活性S-S結合による結晶相光応答錯体分子の構築と光機能の解明

2007 Fiscal Year Final Research Report Summary

Synthesis and Function of Crystalline-state Photoresponsive Metal Complexes with Active S-S Bond

Research Project

Project/Area Number

16350029

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

Principal Investigator

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Project Period (FY)

2004 – 2007

Keywords

Active S-S Bond / Crystalline-state Reaction / Photoresponsive Function / Photochromism / Variable Temperature Solid State ^2H NMR Spectroscopy / Chiral Crystalzation / Absolute Asymmetric Synthesis / 光誘起相転移

Research Abstract

In the crystalline state, the rhodium dinuclear complex[(RhCp^*)_2(μ-CH_2)_2(μ-O_2SSO_2)] (1) with a photoresponsive dithionite group (μ-O_2SSO_2) and two pentamethylcyclopentadienyl ligands (Cp^*=η^5-C_5Me_5) undergoes a 100% reversible unimolecular type T inverse photochromism upon interconversion to [(RhCp^*)_2(μ-CH_2)_2(μ-O_2SOSO)] (2). The photochromism can be followed directly by using stepwise crystal structure analysis.
In this study, we found that the photoreaction of 1 was triggered by absorption of the 510 nm light (charge transfer band from σ(S-S)to σ^*(S-S)and σ^*(Rh-Rh)orbitals

assigned by DFT calculation) and included two important processes:kinetically controlled oxygen-atom transfer to produce four stereoisomers of 2 and thermodynamically controlled isomerization between the four stereoisomers of 2 to afford the most stable isomer. Although the formation rate of the four stereoisomer products was kinetically controlled and the population of the four stereoisomers produc …▾ More

Research Products (114 results)

[Journal Article] Substitution Effects of Cp Ring Benzyl Groups on Photoisomerization of a Rhodium Dithionite Complex in the Crystalline State 2008

[Journal Article] Self-assembled All-inorganic Chiral Polyoxovanadate：Spontaneous Resolution of Nitrated-incorporated Octadecavanadate 2008

[Journal Article] Substitution Effects of Cp Ring Benzyl Groups on Photoisomerization of a Rhodium Dithionite Complex in the Crystalline State 2008

[Journal Article] Self-assembled All-inorganic Chiral Polyoxovanadate: Spontaneous Resolution of Nitrated-incorporated Octadecavanadate 2008

[Journal Article] ロジウムおよびイリジウム二核錯体による無機硫黄の変換(Account) 2007

[Journal Article] Synthesis and Structural Characterization of a Photoresponsive Organodirhodium Complex with Active S-S Bonds：[(Cp^<Ph>Rh)(μ-CH_2)(μ-O_2SSO_2)](Cp^<Ph>=η^5-C_5Me_4Ph) 2007

[Journal Article] Mixed-Valence States Stabilized by Proton Transfer in a Hydrogen-Bonded Biimidazolate Rhenium Dimer 2007

[Journal Article] Reduced Polyoxovanadates in Non-aqueous Medial Conden sation Reaction of Polyoxovanadates by Reductive or Oxidative Coupling 2007

[Journal Article] Stepwise Synthesis of Disk and Ball Shaped Polyoxovanadates：All-Inorganic Coordination Chemistry of Polyoxovanadates 2007

[Journal Article] Transformation of Inorganic Sulfurs Using Rhodium/Iridium Dinuclear complexes 2007

[Journal Article] Synthesis and Structural Characterization of a Photoresponsive Organodirhodium Complex with Active S-S Bonds：[(Cp^<ph>Rh)(μ-CH_2)(μ-O_2SSO_2)](Cp^<ph>=η^5-C_5Me_4Ph) 2007

[Journal Article] Direct Observation of Photochromic Dynamics in Crystalline-state of an Organorhodium Dithionite Complex 2006

[Journal Article] Synthesis and Structural Characterization of a Photochromic Dirhodium Dithionite Complex：[(Cp^<ph>Rh)(μ-CH_2)(μ-O_2SSO_2)] (Cp^<Ph>=η^5-C_5Me_4Ph) 2006

[Journal Article] Structures and Phase Transition of Multi-layered Water Nanotube Confined to Nanochannels 2006

[Journal Article] Mixed-Valence States Stabilized by Proton Transfer in a HydrogenBonded Biimidazolate Rhenium Dimer 2006

[Journal Article] Direct Observation of Photochromic Dynamics in Crystalline-state of an Organorhodium Dithionite Complex 2006

[Journal Article] Synthesis and Structural Characterization of a Photochromic Dirhodium Dithionite Complex：[(Cp^<ph>Rh)(μ-CH_2)(μ-O_2SSO_2)] (Cp^<ph>=η^5-C_5Me_4Ph) 2006

[Journal Article] Synthesis and Crystal Structure of an Open Capsule-type Octanuclear Heterometallic Sulfide Cluster with a Linked Incomplete Double Cubane Framework without an Intramolecular Inversion Center 2005

[Journal Article] Synthesis and Characterization of a Twin Cubane-Type Molybdenum-Rhodium-Sulfur Cluster, [{Mo_3RhCp*S_4(H_2O)_7(O)}_2]. X-ray Structure of [{Mo_3RhCp*S_4(H_2O)_7(O)}_2] (CH_3C_6H_4-SO_3)_8-14H_2O 2005

[Journal Article] Preparation, Crystal Structures and Spectroscopic Properties of Novel[M^<III>Cl_<3-n>(P)_<3+n>]^<n+> (M=Co, Rh；n=0, 1, 2 or 3) Series of Complexes Containing Tripodal Tridentate Phosphine, 1, 1, 1-tris (DimeThylphosphinomethyl) ethane 2005

[Journal Article] Cyclic Polyvanadates Incorporating Template Transition Metal Cationic Species：Synthesis and Structures of Hexavanadate [PdV_6O_<18>]^<4->, Octavanadate [Cu_2V_8O_<24>]^<4->, and Decavanadate [Ni_4V_<10>O_<30>(OH)_2(H_2O)_6]^<4-> 2005

[Journal Article] Synthesis and Crystal Structure of an Open Capsule"type Octanuclear Heterometallic Sulfide Cluster with a Linked Incomplete Double CubaneFramework without an Intramolecular Inversion Center 2005

[Journal Article] Synthesis and Characterization of a Twin Cubane-Type MolybdenumRhodium-Sulfur Cluster, [{Mo_3RhCp^*S_4(H_2O)7(O)}_2]. X-ray Structure of [{Mo_3RhCp^*S_4(H_2O)_7(O)}_2] (CH_3C_6H_4-SO_3)_8・14H_2O 2005

[Journal Article] Preparation, Crystal Structures and Spectroscopic Properties of Novel [M^<III>Cl_<3-n>(P)_<3+n>]n^+ (M = Co, Rh ; n = 0, 1, 2 or 3) Series of Complexes Containing Tripodal Tridentate Phosphine, 1,1,1-tris(Dimethylphosphinomethy1)ethane 2005

[Journal Article] Cyclic Polyvanadates Incorporating Template Transition Metal Cationic Species : Synthesis and Structures of Hexavanadate [PdV_6O_18]^4, Octavanadate [Cu_2V_8O_24]^4, and Decavanadate [Ni_4V_10O_30(OH)_2(H_2O_6)]^4 2005

[Journal Article] Nucleophilicity of Ligated S_2^<2-> Ions. Conversion of Organic Chlorides in Organosulfur Compounds in cis-[(MCp^*)_2(μ-CH_2)_2(μ-S_2R)]^+ (M=Rh, Ir) 2004

[Journal Article] Novel Nucleophilic Reactivity of Disulfido Ligands Coordinated Parallel to M-M (M=Rh, Ir) Bonds 2004

[Journal Article] Activation of C-Cl and C-H Bonds by Ligated S_2^<2-> in Unusual Way. Conversion of Organic Chlorides into Organosulfur Compounds Coordinated to Iridium Metal Atom in cis-[(IrCp^*)_2(μ-CH_2)_2(μ-S_2R)]^+ 2004

[Journal Article] Pyridine-2-sulfonates as Versatile Ligands for the Synthesis of Novel Coordinative and Hydrogen-bonded Supramolecles 2004

[Journal Article] Nucleophilicity of Ligated S22" Ions. Conversion of Organic Chlorides into Organosulfur Compounds in cis-[(MCp^*)_2(μ-CH_2)_2(μ-S_2R)]+(M=Rh, Ir) 2004

[Journal Article] Novel Nucleophilic Reactivity of Disulfido Ligands Coordinated Parallel to M-M (M = Rh, Ir) Bonds 2004

[Journal Article] Activation of C-Cl and C-H Bonds by Ligated S_2^2- in Unusual Way. Conversion of Organic Chlorides into Organosulfur Compounds Coordinated to Iridium Metal Atom in cis-[(IrCp^*)_2(μ-CH_2)_2(μ-S_2R)]^+ 2004

[Journal Article] Pyridine-2-sulfonates as Versatile Ligands for the Synthesis of Novel Coordinative and Hydrogen-bonded Supramolecles 2004

[Journal Article] Reaction Dynamics Studies on Crystalline-state Photochromism of Rhodium Dithionite Complexes

[Presentation] ジチオナイト錯体の結晶相フォトクロミズム：反応空間をつくる配位子の動的挙動 2008

[Presentation] ジチオナイト錯体の結晶相フォトクロミズム：結晶相反応におよぼすペンタメチルシクロペンクジエニル配位子の置換基効果 2008

[Presentation] ロジウムジチオナイト錯体のキラル結晶中でのフォトクロミズム 2008

[Presentation] Control of crystalline-state photochromic reaction by fine-tuning of phtoresponsive space 2007

[Presentation] All-Inorganic Dinuclear Cobalt Complex with Inorganic Porphhyrin Type Ligand" 2007

[Presentation] Template Synthesis of a Spherical Polyoxovanadate(V) by Oxidative Coupling 2007

[Presentation] All-inorganic dinuclear cobalt complex with inorganic porphhyrin type ligand 2007

[Presentation] Template synthesis of a spherical polyoxovanadate(V) by oxidative coupling 2007

[Presentation] Exchange Reaction of Oxo Anions on Tripodal Molybdenum Cluster 2007

[Presentation] Coordination Chemistry of Polyoxovanadates as Macrocyclic Ligands 2007

[Presentation] Exploration of dynamics of photoreaction and morphology change of dithionite complex in crystalline-state 2007

[Presentation] Crystalline-state photochromism of rhodium dithionite complexes having pentamethylcyclopen tadienyl derivatives 2007

[Presentation] Exchange reaction of oxo anions on tripodal molybdenum cluster 2007

[Presentation] Coordination chemistry of polyoxovanadates as macrocyclic ligands 2007

[Presentation] Control of Crystalline State Photochromic Reaction 2007

[Presentation] 新規骨格を有するポリオキソメタレートの合成 2007

[Presentation] 環状酸化物配位子を用いた第一系列遷移金属錯体 2007

[Presentation] 還元型モリブデートの二量化反応 2007

[Presentation] テンプレートを用いた球状トリアコンタバナデート(V)の合成 2007

[Presentation] アルコキソチクンクラスターと金属塩の反応 2007

[Presentation] 固体重水素NMRによるジチオナイト錯体の配位子回転運動に関する研究 2007

[Presentation] Co-Mo担持金属醒化物クラスターの四面体部位置換反応 2007

[Presentation] ヒドリド配位子を持つ種々のイリジウム二核錯体の合成、構造および反応性 2007

[Presentation] サイクリックポリオキソバナデート配位子を用いた第一系列遷移金属錯体 2007

[Presentation] ロジウムジチオナイト錯体の結晶相光異性化反応におけるプロピル置換基の効果 2007

[Presentation] 光機能化したシクロペンタジエニル誘導体を用いたランタニド錯体の合成と性質 2007

[Presentation] テンプレートを用いた球状トリアコンタバナデート(V)の合成 2007

[Presentation] ジチオナイト基を持つロジウム複核錯体の結晶相光異性化反応における光強度依存性 2007

[Presentation] ジチオナイト錯体が示す結晶相光異性化反応と配位子の動的挙動との相関 2007

[Presentation] Co-Mo担持金属酸化物クラスターの四面体部位置換反応 2007

[Presentation] ロジウムジチオナイト錯体の結晶相光異性化反応におけるナフチル基の効果 2007

[Presentation] Exploration of Dynamics of Photoreaction and Morphology Change of Dithionite Complex in Crystalline-state 2007

[Presentation] Crystalline-state Photochromism of Rhodium Dithionite Complexes Having Pentamethylcyclopentadienyl Derivatives 2007

[Presentation] Stepwise Synthesis of Disk, Bowl and Ball Shaped Polyoxovanadates：All-Inorganic Coordination Chemistry 2006

[Presentation] Stepwise synthesis of disk, bowl and ball shaped polyoxovanadates:AlHnorganic coordination chemistry 2006

[Presentation] コバルト錯体担持型モリブデン酸化物クラスターの四面体ユニット置換反応 2006

[Presentation] ジオチナイト基をもつCpRh二核錯体の結晶相異性化反応の温度依存性 2006

[Presentation] 光機能化したペンタメチルシクロペンタジエニル配位子による新規サマリウム錯体の合成と性質 2006

[Presentation] ロジウム二核錯体上でのジスルフィド配位子の酸化反応メカニズム 2006

[Presentation] 新規骨格を有するバナジウム酸化物クラスターの合成 2006

[Presentation] ジオチナイト錯体の結晶相光異性化反応における反応ダイナミクス 2006

[Presentation] 結晶相光異性化反応における置換基効果2：テトラメチルシクロペンタジエニル配位子を用いたロジウムジオチナイト錯体の合成と性質 2006

[Presentation] コバルト錯体担持型モリブデン酸化物クラスターの四面体ユニット置換反応 2006

[Presentation] 還元型タングステンドーソン構造のアセテート置換反応 2006

[Presentation] 結晶相光異性化反応における置換基効果1：ベンジル置換基を有するロジウムジオチナイト錯体の合成と性質 2006

[Presentation] 光機能化したペンタメチルシクロペンタジエニル誘導体のアルカリ金属塩の合成とその光化学特性 2006

[Presentation] Formation of Hexacosavanadate by Reductive Coupling Reaction of Decavanadate 2005

[Presentation] Benzoate Derivatives of Lacunary Dawson-Type Tetradecamolybdate 2005

[Presentation] All-Inorganic Coordination Chemistry of Polyoxovanadates：Chemistry Between Polyoxovanadates and Metal Cationic Species 2005

[Presentation] Formation of hexacosavanadate by reductive coupling reaction of decavanadate, Polyoxometalate Chemistry for Molecular Design and Nanoengineering 2005

[Presentation] Benzoate derivatives of lacunary Dawson-type tetradecamolybdate, Polyoxometalate Chemistry for Molecular Design and Nanoengineering 2005

[Presentation] All-inorganic coordination chemistry of polyoxovanadates：Chemistry between polyoxovanadates and metal cationic species, Polyoxometalate Chemistry for Molecular Design and Nanoengineering 2005

[Presentation] Synthesis of Crown-Ring, Bowl and Ball Shaped Polyoxovanadate(V) with Templates 2005

[Presentation] Synthesis of crown-ring, bowl and ball shaped polyoxovanadate(V) with templates 2005

[Presentation] α-ジスルフォン錯体の結晶相光異性化反応における反応空間ダイナミクス：固体NMRおよびX線結晶構造解析による検討 2005

[Presentation] 欠損型Dawson構造を持つテトラデカモリブデートの安息香酸誘導体 2005

[Presentation] 結晶相光異性化反応における置換基効果：フェニル置換基を有するα-ジスルフオンロジウム二核錯体の合成と性質 2005

[Presentation] 光応答部位を導入した新組サマリウム錯体の合成と性質 2005

[Presentation] 亜鉛イオンを含むテトラバナデートの合成 2005

[Presentation] ロジウム二核錯体上でのオキシジスルフィド誘導体の変換反応 2005

[Presentation] テンプレートを用いた新規バナジウムクラスターの合成 2005

[Presentation] 酸化還元能を持つポリオキソタングステートの合成 2005

[Presentation] Cyclic polyvanadates incorporating templatetransition metal cationic species 2004

[Presentation] Construction of chloride-encapsulated spherical vanadate from cyclic polyvanadate 2004

[Presentation] 新規骨格構造をもつバナジウム酸化物クラスターの合成 2004

[Presentation] パラジウム(II)を含む環状ヘキサバナデートの合成 2004

[Presentation] 結晶相光応答錯体：硫黄酸化物イリジウム二核錯体の合成と構造 2004

[Presentation] 結晶相光異性化能を持つロジウム二核錯体の合成 2004

[Presentation] 酸化還元能をもつ酢酸架橋モリブデン酸化物クラスターの合成 2004

[Presentation] クロム(VI)酸配位金属錯体の合成と性質 2004

[Presentation] SI-MS及び多核NMRによる, VO_3^-, WO_4^2-, Mo_2O_7^2-の溶液内挙動の研究 2004

[Presentation] Cyclic Polyvanadates Incorporating Template Transition Metal Cationic Species 2004

[Presentation] Construction of Chloride-encapsulated Spherical Vanadate from Cyclic Polyvanadate 2004

[Book] Reaction Dynamics Studies on Crystalline-state Photochromism of Rhodium Dithionite Complexes, in “Molecular Nanodynamics-Active Surfaces and Single Crystals" edited by Hiroshi Fukumura, Masahiro Irie, Yasuhiro Iwasawa, Hiroshi Masuhara and Kohei Uosaki. 2008

[Book] Reduced Polyoxovanadates in Non-aqueous Media：Condensation Reaction of Polyoxovanadates by Reductive or Oxidative Coupling, Chapter 2, pp. 15-32in “Vanadium Biochemistry" edited by Manuel Aureliano Alves 2007

[Book] Stepwide Synthesis of Disk- and Ball-Shaped Polyoxovanadates : All-inorganic Coordination Chemistry of Polyoxovanadates, Chapter 29 in “Vanadium : The Versatile Metal" edited by Kenneth Kustin, Joao Costa Pessoa, Debbie C. Crans 2007

[Patent(Industrial Property Rights)] 重合体の製造方法 2008

[Patent(Industrial Property Rights)] ポリシランの製造方法 2008

[Patent(Industrial Property Rights)] 二核金属錯体およびその製造方法 2007

[Patent(Industrial Property Rights)] 発光性金属錯体およびその製造方法 2007

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