

Reactivity of Distorted Tetrahedral Copper(II) Complex toward O₂ and H₂O

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Peptidylglycine α -hydroxylating monooxygenase (PHM) performs stereospecific hydroxylation of C–H bonds at a single copper center Cu_M, where a mononuclear tetrahedral Cu/O₂ intermediate is involved as a reactive intermediate.¹ However, little is known about the dioxygen activation mechanism on such a tetrahedral copper reaction center. Recently, we have developed a series of copper(II) complexes supported by a tridentate N₃ ligand (TMG₃tach), which induces a tetrahedral geometry with a labile coordination site.²

In this study, the reactivity of (TMG₃tach)Cu^{II}Br was examined to find that the ligand hydroxylation took place when the complex was treated with O₂ at 70 °C in acetonitrile. Furthermore, we have found that (TMG₃tach)Cu^{II}Br was reduced by H₂O to form the Cu(I) complex. In order to get information about the mechanisms of these reactions, we have examined the intrinsic reactivity of a series of (TMG₃tach)Cu^{II}X (X = F, Cl, Br, and I) to find that homolytic cleavage of the Cu^{II}–X bond easily occurred to form Cu^I and X• as the key reactive intermediates (Figure 1). Oxidation ability of external substrates such as phenol derivatives by (TMG₃tach)Cu^{II}X was also examined.

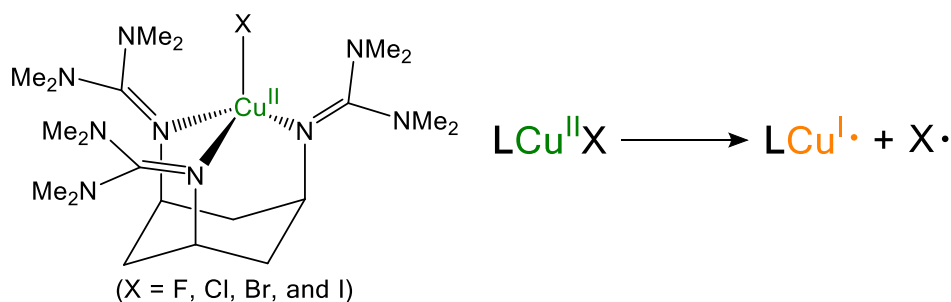


Fig 1. Homolytic cleavage of Cu^{II}–X bond to form Cu^I and X•

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- 2) S. Itoh, et al., *Inorg. Chem.*, **2017**, 56, 9634–9645.