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catalyzed by transition metal
complexes.

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Biomimetic metal-radical reactivity: aerial oxidation of alcohols, amines, aminophenols and catechols catalyzed by transition metal complexes

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Abstract

The contributions of the authors to the research program 'Radicals in Enzymatic Catalysis' over the last ca. 5 years are summarized. Significant efforts were directed towards the design and testing of phenol-containing ligands for synthesizing radical-containing transition metal complexes as potential candidates for catalysis of organic substrates like alcohols, amines, aminophenols and catechols. Functional models for different copper oxidases, such as galactose oxidase, amine oxidases, phenoxazinone synthase and catechol oxidase, are reported. The copper complexes synthesized can mimic the function of the metalloenzymes galactose oxidase and amine oxidases by catalyzing the aerial oxidation of alcohols and amines. Even methanol could be oxidized, albeit with a low conversion, by a biradical-copper(II) compound. The presence of a primary kinetic isotope effect, similar to that for galactose oxidase, provides compelling evidence that H-atom abstraction from the α -C-atom of the substrates is the rate-limiting step. Although catechol oxidase and phenoxazinone synthase contain copper, manganese(IV) complexes containing radicals have been found to be useful to study synthetic systems and to understand the naturally occurring processes. An 'on-off' mechanism of the radicals without redox participation from the metal centers seems to be operative in the catalysis involving such metal-radical complexes.

Keywords: [aerial oxidation](#); [catalysis](#); [copper oxidases](#); [functional models](#); [radicals](#); [transition metal complexes](#)

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