Redox Behavior and Catalytic Oxidation Reactions of Alcohols by a New Ruthenium(III)–Dioxolene–Amine Complex of Bis(2-pyridylmethyl)-2-aminoethylamine

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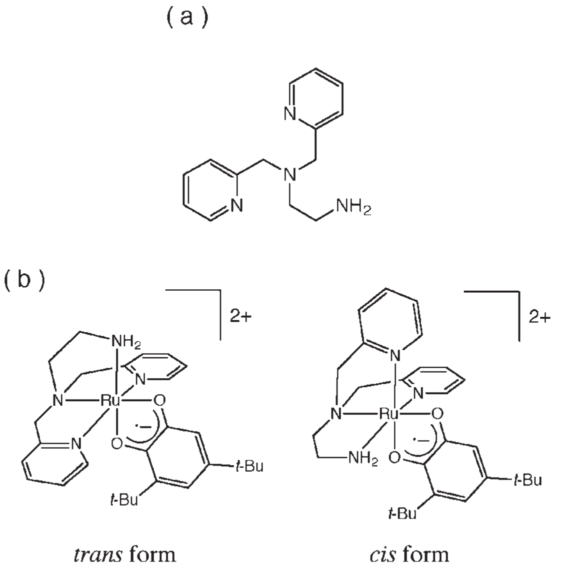
A ruthenium–dioxolene–amine complex, $[Ru^{III}(NH_2\text{-}L)(Bu_2sq)](PF_6)_2\cdot 0.5H_2O$ (NH_2-L = bis(2-pyridylmethyl)-2-aminoethylamine, $Bu_2sq^- = $ 3,5-di-*tert*-butylsemiquinonate), was newly prepared. The complex undergoes spontaneous one-electron reduction under basic conditions in MeOH and works as an electrocatalyst in the oxidation of benzyl alcohol to benzaldehyde under electrolysis at +0.4 V (vs SCE).

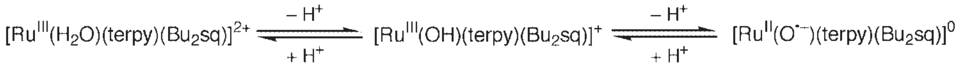
The oxidation reactions of alcohols forming aldehydes and ketones are fundamental molecular transformations in organic syntheses, and a variety of reagents have been employed in those oxidation reactions.[1] In biological systems, the oxo-metal species included in metal proteins are believed to work as the active centers to oxidize various biological substrates.[2,3] Meyer and co-workers have developed a versatile synthetic route for high-valent $O{=}Ru^{IV}$ complexes by sequential proton and electron losses of the corresponding Ru(II)–OH_2 complexes, $[Ru^{II}(H_2O)(terpy)(bpy)]^{2+}$ and $[Ru^{II}(H_2O)(bpy)_2(py)]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine, py = pyridine).[4] Several $O{=}Ru^{IV}$ complexes have proven to be active in the oxidation of some organic substrates.[4a] Recently, we have reported that $[Ru^{III}(H_2O)(terpy)(Bu_2sq)](ClO_4)_2$ ($Bu_2sq^- = $ 3,5-di-*tert*-butylsemiquinonate) is reversibly converted to an unusual oxyl radical complex, $[Ru^{II}(O^{\bullet -})(terpy)(Bu_2sq)]^0$, under basic conditions without using any oxidants (Scheme 1).[5] The reactivity of the oxyl radical complex toward the oxidation of alcohols was lower than that of $O{=}Ru^{IV}$. On the other hand, 2-PrOH was oxidized to acetone by an analogous ruthenium(III)–dioxolene–ammine complex,[6] $[Ru^{III}(NH_3)(terpy)(Bu_2sq)](ClO_4)_2$, in the presence of a methanolic solution of BuOK. The same oxidation reaction catalytically proceeded under the electrochemical oxidation of $[Ru^{III}(NH_3)(terpy)(Bu_2sq)]^{2+}$ at +0.35 V (vs SCE) in MeOH. However, the amino group of the complex was gradually substituted with MeO^- in the progress of the oxidation reactions, and the catalytic activity of the complex decreases with time due to the formation of $[Ru^{III}(OMe)(terpy)(Bu_2sq)]^+$, which has no activity to oxidize alcohols under similar reaction conditions. Protection of the amino group of $[Ru^{III}(NH_3)(terpy)(Bu_2sq)]^{2+}$ from the replacement of MeO^- is expected to improve the catalytic activity for the oxidation reaction of alcohols. We, therefore, prepared a new ruthenium–dioxolene–amine complex, $[Ru^{III}(NH_2\text{-}L)(Bu_2sq)](PF_6)_2\cdot 0.5H_2O$ (NH_2-L = bis(2-pyridylmethyl)-2-aminoethylamine (Fig. 1a), $Bu_2sq^- = $ 3,5-di-*tert*-butylsemiquinonate), in the hope that the NH_2 group of NH_2-L would be inert for the substitution reaction by MeO^-, and examined the catalytic activity toward the oxidation reaction of alcohols under basic conditions.

A ruthenium(III)–dioxolene–amine complex, $[Ru^{III}(NH_2\text{-}L)(Bu_2sq)](PF_6)_2\cdot 0.5H_2O$ ($[\mathbf{1}](PF_6)_2\cdot 0.5H_2O$), was obtained by the addition of 2 equiv of *tert*-BuOLi to a 2:2:1 mixture of $[\{Ru^{II}(NH_2\text{-}L)\}_2(\mu\text{-}Cl)_2](PF_6)_2$,[15] $AgBF_4$, and 3,5-di-*tert*-butylcatechol (Bu_2catH_2) in acetone. The geometry of $[\mathbf{1}](PF_6)_2\cdot 0.5H_2O$ presumably takes a hexa-coordinate structure with four nitrogen atoms of tetradentate NH_2-L and two oxygen atoms of bidentate Bu_2sq^-. There would be two possible isomers with regard to the orientation of the coordination mode of NH_2-L to a ruthenium ion: The two pyridyl groups in NH_2-L are located at either a *cis*- or *trans*-position with each other (Fig. 1b).[5] Several attempts to separate those two isomers by chromatography were unsuccessful, because the product showed only one band in chromatograms. All the physicochemical data of isolated $[Ru^{III}(NH_2\text{-}L)(Bu_2sq)](PF_6)_2$ are reasonably explained by the single pure complex, though it is not clear whether the product is a mixture of the two isomers in Fig. 1b or a pure form of either of them. The effective magnetic moment of $[\mathbf{1}](PF_6)_2\cdot 0.5H_2O$ in the powder sample was 2.79 B.M.



trans form *cis* form

Fig. 1. The schematic structure of NH_2-L (a) and two proposed structures of $[\mathbf{1}]^{2+}$ (b).



Scheme 1.

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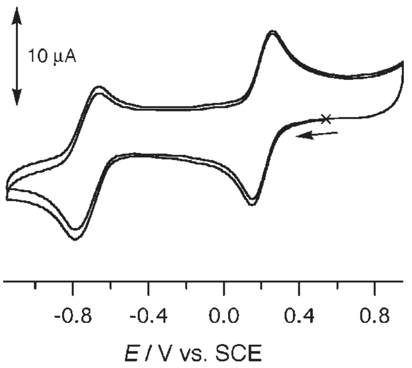


Fig. 2. A cyclic voltammogram of [**1**]$(PF_6)_2\cdot 0.5H_2O$ (1 mM) in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 at room temperature under N_2; $dE/dt = 100\,mV\,s^{-1}$; a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/0.01 M $AgNO_3$ reference electrode (SCE − 250 mV).

at 300 K. The value is close to the spin-only one ($\mu_{s.o.} = 2.45$ B.M.) expected from the magnetically isolated {Ru(III)–sq} framework. The CT band resulting from the {Ru(III)–sq} framework was observed at 618 nm (ε: $7890\,M^{-1}\,cm^{-1}$) and 592 nm (ε: $5540\,M^{-1}\,cm^{-1}$) in the electronic absorption spectrum of [**1**]$(PF_6)_2\cdot 0.5H_2O$ in CH_2Cl_2 and MeOH, respectively. The cyclic voltammograms (CV) of [**1**]$(PF_6)_2\cdot 0.5H_2O$ in CH_2Cl_2 showed two quasi-reversible redox waves at $E^1{}_{1/2} = +0.20$ V and $E^2{}_{1/2} = -0.77$ V (vs SCE), and the rest potential of the solution (+0.52 V) is located at the positive side of the redox couple at $E^1{}_{1/2} = +0.20$ (Fig. 2). The redox waves at $E^1{}_{1/2}$ and $E^2{}_{1/2}$ are assigned to the $[Ru(III)–sq]^{2+}/[Ru(II)–sq]^{+}$ and $[Ru(II)–sq]^{+}/[Ru(II)–cat]^{0}$ (sq^- = semiquinonate and cat^{2-} = catecholate) couples, respectively.[6a,7] Based on the analogous redox couples at $E^1{}_{1/2} = +0.34$ and $E^2{}_{1/2} = -0.46$ V of $[Ru^{III}(NH_3)(terpy)(Bu_2sq)](ClO_4)_2$, the $E^1{}_{1/2}$ and $E^2{}_{1/2}$ values of [**1**]$^{2+}$ shifted cathodically by 0.14 and 0.31 V, respectively, indicating that the σ-donor character of NH_2-L generated by primary amine, tertiary amine, and two pyridyl groups is stronger than that of a combination of NH_3 and the terpy ligand in $[Ru^{III}(NH_3)(terpy)(Bu_2sq)](ClO_4)_2$. Electrochemical reduction of [**1**]$^{2+}$ at −0.2 V (vs SCE) generating [**1**]$^{+}$ with the {Ru(II)–sq} framework[6,7] in CH_2Cl_2 resulted in red shift of the MLCT band from 618 to 888 nm. In accordance with this, the EPR spectrum of the electrolyte solution showed an isotropic broad signal at $g = 2.015$ assignable to a semiquinonate radical at 193 K. A large g value compared with the free spin value ($g = 2.0023$) implies that [**1**]$^{+}$ has more or less the electronic state of the {Ru(III)–cat} framework as a resonance form of the {Ru(II)–sq} core.[8–10]

The gradual addition of a methanol solution of *tert*-BuOLi to [**1**]$^{2+}$ in MeOH results in the emergence of a new absorption band at 894 nm at the expense of the absorption band at 592 nm, with an appearance of an isosbestic point at 724 nm (Fig. 3).[11,12] The spectral changes caused at the presence of one-equiv of *tert*-BuOLi, and further addition of the base to the solution did not give any influence on the spectra. The final spectrum is fully consistent with that of [**1**]$^{+}$ generated by the electrochemical reduction of [**1**]$^{2+}$ at −0.2 V in MeOH. In accordance with this, an ESI-mass signal of dicationic [**1**]$^{2+}$ ($m/z = 282.098$) completely disappeared after the addition of 1 equiv of *tert*-BuOLi to the methanolic solution of [**1**]$^{2+}$, and the signal originated from monocationic $[Ru^{II}(NH_2\text{-}L)(Bu_2sq)]^{+}$ (obsd. $m/z = 564.202$, calcd $m/z = 564.205$) developed. In addition, LC analysis of the resultant solution proved the formation of formaldehyde as the two-electron oxidation product of MeOH in 28% yield (based on [**1**]$(PF_6)_2$). Thus, spontaneous reduction of [**1**]$^{2+}$ having the $\{Ru(III)–sq\}^{2+}$ framework to [**1**]$^{+}$ with the $\{Ru(II)–sq\}^{+}$ one in MeOH under basic conditions is caused by the oxidation reaction of the solvent molecule to formaldehyde. The low yield of formaldehyde compared with the stoichiometric conversion from [**1**]$^{2+}$ to [**1**]$^{+}$ may be ascribed to the instability of the formaldehyde in basic media. In other words, [**1**]$^{2+}$ has the ability to oxidize MeOH with the generation of [**1**]$^{+}$. We, therefore, carried out the oxidation reaction of MeOH used as the solvent under the controlled potential electrolysis of [**1**]$(PF_6)_2\cdot 0.5H_2O$ (10 µmol) in the presence of 100 equiv of *tert*-BuOLi at +0.4 V. The electrolysis smoothly proceeded as far as the base exists in the solution and almost stopped after 100 C passed in the electrolysis, suggesting that the oxidation reaction of MeOH took place under the experimental conditions. It is worthy of note that $[Ru^{III}(NH_3)(terpy)(Bu_2sq)]^{2+}$ gradually loses catalytic activity in the electrochemical oxidation reaction of MeOH because of the formation of $[Ru^{III}(OMe)(terpy)(Bu_2sq)]^{+}$ in the presence of MeO^{-}.[7] On the other hand, [**1**]$^{2+}$ keeps the catalytic activity in the electrochemical oxidation of MeOH even in the presence of large excess amounts of MeO^- (in a methanolic solution of *tert*-BuOLi, the solution contains MeO^- and *tert*-BuOH), indicating that the NH_2-L ligand ligated on [**1**]$^{2+}$ remains unchanged in the oxidation reaction. Benzyl alcohol was also catalytically oxidized by [**1**]$^{2+}$ under basic conditions, since the electrolysis of [**1**]$(PF_6)_2\cdot 0.5H_2O$ (10 µmol) at +0.4 V in the presence of 10 equiv of *tert*-BuOLi in $CH_2Cl_2/PhCH_2OH$ (4:1 v:v) produced 63 µmol of benzaldehyde (GC-MS analysis) after the consumption of 10 C in the electrolysis. The rate of the oxidation reaction of benzyl alcohol was about 1/3 compared with that of MeOH due to the steric hindrance.

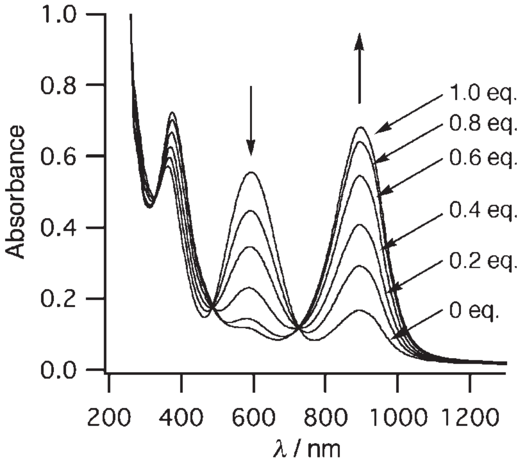
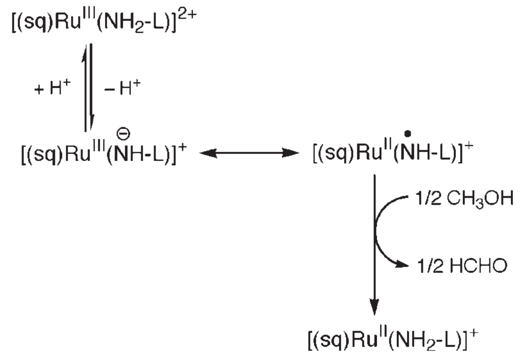


Fig. 3. The electronic absorption spectra of [**1**]$(PF_6)_2\cdot 0.5H_2O$ in MeOH (1 mM) in the presence of various amounts of *tert*-BuOLi at 298 K.[11]

The catalytic activity of [**1**]$^{2+}$ toward the oxidation of alcohols under basic conditions is reasonably inferred from the



Scheme 2.

acid–base equilibria among $[Ru^{III}(H_2O)(terpy)(Bu_2sq)]^{2+}$, $[Ru^{III}(OH)(terpy)(Bu_2sq)]^{+}$, and $[Ru^{II}(O^{\bullet -})(terpy)(Bu_2sq)]^{0}$: Treatment of $[\mathbf{1}]^{2+}$ with 1.0 equiv of *tert*-BuOLi dissociates a primary amino proton, which will induce intramolecular one-electron transfer from the $(NH\text{-}L)^{-}$ group to the $\{Ru^{III}\text{–}sq\}$ unit. As a result, the radical character will be generated on the nitrogen atom of the primary amino group. Abstraction of hydrogen from alcohols by $[Ru^{II}({}^{\bullet}NH\text{-}L)(Bu_2sq)]^{+}$ would produce $[Ru^{II}(NH_2\text{-}L)(Bu_2sq)]^{+}$ ($[\mathbf{1}]^{+}$) (Scheme 2). Thus, the ruthenium–dioxolene complex having $\{({}^{\bullet}N)Ru^{II}\text{–}sq\}$ framework is the most possible active species in the catalytic oxidation of $PhCH_2OH$ and MeOH.

Experimental

Physical Measurements. Elemental analysis was carried out at the Research Center for Molecular-scale Nanoscience, Institute for Molecular Science. Magnetic measurement was carried out on a powder sample with a Quantum Design MPMS-7 magnetometer, in the temperature range of 2–300 K. Diamagnetic correction was applied using Pascal's constants. The effective magnetic moment was calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. Electronic absorption spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. The EPR spectrum was measured with a JEOL X-band spectrometer (JES-FA200) using an attached VT (Variable Temperature) apparatus. ESI-TOF mass spectra were obtained with a micromass LCT time of flight mass spectrometer. Cyclic voltammograms of the complex were measured with an ALS/chi Model 660 Electrochemical Analyzer. The controlled potential electrolysis was performed on a Toho Model PS-08 8-channel potentiostat/galvanostat using the H-tube cell separated with anion exchange membrane. GC-MS experiments were performed on a Shimadzu GSMS-QP5050. LC analysis was performed on a Tosoh DP-8020 instrument equipped with a Shiseido Capcell-Pack C_{18} column (4.6 × 250 mm).

Preparation. $[\{(\eta\text{-}C_6H_6)RuCl_2\}_2]$ and bis(2-pyridylmethyl)-2-aminoethylamine (NH_2-L) were prepared according to the literature methods.[13,14]

$[Ru^{III}(NH_2\text{-}L)(Bu_2sq)](PF_6)_2 \cdot 0.5H_2O$ ($[\mathbf{1}](PF_6)_2 \cdot 0.5H_2O$). To an acetone solution (25 mL) of bis-μ-chloride dimer precursor,[15] $[\{Ru(NH_2\text{-}L)\}_2(\mu\text{-}Cl)_2](PF_6)_2$ (200 mg, 0.2 mmol), was added $AgBF_4$ (78 mg, 0.4 mmol) in acetone (2 mL). After heating for 2 h, the resulting AgCl was filtered off. A methanolic solution of sodium 3,5-di-*tert*-butylcatecholate (90 mg, 0.4 mmol) and *tert*-BuOLi (64 mg, 0.8 mmol) was added to the filtrate, and then the solution was stirred for 24 h under N_2 at room temperature. The reaction mixture was evaporated to dryness under reduced pressure, and then the crude products were washed with diethyl ether to remove blue $[Ru^{III}(Bu_2sq)_3]$ from the mixture. The residue was dissolved in a minimum amount of MeOH. The addition of an aqueous solution of NH_4PF_6 (30 mL) to the solution precipitated the ruthenium–dioxolene–amine complex as a blue powder. Anal. Found: C, 38.90; H, 4.45; N, 6.29%. Calcd for $C_{28}H_{39}N_4O_{2.5}F_{12}P_2Ru$: C, 38.99; H, 4.56; N, 6.49%. ESI-mass: $m/z = 282.0981$ for $[Ru^{III}(NH_2\text{-}L)(Bu_2sq)]^{2+}$ in MeOH.

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11 A weak band emerged at 894 nm resulted from $[\mathbf{1}]^{+}$ in the absorption spectrum of $[\mathbf{1}]^{2+}$ in MeOH even in the absence of bases. The absorbance at 894 nm slowly increased with time. Furthermore, the rate of the increase in the absorption band at 894 nm in electronic absorption spectra of $[\mathbf{1}]^{2+}$ in MeOH increased with dilution of the complex, indicating that spontaneous reduction of $[\mathbf{1}]^{2+}$ is triggered by the dissociation of amino proton of the ligand in MeOH.

12 The reduction of $[\mathbf{1}]^{2+}$ to $[\mathbf{1}]^{+}$ was also observed in the CV of the complex; an addition of 1.0 equiv of *tert*-BuOLi to a methanolic solution of $[\mathbf{1}]^{2+}$ shifted the rest potential of the solution from +0.52 to −0.25 V across the redox couple at $E^1{}_{1/2} = +0.20$ V without changing the pattern of the two redox couples ($E^1{}_{1/2}$ and $E^2{}_{1/2}$).

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15 To a suspension of $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ (270 mg, 0.54 mmol) in degassed EtOH (30 mL) was added an EtOH (5 mL) solution of NH_2-L (200 mg, 0.82 mmol), and then the mixture was stirred for 4 h at 70 °C under N_2. After cooling to room temperature, NH_4PF_6 (360 mg, 2.16 mmol) was added to the reaction mixture, and the solution was stirred for 1 h at 50 °C under N_2. The resulting brown powder was filtered off and washed with EtOH and Et_2O. ESI-mass data: $m/z = 379.03$ for $[\{Ru(NH_2\text{-}L)\}_2(\mu\text{-}Cl)_2]^{2+}$.