

二核ロジウム錯体上での無機硫黄の循環の化学

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2003 Fiscal Year Final Research Report Summary

INORGANIC SULFUR CYCLE ON DINUCLEAR RHODIUM COMPLEX

Research Project

Project/Area Number

13440200

Research Category

Grant-in-Aid for Scientific Research (B)

Allocation Type

Single-year Grants

Section

一般

Research Field

Inorganic chemistry

Research Institution

KANAZAWA UNIVERSITY (2003)
Osaka City University (2001-2002)

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Project Period (FY)

2001 - 2003

Keywords

Inorganic Sulfur Cycle / Dinuclear Rhodium Complexes / Disulfido / Oxysulfido Complexes / Reduction of Sulfur Oxides / Thioisulfonato Complexes / α -Disulfone Complexes / α -Disulfoxido Complexes

Research Abstract

Inorganic sulfur species with oxidation states between -2 and +6 have been isolated as the ligands in the rhodium dinuclear complexes from the oxygenation of disulfido complex $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-S}_2)]$ (1) with O_2 in the air. The isolated oxysulfur complexes are the thioisulfonato complex $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-SSO})]$ (2), thioisulfonato complex $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-SS(O)}_2)]$ (3), α -disulfoxido complex $\text{cis}-[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-S(O)SO})]$ (4), and traps- $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-S(O)SO})]$ (5). Using peroxides such as m-CPBA, complex 1 as well as 2 and 3 gave the α -disulfone complex $[(\text{RhCp}^*)_2(\mu\text{-CH}_2)_2(\mu\text{-S(O)}_2\text{SO}_2)]$ (6). These dinuclear complexes have a dithiodirhodium metalacycle framework where the S-S moiety coordinates to the Rh-Rh group in a side-on fashion. The strong

electron donation group of Cp^{*}Rh-RhCp^{*} allows the high grade oxygenated sulfur species of α-disulfone to work still as the didentate ligand through both S atoms. In this research the reactivity of the isolated oxysulfur complexes towards electrophiles and nucleophiles has been explored. Complex 6 is readily reduced to 3 by NaBH₄, not to 1. Although we did not succeed yet in the reduction of 3 to 1, but found that the reaction of 3 with I₂ or ICH₂CH₂I produces the precursor of 1, [(RhCp^{*})₂(μ-CH₂)₂(μ₄-S₄)]²⁺. The artificial sulfur cycle on the Rh-Rh bond is completed.

Research Products (22 results)

All	2003	2002	2001
All	Journal Article	Book	

[Journal Article] Introduction of Chirality to the Remote, Open Face of Metalloporphyrin through Coordination to the Metal of Specially Designed Pendant Arm	2003	▼
[Journal Article] Design and synthesis of copper complexes of novel ligands based on the pyridine thiolate group	2003	▼
[Journal Article] Synthesis of (μ-alkoxo)bis(μ-carboxylato)-dirutenium complex having porphyrin moieties as a potential photo-harvesting functionality	2003	▼
[Journal Article] Synthesis of a Reduced Tridecavanadate Dimer Linked by Eight Hydrogen Bonds	2003	▼
[Journal Article] Synthesis and behavior in solution of the triple cubane- and windmill-type framework isomers of an organorhodium tungsten oxide cluster [(Cp [*] Rh) ₄ W ₄ O ₁₆]	2003	▼
[Journal Article] Introduction of Chirality to the Remote, Open Face of Metalloporphyrin through Coordination to the Metal of Specially Designed Pendant Arm	2003	▼
[Journal Article] Synthesis of (μ-alkoxo)bis(μ-carboxylato)-dirutenium complex having porphyrin moieties as a potential photo-harvesting functionality	2003	▼
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[Journal Article] Synthesis and behavior in solution of the triple cubane- and windmill-type framework isomers of an organorhodium tungsten oxide cluster [(Cp [*] Rh) ₄ W ₄ O ₁₆]	2003	▼
[Journal Article] meso-Tetraphenylporphyrin Having Hexa-maltosyl and Decyl Chain as an Amphiphilic Photosensitizer toward Photodynamic Therapy	2002	▼
[Journal Article] Self-Organizing Super-Structures Formed from Hydrogen Bonded Biimidazaolate Metal Complexes	2002	▼
[Journal Article] Mononuclear-Dinuclear Helicate Interconversion of Dibromo{N,N'-bis[(S)-1-2-(pyridyl)ethyl]pyridine-2,6-dicarboxamidate}copper(II) via a Deprotonation-Protonation Process	2002	▼
[Journal Article] Thia-calix[n]pyridines, synthesis and coordination to Cu(I,II) ions with both N and S donor atoms	2002	▼
[Journal Article] Structure and Reactivity of a Novel Parallel Thiosulfite (SSO ₂ -S,S') Rhodium Dinuclear Complex	2002	▼
[Journal Article] Self-Organizing Super-Structures Formed from Hydrogen-Bonded Biimidazaolate Metal Complexes	2002	▼
[Journal Article] Mononuclear-Dinuclear Helicate Interconversion of Dibromo{N,N'-bis[(S)-1-2-(pyridyl)ethyl]Pyridine-2,6-dicarboxamidate}copper(II) via a Deprotonation-Protonation Process	2002	▼
[Journal Article] Thia-calix[n]pyridines, synthesis and coordination to Cu(I, II) ions with both N and S donor atoms	2002	▼
[Journal Article] Cesium(I)-Mediated 3-D Superstructures by One-Pot Self-Organization of Hydrogen-Bonded Nickel Complexes	2001	▼
[Journal Article] Cesium(I)-Mediated 3-D Superstructures by One-Pot Self-Organization of Hydrogen-Bonded Nickel Complexes	2001	▼
[Journal Article] meso-Tetraphenylporphyrin Having Hexa-maltosyl and Decyl Chain as an Amphiphilic Photosensitizer toward Photodynamic Therapy	2001	▼
[Book] 集積型金属錯体の科学-物質機能の多様性を求めて-	2003	▼
[Book] Polyoxometalate Chemistry for Nano-composite Design	2002	▼

