Coupling of Ground-State Molecular Vibrations to Low-Energy Electronic Transition of Ruthenium(III,II) Porphyrin Dimers

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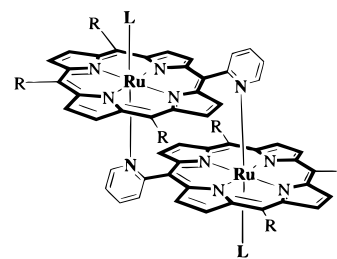Yoshiyuki Morioka,*,‡ Kohei Uosaki,*,† and Yoichi Sasaki†

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The mixed-valence state of compounds with multiple redox centers has been a subject of considerable scientific interests.[1−9] Some of these compounds show characteristic intervalence-charge-transfer bands in the near-IR region. Typical examples are mixed-valence multinuclear metal complexes such as Creutz-Taube ions[4] and lanthanide porphyrin sandwich complexes.[9] The charge-transfer transition of the lanthanide complexes shows a strong vibronic structure at around 8000 cm^{-1}. Other intriguing examples are the cation radicals of the special pair of bacterio-chlorophyll (BChl). The radicals show a broad but distinct optical absorption ascribable to the intervalence transition, which occurs in the mid-IR region down to 2600 cm^{-1}.[10] A striking feature is that the broad band shows a derivative-like dispersion form at around 2100 cm^{-1}. In these systems of radicals of the special pair and the lanthanide complexes, the broad band shape of the low-energy electronic transitions and the vibronic structures have been regarded as overlapping transitions from the ground state to various vibrational levels of the excited electronic state. Thus, they have been essentially analyzed using the Franck−Condon factor calculation.[9,11]

However, in the cases where the intervalence transition is extremely low in energy (<2100 cm^{-1}) and appears in the wavenumber region of vibrational fundamentals (transitions of v = 0 to 1), another type of the electron−vibration coupling takes place, which has been observed in one-dimensional organic conductors.[3,12] This coupling, termed EMV (electron−molecular vibration) coupling, occurs between the discrete vibrational levels of the electronic ground state and the vibronic continuum of the low-lying electronic excited state. The EMV coupling results in a "derivative-like band structure" of the vibrational mode in the broad electronic band of the mid-IR spectra. The derivative-like

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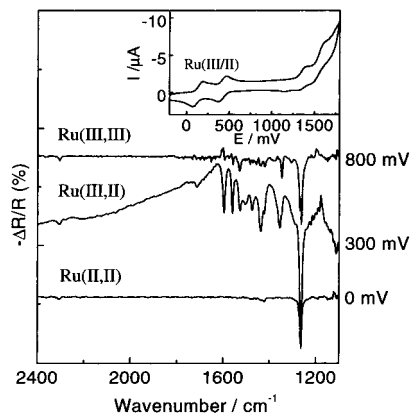

1 (L = Py, R = 4-tert-butylpheny)
2 (L = PyCN, R = 4-tert-butylphenyl)

Figure 1. Ruthenium porphyrin dimers **1** and **2**.

band structure is characteristic of the coupling between a discrete energy level and a continuum, and is often referred to "antireso-nance".[13] To our knowledge, the EMV coupling reported so far is restricted to systems in the solid-state such as MEM(TCNQ)$_2$[3,14] and [Os(OEP)(pyz)(PF$_6$)$_x$]$_n$.[15] MEM(TCNQ)$_2$ shows a prominent coupling of conduction electrons and vibrational modes in the range around 2200−100 cm^{-1}. A pyrazine-bridged mixed-valence osmium porphyrin polymer, [Os(OEP)(pyz)(PF$_6$)$_x$]$_n$, in fluorolube mull, also shows an antiresonance at around 1500 cm^{-1}.[15]

We report here the first example of well-defined molecular compounds that show a remarkable electron-molecular-vibration coupling in the range 2000−700 cm^{-1} both in the solid state and in solution. The molecules are cofacial ruthenium porphyrin dimers with a Ru$_2$(III,II) oxidation state. The most remarkable feature is that the entire range of porphyrin vibrations all shows a strong antiresonance coupling with an electronic transition, this coupling appearing even in solution spectra.

The cofacial ruthenium porphyrin dimers, [Ru^{II}(2-PytB$_3$P)(Py)]$_2$ **1** (Ru$_2$(II,II)) and [Ru^{II}(2-PytB$_3$P)(PyCN)]$_2$ **2**, shown in Figure 1, were prepared by the method reported previously.[16] They exhibited stepwise electrochemical oxidations at the metal centers Ru$_2$(II,II)/(III,II) and Ru$_2$(III,II)/(III,III) due to strong interactions between the cofacially arranged ruthenium porphyrin units. The one-electron oxidation of **1** by stoichiometric titration with I$_2$ enabled us to isolate a mixed-valence complex of [Ru(2-PytB$_3$P)]$_2$I.

In situ Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) was applied to the study of interfacial electrochemistry.[17] The measurements were carried out using a Bio-Rad FTS-30 spectrometer equipped with a HgCdTe detector cooled with liquid-N$_2$. A gold working electrode (diameter, 8 mm) was pushed against the CaF$_2$ window by a micrometer head. Since the solution layer between the electrode and the window was very thin ($\sim$1 μm), the electrochemical reactions of the species were completed instantaneously when the electrode potential changed. A total of 128 interferograms with a resolution of 4 cm^{-1} were collected at each potential, where R is the reflectance at 0 potential and ΔR is the difference in reflectance at the measured potential versus 0 potential. The results are presented in the form of the normalized reflectance decrease, $-\Delta R/R$, which corresponds to the absorption change from Ru$_2$(II,II).

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(14) Abbreviations: 2-PytB$_3$P = 5-(2-pyridyl)-10,15,20-tri(4-*tert*-butyl)-phenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; PyCN = 4-cyanopyridine (isonicotinonitrile); TBA(PF$_6$) = *n*-tetrabuthylammonium hexafluorophosphate; MEM(TCNQ)$_2$ = *N*-methyl-*N*-ethylmorpholinium-tetracyanoquinodimethane.
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Figure 2. In situ FT-IRRAS of the [Ru(2-PytB$_3$P)(Py)]$_2$ **1** (Ru$_2$(II,II)) system in 0.1 M TBA(PF$_6$)-CH$_2$Cl$_2$ solution at around 23 °C. Concentration of the dimer is ∼0.5 mM. Inset is a cyclic voltammogram of **1**.

Figure 2 shows in situ IRRAS spectra of **1** at potentials of 0, 300, and 800 mV versus Ag/AgCl, respectively. Compared to a cyclic voltammogram observed under the same conditions, shown in the inset, the Ru complex is expected to exist as Ru$_2$(II,II), Ru$_2$(III,II), and Ru$_2$(III,III) at these potentials, respectively. It is remarkable that a broad absorption band was observed in the region between 2000 and 1000 cm^{-1} in the spectrum of Ru$_2$(III,II), while this absorption band is absent in the IRRAS spectra of Ru$_2$-(II,II) and Ru$_2$(III,III). Significant intensity changes of several vibrational bands were observed in the region of less than 1700 cm^{-1}. Similar band changes in the mid-IR region were also observed in the KBr pellet for Ru$_2$(III,II), as shown in Figure 3.[18] The system of **2** gave the same spectral contour. These results demonstrate that the coupled spectra are characteristic of the Ru$_2$-(III,II) electronic states.

The solvent-subtracted solution spectrum of Ru$_2$(III,II) in a low concentrated (0.03 mM) CH$_2$Cl$_2$ solution, measured by using a 0.1 mm cell with KRS-5 windows, is almost the same as the spectra of the KBr disk of Ru$_2$(III,II) and also of Ru$_2$(III,II) in the FT-IRRAS cell. Such a coupled broad band in the IR region of 4000−250 cm^{-1} was neither observed in the corresponding monomer complexes of Ru^{II}(2-PytB$_3$)(Py)$_2$ and [Ru^{III}(2-PytB$_3$)-(Py)$_2$]$^+$, nor in the mixed-valence carbonyl dimer complex of [Ru-(2-PytB$_3$P)(CO)]$_2$$^+$, where oxidation of porphyrin rings occurs.

The observed spectra described above suggest that the anomalous infrared band shape of Ru$_2$(III,II) may be explained by assuming an intervalence transition at around 1500 cm^{-1}.[19] According to the EMV coupling theory for the dimer-system with an unpaired electron given by Rice et al.,[3] the broad band is

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(18) This similarity between the FT-IRRAS difference spectrum and the general IR spectrum (KBr disk) again signifies that the spectrum is characteristic of the Ru$_2$(III, II) state, because the relation can be observed only when the molar absorptivity, $\epsilon_{III,II}$, of the unique Ru$_2$(III,II) spectrum in FT-IRRAS measurements is significantly larger than that of Ru$_2$(II,II), that is, $\epsilon_{III,II} \gg \epsilon_{II, II}$ in eq 1 for the difference spectrum, where, for example, C$_{III,II}$ is the concentration of Ru$_2$(III,II).

$$\text{Absorbance} = \epsilon_{III,II} C_{III,II} + \epsilon_{II,II}C_{II,II} - \epsilon_{II,II}(C_{III,II} + C_{II,II})$$
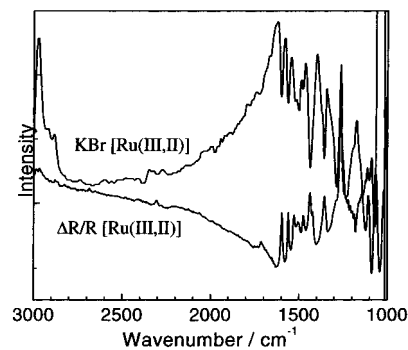$$= (\epsilon_{III,II} - \epsilon_{II,II})C_{III,II} \qquad (1)$$

Figure 3. Comparison between the spectra of Ru$_2$(III,II) obtained by FT-IRRAS and IR−KBr disk methods.

Figure 4. IR spectrum (KBr disk) of [Ru(2-PytB$_3$P)(Py)]$_2$I with a Ru$_2$-(III,II) oxidation state (solid line) and its calculated spectrum (dotted line).

modified by totally symmetric monomer vibrations and antiresonance peaks at frequencies of the vibrational modes. To confirm this coupling in the present system, the KBr spectrum of Ru$_2$-(III,II) was compared with a calculated spectrum based on the dielectric function similar to eq 2.26 in ref 3. An excellent agreement between both spectra was obtained as shown in Figure 4, by adjusting parameters in the EMV model and assuming a strongly active infrared band at 1642 cm^{-1}.

In conclusion, IR spectra (KBr mull and in solution) and in situ FT-IRRAS measurements disclosed the presence of antiresonance couplings of ground-state molecular vibrations to an electronic transition in the dimer ion of [Ru(2-PytB$_3$P)]$_2$$^+$ in the range of 2000−700 cm^{-1}. The spectrum contour is very similar to that of cation radicals of BChl which show several antiresonance-like peaks at around 2100 cm^{-1}.
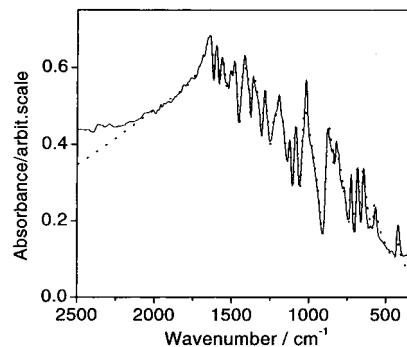
Supporting Information Available: Calculation procedures for the simulation of the IR spectrum (KBr disk) of [Ru(2-PytB$_3$P)(Py)]$_2$I, that is, Ru$_2$(III,II) of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) This broad band at around 1500 cm^{-1} in the present study is ascribed to an intervalence transiton band. Another intervalence transition in this system has been observed at 6670 cm^{-1} (1500 nm).[16] The relation between the two bands is now under investigation. The presence of such multiple transitions is documented in ref 6.