

## COMMUNICATIONS TO THE EDITOR

**Interaction of Superoxide with Copper(II) Complex of a Doubly Deprotonated Dioxotetraamine Macrocyclic Ligand**

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Functional transformations that are catalyzed by enzymatic systems generally proceed with high catalytic efficiency and stereospecificity. Particular attention has been afforded to the copper containing metalloenzymes because copper is essential to most life forms; it is the third most abundant trace metal in humans.<sup>1</sup>

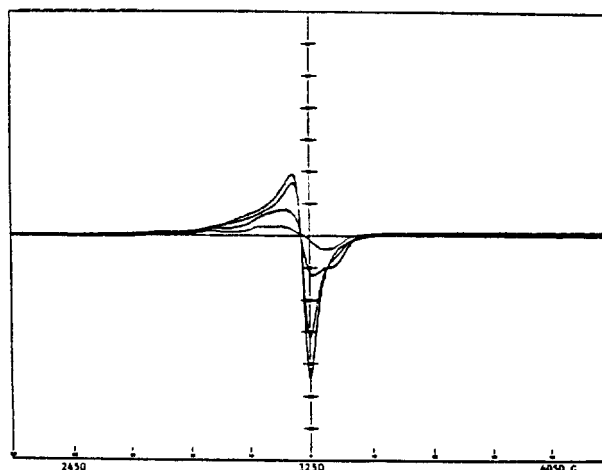
Galactose oxidase (D-galactose: oxygen 6-oxidoreductase, EC 1.1.3.9), a copper(II) containing metalloenzyme, catalyzes the oxidation of galactose.<sup>2</sup> The enzyme was found to consume dioxygen in the reaction and to produce hydrogen peroxide as a by-product. It has been shown that a variety of primary alcohols can serve as a substrate for this enzyme. Oxygen is the primary oxidant; however, ferricyanide can replace oxygen as the oxidant. The mechanism of the enzymatic reaction is at present uncertain, although several different mechanisms<sup>3-5</sup> have been suggested.

Meanwhile, superoxide ( $O_2^-$ ) is an effective one-electron reductant for a large number of metal ions and their complexes.<sup>6</sup> Also superoxide is an one-electron oxidant, but oxidation of metal complexes by superoxide has been much less studied.<sup>6</sup>

Although copper(II)-superoxide complexes have been proposed as intermediates in Cu(I) autoxidation reactions,<sup>7</sup> in reactions of Cu(II) with superoxide in aqueous media,<sup>6</sup> and in the enzymatic reaction of galactose oxidase,<sup>3</sup> there are few reports about direct detection of copper(II)-superoxide complexes.<sup>8</sup> Thus, this study of the interaction of superoxide with copper(II) complex of a doubly deprotonated dioxotetraamine macrocyclic ligand which has been prepared as a model complex of galactose oxidase active site was undertaken, in attempting to understand the active site chemistry of galactose oxidase.

The copper(II) complex of a doubly deprotonated dioxotetraamine macrocyclic ligand 1,8-dibenzyl-1,4,8,11-tetraazacyclotetradecane-5,12-dione [Cu(II)DBTA] has been prepared as a model complex of the galactose oxidase active site.<sup>9</sup> The EPR spectrum of Cu(II)DBTA itself in acetonitrile under anaerobic conditions at 77 K is shown as the highest intensity line in Figure 1, and strongly suggests that the copper(II) atom in Cu(II)DBTA is coordinated to four nitrogens in a square planar geometry. The EPR  $g$  parameter from Cu(II)DBTA itself was observed to be 2.078.

Cyclic voltammograms of Cu(II)DBTA in  $CH_3CN$  between +2.0 and -2.0 V at different scan rates (using 0.1 M



**Figure 1.** EPR spectra of 1.0 mM Cu(II)DBTA with different amounts of added  $O_2^-$  in  $CH_3CN$  at 77 K. Highest intensity line is starting solution, lowest intensity line is after addition of about 10 equiv of  $O_2^-$ . Spectra were recorded at 1.6 G field modulation intensity and 21.4 mW microwave power; 3217 G corresponds to  $g = 2.078$ .

$[CH_3(CH_2)_3]_4NBF_4$ , TBABF<sub>4</sub>, as supporting electrolyte and a glossy carbon electrode) under anaerobic conditions were measured. The cyclic voltammograms on the copper(II)/copper(I) and copper(II)/copper(I) redox system indicated quasi-reversible profiles with an  $E_{1/2}(Cu^{II}/Cu^{I})$  value of 0.916 V and an  $E_{1/2}(Cu^{II}/Cu^I)$  value of -1.078 V vs. Ag/AgCl reference electrode at a scan rate 100 mV sec<sup>-1</sup>. The visible spectrum of Cu(II)DBTA in  $CH_3CN$  under the anaerobic condition showed two bands at 470 nm ( $\epsilon$  154) and 620 nm ( $\epsilon$  45). The UV/vis concentration of Cu(II)DBTA exhibited a faint pink color.

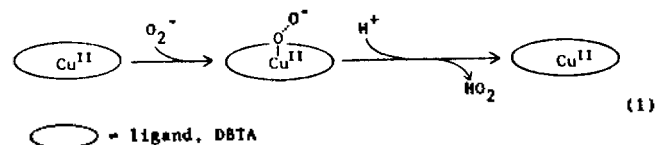
Addition of 18-crown-6 ether solubilized  $KO_2$  to solution of Cu(II)DBTA in  $CH_3CN$  under anaerobic conditions caused the EPR spectra to disappear as shown in Figure 1. Decomposition of superoxide by addition of  $CF_3COOH$  as a proton source caused the intensity of the Cu(II) EPR signal to reappear. If Cu(II)DBTA is reduced by superoxide to produce Cu(I) species and dioxygen, the intensity of the Cu(II) EPR signal cannot reappear by addition of  $CF_3COOH$ . This observed EPR spectral behavior strongly suggests that the

interaction of Cu(II)DBTA with superoxide results in an ERP-silent five-coordinate complex.

Cyclic voltammogram of Cu(II)DBTA plus superoxide (>1.0 equiv) in CH<sub>3</sub>CN under the anaerobic condition showed a new irreversible wave centered at -0.47 V, using 0.1 M TBABF<sub>4</sub> as supporting electrolyte and a glossy carbon electrode. The new wave centered at -0.47 V is attributed to reduction of coordinated superoxide to peroxide followed by irreversible oxidation.

Addition of ca. 1 equiv of superoxide to solution of Cu(II)DBTA in CH<sub>3</sub>CN under the anaerobic condition caused a little blue shift and an increase in intensity at the short-wavelength absorption band. Similar visible spectra were obtained from interaction of Cu(II)DBTA with (CH<sub>3</sub>)<sub>4</sub>NOH or C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>ONa in CH<sub>3</sub>CN. The similarity of the visible spectra of the products formed by interaction with O<sub>2</sub><sup>-</sup>, OH<sup>-</sup>, and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O<sup>-</sup> implies that they are all structurally similar five-coordinate Cu(II) complexes.

On the basis of the EPR spectra, visible spectra, and cyclic voltammetric studies, the interaction of Cu(II)DBTA with superoxide in CH<sub>3</sub>CN under the anaerobic condition leads to the formation of copper(II)-superoxide complex, which can be easily decomposed to HO<sub>2</sub> and the copper(II) complex by a proton source (eq. 1).



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### References

1. T. Vanngard, In "Biological Applications of Electron Spin Resonance", H. M. Swartz, J. R. Bolton, and D. C. Borg, Ed., Wiley-Interscience: New York, p. 411, 1972.
2. J. A. D. Cooper, S. Wilfrid, B. Metry, and H. Medina, *J. Biol. Chem.*, **234**, 445 (1959).
3. G. A. Hamilton, P. K. Adolf, J. de Jersey, G. C. DuBois, G. R. Dyrkacz, and R. D. Libby, *J. Am. Chem. Soc.*, **100**, 1899 (1978).
4. M. J. Ettinger and D. J. Kosman, In "Copper Proteins", T. G. Spiro, Ed., Wiley-Interscience: New York, p. 219, 1981.
5. L. Cleveland, R. E. Coffman, P. Coon, and L. Davis, *Biochemistry*, **14**, 1108 (1975).
6. D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res.*, **14**, 393 (1981).
7. A. D. Zuberbuhler, In "Metal Ions in Biological Systems", H. Sigel, Ed., M. Dekker: New York, Vol. 5, pp. 325-368, 1976.
8. M. Nappa, J. S. Valentine, A. R. Miksztal, H. J. Schugar, and S. S. Isied, *J. Am. Chem. Soc.*, **101**, 7744 (1979).
9. J. T. Groves and K.-T. Park, In "The Role of Oxygen in Chemistry and Biochemistry", W. Ando and Y. Moro-oka, Ed., Elsevier: Amsterdam, pp. 541-548, 1988.

## Formation and Characterization of the 19-Electron Rhenium Radical

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Paramagnetic 17- or 19-electron complexes play a vital role in the organometallic chemistry because many reactions have been found in which these complexes are involved as intermediates.<sup>1</sup> For example, several substitution reactions have been found to proceed more rapidly when a small anodic or cathodic current was passed through the solution.<sup>2</sup> The isolation and characterization of paramagnetic complexes are relatively rare due to the instability of transient species. Recently, Brown and coworkers<sup>3</sup> described the formation of persistent metal-centered substituted transition metal carbonyl radical, M(CO)<sub>3</sub>L<sub>2</sub> (M = Mn, Re; L = P-c-Hx<sub>3</sub>), whose stability is ascribable to the large cone angle of the phosphine ligand. The 19-electron complex, Co(CO)<sub>3</sub>L<sub>2</sub> [L<sub>2</sub> = 2,3-bis(diphenylphosphino) maleic anhydride], was first synthesized from Co<sub>2</sub>(CO)<sub>8</sub> and L<sub>2</sub> by Fenske<sup>4</sup>,

who showed that the unpaired electron is delocalized over the Co atom and the π\* system of the L<sub>2</sub> ligand. Further evidence for the formation of 19-electron adducts has been obtained by photochemical reaction of a metal-metal bonded complex with ligands possessing a low-energy π\* orbital such as quinones<sup>5</sup>, α-diimines<sup>6</sup>, and substituted pyridines<sup>7</sup>. The ease of the formation of transient Re(CO)<sub>5</sub> radical from the dimer Re<sub>2</sub>(CO)<sub>10</sub> by photochemical method<sup>8</sup> prompted us to study the 19-electron species, Re(CO)<sub>4</sub>L<sub>2</sub> with ESR spectroscopy.

The ESR spectrum of a THF solution of Re<sub>2</sub>(CO)<sub>10</sub> (10 mM) and L<sub>2</sub> [2,3-bis(diphenylphosphino) maleic anhydride] (10 mM) in the dark at room temperature is shown in Figure 1. The radical, which is stable four hours in the dark, exhibits the 1:2:1 triplets arising from two equivalent <sup>31</sup>P nuclei. The