# Investigations of dioxygen activation mechanisms by dimetal complexes

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	キーワード (Ja):
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	作成者: Suzuki, Masatatsu
	メールアドレス:
	所属:
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## 2003 Fiscal Year Final Research Report Summary

### Investigations of dioxygen activation mechanisms by dimetal complexes

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Project/Area Number
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Research Institution
Kanazawa University
Principal Investigator
SUZUKI Masatatsu Kanazawa University, Department of Chemistry, Prof. of Chemistry, 理学部, 教授 (20091390)
Co-Investigator(Kenkyū-buntansha)
FURUTACHI Hideki Kanazawa University, Department Chemistry, Assistant Prof. of Chemistry, 大学院・自然科学研究科, 助手 (40332663)
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December Allestonet

#### Research Abstract

<Reversible four electron redox conversion of dioxygen by copper complexes > A series of copper(I) complexes ( $[Cu(L)]^+$ ) having tripodal tetradentate ligands (L) was synthesized and reactivity of their complexes with O\_2 was investigated. Reaction of copper(I) complexes ( $[Cu(L)]^+$  generated bis( $\mu$ -oxo)dicopper(III) complexes, which showed reversible conversion to copper(I) complexes by bubbling of N\_2. Furthermore, it was also found that bis( $\mu$ -oxo)dicopper(III) complexes have monooxygenase activity for the supporting ligands. Reactivity can be modulated by stereochemical electronic effect of the supporting ligands

<Reaction intermediates of nickel complexes having a variety of dioxygen active species formed by the reaction with  $H_2O_2$ > Reaction of a bis( $\mu$ -hydroxo)Ni(II)\_2 having a series of tetradentate tripodal ligands having methyl substituents with  $H_2O_2$  at low temperature resulted in a successive formation a bis( $\mu$ -oxo)Ni(III)\_2 a bis( $\mu$ -superoxo)Ni(II)\_2, and a bis( $\mu$ -alkylperoxo)Ni(II)\_2 complexes as the intermediates for the conversion of a methyl substituent of ligands to carboxylate and alkoxide ligands

<Reversible O-O bond cleavage and formation of a peroxo group of an iron(III) complex having a peroxycarbonate > A peroxcarbonate iron(III) complex ([Fe(qn)\_2(O\_2C(O)O)]^-(1)) was synthesized. The complex is stable at -35 $^{\circ}$ C in acetonitrile, whereas it decomposes at 20 $^{\circ}$ C. Decomposition of an ^<18>O-labeled [Fe(qn)\_2(^<18>O-^<18>OC(O)O)]^-complex (1-^<18>O-^<18>O) at 20 $^{\circ}$ C in acetonitrile was investigated by resonace Raman and ESI-MS spectroscopies. They

 $revealed that the $$^{18}$-$^{18}$- of the peroxocarboante ligand is converted through $$^{16}$- of the peroxocarboante ligand is converted through $$^{1$ ^<16>OC(0)0 during thermal decomposition. This is the first example which showed reversible 0-0 bond cleavage and formation for iron complexes

#### Research Products (36 results)

All Other All Publications

[Publications] H.Furutachi, M.Suzuki, et al.: "A Rare μ\_3-η^1;η^2 Peroxo Bridge between Two Col^<II>Pb^<II> Dinuclear Units and Hydrolytic Conversion into a Hydroxo-Bridged Co^<III>Pb^<II> Complex"Chemistry. Letters. 763-764 (1999) [Publications] H.Furutachi, M.Suzuki, et al.: "Oxygenation of Heterodinuclear Di( $\mu$ -phenoxo)Co^<II>M^<II> (M = Mn, Fe or Co) Complexes having "Co(salen)" Entity in a Macrocyclic Framework" Journal of Chemical Society, Dalton transaction. 2197-2203 (1999) [Publications] M.Kodera, M.Suzuki, et al.: "Crystal Structure and Reversible O\_2 Binding of a Room Temperature Stable  $\mu$ - $\eta$ ^2: $\eta$ ^2 Peroxodicopper(II) Complex of a Sterically Hindered Hexapyridine Dinucleating Ligand"Journal of the American Chemical Society. 121. 11006-11007 (1999) [Publications] K.Siren, M.Suzuki, et al.: "Synthesis, Structures, and Properties of Bis(μ-oxo)nickel(III) and Bis(μ-superoxo)nickel(II) Complexes: An Unusual Conversion of a Ni(III)\_2(μ-O)\_2 Core into a Ni(II)\_2(μ-OO)\_2 Core by H\_2O\_2 and Oxygenation of Ligand"Journal of the American Chemical Society, 122. 254-262 (2000) [Publications] M.Suzuki, H.Okawa, et al.: "Bimetallic Dioxygen Complexes Derived from 'End-off' Compartmental Ligands" Coordination Chemistry Review. 200-202. 105-129 (2000) [Publications] H.Hayashi, M.Suzuki, et al.: "A Bis(µ-oxo)dicopper(III) Complex with Aromatic Nitrogen Donors: Structural Characterization and Reversible Conversion between Copper(I) and  $Bis(\mu-oxo)dicopper(III)$  Species" Journal of the American Chemical Society. 122. 2124-2125 (2000) [Publications] H.Furutachi, M.Suzuki, et al.: "Dinuclear Co^<II>M^<II> (M = Pb, Co) Complexes Having a 'Co(salen)' Entity in a Macrocyclic Framework: Ligand Modulation Effect and Neighboring M^<II> Effect upon Oxygenation at the 'Co(salen)' Center." Journal of Chemical Society, Dalton transaction. 2761-2769 (2000) [Publications] H.Furutachi, M.Suzuki, et al.: "Bis(μ-οχο)(μ-hydroxo)triiron(III) and (μ-οχο)(μ-hydroxo)diiron(III) Core Complexes with Tripodal Ligands Having a Terminal Calboxylate Group. "Chemistry Letters. 1132-1133 (2000) [Publications] M.Shinoura, M.Suzuki, et al.: "A Heterodinuclear Co^<II>Cu^I Complex with Co(salen) in a Macrocyclic Framework. Oxygenation Studies in Comparison with Analogous Cu^<II>Cu^I and Co^<II>Pb^<II> Complexes. "Inorganic Chemistry. 39. 4520-4526 (2000) [Publications] K. Yamaguchi, M. Suzuki, et al.: "Hydrolysis of Phosphodiester with Hydroxo- or Carboxylate-bridged Dinuclear Ni(II) and Cu(II) Complexes" Journal of Chemical Society, Chemical Communication. 375-376 (2001) [Publications] K.Shiren, M.Suzuki, et al.: "Synthesis, Structures, and Magnetic Properties of Heterodimetal Bis(µ-hydroxo)Chromium(III)Nickel(II) Complexes with Tpa Derivatives Having Sterically Bulky Substituents"Inorganic Chemistry. 41. 1598-1605 (2002) [Publications] K.Hashimoto, M.Suzuki, et al.: "A New Mononuclear Iron(III) Complex Containing Peroxocarbonate Ligand"Angewandte Chemie International Edition. 41. 1202-1205 (2002) [Publications] H.Hayashi, M.Suzuki, et al.: "Modulation of the Copper-Dioxygen Reactivity by Stereochemical Effect of Tetradentate Tripodal Ligends" Chemistry Letters. 416-417 (2002) [Publications] Furutachi, H., Suzuki, M.et al.: "Regioselective Hydroxylation of Xylyl Linker in a Diiron(III) Complex having a Carboxylate-Rich Ligand with H\_2O\_2"Journal of Chemical Society, Chemical Communication. 1900-1901 (2002) [Publications] M.Mizuno, M.Suzuki, et al.: "Ligand Effect on Reversible Conversion between Copper and Bis(µ-oxo)Dicopper(III) Complex with a Sterically Hindered Tetradentate Tripodal Ligand and Monooxygenase Activity of Bis(µ-oxo)Dicopper(III) Complex"Inorganic Chemistry, 42, 8534-8544 (2003) [Publications] Kodera, M, Suzuki, M. et al.: "Synthesis, Structure and Greatly Improved Reversible  $O_2$  Binding in a Structurally Modulated  $\mu$ - $\eta$ ^2: $\eta$ ^2-Peroxodicopper(II) Complex with Room-Temperature Stability"Angewandte Chemie International Edition. 43. 334-337 (2004) [Publications] Komiyama, K, Suzuki, M. et al.: "Dioxygen Reactivity of Copper(I) Complexes with Tetradentate Tripodal Ligands Having Aliphatic Nitrogen Donors: Synthesis Structures, and Properties of Peroxo and Superoxo Complexes Bulletin Chemical Society of Japan. 77. 59-72 (2004) [Publications] Chow, J., Suzuki, M.et al.: "Formation and Characterization of a Bis(µ-allrylperoxo)dinickel(II) Complex as a Reaction Intermediate for Oxidation of Methyl Getup of Me\_2-tpa Ligand to Carboxyl ate and Alkoxide Ligands" Angewandte Chemie International Edition. (in press). (2004)

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