

Coordination chemistry and catalytic activity of a NiSOD related metallopeptide

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Nickel superoxide dismutases (NiSOD) are capable of catalyzing the decomposition of superoxide anion radical in several *Streptomyces* and cyanobacteria. The absence of these enzymes results in elevated level of superoxide anion concentration which may cause oxidative stress and extensive cellular damage. In the last few years, our research group intensively studied metallopeptides mimicking the nickel binding motif in NiSOD enzyme by applying the systematic active site tailoring approach.^{1,2} In this presentation, we report a thorough equilibrium, spectroscopic, computational and SOD activity study on a new metallopeptide, in which penicillamine as a natural decomposition product of the antibiotic was introduced into the peptide chain. The nickel(II) and nickel(III) complexes of the metallopeptide possess the same coordination environment than that observed in the native enzyme, however, the methyl substituents of penicillamine moiety alter the thermodynamic and electronic parameters. Our recently developed kinetic method for studying the SOD activity made possible to establish a multi-step kinetic model which incorporates the decomposition of the superoxide anion, the dismutation cycle and the degradation of the catalyst. The metallopeptide effectively catalyzes the dismutation process, however, the simultaneous intramolecular redox decomposition of the Ni(III) form of the catalyst eventually ceases the dismutation process.³

References

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