Partial Reduction of Imidazolate Bridged Binuclear Copper(II) Complex with Glycylglycine in Aqueous Solution

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Received August 3, 1984

There is much interest in imidazolate bridged binuclear copper(II) complexes [1–4], since the imidazolate bridged copper(II)–zinc(II) pair has been shown to be involved in the active site of bovine erythrocyte superoxide dismutase [5]. This enzyme has been known to catalyze disproportionation of superoxide with alternate redox of the copper atom accompanied by breaking and reforming of the imidazolate bridge [6]. In order to ascertain the function of the imidazolate bridge in the electron transfer reaction, we are investigating redox properties of the binuclear copper(II) complexes as models for the active center of the enzyme [7].

We report here a new reduction mechanism of an imidazolate bridged binuclear copper(II) complex with glycylglycine ($[(GlyGly)_2Cu_2(Im)]^-$) in aqueous solution. This complex has been well characterized [8, 9] and its dimeric structure was shown to be stable in aqueous solution above pH 9 [10], partial reduction being carried out by adding sodium dithionite as a reducing agent under anaerobic conditions. ESR spectra of the original and partially reduced complexes are shown in Fig. 1. When 50% of the copper atoms were reduced, which corresponds to one-electron reduction per molecule (Fig. 1(b)), a new signal, superimposed by a broad signal in the $g_\perp$ region, appeared in the spectrum. This new signal is consistent with that of the mononuclear copper(II) complex with glycylglycine ([(GlyGly)Cu]) shown in Fig. 1(d). A Dc-polarogram of the partially reduced solution showed a cathodic wave at $E_{1/2}$ = −0.36 V *vs.* SCE, which agrees well with that of the [(GlyGly)Cu] which appeared at $E_{1/2}$ = −0.38 V. These results indicate that the mononuclear [(GlyGly)Cu] is formed from the binuclear $[(GlyGly)_2Cu_2(Im)]^-$ by partial reduction. This change can be explained as the reduction of one copper atom in the binuclear center followed by the bridge breaking at the position between imidazolate and another side of the copper atom. The remaining broad signal appears to show that a small amount of the original binuclear complex was still involved in the solution. Electrons from the reducing agent seem to be transferred in part to the [(GlyGly)Cu], and a small amount of the original complex remained intact in the solution. When more than 90% of the copper atoms were reduced (Fig. 1(c)), the blue color of the solution turned to yellow (λ_{max} 317 nm), the intensity of the signal became smaller and the ESR signal changed further to become almost the same as that of the copper(II) complex with two glycylglycines ($[(GlyGly)_2Cu]^{2-}$) shown in Fig. 1(e). This change suggests that the glycylglycine ligand of the reduced copper complex was liberated to the bulk solution, which was then bound to the cupric complex in the solution to result in the formation of cuprous hydroxide and $[(GlyGly)_2Cu]^{2-}$. This additional electron transfer appeared to take place also at 50% reduction but only to a small extent, and the signal of $[(GlyGly)_2Cu]^{2-}$ was observed very faintly in Fig. 1(b).

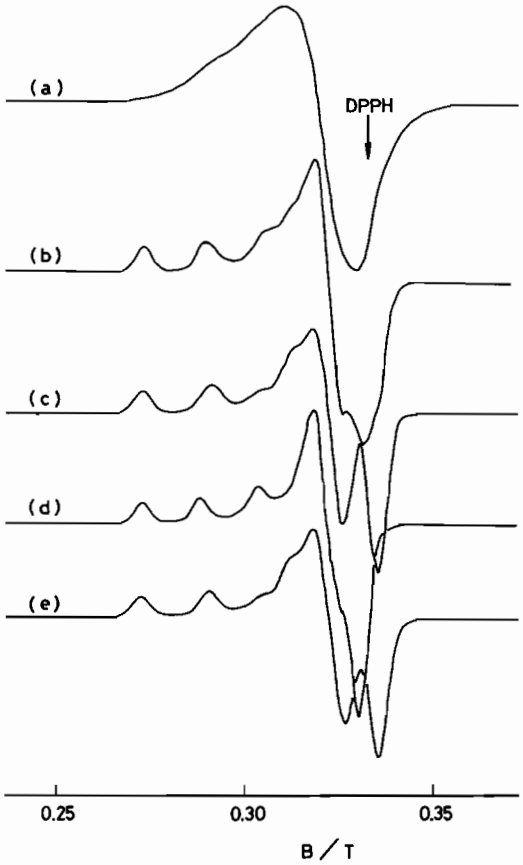

Fig. 1. ESR spectra of frozen (77 K) aqueous solution of (a): $[(GlyGly)_2Cu_2(Im)]^-$; (b) and (c): 50% and 90% reduction of (a), respectively; (d): [(GlyGly)Cu]; and (e): $[(GlyGly)_2Cu]^{2-}$ at pH 11.0 ± 0.2 containing 1.0 M of $NaClO_4$.

We conclude that the binuclear complex $[(GlyGly)_2Cu_2(Im)]^-$ accepts one electron with the imidazolate bridge breaking and upon further electron intro-

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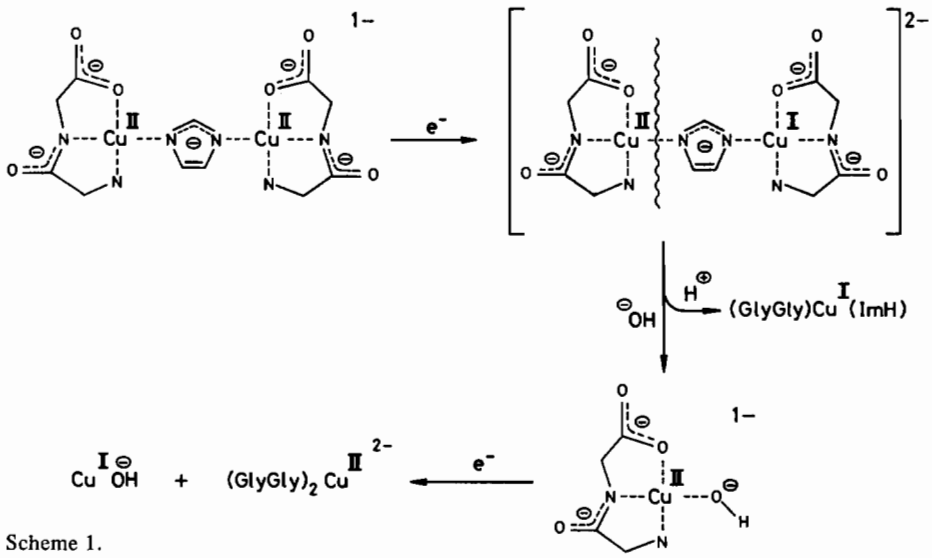

Scheme 1.

duction, the glycylglycine ligand is transferred intermolecularly as shown in Scheme 1. The bridge breaking intermolecularly as shown in Scheme 1. The bridge breaking position in this study was between imidazolate and the copper(II) atom, whereas the position postulated in the enzyme was at the opposite side between imidazolate and the copper(I) atom. This difference and the structural changes observed in this model study may shed some light on the conformational changes at the active site of the enzyme during electron transfer catalysis.

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