# 六座二核化配位子の二核銅錯体が触媒するメタン酸化

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Methane oxidation catalyzed by dicopper complex with hexadentate binucleating ligand

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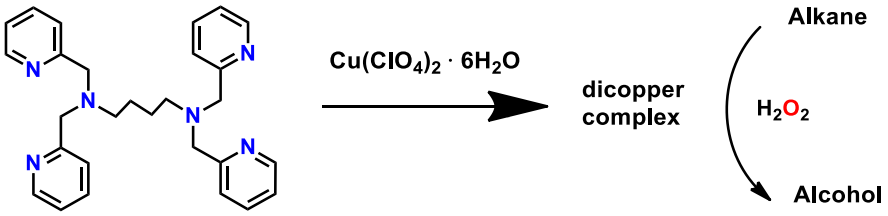
Cu-enzyme particulate methane monooxygenases (pMMO) catalyze oxidation of methane to methanol at ambient conditions. The mono- and multi-copper sites are proposed as the active site structure of pMMO, and the $O_2$-activation mechanism and the active species in the methane oxidation have not been clarified yet. Recently, we found that a monocopper complex of Medpa tridentate ligand $[Cu^{II}(Medpa)]^{2+}$ (**1**) gave large TOF 120 $min^{-1}$ in the cyclohexane oxidation with $H_2O_2$ and proposed that μ-oxyl radical dicopper species $[Cu_2(\mu\text{-}O\bullet)(\mu\text{-}OH)(Medpa)_2]^{2+}$ is formed as the active species. In the $H_2O_2$ activation via a monocopper pathway, however, **1** catalyzes Fenton type reaction where the supporting ligand is oxidized by HO• to decrease TON. In this study, we synthesized a dinucleating ligand *N,N,N',N'*-tetra(2-picolyl)butane-1,4-diamine (L) where two dpa units are connected by a $C_4$-alkyl tether. A dicopper(II) complex of L $[Cu^{II}(L)]^{2+}$ (**2**) suppressed the Fenton type reaction to improve catalytic activity. Here, we report the synthesis, structure, and methane oxidation of complex **2**.

*Keywords : Dicopper(II) complex; Alkane oxidation; methane oxidation; reaction mechanism*

メタン資化細菌にはメタン酸化を触媒する膜結合型銅タンパク質である pMMO が存在する．我々は，三座配位子 *N*-methyldi(2-piycolyl)amine (Medpa)を用いて単核銅錯体$[Cu(Medpa)]^{2+}$ (**1**)を合成し，これが $H_2O_2$ によるシクロヘキサン酸化を高速に触媒することを見出した．この反応では 2 分子の **1** と $H_2O_2$ の反応で μ-oxyl radical 二核銅活性種$[Cu_2(\mu\text{-}O\bullet)(\mu\text{-}OH)(Medpa)_2]^{2+}$が生じ，これが高い酸化活性を示すと考えられる．しかし，**1** の単核経由の Fenton 反応で HO•が生じて配位子の酸化分解が起こり TON は低下した．本研究では二核銅による $H_2O_2$ 活性化を効率化するため 2 つの dpa を $C_4$-alkyl tether で繋いだ二核化配位子 *N,N,N',N'*-tetra(2-picolyl)butane-1,4-diamine (L)を用いて二核銅錯体$[Cu^{II}_2(L)]^{2+}$(**2**)を合成した. **2** を触媒に用いると二核構造の安定化で $Cu_2(\mu\text{-}O\bullet)$の生成が有利になり，単核経由の Fenton 反応が抑えられるので TON が大きく向上した．今回は, **2** の合成，構造，触媒活性などについて報告する．

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