Transition Metal-Radical Complexes and Their Catalytic Reactivity

Abstract:

Galactose Oxidase (GOase), Amine Oxidases (AOs) and Phenoxazinone Synthase (PHS) are copper containing metalloenzymes. Mononuclear, Copper(II) ion containing enzymes, GOase and AOs catalyze aerial oxidation of primary alcohols and amines to the corresponding aldehydes, respectively. PHS is a pentanuclear, Copper containing metalloenzyme, which catalyzes aerial 6-electron oxidative coupling of two molecules of 2-aminophenol derivative to phenoxazinone chromophore. Active site of GOase contains a Cu(II) ion with a Tyr 272 radical. One Cu(II) ion with an organic cofactor, like, topa-quinone or lysyl tyrosyl quinone, depending on the class of the AOs, are known as active site(s) for AOs. The active site of PHS contains four Cu(II) ions. All these catalytic processes are proposed to go through radical-based mechanism.

Biradical-containing copper complexes, symbolically, $[Cu^{II}(L^{\bullet\bullet})]^0$ and $[Cu^{II}(L^{X\bullet})_2]^0$, have been found to oxidize primary alcohols like, benzyl alcohol, ethanol, methanol to their corresponding aldehydes in the presence of air. Therefore, they act as functional models for GOase.

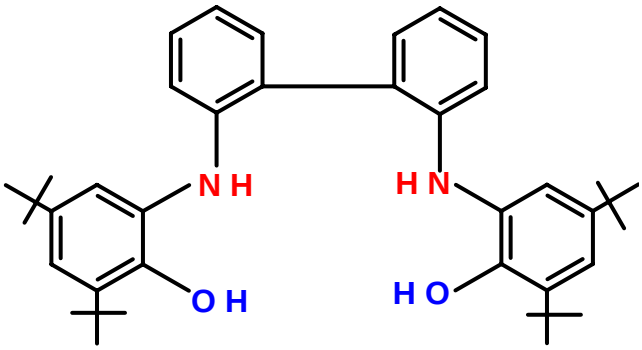
Tetranuclear-tetraradical-containing cubane shaped Cu(II) complex, $[Cu^{II}_4(L^{CH_2OH\bullet})_4]^0$ catalyzes aerial oxidation of 2-aminophenol to phenoxazinone chromophore. Hence, the function of PHS has been mimicked.

To mimic the function of AOs and PHS, mononuclear-monoradical-containing Mn(IV) complex, $[Mn^{IV}(L^{COOH\bullet})(L^{COOH})]NHEt_3$, has been used and found to catalyze aerial oxidative deamination of primary amines like, benzyl amine, ethylenediamine, 2-aminoethanol to the corresponding Schiff-base products or aldehydes. 2-aminophenol has been converted to phenoxazinone chromophore by catalytic activity of the complex in the presence of air.

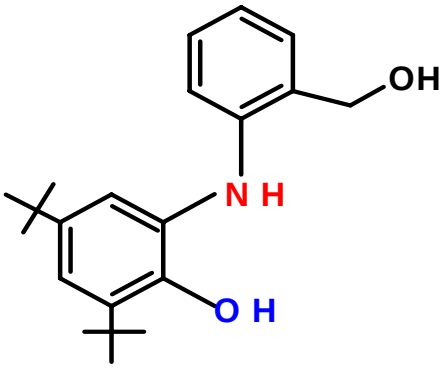
Kinetic studies and mechanistic investigations prove unambiguously that radical(s) participate(s) in the catalytic processes.

Use of radical-containing transition metal complexes as catalysts thus provide deeper insight of the metalloenzymes and are examples of bio-inspired catalysts which might be important for industrial purposes.

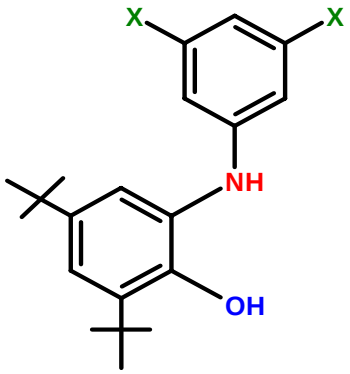
The ligands used in this thesis are;



H_4L



$H_3L^{CH_2OH}$



X = -^{t}Bu

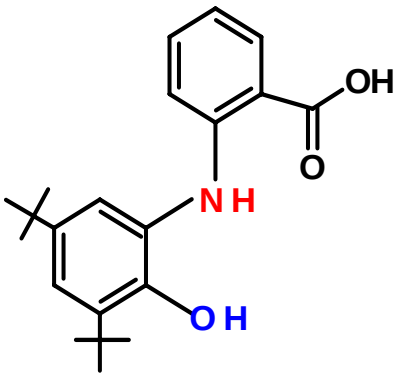
-OMe

-H

-F

-CF_3

H_2L^x



H_3L^{COOH}

Additionally, some other radical-containing complexes are described.