Development of Functional Metal Complexes Having Active Oxygen Species Controlled by Coordination Sphere

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Research Project

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Research Institution	Kanazawa University
Principal Investigator	**SUZUKI Masatatsu** Kanazawa University, Graduate School of Natural Science and Technology, Division of Material Sciences, Professor (20091390)
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Research Abstract	The purpose of this project is the development of metal complexes having active-oxygen species. In order to syntheses such complexes, we have developed new coordination environments, where the first and second coordination spheres can cooperatively function. 1. Synthesis of (μ-η^2:η^2-Peroxo)Cu(II)_2 Complexes as Functional Models for Tyrosinase and Methane Monooxygenase: We have succeeded in synthesis of (μ-η^2:η^2-peroxo)Cu(II)_2 complexes, [Cu_2(O_2) (H-L)]^<2+> (oxy-H-1), where H-L = 1, 3-bis [bis (6-methyl-2-pyridylmethyl)aminomethyl]benzene, which can perform not only hydroxylation of the m-xylyl linker of H-L, but also epoxidation of styrene via an electrophilic addition of the peroxide to the C=C bond. In addition, oxy-H-1 can oxidize various aliphatic C-H bonds having the bond dissociation energies (BDE) 75 - 92 kcal mol^<-1> via H-atom abstraction. A linear correlation between log k (the second order rate constants of oxidation) and BDE was observed. 2. Synthesis of (μ-Peroxo)diiron (III) Complex as a Functional Model for Toluene Monooxygenase: We have succeeded in synthesis of two types of peroxodiiron (III) complexes, [Fe_2(LPh4) (RCO_2) (O_2)]^<2+> (R = Ph_3C (oxy-l) and Ph (oxy-2)), the former leads to regioselective hydroxylation of a phenyl group of LPh4 and the latter exhibits reversible deoxygenation (LPh4 = N,N,N',N'-tetrakis[(1-methyl-2-phenyl-4-imidazolyl)methyl]-1,3-diamino-2-propanolate). This is the first example of the peroxodiiron (III) complex which is capable of arene hydroxylation. The reactions mimic toluene monooxygenase and hemerythrin reactivity, respectively.

Report (5 results)

2007 Annual Research Report Final Research Report Summary

2006 Annual Research Report

2005 Annual Research Report

2004 Annual Research Report

Research Products (40 results)

All | 2008 | 2007 | 2006 | 2005 | 2004

All | Journal Article | Presentation | Book

[Journal Article] Regioselective Arene Hydroxylation Mediated by a (μ-Peroxo)diiron(III) Complex : A Functional Model for Toluene Monooxygenase 2007

[Journal Article] Ligand Effects on Dioxygen Activation by Copper and Nickel Complexes : Reactivity and Intermediates 2007

[Journal Article] Regioselective Arene Hydroxylation Mediated by a (μ-Peroxo)diiron(III) Complex : A Functional Model for Toluene Monooxygenase 2007

[Journal Article] Ligand Effects on Dioxygen Activation by Copper and Nickel Complexes: Reactivity and Intermediates 2007

[Journal Article] Aromatic Hydroxylation Reactivity of a Mononuclear Cu(II)-Alkylperoxo Complex 2007

[Journal Article] Regioselective Arene Hydroxylation Mediated by a (μ-Peroxo)diiron(III) Complex : A Functional Model for Toluene Monooxygenase 2007

[Journal Article] Synthesis and Reactivity of (μ-η^2 : η^2-Peroxo)dicopper(II) Complexes with Dinucleating Ligands : Hydroxylation of Xylyl Linker with a NIH Shift 2007

[Journal Article] Intramolecular Arene Hydroxylation versus Intermolecular Olefin Epoxidation by (μ-η^2 : η^2- Peroxo)dicopper(II) Complex Supported by Dinucleating Ligand 2006

[Journal Article] Intramolecular Arene Hydroxylation versus Intermolecular Olefin Epoxidation by (μ-η ^2 : η^2-Peroxo)dicopper(II) Complex Supported by Dinucleating Ligand 2006

[Journal Article] Sequential Reaction Intermediates in Aliphatic C-H Bond Functionalization Initiated by a Bis(μ-oxo)dinickel(III) Complex 2006

[Journal Article] A Mononuclear Alkylperoxocopper(II) Complex as a Reaction Intermediate in the Oxidation of the Methyl Group of the Supporting Ligand 2006

[Journal Article] Intramolecular Arene Hydroxylation versus Intermolecular Olefin Epoxidation by (μ-η^2:η^2-Peroxo)dicopper(II) Complex Supported by Dinucleating Ligand 2006

[Journal Article] Sequential Reaction Intermediates in Aliphatic C-H Bond Functionalization Initiated by a Bis(μ-oxo)dinickel(III) Complex 2006

[Journal Article] Reversible O-O Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron(III) Complex 2005

[Journal Article] Reversible 0-0 Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron (III) Complex 2005

[Journal Article] Synthesis and Reactivity of a (μ-1,1-Hydroperoxo)(μ-hydroxo)dicopper(II) Cyomplex : Ligand Hydroxylation by a Bridging Hydroperoxo Ligand 2005

[Journal Article] Reversible O-O Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron(III) Complex 2005

[Journal Article] Structure and Dioxygen-reactivity of Copper(I) Complexes Supported by Bis(6-methylpyridin-2-yl-methyl)amine Tridentate Ligands 2005

[Journal Article] Mass Spectrometric and Spectroscopic Studies on Hydrolysis of Phosphoesters by Bis(μ-acetato)-μ-phenolato Dinuclear Metal(II) Complexes (Metal=Mn,Co,Ni, and Zn) 2005

[Journal Article] Structural and Spectroscopic Characterization of (μ-Hydroxo or μ-oxo)(μ-peroxo)diiron(III) Complexes : Models for Peroxo Intermediates of Non-Heme Diiron Proteins 2005

[Journal Article] Synthesis and Reactivity of a (μ-1,1-Hydroperoxo)(μ-hydroxo)dicopper(II) Complex : Ligand Hydroxylation by a Bridging Hydroperoxo Ligand 2005

[Journal Article] Reversible O-O Bond Cleavage and Formation of a Peroxo Moiety of a Peroxocarbonate Ligand Mediated by an Iron(III) Complex 2005

[Journal Article] Structure and Dioxygen-reactivity of Copper(I) Complexes Supported by Bis(6-methylpyridin-2-yl-methyl)amine Tridentate Ligands 2005

[Journal Article] Formation and Characterization of a Bis(μ-alkylperoxo)dinickel(II) Complex as a Reaction Intermediate for Oxidation of Methyl Group of Me_2-tpa Ligand to Carboxylate and Alkoxide Ligands 2004

[Presentation] Reactivity of Peroxodiiron(III), , (μ-η^2 : η^2-Peroxo)dicopper(II), and Bis(μ-oxo)dinickel(II) Complexes 2008

[Presentation] Reactivity of Peroxodiiron(III),(μ-η^2:η^2-Peroxo)dicopper(II), and Bis(μ-oxo)dinickel(II)Complexes 2008

[Presentation] 遷移金属錯体による酸素分子活性化の化学 2008

[Presentation] Reactivity of Peroxodiiron (II), (μ-η^2 : η^2-Peroxo)dicopper(II), and Bis (μ-oxo)dinickel(III) Complexes 2008

[Presentation] Reactivity of Peroxodiiron(III)and Dicopper(II)Complexes: Functional Models for Dioxygen Binding and Activating Diiron and D icopper Metalloenzymes 2007

[Presentation] Reversible Dioxygen Binding vs Arene Hydroxylation Mediated by Peroxo-diiron(III) Complexes 2007

[Presentation] 二核鉄(III)酸素錯体による配位子に組み込んだメチル基の水酸化反応 2007

[Presentation] 過酢酸イオンを含む鉄(III)錯体の合成と反応性 2007

[Presentation] ヒドリド架橋を有する二核ニッケル錯体の合成と反応性 2007

[Presentation] キシレン架橋骨格を有する二核化配位子を含むbis(μ-oxo)二核ニッケル錯体によるアレーン環の水酸化反応 2007

[Presentation] 三座配位子を含むbis(μ-hydroxo)dicopper錯体によるC-H結合活性化 2007

[Presentation] 過炭酸イオンを含む単核鉄(III)錯体の合成と反応性 2007

[Presentation] 金属錯体による酸素分子活性化の化学 2007

[Book] 金属錯体最前線 2006

[Book] 生物無機化学 2005

[Book] 生物無機化学 2005

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