RESEARCH ACTIVITIES VIII Coordination Chemistry Laboratories

Prof. Hiroshi Kitagawa (Kyushu Univ.) and Assoc. Prof. Mitsuru Kondo (Shizuoka Univ.) took the position of the Laboratory of Complex Catalyst from April 2006. Prof. Kazushi Mashima (Osaka Univ.) and Assoc. Prof. Masato Kurihara (Yamagata Univ.) finished their term as Adjunct Prof. of the Laboratory of Complex Catalyst in March 2006. Their effort during their term is gratefully appreciated. Prof. Yoichi Ishii (Chuou Univ.) and Prof. Takashi Hayashi (Osaka Univ.) continue the position of Laboratory of Coordination Bond.

VIII-A Metal Complexes Aimed at Conversion between Chemical and Electrochemical Energies

Metal complexes that have an ability to oxidize organic molecules at potentials more negative than the reduction potential of dioxygen have potential uses for electro-catalysts in fuel cells. Metal–oxo complexes are possible candidates for the oxidation of organic molecules, since metal–oxo species are believed to work as active centers in various metal enzymes, which oxidize various biological substrates under very mild conditions. Mechanistic understandings of the reactivity of metal–oxo species, however, are limited due to the difficulty of preparation of reactive M–O frameworks in artificial systems. On the other hand, reactivity of high valent Ru=O complexes prepared by sequential electron and proton loss of the corresponding Ru–OH₂ ones have been extensively studied and proven to work as oxidants of organic molecules to some extent. We have succeeded reversible conversion between aqua and oxo ligands on Ru–dioxolene frameworks without using any oxidants by taking advantage of dioxolene as a redox active ligand. Along this line, we have been preparing a variety of metal–aqua and –amine complexes bearing a dioxolene ligand aiming at oxidation of hydrocarbons by the corresponding metal–oxo and –imido complexes.

VIII-A-1 Structural Characterization of Ruthenium–Dioxolene Complexes with Ru^{II}–SQ and Ru^{II}–Cat Frameworks

FUJIHARA, Tetsuaki; OKAMURA, Rei; TANAKA, Koji

[Chem. Lett. 34, 1562–1563 (2005)]

The structural and electronic properties of $[Ru^{II}(trpy) (CISQ)(PPh_3)]^+$ (trpy = 2,2':6',2''-terpyridine; CISQ = 4-chlorobenzosemiquinonate) that is prepared from *cis*-[Ru(trpy)(PPh_3)Cl_2] and 4-chlorocatechol (HCICat), and $[Ru^{II}(trpy)(CICat)(PPh_3)]$ obtained by the reduction of the former were examined. Both complexes were characterized by x-ray diffractometry, UV-visible spectroscopy, ESR, and electrochemistry.

VIII-A-2 Reversible Bond Formation and Cleavage of the Oxo Bridge of $[Ru_2(\mu-O)$ (dioxolene)₂(btpyxa)]³⁺ [btpyxa = 2,7-Di-tertbutyl-9,9-dimethyl-4,5-bis(2,2':6',2"-terpyrid-4'yl)xanthene] Driven by a Three-Electron Redox Reaction

WADA, Tohru; TANAKA, Koji

[Eur. J. Inorg. Chem. 19, 3832-3839 (2005)]

The bis(chlororuthenium) complex $[Ru_2Cl_2(3,6-tBu_2sq)_2(btpyxa)](PF_6)_2$ $[3,6-tBu_2sq = 3,6-di-tert-butyl-1,2-benzosemiquinone; btpyxa = 2,7-di-tert-butyl-9,9-dimethyl- 4,5-bis(2,2':6',2''-terpyrid-4'-yl)xanthene]$

and the oxobridged diruthenium complex [$Ru_2(\mu-O)$] (3,6-tBu₂sq)₂(btpyxa)](PF₆)₃ were synthesized, and the redox behavior of these complexes, which contain a non-innocent dioxolene ligand, was investigated by electrochemistry and electrospectrochemistry methods. Dicationic 2^+ undergoes two successive metal-centered one-electron and a simultaneous two-electron ligandbased redox reaction at $E_{1/2} = +0.13$ and +0.09 and $E_{1/2}$ = -0.75 V (vs. SCE), respectively, in CH₂Cl₂. The UV/ Vis/NIR spectrum of tricationic 3^+ shows an intervalence-transition (IT) band at 1333 nm ($\lambda = 1.52 \times 10^4$ M⁻¹ cm⁻¹) in a near-IR region together with two CT bands at 766 ($\lambda = 2.21 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 586 nm (epsilon = $1.13 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in CH₂Cl₂. The mixedvalence complex of 3^+ with an Ru^{IV}–O–Ru^{III} core is reversibly oxidized and reduced to the Ru^{IV}–Ru^{IV} and Ru^{III}–Ru^{III} oxidation states at $E_{1/2} = +0.63$ and -0.01 V, respectively, in CH₂Cl₂. On the other hand, three-electron redn. of $(PF_6)_3$ is accompanied by the cleavage of the Ru–O–Ru bond at $E_p = +0.02$ V to give [{Ru(OMe) (3,5-*t*Bu₂sq)}{Ru(OH₂)(3,5-*t*Bu₂sq)}(btpyxa)]⁺ in MeOH.

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VIII-A-3 A New Series of Molybdenum-(IV), -(V), and -(VI) Dithiolate Compounds as Active Site Models of Molybdoenzymes: Preparation, Crystal Structures, Spectroscopic/ Electrochemical Properties and Reactivity in Oxygen Atom Transfer

SUGIMOTO, Hideki¹; TARUMIZU, Makoto¹; TANAKA, Koji; MIYAKE, Hiroyuki¹; TSUKUBE, Hiroshi¹

(¹Osaka City Univ.)

[Dalton Trans. 21, 3558–3565 (2005)]

A new set of Mo-(IV), -(V), and -(VI) compounds containing 3,6-dichloro-1,2-benzenedithiolate (bdtCl₂) were isolated and characterized by crystallography and other spectroscopic techniques as active site models of arsenite oxidase, one of the molybdoenzymes. MoO2 compounds were prepared in high yields by reaction of MoO₂Cl₂ with bdtCl₂, related dithiolene and thiocatecholate in MeOH at low temp. The bdtCl₂ ligand particularly stabilized the MoO compounds with oxidation states of +4 and +5 as well as the MoO₂ compound with an oxidation number of +6. (Et₄N)₂[Mo^{VI}O₂ $(bdtCl_2)_2$] (1) $(Et_4N)_2[Mo^{IV}O(bdtCl_2)_2]$ (2) and (Et_4N) $[Mo^{V}O(bdtCl_{2})_{2}]$ (3) were successfully isolated, whereas (Et₃NH)₂[MoO₂(thiocatecholate)₂] (6) gradually decomposed in MeCN. A distorted octahedral structure similar to that of **1** was suggested for the structure of the active site of the oxidized form of arsenite oxidase from a comparison of their bond distances and angles. The bond distances and angles around the Mo(IV) atom in 2 were similar to those around the Mo(IV) center in the reduced form of arsenite oxidase. The reversible 2/3 couple exhibited a more positive redox potential than common MoO dithiolene compounds. 1 underwent an irreversible proton-coupled reduction process to yield 2. An O atom transfer reaction of 1 with PPh3 afforded 2 and OPPh₃, and proceeded in second order as v = -d/dt $[MoO_2] = k[MoO_2][PPh_3]$. The structures and properties of the oxo-bridged dinuclear compound, $(Et_4N)_2[Mo^{VI}O_2]$ $(bdtCl_2)]_2(\mu-O)$ (4), a dimer of $bdtCl_2$ (5) and 6 were also characterized.

VIII-A-4 Reversible Hydride Generation and Release from the Ligand of [Ru(pbn)(bpy)₂](PF₆)₂ Driven by a Pbn-Localized Redox Reaction

KOIZUMI, Take-aki; TANAKA, Koji

[Angew. Chem., Int. Ed. 44, 5891-5894 (2005)]

 $[Ru(pbn)(bpy)_2](PF_6)_2$ (1, pbn = 2-(2-pyridyl)benzo [b]-1,5-naphthyridine, bpy = 2,2'-bipyridine) was prepared and characterized by x-ray crystallography. Electrochemical reduction of 1 in an acidic solvent gives $[Ru(pbnH_2)(bpy)_2]^{2+}$ (2), which releases the hydrogen as hydride. This catalytic system reduces substrates (for example, acetone) with two electrons and protons from water, and thus operates in a similar way to the NAD⁺/ NADH redox couple.



 $[Ru] = [Ru(bpy)_2]$

VIII-A-5 Mononuclear Five-Coordinate Molybdenum(IV) and -(V) Monosulfide Complexes Coordinated with Dithiolene Ligands: Reversible Redox of Mo(V)/Mo(IV) and Irreversible Dimerization of [Mo^VS]⁻ Cores to a Dinuclear [Mo^V₂(μ-S)₂]²⁻ Core

SUGIMOTO, Hideki¹; SAKURAI, Takashi¹; MIYAKE, Hiroyuki¹; TANAKA, Koji; TSUKUBE, Hiroshi¹

(¹Osaka City Univ.)

[Inorg. Chem. 44, 6927–6929 (2005)]

A mononuclear five-coordinate Mo(IV) monosulfide complex, $(Et_4N)_2[MoS(L)_2]$ (L = cyclohexene-1,2-di thiolate) (1), was obtained and characterized by IR, UVvisible spectroscopic methods, and x-ray crystallography. 1 was oxidized by an equiv. ferrocenium cation to give the corresponding mononuclear Mo(V) complex, (Et_4N) [MoS(L)₂] (2), which was stable for a few minutes under a lower concentration than 0.3 mM and then further dimerized to $(Et_4N)_2[Mo(L)_2]_2(\mu-S)_2$ (3).

VIII-A-6 Synthesis and Crystal Structures of $[W(3,6\text{-dichloro-1},2\text{-benzenedithiolate})_3]^{n-}$ (n = 1, 2) and [Mo(3,6-dichloro-1,2-) benzenedithiolate $)_3]^{2-}$: Dependence of the Coordination Geometry on the Oxidation Number and Counter-Cation in Trigonal-Prismatic and Octahedral Structures

SUGIMOTO, Hideki¹; FURUKAWA, Yuuki¹; TARUMIZU, Makoto¹; MIYAKE, Hiroyuki¹; TANAKA, Koji; TSUKUBE, Hiroshi¹ (¹Osaka City Univ.)

[Eur. J. Inorg. Chem. 15, 3088–3092 (2005)]

 $(Et_4N)_2[W(bdtCl_2)_3]$ (1a), $(Ph_4P)_2[W(bdtCl_2)_3]$ (1b), $(Et_4N)[W(bdtCl_2)_3]$ (2a), $(Ph_4P)[W(bdtCl_2)_3]$ (2b), $(C_5NH_6)[W(bdtCl_2)_3]$ (2c), and $(Et_3NH)_2[Mo(bdtCl_2)_3]$ (**3a**) (bdtCl₂ = 3,6-dichloro-1,2-benzenedithiolate) were prepared and characterized by x-ray crystallography, UV/visible spectroscopic, and electrochemical methods. Versatile geometrical changes around the W centers were observed. The trigonal-prismatic structure of the W center in (Et₄N)₂[W(bdtCl₂)₃] (1a) is changed to an intermediate structure between trigonal prismatic and octahedral upon solid-state oxidation of the complex of **2a.** Replacement of the countercation of **1a** with Ph_4P^+ also resulted in geometrical changes and somewhat of an octahedral contribution is included in 1b. However, almost the same coordination structures are present in structures 2a, 2b, and 2c, with an oxidation number of

+5. These structures adopt an intermediate geometry between trigonal prismatic and octahedral. No geometrical change was observed upon changing the metal center from W to Mo in $[M(bdtCl_2)_3]^{2-}$ (M = W and Mo).

VIII-A-7 Synthesis, Structures and Electrochemical Properties of Ruthenium (II) Complexes Bearing Bidentate 1,8-Naphthyridine and Terpyridine Analogous (N,N,C)-Tridentate Ligands

KOIZUMI, Take-aki; TOMON, Takashi; TANAKA, Koji

[J. Organomet. Chem. 690, 4272–4279 (2005)]

1,8-Naphthyridine (napy) and terpyridine-analogous (N,N,C) tridentate ligands coordinated ruthenium (II) complexes, [RuL(napy-kappa2,N,N')(dmso)](PF₆)₂ (1: L = L1 = N"-methyl-4'-methylthio-2,2':6',4"-terpyridinium, 2: L = L2 = N"-methyl-4'-methylthio-2,2': 6',3"-terpyridinium) were prepared and their chemical and electrochemical properties were characterized. The structure of complex 1 was determined by x-ray crystallographical study, showing that it has a distorted octahedral coordination style. The cyclic voltammogram of 1 in DMF exhibited two reversible ligand-localized redox couples. On the other hand, the CV of 2 shows two irreversible cathodic peaks, due to the Ru-C bond of 2 containing the carbenic character. The IR spectra of 1 in CO₂-saturated CH₃CN showed the formation of Ru-(η -CO₂) and Ru-CO complexes under the controlled potential electrolysis of the solution at -1.44 V (vs. Fc/Fc^+). The electrochemical reduction of CO_2 catalyzed by 1 at -1.54 V (vs. Fc/Fc⁺) in DMF (-0.1 M Me₄NBF₄) produced CO with a small amt. of HCO₂H.



VIII-A-8 Dioxo-Molybdenum(VI) and Mono-Oxo-Molybdenum(IV) Complexes Supported by New Aliphatic Dithiolene Ligands: New Models with Weakened Mo:O Bond Characters for the Arsenite Oxidase Active Site

SUGIMOTO, Hideki¹; HARIHARA, Makoto¹; SHIRO, Motoo¹; SUGIMOTO, Kunihisa¹; TANAKA, Koji; MIYAKE, Hiroyuki¹; TSUKUBE, Hiroshi¹

(¹Osaka City Univ.)

[Inorg. Chem. 44, 6386–6392 (2005)]

The *cis*-dioxomolybdenum(VI) complexes, $[MoO_2 (LH)_2]^{2-}$ (**1b**), $[MoO_2(LS)_2]^{2-}$ (**2b**), and $[MoO_2(LO)_2]^{2-}$ (**3b**) (LH = cyclohexene-1,2-dithiolate, LS = 2,3dihydro-2H-thiopyran-4,5-dithiolate, and LO = 2,3dihydro-2H-pyran-4,5-dithiolate), with new aliphatic dithiolene ligands were prepared and studied by IR and UV-visible spectroscopic and electrochemical methods. The mono-oxomolybdenum(IV) complexes, [MoO $(LH)_2]^{2-}$ (1a), [MoO(LS)_2]^{2-} (2a), and [MoO(LO)_2]^{2-} (3a), were further characterized by x-ray crystal structural determinations. The IR and resonance Raman spectroscopic studies suggested that these *cis*-dioxo Mo(VI) complexes (1b-3b) have weaker Mo=O bonds than the common Mo^{VI}O₂ complexes. Complexes 1b-3b also exhibited strong absorption bands in the visible regions assigned as charge-transfer bands from the dithiolene ligands to the *cis*-MoO₂ cores. Because the O atoms of the *cis*-Mo^{VI}O₂ cores are relatively nucleophilic, these complexes are unstable in protic solvents and protonation might occur to produce Mo^{VI}O(OH), as observed with the oxidized state of arsenite oxidase.

VIII-A-9 Electronic Structural Changes between Nickel(II)–Semiquinonato and Nickel(III)– Catecholato States Driven by Chemical and Physical Perturbation

OHTSU, Hideki; TANAKA, Koji

[Eur. J. Chem. A 11, 3420–3426 (2005)]

The selective synthesis of tetracoordinate squareplanar low-spin nickel(II)-semiquinonato (Ni^{II}-SQ) and nickel(III)-catecholato (Ni^{III}-Cat) complexes, [Ni(L) $(SQ/CAT)](PF_6)$ (L = dibenzyl(2-pyridylmethyl)amine, SQ = 3,5-di-*tert*-butylsemiquinonate, CAT = 3,5-di-*tert*butylcatecholate), 1 and 2, respectively, was achieved by using bidentate ligands with modulated nitrogen-donor ability to the nickel ion. The electronic structures of 1 and $\hat{2}$ were revealed by XPS and EPR measurements. The absorption spectra of 1 and 2 in a noncoordinating solvent, dichloromethane (CH_2Cl_2) , are completely different from those in THF, being a coordinating solvent. As expected the gradual addition of DMF, which is also a coordinating solvent like THF, into a solution of 1 or 2 in CH₂Cl₂ leads to color changes from blue (for 1) and brown (for 2) to light green, which is the same color observed for solutions of 1 or 2 in THF. Also, the same color changes are induced by varying the temp. Such spectral changes are attributable to the transformation from square-planar low-spin Ni^{II}-SQ and Ni^{III}-Cat complexes to octahedral high-spin Ni^{II}-SQ ones, caused by the coordination of two solvent molecules to the nickel ion.

VIII-A-10 Electrochemical Hydrogenation of $[Ru(bpy)_2(napy-\kappa N)(CO)]^{2+}$: Inhibition of Reductive Ru–CO Bond Cleavage by a Ruthenacycle

TOMON, Takashi; KOIZUMI, Take-aki; TANAKA, Koji

[Angew. Chem., Int. Ed. 44, 2229–2232 (2005)]

A 5-membered metallacycle (2^+) hydrogenated at the 4-position of the naphthyridine ligand (3^+) is formed by the electrochemical reduction of $[Ru(bpy)_2(napy-\kappa N)$ (CO)]²⁺ (1^{2+} ; bpy = 2,2'-bipyridine, napy = 1,8-naph-thyridine) at -1.40 V in H₂O. Chemical or electro-

chemical oxidation of 3^+ regenerates 1^+ through 2^+ in almost quantitative yield.



VIII-A-11 Synthesis, Chemical- and Electrochemical Properties of Ruthenium(II) Complexes Bearing 2,6-Bis(2-naphthyridyl)pyridine

KOIZUMI, Take-aki; TANAKA, Koji

[Inorg. Chim. Acta 358, 1999–2004 (2005)]

Ruthenium complexes with a terpyridine-analogous ligand, 2,6-bis(2-naphthyridyl)- pyridine (**I**, bnp), were synthesized and their chemical and electrochemical properties studied. The structures of $[Ru(bnp)(tpy)](PF_6)_2$ (**1**) and $[Ru(bnp)_2](PF_6)_2$ (**2**) were determined by x-ray structure analysis. The bnp localized redox potentials of **1** and **2** showed significant positive shift by 260–290 mV relative to the analogous Ru–terpyridine complexes.

VIII-A-12 Synthesis and Electrochemical Properties of Bis(bipyridine)ruthenium(II) Complexes Bearing Pyridinyl- and Pyridinylidene Ligands Induced by Cyclometalation of N-Methylated Bipyridinium Analogs

KOIZUMI, Take-aki; TOMON, Takashi; TANAKA, Koji

[J. Organomet. Chem. 690, 1258–1264 (2005)]

Ruthenium cyclometalated complexes with N-monomethylated 2,4'- and 2,3'-bipyridine N,C-ligands were prepared and characterized. Reaction of $[(bpy)_2RuCl_2]$ (bpy = 2,2'-bipyridine) with 1-methyl-4-(2-pyridinyl) pyridinium (HL₁·PF₆) and 1-methyl-3-(2-pyridinyl) pyridinium (HL₂·PF₆) hexafluorophosphates and AgPF₆ afforded cyclometalated complexes $[(bpy)_2Ru(L_1-C3, N')][PF_6]_2$ (1) and carbenoid complex I (2), respectively. Structure of **2** was confirmed by low-field shift of the C4-carbon of the cyclometalated bipyridinium ligand and by x-ray structure determination. The ligand-localized redox potentials of **1** and **2** also revealed the substantial difference in the electron donating ability of both ligands.

VIII-A-13 Stabilization and Destabilization of the Ru–CO Bond during the 2,2'-Bipyridin-6-Onato (bpyO)-Localized Redox Reaction of [Ru(terpy)(bpyO)(CO)](PF₆)

TOMON, Takashi; KOIZUMI, Take-aki; TANAKA, Koji

[Eur. J. Inorg. Chem. 2, 285-293 (2005)]

Two stereoisomers of [Ru(terpy)(bpyO)(CO)](PF₆) $([1]^+ \text{ and } [2]^+; \text{ terpy} = 2,2':6',2''-\text{terpyridine, bpyO} =$ 2,2'-bipyridin-6-onato) were prepared. The pyridonato moiety in the bpyO ligand of $[1]^+$ and $[2]^+$ is located trans and *cis*, respectively, to CO. Treatment of $[1]^+$ and $[2]^+$ with HPF₆ produced $[1H]^{2+}$ and $[2H]^{2+}$, both of which contain bpyOH (bpyOH = 6-hydroxy-2,2'-bipyridine). The difference in the *pKa* values of $[1H]^{2+}$ (3.5) and [2H]²⁺ (3.9) reflects the stronger electronic interaction between CO and the pyridonato moiety in the bpyO ligand in the trans position compared with that in the *cis* position. The molecular structures of $[1](PF_6)$, $[2](PF_6) \cdot H_2O$ and $[2H](PF_6)_2 \cdot 2H_2O$ were determined by x-ray structure analyses. $[1]^+$ and $[2]^+$ undergo one reversible reduction at $E_{1/2} = -1.65$ V and -1.51 V, respectively, and one irreversible reduction at $E_{p,c}$ = -2.07 and $E_{p,c} = -2.13$ V, respectively. Both reductions are assigned to redox reactions localized at the terpy and bpyO ligands. Irreversible reduction of $[1]^0$ results from reductive cleavage of the Ru-CO bond of [1]⁻. However, a two-electron oxidation of $[2]^-$ almost regenerates $[2]^+$ because of the depression of the reductive Ru-CO bond cleavage of $[2]^-$ due to cyclometalation formed by an attack of O of bpyO to the C of the Ru-CO bond. An unusually large shift of the v(C=O) band on going from $[2]^0$ (1950 cm⁻¹) to $[2]^-$ (1587 cm⁻¹) also supports a reversible cyclometalation driven by the bpyO-localized redox reaction.



VIII-A-14 Electronic Structural Changes between Nickel(II)–Semiquinonato and Nickel(III)–Catecholato States Driven by Chemical and Physical Perturbation

OHTSU, Hideki; TANAKA, Koji

[Eur. J. Chem. A 11, 3420–3426 (2005)]

The selective synthesis of tetracoordinate squareplanar low-spin nickel(II)–semiquinonato (Ni^{II}–SQ) and nickel(III)–catecholato (Ni^{III}–Cat) complexes, [Ni(L) (SQ/CAT)](PF₆) (L = dibenzyl(2-pyridylmethyl)amine, SQ = 3,5-di-*tert*-butylsemiquinonate, CAT = 3,5-di-*tert*butylcatecholate), **1** and **2**, respectively, was achieved by using bidentate ligands with modulated nitrogen-donor ability to the nickel ion. The electronic structures of **1** and **2** were revealed by XPS and EPR measurements. The absorption spectra of **1** and **2** in a noncoordinating solvent, dichloromethane (CH₂Cl₂), are completely different from those in THF, being a coordinating solvent. As expected the gradual addition of DMF, which is also a coordinating solvent like THF, into a solution of **1** or **2** in CH₂Cl₂ leads to color changes from blue (for **1**) and brown (for **2**) to light green, which is the same color observed for solutions of **1** or **2** in THF. Also, the same color changes are induced by varying the temp. Such spectral changes are attributable to the transformation from square-planar low-spin Ni^{II}–SQ and Ni^{III}–Cat complexes to octahedral high-spin Ni^{II}–SQ ones, caused by the coordination of two solvent molecules to the nickel ion.

Ρh

Мe

[Ni^{II}(Py(Bz)₂)(*t*Bu₂SQ)](PF₆)

[Ni^{III}(MePy(Bz)₂)(tBu₂Cat)](PF₆)