

Structural Variety of Copper(II)-Peroxide Adducts and Its Relevance to DNA Cleavage

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The reactivity of copper(II) compounds with several tetradentate ligands towards some spin-trapping reagents was studied in the presence of hydrogen peroxide. The compounds used in this study are roughly divided into two groups based on the reactivity towards 2,2,6,6-tetramethyl-4-piperidinol (and also 2,2,6,6-tetramethyl-4-piperidone), which are trapping agents for singlet oxygen, $^1\text{O}_2(^1\Delta_g)$; The A-group compounds exhibited a high activity to form the corresponding nitron radical, which was detected by ESR spectroscopy, but corresponding activity of the B-group compounds was very low. The A-group compounds defined as above exhibited high activity for cleavage of DNA (supercoiled Form I) in the presence of hydrogen peroxide, yielding DNA Form II (relaxed circular) or Form III (linear duplex) under our experimental conditions ($[\text{Cu(II)}]=0.1\sim 0.5\text{ mM}$). On the other hand, the B-group compounds effected complete degradation of the DNA (double-strand scission) under the same experimental conditions, formation of Form II or Form III DNA was negligible. Two different DNA cleavage patterns observed for A- and B-group compounds were elucidated by the different structural property of the copper(II)-peroxide adducts, which is controlled by the interaction through both DNA and the peripheral group of the ligand system.

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