

Properties of Imidazolate Bridged Copper(II)–Zinc(II) Complexes

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Compounds modelling the active centre of bovine erythrocyte superoxide dismutase (BESOD) have been synthesized with imidazolate bridged copper(II)–zinc(II) pairs, and the influence of the Zn^{II} on the properties of the Cu^{II} is shown.

The active centre of bovine erythrocyte superoxide dismutase (BESOD), which catalyses the dismutation of toxic superoxide to dioxygen and hydrogen peroxide,¹ has been shown to consist of a copper(II) and a zinc(II) ion bridged by a histidyl imidazolate residue, by X-ray crystallographic studies.² The Cu^{II} was shown to play a direct role in the catalytic electron transfer mechanism.³ The role of Zn^{II}, however, has not been

clearly explained, but may organize the peptide chain of the active centre,⁴ or attenuate the p*K*_a value of the pyrrole hydrogen of the imidazole.⁵ It is of interest to know whether, or how the Zn^{II} affects the properties of the Cu^{II}. Model complexes have been synthesized and their magnetic exchange couplings,⁶ solution properties,⁷ and reduction features⁸ have been reported. All these complexes have

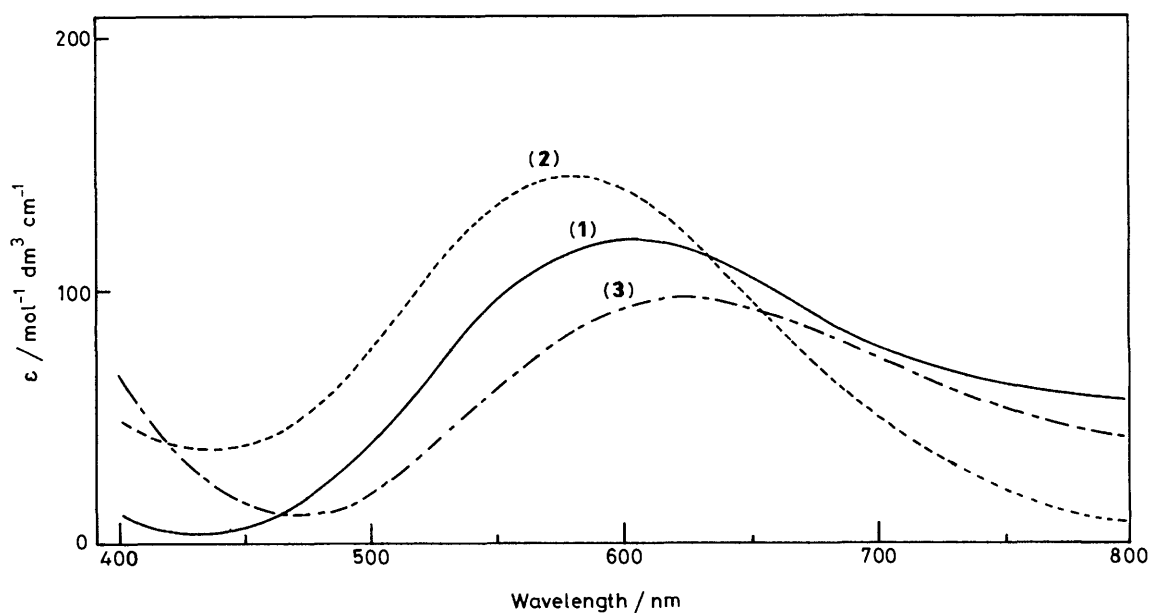
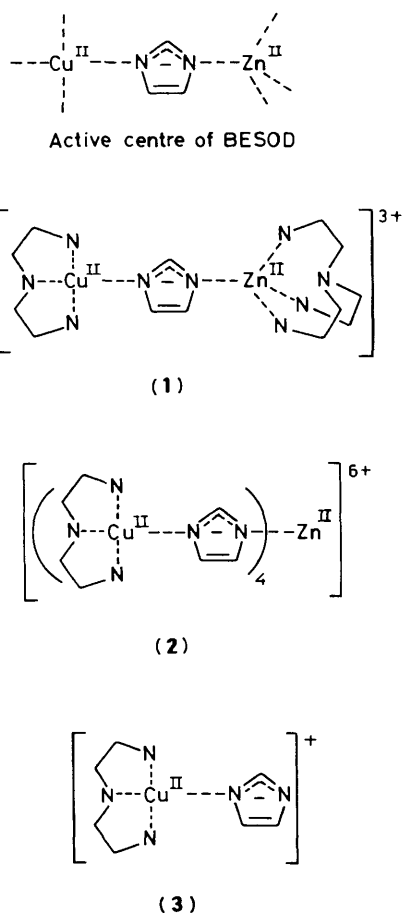


Figure 1. Visible absorption spectra of (1) CuImZn, (2) (CuIm)₂Zn, and (3) CuIm in dimethyl sulphoxide at 25 °C.



homo-binuclear Cu^{II} centres, but now we report on the static properties of imidazolate (Im) bridged hetero-nuclear Cu^{II} – Zn^{II} complexes as new model compounds for the active centre of the enzyme.

The model compounds (1) (binuclear, CuImZn) and (2) [pentanuclear, $(\text{CuIm})_4\text{Zn}$] were obtained by adding the mononuclear Cu^{II} complex (3) (CuIm) to a stoichiometric amount of the Zn^{II} -tris(2-aminoethyl)amine complex, and to a quarter of that amount of free Zn^{2+} in ethanol.[†]

Visible absorption spectra of these complexes are shown in Figure 1. The absorption maxima shifted to shorter wavelengths and the extinction coefficients (denoted per Cu^{II} atom) increased when the complex structure was changed from mononuclear to binuclear and to pentanuclear form. The imidazolate bridged homo-binuclear Cu^{II} -diethylenetriamine complex showed an absorption maximum at 586 nm (ϵ 113 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). As the absorption in this region arises from a d–d transition of the Cu^{II} , these spectral alterations suggest changes in the d-orbitals of the Cu^{II} atoms. E.s.r. spectra of complexes (2) and (3) had broad single peak signals at the temperature of liquid nitrogen (g_{\parallel} 2.065 and 2.101, respectively) as in the case of homo-nuclear Cu^{II} complexes,⁹ whereas complex (1) showed a signal characteristic of its tetragonal symmetry (g_{\parallel} 2.213, g_{\perp} 2.059). This change in signal appears to indicate that Zn^{II} has an effect on the ligand field of the Cu^{II} .

The redox property of these complexes was studied from their polarograms, shown in Figure 2. Cathodic waves observed here were derived from the reduction of Cu^{II} , and those of Zn^{II} appeared at more negative potentials. As these

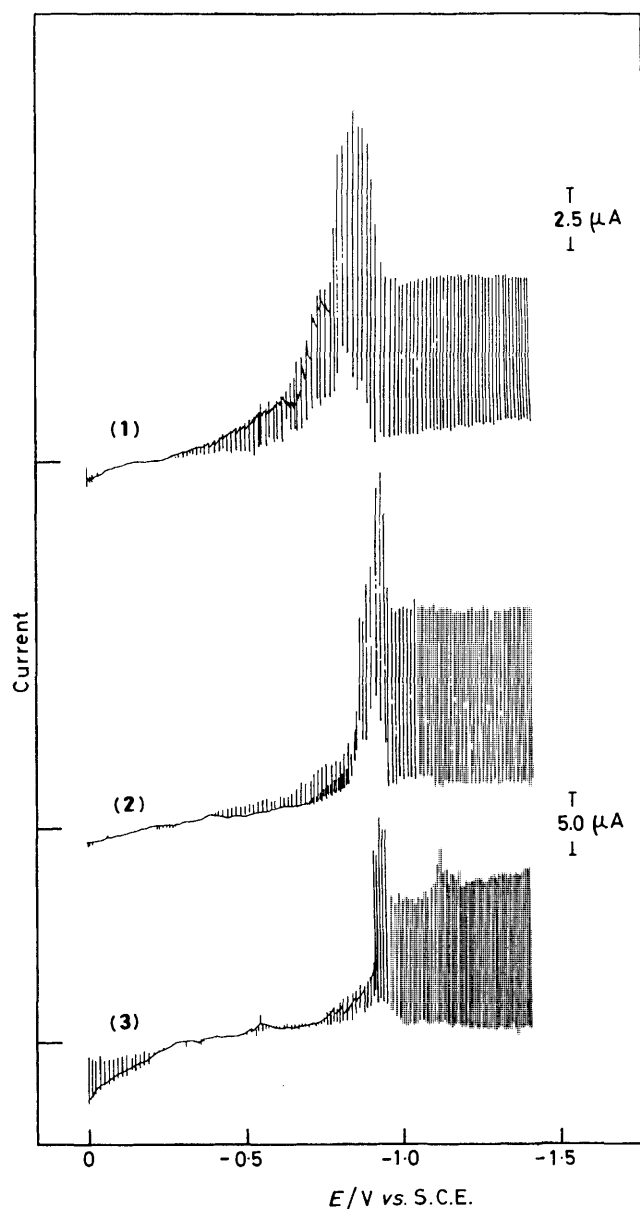


Figure 2. D.c.-polarograms of (1) CuImZn , (2) $(\text{CuIm})_4\text{Zn}$, and (3) CuIm at 25°C in dimethyl sulphoxide containing 0.1 M tetraethylammonium perchlorate.

waves implied irreversible reduction, as reported in the case of homo-binuclear complexes,¹⁰ the redox potential could not be obtained. However, the potential at which the cathodic current increases in the polarogram seems to give some idea of this value. The potential shifted towards positive in complex (2) and was more positive in complex (1) than in complex (3), indicating that the potential at which Cu^{II} is reduced is in the following order: complex (1) > complex (2) > complex (3). The presence of Zn^{II} increases the electron accepting ability of the Cu^{II} .

These results indicate that the properties of the Cu^{II} changed when it was linked to the Zn^{II} by an imidazolate bridge, probably because of electron deviation through the imidazolate bridge. Therefore, we suggest that in the case of the BESOD, where Cu^{II} and Zn^{II} are bridged by an imidazolate in the same way, Zn^{II} affects the electronic properties of Cu^{II} . Bridge breaking and reforming during

[†] Complexes (1) and (2) gave satisfactory elemental analyses.

catalysis may regulate or even control the two-step inverse electron transfer between superoxide and the active centre.

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