridged binuclear complex that gives not only equilibrium constants for the formation and scission of the imidazolate-bridge linkage, but also all of the complex species present in solution at equilibrium.

Experimental

Materials

Reagents were of the highest grade commercially available, and distilled deionized water was used throughout.

Preparation of the Imidazolate-bridged Binuclear Copper(II) Complex with Glycylglycine, ([GlyGly-$Cu^{II}Im^{-}Cu^{II}$GlyGly]$^{-}$)

To a stirred aqueous solution (50 cm^3) of copper-(II) complex with glycylglycine, [GlyGly$Cu^{II}H_2O$] (0.846 g, 4 mmol), the synthesis of which is reported elsewhere [15], was added imidazole (0.136 g, 2 mmol). By the addition of sodium hydroxide, the solution was adjusted to pH 11, and then 30 cm^3 of dimethylformamide was added. The mixture was evaporated to half of its volume under reduced pressure. After being left overnight, dark blue crystals of the desired binuclear complex as a sodium salt were collected by filtration, washed with ether, and dried under reduced pressure. *Anal.* Found: C, 26.17; H, 3.55; N, 16.48. Calc. for $Na[(C_4H_6O_3N_2)_2Cu_2(C_3H_3N_2)]\cdot 1.5H_2O$: C, 26.19; H, 3.60; N, 16.66%. This procedure gave rise to the binuclear complex of 1.5 hydrate, while Nakahara *et al.* reported the hexahydrate [7, 14].

Methods

Potentiometric titration and ESR measurements were made as described previously [15]. To find the equilibrium constants for the formation of the binuclear complex, titration of three complex systems ($Cu(ClO_4)_2$:glycylglycine:imidazole = 1:1:0, 1:1:1/2, and 1:1:1) was carried out. All of the complex solutions ([Cu^{II}] = 1.0×10^{-2} mol dm^{-3}) were titrated with 1.0 mol dm^{-3} of sodium hydroxide at an ionic strength μ = 1.0 ($NaClO_4$) under a nitrogen atmosphere. ESR spectra were recorded at 77 K. Instrumental settings were 6 mW for microwave power, with a modulation amplitude of 2.0 gauss, time constant of 0.3 s, and sweep rate of 0.025 T min^{-1}.

Results and Discussion

Potentiometric Titration of Cupric Perchlorate–Glycylglycine–Imidazole Systems

Potentiometric titration of three complex systems, in which the cupric perchlorate–glycylglycine–imidazole ratios were 1:1:0 (the system without imidazole), 1:1:1/2 (the system with 1/2 imidazole), and 1:1:1 (the system with equimolar imidazole), was carried out in aqueous solution. The results are shown in Fig. 1.

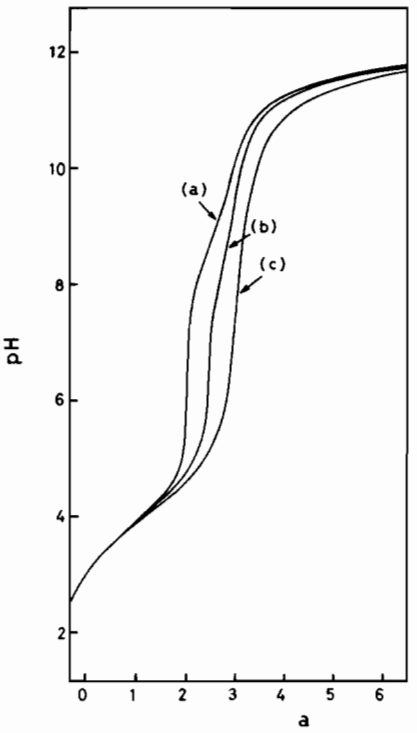

Fig. 1. Potentiometric titration curves for three complex systems of Cu^{II}:glycylglycine:imidazole, (a) 1:1:0, (b) 1:1:1/2, and (c) 1:1:1, at 25.0 ± 0.1 °C and μ = 1.0. [Cu^{II}] = 1.0×10^{-2} mol dm^{-3}. a = mol of standard NaOH added per mol of Cu^{II}.

Below pH 4, the three systems had the same potentiometric responses. At this region of pH, glycylglycine coordinated to the Cu^{2+} ion [13, 16] and imidazole had no effect on the titration. From pH 4 to 7, differences appeared in the systems. The protonated imidazole ($HImH^+$) in solution coordinated to [GlyGly$Cu^{II}H_2O$] with deprotonation followed by liberation of the coordinated H_2O molecule. Although the pK_a value for imidazole is 7.1, its coordination to [GlyGly$Cu^{II}H_2O$] had already begun at pH 4. The titration curve for the complex system containing 1/2 imidazole was in the middle of the two other curves. The equilibrium constant for the formation of copper(II) complex with glycylglycine (K_1) and that with additional imidazole (K_2) were obtained as 2.50×10^{-6} mol dm^{-3} and 1.19×10^{-3} mol dm^{-3}, respectively.

$$Cu^{2+} + \text{glycylglycine} \overset{K_1}{\rightleftharpoons} [\text{GlyGly}Cu^{II}H_2O] + 2H^+ \quad (1)$$

$$[GlyGlyCu^{II}H_2O] + HImH^+ \overset{K_2}{\rightleftharpoons} [GlyGlyCu^{II}ImH] + H^+ + H_2O \quad (2)$$

Above pH 7, the three titration curves were quite different. In the first system with $[GlyGlyCu^{II}H_2O]$, a relatively flat zone around pH 8.5 was seen; it was ascribed to deprotonation of the coordinated water molecule, which resulted in the two kinds of complexes shown as follows:

$$2[GlyGlyCu^{II}H_2O] \overset{K_3}{\rightleftharpoons} [GlyGlyCu^{II}(OH^-)Cu^{II}GlyGly]^- + H^+ + H_2O \quad (3)$$

$$[GlyGlyCu^{II}H_2O] \overset{K_4}{\rightleftharpoons} [GlyGlyCu^{II}OH^-]^- + H^+ \quad (4)$$

The first is a binuclear complex bridged by an OH^- ion [eqn. (3)] and the second, a mononuclear complex with an OH^- ion [eqn. (4)]; both have been studied elsewhere [15]. Their equilibrium constants K_3 and K_4 were 8.71×10^{-6} mol dm^{-3} and 4.90×10^{-10} mol dm^{-3}, respectively.

In the second case, that with 1/2 imidazole, there was no typical buffer zone visible, but there was a small inflection around pH 8.5. This titration curve gradually approached that of the first $[GlyGlyCu^{II}H_2O]$ system as the pH value rose, which suggested that one proton per Cu^{II} atom, as in the previous system, was released at pH above 7. Half of the protons would come from the 1/2 $HImH^+$ when it was coordinated to $[GlyGlyCu^{II}H_2O]$ [eqn. (2)] and the other half of the protons either from $[GlyGlyCu^{II}ImH]$ or from the remaining $[GlyGlyCu^{II}H_2O]$. At any rate, at pH 11, crystals of the imidazolate-bridged binuclear copper(II) complex were isolated as a sodium salt, $Na[(GlyGly)_2Cu_2Im^-]$, in good yield, as shown in the Experimental Section, so the major complex species here in solution would be the binuclear complex. Therefore, the second half of the protons would come from the process of binuclear complex formation, of which the equilibrium constant was 7.46×10^{-5} mol dm^{-3}.

$$[GlyGlyCu^{II}H_2O] + [GlyGlyCu^{II}ImH] \overset{K_5}{\rightleftharpoons} [GlyGlyCu^{II}(Im^-)Cu^{II}GlyGly]^- + H^+ + H_2O \quad (5)$$

In the third case, that of equimolar imidazole, the titration curve was farthest to the right side. The difference with the first system without imidazole at pH 7 corresponded to one proton, and that at pH 11.5, to 0.75 proton per Cu^{II} atom. The former can be explained by eqn. (2), in which one proton is released per Cu^{II} atom with coordination of the equimolar $HImH^+$ to give rise to $[GlyGlyCu^{II}ImH]$. The latter is slightly more complicated. Since the first system, the reference, released one proton between pH 7 and 11.5, this difference at pH 11.5 showed the liberation of about two protons in total. Hence, the second deprotonation seemed to take place in the $[GlyGlyCu^{II}ImH]$. Although the deprotonated complex could not be isolated, probably because of its low stability, it seems probable that the pyrrole hydrogen of the coordinated imidazole was deprotonated. In a similar case, that in which diethylenetriamine (dien) takes the place of the GlyGly ligand, the deprotonated complex of $[(dien)Cu^{II}Im^-]ClO_4$ was isolated as a single crystal and its molecular structure was verified by X-ray crystallographic analysis [17].

$$[GlyGlyCu^{II}ImH] \overset{K_6}{\rightleftharpoons} [GlyGlyCu^{II}Im^-]^- + H^+ \quad (6)$$

The equilibrium constant for the deprotonation, K_6, was obtained as 6.03×10^{-11} mol dm^{-3}. This value suggested that the deprotonated complex might also be involved in the binuclear complex system at very high pH where the imidazolate bridge becomes unstable.

$$[GlyGlyCu^{II}(Im^-)Cu^{II}GlyGly]^- + H_2O \overset{K_7}{\rightleftharpoons} [GlyGlyCu^{II}Im^-]^- + [GlyGlyCu^{II}OH^-]^- + H^+ \quad (7)$$

The equilibrium constant for the dissociation of the binuclear complex, K_7, was given by $(K_4K_6)/K_5$, which was obtained as 3.96×10^{-16} mol dm^{-3}. These seven equilibrium constants, from K_1 to K_7, could quite satisfactorily explain the three titration results shown in Fig. 1.

ESR Spectra of the Complexes in Solution

ESR spectra of the three complex systems with zero, 1/2, and equimolar imidazole were studied in aqueous solutions under various pH conditions. The purpose was to identify by ESR spectroscopy the complex species present in the solution.

Figures 2 and 3 show the pH dependence of the ESR spectra of the systems without and with equimolar imidazole, respectively. When the pH of the solution was raised from 2 to 6, glycylglycine and imidazole molecules coordinated to Cu^{II}, and the ESR spectra changed. From the titration results for the system without imidazole, we calculated that more than 90% of the glycylglycine molecules were coordinated at above pH 4.7. So the clear signal observed at pH 5.3, as shown in Fig. 2b, was ascribed to $[GlyGlyCu^{II}H_2O]$. Imidazole became coordinated at a slightly higher pH region. The coordination process is seen in Fig. 3 from (a) to (d). At pH 4.5, complex formation was underway, and a spectrum with poor resolution and probably built up from

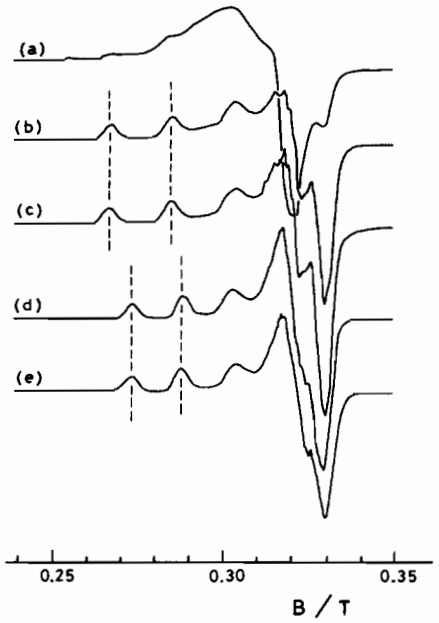

Fig. 2. ESR spectra of a frozen aqueous solution (at 77 K) of the copper(II) complex with glycylglycine (Cu^{II}:glycylglycine:imidazole = 1:1:0) at (a) pH 4.0; (b) pH 5.3; (c) pH 7.2; (d) pH 9.9; and (e) pH 12.8.

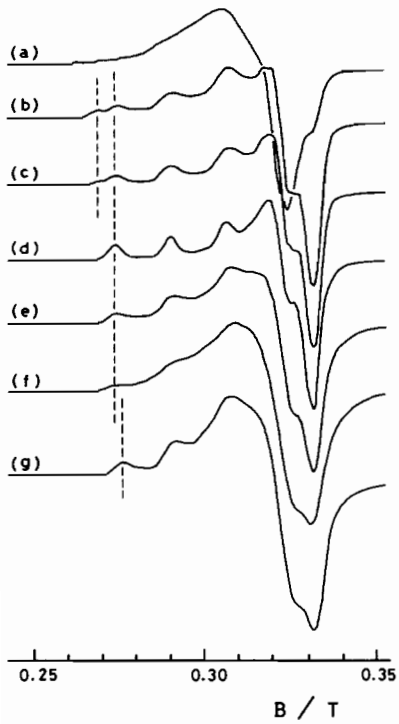

Fig. 3. ESR spectra of a frozen aqueous solution (at 77 K) of the copper(II) complex with glycylglycine and equimolar imidazole (Cu^{II}:glycylglycine:imidazole = 1:1:1) at (a) pH 4.5; (b) pH 5.4; (c) pH 6.0; (d) pH 9.1; (e) pH 10.0; (f) pH 10.5; and (g) pH 12.5.

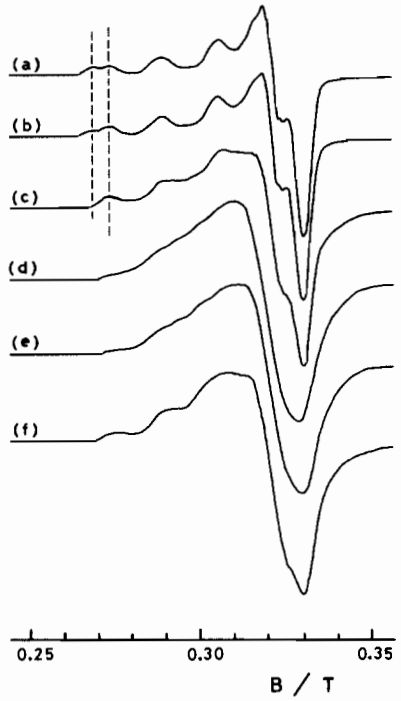

Fig. 4. ESR spectra of a frozen aqueous solution (at 77 K) of the copper(II) complex with glycylglycine and 1/2 imidazole (Cu^{II}:glycylglycine:imidazole = 1:1:1/2) at (a) pH 6.8; (b) pH 8.1; (c) pH 9.5; (d) pH 10.0; (e) pH 11.0; and (f) pH 12.0.

several complex species was obtained (Fig. 3a). A clear spectrum of [GlyGlyCu^{II}ImH] was observed first at pH 6.5 (the same signal as Fig. 3d). At pH 5.4, where most of the glycylglycine molecules were already coordinated to Cu^{II} while about half of the imidazole molecules were not, as calculated from the titration results, two kinds of signals were observed. The signals were most easily distinguished at the low-field edge of the $g_{\|}$ region. With increasing pH, the signal of [GlyGly$Cu^{II}H_2O$] appearing at 0.268 T decreased, while the other signal of [GlyGlyCu^{II}ImH] at 0.273 T increased. The spectral changes showed that coordination of imidazole to [GlyGly$Cu^{II}H_2O$] took place around pH 5.4. This result was compatible with the titration results, which showed that deprotonation occurred at the midpoint pH of 5.5.

ESR spectra of the system containing 1/2 imidazole at various pH values are shown in Fig. 4. At pH 6.8, where almost all of the imidazole molecules were coordinated to the Cu^{II} atom, two signals were observed (Fig. 4a). By comparing this spectrum with those of [GlyGly$Cu^{II}H_2O$] and [GlyGlyCu^{II}ImH], shown in Fig. 5, we saw that the 1/2 imidazole was coordinated to Cu^{II} to form [GlyGlyCu^{II}ImH], which leaves half of the complex as [GlyGlyCu^{II}-H_2O]. When the pH of the solution was raised to 9.5, the signal of [GlyGly$Cu^{II}H_2O$] disappeared, which showed that the coordinated H_2O molecule was

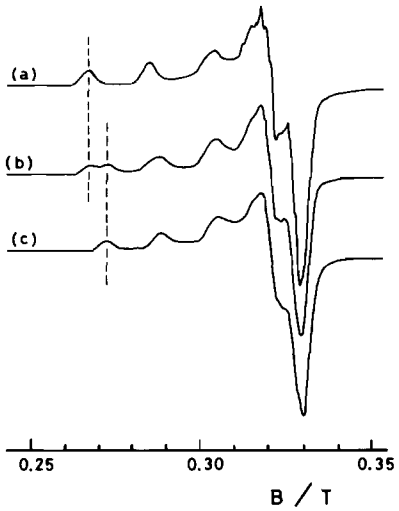

Fig. 5. ESR spectra of a frozen aqueous solution (at 77 K) of the copper(II) complex with glycylglycine and (a) zero, (b) 1/2, and (c) equimolar imidazole at pH 7.0 ± 0.2. The spectra of (a) and (c) are of $[GlyGlyCu^{II}H_2O]$ and $[GlyGlyCu^{II}ImH]$, respectively.

deprotonated. Then, at pH 10.0, the signal of $[GlyGlyCu^{II}ImH]$ became smaller and a broad, single signal appeared at the same magnetic field (Fig. 4d). This kind of signal has been reported in binuclear copper(II) complexes where two Cu^{II} atoms are connected by a bridging molecule [6, 18, 19]. Therefore, these spectral changes suggested the following reactions: (1) deprotonation of the coordinated H_2O of $[GlyGlyCu^{II}H_2O]$, and (2) formation of a binuclear complex $[GlyGlyCu^{II}Im^-Cu^{II}GlyGly]^-$ from $[GlyGlyCu^{II}ImH]$ and $[GlyGlyCu^{II}OH^-]^-$ with a deprotonation of the pyrrole hydrogen of $[GlyGlyCu^{II}ImH]$, and with a liberation of the coordinated OH^- of $[GlyGlyCu^{II}OH^-]^-$. These reactions seem to be likely because the binuclear complex itself was isolated as pure crystals under the conditions in which the broad, single signal was observed (see Experimental). This binuclear complex was so stable in aqueous solution at pH 11.0 that no spectral change was seen after the solution was left for a few months. However, when the solution was more basic, other signals appeared in addition to the broad, single one (Fig. 4f). We concluded from these results that although the binuclear structure was stable at pH 9.8–11.5 where the broad, single signal was observed, it became unstable at higher pH values.

With $[GlyGlyCu^{II}H_2O]$, the spectrum changed within the pH region from 7.2 to 9.9, as shown in Fig. 2. We attributed these changes to a deprotonation of the coordinated water molecule of $[GlyGlyCu^{II}H_2O]$ to give rise to $[GlyGlyCu^{II}OH^-]^-$, as reported previously [15].

The spectrum of $[GlyGlyCu^{II}ImH]$ also changed with rises in pH above 9.1. The axial signal that was seen at pH 9.1 (Fig. 3d) changed to a broad, single one at pH 10.5 (Fig. 3f), as with the binuclear complex system. At pH 12.5, it changed into another new axial signal (Fig. 3g). The pyrrole hydrogen of the coordinated imidazole seemed to be deprotonated at around pH 10, as mentioned in the section about potentiometric titration, so these spectral changes seemed to be derived from the deprotonation. The broad, single signal midway between pH 10 and 11 seemed to appear because of the formation of an imidazolate-bridged binuclear complex that was built up from deprotonated $[GlyGlyCu^{II}Im^-]^-$ and the remaining $[GlyGlyCu^{II}ImH]$. The Im^- seemed to act as a bridging molecule and the ImH as an apical ligand of one of the two Cu^{II} atoms. Lehn *et al.* have reported a similar kind of binuclear complex with imidazoles at the apical site of both Cu^{II} atoms [20]. Another possible reason for the appearance of the broad, single signal is formation of a polynuclear complex. An example of such formation was reported in a study of $[(dien)Cu^{II}Im^-]ClO_4$; the imidazolate ligand coordinated intermolecularly to another Cu^{II} to form imidazolate-bridged polynuclear structure [17]. Intermolecular complexation may also broaden the signal. In the present case, the former possibility seemed more probable, since the broad, single signal was most distinct at pH 10.5, where about half of the complex was probably deprotonated. Therefore, the new signal observed at pH 12.5 (Fig. 3g) was ascribed to that of the deprotonated complex of $[GlyGlyCu^{II}Im^-]^-$. Lippard *et al.* reported a weak Cu^{II}–ImH bond that was easily cleaved so that the ImH was replaced by an OH^- ion at high pH values [3, 18], but this was not the case here. The signal was different from that of $[GlyGlyCu^{II}OH^-]^-$, as is clear in Fig. 6 (compare a and c). The Cu^{II}–ImH bond in this complex seemed to be so strong that the imidazole ligand was not displaced by hydroxide ions, while the pyrrole hydrogen of the imidazole ligand was acidic enough to be deprotonated by the hydroxide ion to give rise to Cu^{II}–Im^-.

In the system with 1/2 imidazole, the binuclear complex, $[GlyGlyCu^{II}Im^-Cu^{II}GlyGly]^-$, became unstable at pH above 11.5. With further rises in the pH of the solution, the spectrum changed (Fig. 4f). This spectrum was reconstituted by addition of the spectra of $[GlyGlyCu^{II}Im^-]^-$ and $[GlyGlyCu^{II}OH^-]^-$, as seen in Fig. 6, so the binuclear structure was broken at the imidazolate bridge followed by coordination of an OH^- ion to give the above two complexes. This result was compatible with the titration results, which showed that there was additional deprotonation at the binuclear complex at pH above 11 [eqn. (7)].

In conclusion, the imidazolate-bridge linkage in the binuclear copper(II) complex with glycylglycine was stable only in a narrow region of pH between 9.8 and 11.5 in aqueous solution. The linkage could

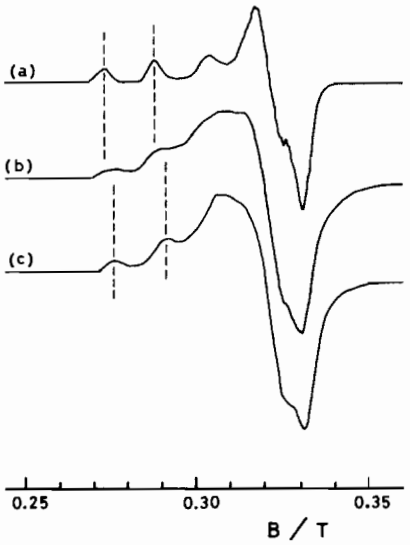

Fig. 6. ESR spectra of a frozen aqueous solution (at 77 K) of the copper(II) complex with glycylglycine and (a) zero, (b) 1/2, and (c) equimolar imidazole at pH 12.2 ± 0.2. The spectra of (a) and (c) are of $[GlyGlyCu^{II}OH^-]^-$ and $[GlyGlyCu^{II}Im^-]^-$, respectively.

be broken by protonation at lower pH and by competition with OH^- ions at higher pH values.

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