

合目的反応場の構築による酸素活性種を含む金属錯体の協奏的機能制御

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

Research Project

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Review Section	Science and Engineering
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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Project Status	Completed (Fiscal Year 2007)
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All 

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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, [Cu₂(O₂)(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, [Fe₂(LPh₄)(RCO₂)(O₂)]²⁺ (R = Ph₃C (oxy-1) 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)dycopper(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)dycopper(II) Complex Supported by Dinucleating Ligand	2006	▼
[Journal Article] Intramolecular Arene Hydroxylation versus Intermolecular Olefin Epoxidation by (μ - η^2 : η^2 -Peroxo)dycopper(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)dycopper(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	▼
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[Journal Article] Synthesis and Reactivity of a (μ -1,1-Hydroperoxo)(μ -hydroxo)dycopper(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] 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	▼
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[Presentation] Reactivity of Peroxodiiron(III), (μ - η^2 : η^2 -Peroxo)dycopper(II), and Bis(μ -oxo)dinickel(II) Complexes	2008	▼
[Presentation] Reactivity of Peroxodiiron(III),(μ - η^2 : η^2 -Peroxo)dycopper(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)dycopper(II), and Bis (μ -oxo)dinickel(III) Complexes	2008	▼
[Presentation] Reactivity of Peroxodiiron(III)and Dycopper(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	▼
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[Presentation] キシレン架橋骨格を有する二核配位子を含む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)dycopper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	▼
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