Reduction Properties of an Imidazolate Bridged Binuclear Copper(II) Complex

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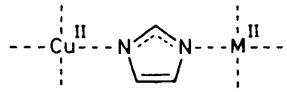
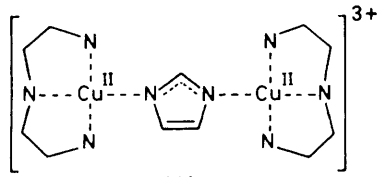
The imidazolate bridged binuclear copper(II) complex (**1**) was one-electron reduced in aqueous solution under anaerobic conditions with the bridge breaking to form two mononuclear complexes (**2**) and (**5**), which were converted to the original binuclear complex by reversible oxidation with molecular oxygen.

An imidazolate bridged copper–zinc system forms the active site of bovine erythrocyte superoxide dismutase (BESOD),[1] which catalyses the dismutation of superoxide.[2] Alternate reduction and reoxidation of the copper atom with reversible breaking and reforming of the imidazolate bridge is thought to happen during catalysis.[3] It is interesting then to know whether this kind of bridge breaking and reforming takes place in a simple low-molecular weight binuclear copper

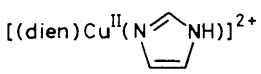


M^{II} = Cu^{II} Imidazolate bridged binuclear copper(II) complex in this study.
= Zn^{II} Active centre in BESOD.



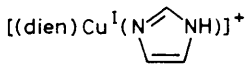
(1)

$[(dien)Cu^{II}]^{2+}$ (2)



(3)

$[(dien)Cu^{I}]^{+}$ (4)



(5)

complex by an electron transfer reaction in the same way as in the enzyme system.

We report here on the partial reduction of an imidazolate bridged binuclear copper(II) complex of diethylenetriamine (dien) (**1**), in aqueous solution under anaerobic conditions as a model for the BESOD enzyme system.[4] Although several types of imidazolate bridged multinuclear complexes have been prepared,[5,6] and structural,[6,7] and magnetic susceptibility studies[8] on these complexes have been reported, no work on the reduction mechanism of such complexes has ever been presented.

Complex (**1**) tends to dissociate into the two mononuclear complexes (**2**) and (**3**) under either low or high pH conditions. The binuclear structure of (**1**), characterized by its single and broad e.s.r. signal,[9] was stabilised in the narrow pH range of 9.5—10.5 wherein the partial reduction of (**1**) was carried out. The pH of the solution was adjusted with a few drops of deoxygenated sodium hydroxide or perchloric acid solution. The extent of the partial reduction was varied either by changing the amount of sodium dithionite added to the solution or by using an electrochemical method of controlled potential coulometry.

The e.s.r. spectra in Figure 1 show a drastic change in the shape of the broad signal of (**1**) with reduction as a diamagnetic copper(I) complex was formed with a new copper(II) complex different from the original complex (**1**). When complex (**1**) was reduced by more than one electron equivalent either by the addition of sodium dithionite [spectrum (C) in Figure 1] or by an electrochemical technique [spectrum (D)], the signal became quite similar to that [in (E)] of a solution containing a mixture of the imidazole-free Cu^{II} complex (**2**) and the imidazole-bound Cu^{I} complex (**5**).† These signals due to partially reduced (**1**) [in (C) and (D)] are completely different to the signal [in (F)] of the imidazole-bound Cu^{II} complex (**3**). These data suggest a mechanism by which one-electron transfer to (**1**) and, consequently, the

† A solution of complex (**5**) was obtained by adding dien and imidazole to an aqueous solution of $Cu(MeCN)_4ClO_4$[10] under anaerobic conditions.

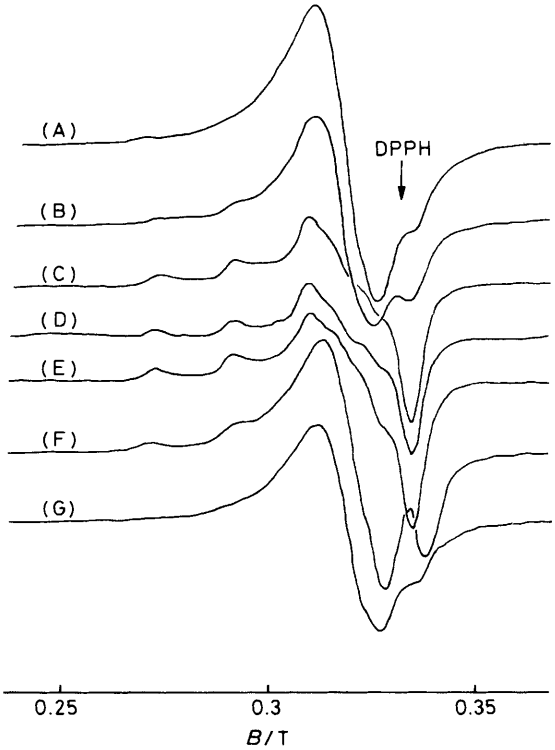
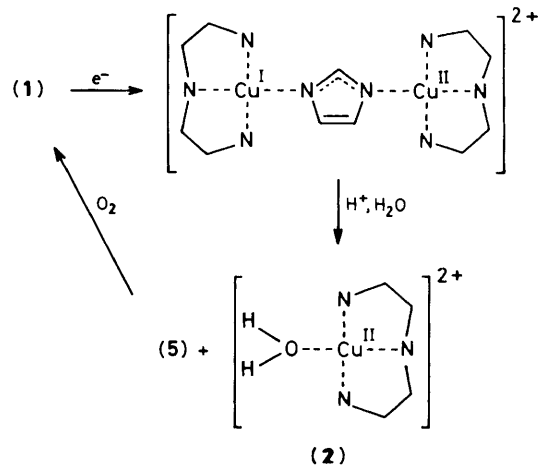


Figure 1. E.s.r. spectra of frozen aqueous solutions (77 K; $[NaClO_4]$ = 0.50 M; pH 10 ± 0.2) of (A) the imidazolate bridged binuclear Cu^{II} complex (**1**); the partially reduced states of (**1**) prepared by addition of (B) 0.5 electron equivalent; (C) greater than one electron equivalent (sodium dithionite); and (D) prepared by controlled-potential electrolysis at −1.0 V *vs.* saturated calomel electrode; (E) a 1 : 1 mixture of the imidazole-free Cu^{II} complex (**2**) and imidazole-bound Cu^{I} complex (**5**); (F) the imidazole-bound Cu^{II} complex (**3**); and (G) the complex formed by bubbling O_2 through the solution in (C).



Scheme 1

reduction of one copper(II) centre would sequentially break the imidazolate bridge, protonate the imidazolate anion, and ultimately produce complexes (**2**) and (**5**), as shown in Scheme 1. The structural change caused by partial reduction was also observed in the mononuclear imidazole-bound Cu^{II} complex (**3**). When it was partially reduced, the e.s.r. signal [in (F)] changed to a new signal quite similar to that in (C), which indicated the formation of the imidazole-free Cu^{II} complex (**2**). This result can be explained by migration of the imidazole

ligand from the starting Cu^{II} complex to the reduced Cu^{I} complex. It is reasonable, then, to conclude that the copper(I) complex formed is stabilized by the neutral imidazole ligand formed by bridge breaking in (**1**) on reduction.

Bubbling of dioxygen through the solution of partially reduced (**1**) restored its original blue colour‡ and the e.s.r. signal changed to that in (G), which is almost superimposable on the original signal in (A). This indicates reformation of the binuclear complex (**1**) from the complexes (**2**) and (**5**). Complete reversibility was maintained even after several reduction-oxidation sequences.

It is of interest that complex (**1**) undergoes reversible bridge breaking and reforming in a reversible structural change from a binuclear to a mononuclear form with accompanying change in the oxidation state of one of the copper atoms. This is analogous to the proposed mechanism of catalysis at the active centre of BESOD.

Received, 25th July 1983; Com. 1002

‡ λ_{max} 581 nm (ε 165 $dm^3\ mol^{-1}\ cm^{-1}$).

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