

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

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(¹Osaka City Univ.)

[Dalton Trans. **21**, 3558–3565 (2005)]

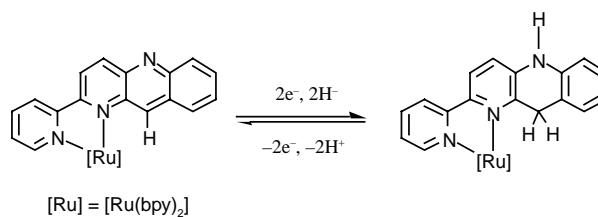
A new set of Mo-(IV), -(V), and -(VI) compounds containing 3,6-dichloro-1,2-benzenedithiolate (bdtCl₂) were isolated and characterized by crystallography and other spectroscopic techniques as active site models of arsenite oxidase, one of the molybdoenzymes. MoO₂ compounds were prepared in high yields by reaction of MoO₂Cl₂ with bdtCl₂, related dithiolene and thio-catecholate 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(bdtCl₂)₂] (**1**) (Et₄N)₂[Mo^{IV}O(bdtCl₂)₂] (**2**) and (Et₄N)[Mo^VO(bdtCl₂)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 $v = -d/dt [\text{MoO}_2] = k[\text{MoO}_2][\text{PPh}_3]$. The structures and properties of the oxo-bridged dinuclear compound, (Et₄N)₂[Mo^{VI}O₂(bdtCl₂)₂](μ-O) (**4**), a dimer of bdtCl₂ (**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](PF₆)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(pbnH₂)(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.



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

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[Inorg. Chem. **44**, 6927–6929 (2005)]

A mononuclear five-coordinate Mo(IV) monosulfide complex, (Et₄N)₂[MoS(L)₂] (L = cyclohexene-1,2-dithiolate) (**1**), was obtained and characterized by IR, UV-visible spectroscopic methods, and x-ray crystallography. **1** was oxidized by an equiv. ferrocenium cation to give the corresponding mononuclear Mo(V) complex, (Et₄N)[MoS(L)₂] (**2**), which was stable for a few minutes under a lower concentration than 0.3 mM and then further dimerized to (Et₄N)₂[Mo(L)₂]₂(μ-S)₂ (**3**).

VIII-A-6 Synthesis and Crystal Structures of [W(3,6-dichloro-1,2-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

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

(Et₄N)₂[W(bdtCl₂)₃] (**1a**), (Ph₄P)₂[W(bdtCl₂)₃] (**1b**), (Et₄N)[W(bdtCl₂)₃] (**2a**), (Ph₄P)[W(bdtCl₂)₃] (**2b**), (C₅NH₆)[W(bdtCl₂)₃] (**2c**), and (Et₃NH)₂[Mo(bdtCl₂)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 counteranion of **1a** with Ph₄P⁺ 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

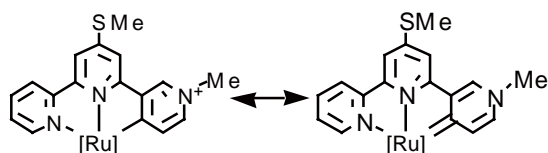
+5. These structures adopt an intermediate geometry between trigonal prismatic and octahedral. No geometrical change was observed upon changing the metal center from W to Mo in $[M(\text{bdtCl}_2)_3]^{2-}$ ($M = \text{W}$ and Mo).

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, $[\text{RuL}(\text{napy-}\kappa\text{pa}2, \text{N}, \text{N}')(\text{dmsO})](\text{PF}_6)_2$ (**1**: $L = \text{L1} = \text{N}''\text{-methyl-4'-methylthio-2,2':6',4''-terpyridinium}$, **2**: $L = \text{L2} = \text{N}''\text{-methyl-4'-methylthio-2,2':6',3''-terpyridinium}$) 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 CO_2 -saturated CH_3CN showed the formation of Ru–(η - CO_2) 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 Me_4NBF_4) produced CO with a small amt. of HCO_2H .



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

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[*Inorg. Chem.* **44**, 6386–6392 (2005)]

The *cis*-dioxomolybdenum(VI) complexes, $[\text{MoO}_2(\text{LH})_2]^{2-}$ (**1b**), $[\text{MoO}_2(\text{LS})_2]^{2-}$ (**2b**), and $[\text{MoO}_2(\text{LO})_2]^{2-}$ (**3b**) ($\text{LH} = \text{cyclohexene-1,2-dithiolate}$, $\text{LS} = 2,3$ -dihydro-2H-thiopyran-4,5-dithiolate, and $\text{LO} = 2,3$ -dihydro-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, $[\text{MoO}(\text{LH})_2]^{2-}$ (**1a**), $[\text{MoO}(\text{LS})_2]^{2-}$ (**2a**), and $[\text{MoO}(\text{LO})_2]^{2-}$ (**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 $\text{Mo}^{\text{VI}}\text{O}_2$ 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*- MoO_2 cores. Because the O atoms of the *cis*- $\text{Mo}^{\text{VI}}\text{O}_2$ cores are relatively nucleophilic, these complexes are unstable in protic solvents and protonation might occur to produce $\text{Mo}^{\text{VI}}\text{O}(\text{OH})$, 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 square-planar low-spin nickel(II)–semiquinonato ($\text{Ni}^{\text{II}}\text{-SQ}$) and nickel(III)–catecholato ($\text{Ni}^{\text{III}}\text{-Cat}$) complexes, $[\text{Ni}(\text{L})(\text{SQ}/\text{CAT})](\text{PF}_6)$ ($L = \text{dibenzyl}(2\text{-pyridylmethyl})\text{amine}$, $\text{SQ} = 3,5\text{-di-}i\text{-tert-butylsemiquinonato}$, $\text{CAT} = 3,5\text{-di-}i\text{-tert-butylcatecholato}$), **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 (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 CH_2Cl_2 leads to color changes from blue (for **1**) or 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 $\text{Ni}^{\text{II}}\text{-SQ}$ and $\text{Ni}^{\text{III}}\text{-Cat}$ complexes to octahedral high-spin $\text{Ni}^{\text{II}}\text{-SQ}$ ones, caused by the coordination of two solvent molecules to the nickel ion.

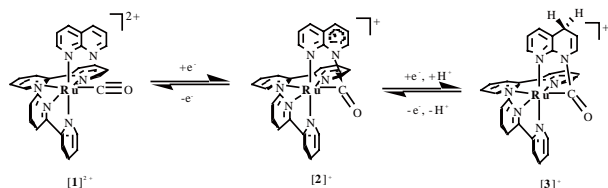
VIII-A-10 Electrochemical Hydrogenation of $[\text{Ru}(\text{bpy})_2(\text{napy-}\kappa\text{M})(\text{CO})]^{2+}$: Inhibition of Reductive Ru–CO Bond Cleavage by a Ruthenacycle

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 $[\text{Ru}(\text{bpy})_2(\text{napy-}\kappa\text{N})(\text{CO})]^{2+}$ (1^{2+} ; bpy = 2,2'-bipyridine, napy = 1,8-naphthyridine) at -1.40 V in H_2O . 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-naphthridyl)pyridine

KOIZUMI, Take-aki; TANAKA, Koji

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

Ruthenium complexes with a terpyridine-analogous ligand, 2,6-bis(2-naphthridyl)-pyridine (**1**, bnp), were synthesized and their chemical and electrochemical properties studied. The structures of $[\text{Ru}(\text{bnp})(\text{tpy})](\text{PF}_6)_2$ (**1**) and $[\text{Ru}(\text{bnp})_2](\text{PF}_6)_2$ (**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)]

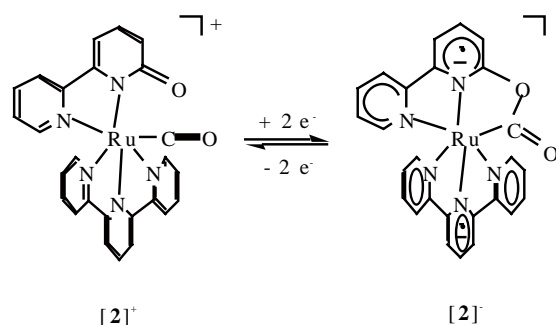
Ruthenium cyclometalated complexes with N-mono-methylated 2,4'- and 2,3'-bipyridine N,C-ligands were prepared and characterized. Reaction of $[(\text{bpy})_2\text{RuCl}_2]$ (bpy = 2,2'-bipyridine) with 1-methyl-4-(2-pyridinyl)pyridinium ($\text{HL}_1 \cdot \text{PF}_6$) and 1-methyl-3-(2-pyridinyl)pyridinium ($\text{HL}_2 \cdot \text{PF}_6$) hexafluorophosphates and AgPF_6 afforded cyclometalated complexes $[(\text{bpy})_2\text{Ru}(\text{L}_1\text{-C}_3, \text{N}^+)](\text{PF}_6)_2$ (**1**) and carbenoid complex **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 $[\text{Ru}(\text{terpy})(\text{bpyO})(\text{CO})](\text{PF}_6)$

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

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

Two stereoisomers of $[\text{Ru}(\text{terpy})(\text{bpyO})(\text{CO})](\text{PF}_6)$ ($[1]^+$ and $[2]^+$; terpy = 2,2':6',2''-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 HPF_6 produced $[1\text{H}]^{2+}$ and $[2\text{H}]^{2+}$, both of which contain bpyOH (bpyOH = 6-hydroxy-2,2'-bipyridine). The difference in the *pK_a* values of $[1\text{H}]^{2+}$ (3.5) and $[2\text{H}]^{2+}$ (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 $[1](\text{PF}_6)$, $[2](\text{PF}_6) \cdot \text{H}_2\text{O}$ and $[2\text{H}](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ 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 $\nu(\text{C}\equiv\text{O})$ 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.



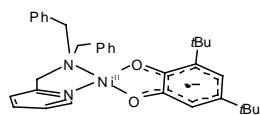
VIII-A-14 Electronic Structural Changes between Nickel(II)–Semiquinonato and Nickel(III)–Catecholato States Driven by Chemical and Physical Perturbation

OHTSU, Hideki; TANAKA, Koji

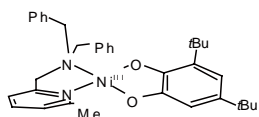
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vent. As expected the gradual addition of DMF, which is also a coordinating solvent like THF, into a solution of **1** or **2** in CH_2Cl_2 leads to color changes from blue (for **1**) and brown (for **2**) to light green, which is the same color observed 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.



$[\text{Ni}^{\text{II}}(\text{Py}(\text{Bz})_2)(\text{tBu}_2\text{SQ})](\text{PF}_6)$



$[\text{Ni}^{\text{III}}(\text{MePy}(\text{Bz})_2)(\text{tBu}_2\text{Cat})](\text{PF}_6)$