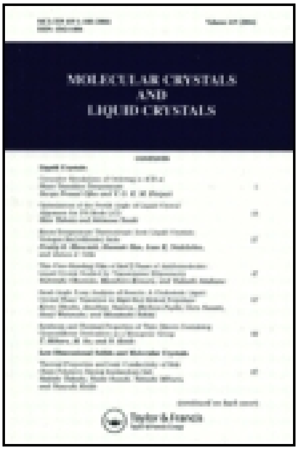

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Comparison with Several Oxidation States of Ruthenium Binuclear Complexes; Ruthenium Analogue for Iron- Protein Active Site Model

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COMPARISON WITH SEVERAL OXIDATION STATES OF RUTHENIUM BINUCLEAR COMPLEXES; RUTHENIUM ANALOGUE FOR IRON-PROTEIN ACTIVE SITE MODEL

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Abstract Alkoxo bridged ruthenium dinuclear complexes as a non-heme diiron protein active site model, $[Ru(III)_2(dhpta)(O_2CR)_2]^-$ (H_5dhpta=1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid, R=CH_3(1), C_6H_5(2), C_6H_4-*p*-OH(3), C_6H_4-*p*-NH_2(4)) exhibited the strongly antiferromagnetically coupled magnetic behavior ($H = -2J \cdot S_1 \cdot S_2$, $-J$=310~470 cm^{-1}). The magnetic interaction between Ru(III) ions varies depending on the bridged carboxylato ligand. The one-electron reduced Ru(II)Ru(III) mixed-valence states by electrolysis shows two absorption bands in the near-IR region, which the lowest energy one might be intervalence charge transfer (IT) band. Hush theory was applied to analyze the IT band in the lowest energy, the electronic coupling integral, H_{ad} was estimated to be 670–870 cm^{-1}. The interaction between the Ru(II)Ru(III) mixed valence state is weaker than that of the Ru(III)Ru(III) states. With one-electron oxidized complex (2), Ru(III)Ru(IV) mixed-valence state, two absorption bands appeared in the near-IR region, and H_{ad} was estimated as 2000 cm^{-1}.

INTRODUCTION

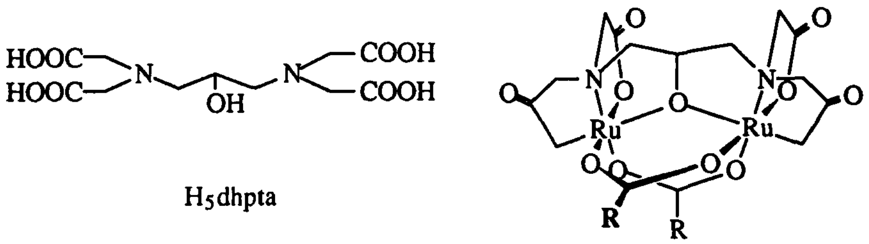
Previously, we reported a series of novel alkoxo bridged ruthenium dinuclear complexes as a non-heme diiron protein active site model such as hemerythrin[1], $[Ru(III)_2(dhpta)(O_2CR)_2]^-$ (H_5dhpta = 1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid, R = CH_3 (1), C_6H_5 (2), C_6H_4-*p*-OH (3), C_6H_4-*p*-NH_2 (4)).[2]

In the present study, we will describe a preliminary account of the spectroscopic properties of Ru(II)Ru(III) and Ru(III)Ru(IV) mixed-valence states and magnetic properties related to the electronic structure of the Ru(III)Ru(III) oxidation state.

EXPERIMENTAL SECTION

Temperature dependent magnetic susceptibilities were measured by the Faraday method with a Cahn RH electrobalance in a 6000 Oe field over the temperature range 70 – 300 K. Magnetic susceptibilities at room temperature were also obtained by the Gouy method. The diamagnetism of the complexes were corrected using the literature values[3] except H_5dhpta.

Cyclic voltammetry was performed in CH_3CN or DMF (0.1M $N(Bu)_4$ (PF_6)) solution with a three-electrode system consisting of a glassy carbon working, and a platinum counter, and an $Ag/AgPF_6$ reference electrode.



H_5dhpta

FIGURE 1 Structures of the bridging ligand, H_5dhpta (left) and its ruthenium complex (right).

RESULTS

Magnetic susceptibility

The temperature dependence of the molar susceptibility was analyzed using an isotropic Heisenberg model for spin-exchange coupled the binuclear center with the spin Hamiltonian $H = -2J \bullet S_1 \bullet S_2 (S_1 = S_2 = 1/2)$, and by treating the coupling constant J, the g value, and temperature-independent paramagnetism TIP. The susceptibility data were fitted to the model equation successfully, and the magnetic susceptibility parameters are summarized in Table 1. The unpaired electrons at Ru(III) centers are strongly coupled antiferromagnetically ($-J$ = 310 – 470 cm^{-1}). The spin-exchange interaction is sensitive to the bridged carboxylate ligands character. In generally the reported g values for ruthenium (III) complexes have been shown anisotropic character. For (μ-hydroxo)bis(μ-carboxylato) binuclear ruthenium complex, a g value of 2.4 has been reported.[4(a)] Thus, the present g value of 2.4 falls within normal two Ru(III) coupled systems.

TABLE 1 Magnetic susceptibility parameters and structural parameters

	g	$-J$ / cm^{-1}	TIP/ emu•mol^{-1}	Ru-O-Ru	Ru—Ru/Å
(1)	2.4	470	263×10^{-6}	124.1(7)*	3.433(3)*
(2)	2.0	310	180×10^{-6}		3.44**
(3)	2.2	312	118×10^{-6}		3.44**
(4)	2.0	320	274×10^{-6}		3.44**

* Referred from X-ray crystallographic data.[2]

** Referred from EXAFS data[6]

For the weak magnetic interaction of two spins ($S = 1/2$) in orthogonal orbitals ϕ_a and ϕ_b, eq. (2) can be derived from the perturbation theory.[6]

$$2J = K_{ab} - \frac{(2H_{ab})^2}{J_{aa} - J_{ab}} \qquad (2)$$

The ferromagnetic term K_{ab} is the potential exchange integral. The antiferromagnetic term is made up the electron exchange integral H_{ab}, and the difference between coulomb repulsion integrals $J_{aa} - J_{ab}$, which is value of 2.6 eV.[7] The ferromagnetic term might well be canceled out by these second order antiferromagnetic contributions. In the case of very strong antiferromagnetic interactions, $2J$ can be expressed as

$$2J \approx -\frac{(2H_{ab})^2}{J_{aa} - J_{ab}} \qquad (3)$$

By substituted the J values in TABLE 1 for eq. (3), the values are obtained as 2230, 1800, 1810, and 1830 cm^{-1} for the complexes (1), (2), (3) and (4), respectively.

Ru(II)Ru(III) mixed valence state

The cyclic voltammogram (CV) of the Ru(III)Ru(III) complexes demonstrated two one-electron reductions and a one-electron oxidation processes at about -1.2 V and -1.6 – -1.8 and 0.60 V *vs* Ag/AgPF$_6$, respectively in a DMF solution. The first reduction processes were reversible or quasi-reversible, and the second reduction and oxidation processes were irreversible.

Controlled potential electrolysis at -1.5 V *vs* Ag/AgPF$_6$ for the first reduction gave a mixed-valence Ru(II)Ru(III) state, exhibiting two near-IR bands at 5500 and

11700 cm^{-1}.[2] Further detailed study will be required for the assignment of these two near IR bands. Here, the lowest near IR was tentatively assigned as IT band. From Hush theoretical treatment for the mixed-valence metal compounds,[8] the degree of electronic coupling between the donor and acceptor, H_{ad}, can be calculated from

$$H_{ad} = 2.05 \times 10^{-2} \sqrt{\frac{\varepsilon_{\max} \bullet \Delta\tilde{\nu}_{1/2}}{\tilde{\nu}_{\max}}} \left(\frac{\tilde{\nu}_{\max}}{r} \right) \qquad (\text{in cm}^{-1}) \qquad (4)$$

where, r is the metal-metal distance (Å), $\varepsilon_{\max}$ is the maximum extinction coefficient of the IT band (mol^{-1} dm^3 cm^{-1}), the bandwidth at half-intensity (cm-1) and $\tilde{\nu}_{\max}$ is the energy of the IT transition at $\varepsilon_{\max}$ (cm^{-1}).. The Ru-Ru distance, r = 3.43 Å, was used on the basis of the X-ray crystallography or EXAFS data for the Ru(III)Ru(III) complexes in TABLE 1. The H_{ad} value is estimated to be 670 - 870 cm-1 for Ru(II)Ru(III) complexes. The value, $\Delta\tilde{\nu}_{1/2}$ can be also calculated from eq. (5) given by Hush

$$\Delta\tilde{\nu}_{1/2} = \sqrt{2.31 \times 10^3 \, \tilde{\nu}_{\max}} \qquad (5)$$

The parameters of the IT band for Ru(II)Ru(III) state are summarized in TABLE 2. Estimated H_{ad} values indicated that Ru(II)Ru(III) complexes have been classified as Class II mixed-valence state according to Robin and Day.[9] The observed $\Delta\tilde{\nu}_{1/2}$ are almost the same to those of calculated values using eq. (3). All the Ru(II)Ru(III) complexes show similar Had values independent of the bridging carboxylate ligand. This result strongly suggests the importance of the Ru-O-Ru frame.

Ru(III)Ru(IV) mixed-valence state

The CV of the complex(2) showed a one-electron oxidation process at 0.75 V *vs* Ag/AgPF6 in CH3CN at -20°C. The oxidation at 0.95 V *vs* Ag/AgPF6 gave a Ru(III)Ru(IV) mixed-valence complex exhibiting two broad near-IR bands at 10000 and 14000 cm^{-1} (FIGURE 2).

From the analysis of the lowest energy band, the parameters calculated from Hush model, $\varepsilon_{\max}$, $\Delta\tilde{\nu}_{1/2}$, and H_{ad} are 2900 mol^{-1} dm^3 cm^{-1}, 3800 cm^{-1}, and 2000 cm^{-1}, respectively. The large H_{ad} values suggest that the Ru(III)Ru(IV) center is strongly coupled in comparison with the Ru(II)Ru(III) state. The electron-exchange integral, H_{ab} for Ru(III)Ru(III) states, calculated from eq. (3), indicate similar values for the Ru(III)Ru(IV) states.

TABLE 2 Data of intervalence charge transfer bands of Ru(II)Ru(III) complexes

	(1)$^-$	(2)$^-$	(3)$^-$	(4)$^-$
$\tilde{\nu}_{max}$ /10^{3}cm^{-1}	5.7	5.5	5.6	5.7
ε_{max} /mol^{-1} dm^3 cm^{-1}	690	1100	890	640
$\Delta\tilde{\nu}_{1/2}$ obsd. /10^{3}cm^{-1}	3.2	3.6	3.3	3.1
$\Delta\tilde{\nu}_{1/2}$ calcd. /10^{3}cm^{-1}	3.6	3.6	3.6	3.6
H_{ad} /10^{3}cm^{-1}	0.67	0.87	0.82	0.64

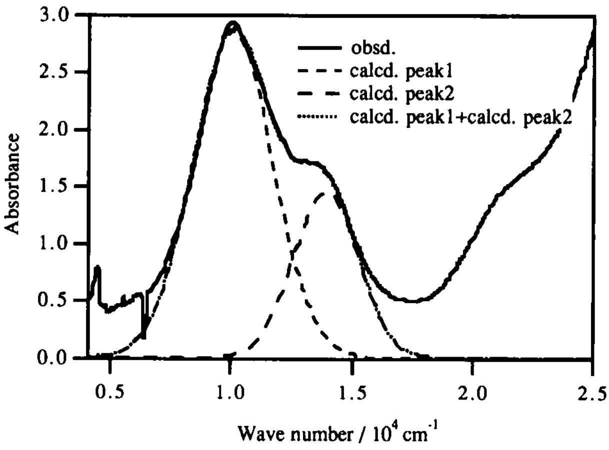


FIGURE 2 near-IR-Vis spectrum of the Ru(III)Ru(IV) mixed valence state for complex(2) in CH3CN

DISCUSSION

Magnetic susceptibility

The characteristic for the present complexes is the alkoxo bridged structure instead of the oxo bridged one in the similar Ru-O-Ru analogs. However, the electronic structure might be essentially the same as the oxo bridged one. The *J* value is dependent on the Ru-O bond length and Ru-O-Ru angle. From the result of X-ray crystallography, EXAFS and NMR^2, all the present complexes have the similar Ru-O-Ru core structure. However, the spin-exchange interaction is sensitive to the bridged carboxylate ligands. Thus, the steric hindrance between the two carboxylato ligands or/and the change of the Ru-O distances and Ru-O-Ru angles is affected significantly for the spin-exchange interaction.

near-IR spectra

Both Ru(II)Ru(III) and Ru(III)Ru(IV) mixed-valence states exhibited two absorption bands in the near-IR region. We assigned the lowest near-IR band as an IT transition. In contrast, the Ru(III)Ru(III) states exhibit no peaks in this region. Since the spectral assignment for many (μ-oxo)bis(μ-carboxylato)diruthenium complexes is based on the MO orbital scheme,[4, 10] further study for the MO calculation is under way.

The electronic structure of several oxidation states

The present Ru-alkoxo-Ru complexes are the first case for giving us the comparison of the electronic coupling between three different states, Ru(II)Ru(III), Ru(III)Ru(III), and Ru(III)Ru(IV). The Ru-oxo distance increases in the order of Ru(III)Ru(IV) < Ru(III)Ru(III) < Ru(II)Ru(III). It has been noted that the J values decrease sharply with lengthening the Fe-O-Fe distance for dinuclear Fe(III)-oxo complexes.[11] The magnitude of electronic coupling increases in the order of Ru(II)Ru(III) < Ru(III)Ru(III) ~ Ru(III)Ru(IV), which follows the increase of Ru-O-Ru distance. Upon the change of carboxylato bridged groups the degree of the interaction is unchanged for the Ru(II)Ru(III) state, but significantly changed for the Ru(III)Ru(III) state. This result might suggest the different pathways between the magnetic coupled orbitals and the electronic superexchange.[12]

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