A Metal-to-Ligand Charge-Transfer Excited State of a Biruthenium(II) Compound Bridged by 2,6-Bis(2-pyridyl)benzodiimidazole

Takeshi Ohno,*,† Koichi Nozaki,† and Masa-aki Haga‡

Chemistry Department, College of General Education, Osaka University, Osaka 560, Japan, and Department of Chemistry, Faculty of Education, Mie University, Tsu, Mie 514, Japan

Received March 11, 1992

A charge-transfer (CT) excited state of a binuclear ruthenium(II) compound with the tetradentate bridging ligand 2,6-bis(2-pyridyl)benzodiimidazole ($dpimbH_2$) was studied by means of emission and transient absorption spectroscopy at 77–300 K. Absorption spectra of the lowest excited states of a mononuclear compound, $Ru(bpy)_2(dpimbH_2)^{2+}$, and a binuclear compound, $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$, were quantitatively determined. The lowest excited states of the Ru(II) compounds were assigned as Ru-to-$dpimbH_2$ CT, and their spectra were compared with the absorption spectra of both the oxidized species ($Ru(bpy)_2(dpimbH_3)^{4+}$) and the reduced species ($[Ru(bpy)_2](dpimbH_2)^{3+}$). The 58 meV lower phosphorescence energy of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ compared with that of the mononuclear compound was accounted for in terms of stabilization of the d_π-orbital (Ru(III)) and the π^*-orbital ($dpimbH_2$). The extent of electronic interaction between ruthenium(III) and ruthenium(II) ions was estimated for the CT states of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ and a mixed-valence compound of $[Ru(bpy)_2]_2(dpimbH_2)^{5+}$ by using emission spectroscopy, Ru(II)-to-Ru(III) CT absorption spectroscopy, and differential voltammetry.

Introduction

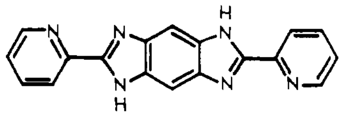
Electronic interactions between ruthenium ions of binuclear compounds in the charge-transfer (CT) excited states have attracted much attention in recent years.[1–7] Since the lowest excited state of RuL_3^{2+} (L = bpy, phen, etc.) is well characterized as a Ru(II)-to-ligand CT state,[8–11] d_π-electrons of an excited metal site (Ru(III)) in excited biruthenium(II) compounds are anticipated to interact with those of an unexcited metal site (Ru(II)). The extent of electronic exchange interaction has seldom been determined for metal-to-ligand CT excited states of binuclear compounds. Interaction energies smaller than 10 meV have been determined for binuclear compounds of ruthenium(II) bridged by 2,2′-bis(2-pyridyl)-5,5′-bibenzimidazole ($bpbimH_2$) or 1,2-bis(2-(2-pyridyl)benzimidazolyl)ethane.[12,13] Emission energy shifts of binuclear compounds compared with the corresponding mononuclear compounds do not necessarily indicate the extent of electronic interaction between ruthenium ions bridged by either 2,3-bis(2-pyridyl)pyrazine[1] or 2,2′-bipyrimidine,[2] because a positive charge on the remote ruthenium ion shifts the reduction potential of the bridging ligand to less negative values,[1,14] which lowers the energy of metal-to-ligand CT emission.

The bridging tetradentate ligand 2,6-bis(2-pyridyl)benzodiimidazole has strong σ-donor properties in comparison with those of bpy, just as 2,2′-bibenzimidazole does.[15] The structure of 2,6-bis(2-pyridyl)benzodiimidazole ($dpimbH_2$) is shown in Figure 1. The CT states of $Ru(bpy)_2(dpimbH_2)^{2+}$ and $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ were studied by means of emission and laser excitation transient spectroscopy. Electronic interaction between ruthenium(III) and ruthenium(II) ions was examined for the CT states of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ and a mixed-valence compound

* To whom correspondence should be addressed.
† Osaka University.
‡ Mie University.

(1) (a) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857–64. (b) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691–7. (c) Wallace, A. W.; Murphy, W. W., Jr.; Petersen, J. D. *Inorg. Chim. Acta* **1989**, *166*, 47–54. (d) Murphy, W. R.; Brewer, K. J.; Gettliffe, G.; Petersen, J. D. *Inorg. Chem.* **1989**, *28*, 81–4. (e) Kalyanasundaram, K.; Nazeeruddin, Md. K. *Inorg. Chem.* **1990**, *29*, 1888–97. (f) Berger, R. M. *Inorg. Chem.* **1990**, *29*, 1920–4. (g) Denti, G.; Campagana, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750–8. (h) Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3728–32.
(2) (a) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370. (b) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660. (c) Sahai, R.; Rillema, D. P.; Shaver, R.; Van Wallendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* **1989**, *28*, 1022–8.
(3) (a) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185–9. (b) Hage, R. *Inorg. Chem.* **1991**, *30*, 3263–9. (c) Haga, M. *Inorg. Chim. Acta* **1980**, *45*, L183. (d) Rillema, D. P.; Sahai, R.; Matthews, P.; Edwards, K.; Shaver, R. J. *Inorg. Chem.* **1990**, *29*, 167–75. (e) Hage, R. *Coord. Chem. Rev.* **1991**, *111*, 161–6.
(4) (a) Elliott, C. M.; Freitag, R. A.; Blaney, D. D. *J. Am. Chem. Soc.* **1985**, *107*, 4647–55. (b) Sahai, R.; Baucom, D. A.; Rillema, D. P. *Inorg. Chem.* **1986**, *25*, 3843–5. (c) Schmehl, R. H.; Auerbach, R. A.; Walcholtz, W. F.; Elliott, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* **1986**, *25*, 2440–5. (d) Furue, M.; Kuroda, N.; Nozakura, S.-I. *Chem. Lett.* **1986**, 1209–12.
(5) (a) De Cola, L.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A.; Vogtle, F.; Ebmeyer, F.; Grammenudi, S. *J. Am. Chem. Soc.* **1988**, *110*, 7210–2. (b) Barigelletti, F.; De Cola, L.; Balzani, V.; Belser, P.; von Zelewsky, A.; Vogtle, F.; Ebmeyer, F.; Grammenude, S. *J. Am. Chem. Soc.* **1989**, *111*, 4662–8. (c) De Cola, L.; Belser, P.; Ebmeyer, F.; Barigelletti, F.; Vogtle, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 495–9.
(6) Ryu, C. K.; Schmehl, R. H. *J. Phys. Chem.* **1989**, *93*, 7961–6.
(7) (a) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 385–7. (b) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885–7. (c) Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2182–93. (d) Furue, M. *Chem. Lett.* **1990**, 2065–8.
(8) Crosby, G. A.; Perkins, W. G.; Klassen, D. M. *J. Chem. Phys.* **1965**, *43*, 1498–1503.
(9) (a) Dallinger, R. F.; Woodruff, W. *J. Am. Chem. Soc.* **1979**, *101*, 4391–3. (b) DeArmond, M. K.; Myrick, M. L. *Acc. Chem. Res.* **1989**, *22*, 364–70. (c) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526–31. (d) McClanahan, S. F.; Dallinger, R. F.; Holler, F. J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 4853–60. (e) Myrick, K. L.; Blakley, R. L.; DeArmond, M. K.; Authur, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 1325–36.
(10) Ohno, T.; Yoshimura, A.; Prasad, D. R.; Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 4723–8.
(11) (a) Orman, L. J.; Chang, Y. J.; Anderson, D. R.; Yabe, T.; Xu, X.; Yu, S.-C.; Hopkins, J. B. *J. Chem. Phys.* **1989**, *90*, 1469–77. (b) Yabe, T.; Orman, K.; Anderson, D. R.; Yu, S.-C.; Xu, X.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 7128–32.
(12) (a) Ohno, T.; Nozaki, K.; Ikeda, N.; Haga, M. In *Electron Transfer in Inorganic, Organic, and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; American Chemical Society: Washington, DC, 1991; pp 215–28.
(13) Ohno, T.; Nozaki, K.; Haga, M. *Inorg. Chem.* **1992**, *31*, 548–55.
(14) (a) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017–21. (b) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125–34.
(15) Haga, M.; Matsumura-Inoue, T.; Yamabe, S. *Inorg. Chem.* **1987**, *26*, 4148–54.

0020-1669/92/1331-4256$03.00/0



dpimbH$_2$

Figure 1. The bridging ligand 2,6-bis(2-pyridyl)benzodiimidazole.

of $[Ru(bpy)_2]_2(dpimbH_2)^{5+}$ by means of emission spectroscopy, Ru(II)-to-Ru(III) CT absorption spectroscopy, and differential voltammetry.

Experimental Section

Materials. Acetonitrile (CH_3CN) was purified by double distillation over P_2O_5. 9,10-Dichloroanthracene (DCA) was used as supplied from Tokyo Kasei. 1,2,4,5-Benzenetetramine tetrahydrochloride (Aldrich) and 2-picolinic acid (Nacalai Tesque) were used without further purification. All other chemicals were of analytical grade and were used as supplied.

Preparation of the Dinucleating Ligand 2,6-Bis(2-pyridyl)benzodiimidazole (dpimbH$_2$). 1,2,4,5-Benzeneteramine tetrahydrochloride (4 g, 14 mmol) in polyphosphoric acid (30 cm^3) was heated in a 500-cm^3 three-neck flask at ~120 °C. Hydrogen chloride gradually evolved. At this stage, the volume of the contents increased remarkably due to the hydrogen chloride gas. It was important to apply gentle heating. After the evolution of hydrogen chloride gas ceased, 2-picolinic acid (3.5 g, 28 mmol) was added.

As the temperature of the flask was gradually increased to 150 °C and then to 200 °C, the red-violet solution became brown and then black-violet. After being heated for 16 h, the resulting solution was cooled at ~100 °C and poured into water (500 cm^3). After the precipitate was collected, it was neutralized with an aqueous solution of sodium carbonate. The dark orange-brown precipitate was recrystallized from ethylene glycol. Yield: 5.57 g. Mp: >280 °C dec. Mass spectrum: m/z = 312 (M^+); M = $^{12}C_{18}H_{12}{}^{14}N_6$. Anal. Calcd for $C_{18}H_{12}N_6 \cdot {}^1/_2H_2O$: C, 67.27; H, 4.08; N, 26.15. Found: C, 67.76; H, 3.86; N, 25.59.

Preparation of the Mononuclear Compound [Ru(bpy)$_2$(dpimbH$_2$)](ClO$_4$)$_2$·2H$_2$O. *Caution*! Perchlorate salts are potentially explosive. Although no detonation tendencies were observed, caution is advised and handling of only small quantities is recommended. Solid dpimbH$_2$ (0.2 g, 0.64 mmol) was added to a 50-cm^3 ethanol–water (1:1 v/v) solution of $Ru(bpy)_2Cl_2$ (0.3 g, 0.62 mmol). The mixture was heated under reflux for 20 h, during which the solution gradually turned dark red. The solution was then evaporated to half-volume and filtered. Excess ligand remained on the filter paper. To the filtrate was added sodium perchlorate (1 g, 7.1 mmol) in water (10 cm^3). The precipitate was collected and purified by column chromatography on SP-Sephadex C-25 resin with CH_3CN/buffer (1:1 v/v), appearing as a yellow band at pH 3.2. The main second red band at pH 5.5 for the desired mononuclear complex was collected. The eluate was evaporated to half-volume, and sodium perchlorate was added to the resulting solution. The precipitate was filtered off and washed with water. Recrystallization from methanol–water (1:4 v/v) gave 0.25 g of red crystals (41% yield). Anal. Calcd for $C_{38}H_{32}N_{10}Cl_2O_{10}Ru$: C, 47.51; H, 3.36; N, 14.58. Found: C, 47.02; H, 3.11; N, 13.11.

Preparation of the Binuclear Compound [Ru(bpy)$_2$]$_2$(dpimbH$_2$)(ClO$_4$)$_4$. A mixture of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (0.3 g, 0.62 mmol) and bridging ligand dpimbH$_2$ (0.094 g, 0.3 mmol) in ethanol–water (1:1 v/v, 60 cm^3) was refluxed for 20 h, during which time the solution became dark red. The solution was evaporated to half-volume and filtered; $NaClO_4$ (1 g, 7.1 mmol) was added to the resulting filtrate. The red-orange precipitate was loaded onto a SP-Sephadex C-25 column and eluted with CH_3CN/buffer (1:1 v/v). The binuclear compound was obtained as a third red band by raising the solution pH to 9 and adding 0.02 mol/dm^3 $NaClO_4$. After evaporation of CH_3CN in the eluate, excess $NaClO_4$ effected the precipitation of the desired complex, which was recrystallized from methanol/water. Yield: 0.2 g (40%). FABMS: m/z = 1438 (M − ClO$_4$), 1339 (M − 2ClO$_4$), 1239 (M − 3ClO$_4$). Anal. Calcd for $C_{58}H_{52}N_{14}C_{14}O_{20}Ru_2$: C, 43.29; H, 3.26; N, 12.19. Found: C, 43.95; H, 2.91; N, 12.27.

Apparatus. A spectrofluorometer (Hitachi Model MPF-2A) was used to record the phosphorescence spectra of the Ru(II) compounds at 300 and 77 K. The Q-switched Nd^{3+}–YAG laser (Quantel Model YG580) used has been described elsewhere.[16]

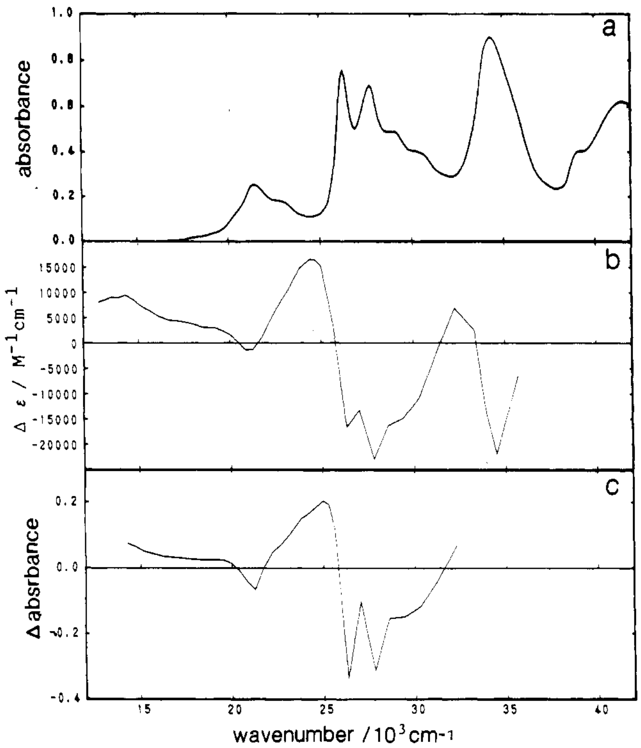


Figure 2. (a) Absorption spectrum of $Ru(bpy)_2(dpimbH_2)^{2+}$ (15 × 10^{-6} mol/dm^3) in methanol/ethanol (1:4 by volume) at 90 K. (b) Transient absorption spectrum of the photoexcited compound in CH_3CN at ambient temperature. (c) Transient spectrum of the photoexcited compound in methanol/ethanol (1:4 by volume) at 90 K.

The temperature of the sample solutions in 89–273 K region was controlled by using a cryostat (Oxford Model DN1704) and a controller (Oxford Model ITC4). A d.c. pulse polarograph (Huso Model HECS-312B) was used to measure the redox potentials of the Ru(II) compounds.

Measurements. The sample solutions of the ruthenium(II) compounds dissolved in acetonitrile or 1:4 methanol/ethanol were deaerated by bubbling with nitrogen more than 12 min. Either $HClO_4$ or CF_3COOH (1 mM) was added to suppress deprotonation from the imino groups of dpimbH$_2$. Pyridine was added as a proton acceptor. Transient absorption spectra after exposure to the second harmonic pulse of the YAG laser were obtained by a procedure described elsewhere.[13]

The difference absorption coefficients of the excited ruthenium(II) compounds were determined from the production of excited 9,10-dichloroanthracene (DCA) in the efficient transfer of excitation energy of the Ru(II) compound in CH_3CN. The formation of the triplet excited state of DCA was determined by monitoring the transient absorbance at 421 nm (ϵ_{421} = 4.5 × 10^4 M^{-1} cm^{-1} [17]). Rate constants for the energy-transfer processes were obtained by plotting the decay rate of phosphorescence against the concentration of DCA added.

Voltammograms were obtained by a procedure described elsewhere.[13] All potentials are referred to the formal potential of the ferrocenium ($Fc^{•+}$)/ferrocene (Fc) couple, which is 0.33 V vs SCE. Absorption spectra of the Ru(II) compounds in 1:4 methanol/ethanol at low temperature were recorded with the use of a Hitachi U-3400 spectrophotometer and an Oxford cryostat. The absorbances of a solute were referred to the stored ones of the neat solvent.

Results

1. Absorption and Emission Spectra of the Ru(II) Compounds. Absorption spectra of $Ru(bpy)_2(dpimbH_2)^{2+}$ and its protonated form, $Ru(bpy)_2(dpimbH_3)^{3+}$, at 90 K are shown in Figures 2a and 3a. Figures 4a and 5a present absorption spectra of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ at 90 K and its deprotonated form, [Ru-

(16) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4871–6.
(17) Kikuchi, K.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1527–34.

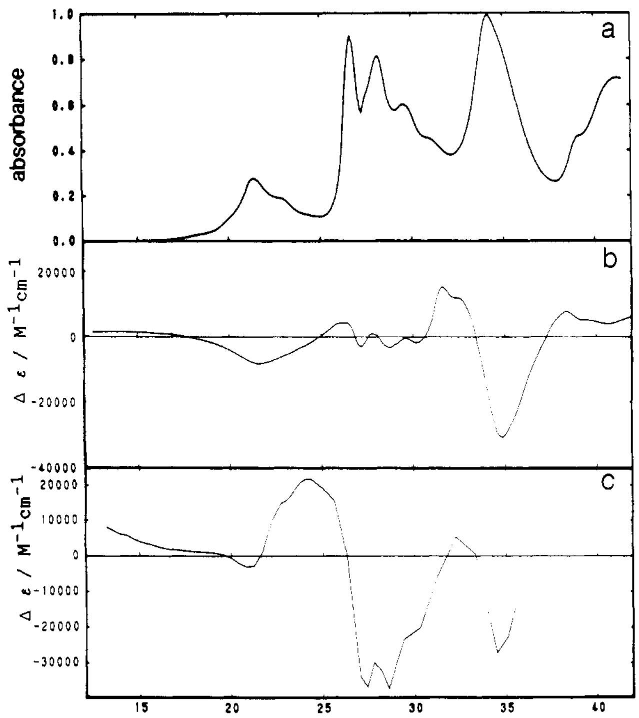


Figure 3. (a) Absorption spectrum of $Ru(bpy)_2(dpimbH_3)^{3+}$ (15×10^{-6} mol/dm^3) in 13 mmol/dm^3 $HClO_4$ in methanol/ethanol (1:4 by volume). (b) Difference spectrum between $Ru^{II}(bpy)_2(dpimbH_3)^{3+}$ and $Ru^{III}(bpy)_2(dpimbH_3)^{4+}$ in 1 mmol/dm^3 $HClO_4$ in CH_3CN. (c) Transient spectrum of the photoexcited compound in 0.1 mmol/dm^3 $HClO_4$ in CH_3CN.

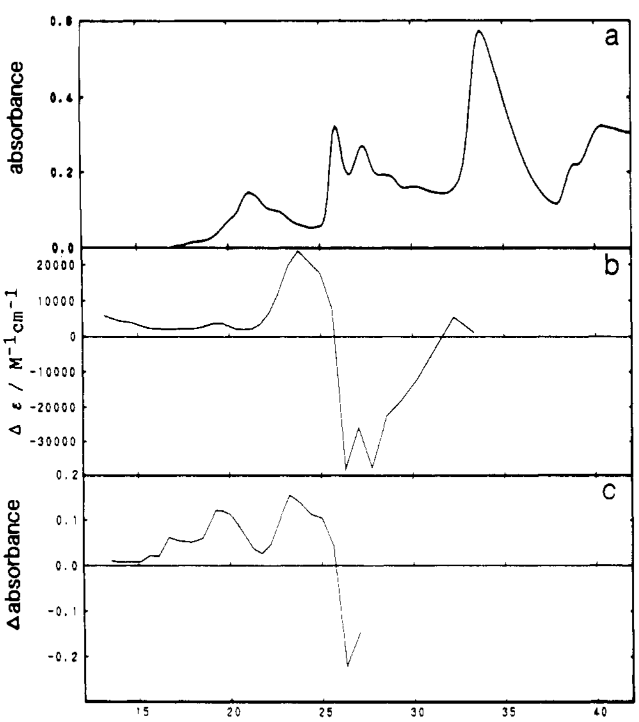


Figure 4. (a) Absorption spectrum of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ (12×10^{-6} mol/dm^3) in 0.1 mmol/dm^3 $HClO_4$ in methanol/ethanol (1:4 by volume). (b) Transient spectrum of the photoexcited compound in 0.1 mmol/dm^3 $HClO_4$ in CH_3CN at ambient temperature. (c) Transient spectrum of the photoexcited compound (2×10^5 mol/dm^3) in the presence of phenothiazine (0.8 mmol/dm^3) in CH_3CN at ambient temperature at 6 μs.

$(bpy)_2]_2(dpimbH)^{3+}$, at 171 K, respectively. A broad charge-transfer band in the (19–25) $\times 10^3$ cm^{-1} region is seen for all the ruthenium(II) compounds studied here with a maximum at 21.3 $\times 10^3$ cm^{-1} and two shoulders around 20×10^3 and 23×10^3 cm^{-1}.

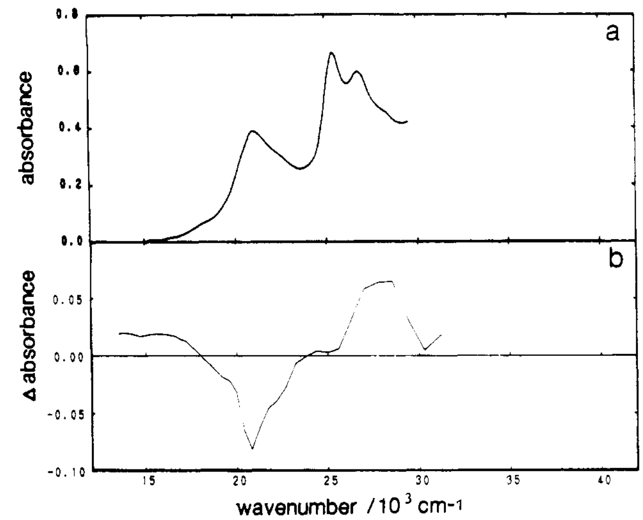


Figure 5. Absorption spectra of $[Ru(bpy)_2]_2(dpimbH)^{3+}$ in 50 mmol/dm^3 pyridine in methanol/ethanol (1:4 by volume) at 171 K: (a) ground state; (b) transient photoexcited state.

Table I. Highest Energy Bands of Emissions at 77 K and Lifetimes of Emissions at 90 and ~300 K

	$\bar{\nu}$/cm^{-1}	τ/ns[a]	τ/ns[b]
$Ru(bpy)_2(dpimbH_2)^{2+}$	16 190	870	2500
$Ru(bpy)_2(dpimbH_3)^{3+}$	15 970	455 330[c]	1970
$Ru(bpy)_2(dpimbH_4)^{4+}$	15 270[d]		
$[Ru(bpy)_2]_2(dpimbH_2)^{4+}$	15 710	606	2700
$[Ru(bpy)_2]_2(dpimbH)^{3+}$	15 360	<35[c]	101[e]
$[Ru(bpy)_2]_2(dpimb)^{2+}$	14 750		

[a] In CH_3CN containing $HClO_4$ (10^{-3} M) at 300 K. [b] In 1:4 methanol/ethanol at 90 K. [c] In 1:4 methanol/ethanol at 286 K. [d] Reference 19. [e] In 1:4 methanol/ethanol at 171 K.

Each of the ruthenium(II) compounds exhibited a long-life emission in the (12.8–16.4) $\times 10^3$ cm^{-1} region at 77 K. Raising the temperature shifted the highest energy peaks of the emissions to lower energy and shortened the lifetimes, which are shown in Table I.

2. Absorption Spectra of the Ru(III) Compound. Electrochemical oxidation of $Ru(bpy)_2(dpimbH_3)^{3+}$ gave rise to a difference absorption spectrum referred to that of the Ru(II) compound (see Figure 3b). The negative bands of the difference spectrum correspond to the bleaching of the CT band at 22×10^3 cm^{-1} and to the shift of the π–π^* (bpy) band from 35×10^3 to 32×10^3 cm^{-1}. The shifted π–π^* transition is seen at 32×10^3 cm^{-1} as a positive band in the difference absorption spectrum. A positive band at $\sim 14 \times 10^3$ cm^{-1} is assigned to $dpimbH_2$-to-Ru(III) CT and bpy-to-Ru(III) CT, as in the cases of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_2(bpbimH_2)^{3+}$.[13]

Quantitative one-electron oxidation of the biruthenium(II) compound in CH_3CN (0.1 mol/dm^3 tetra-*n*-butylammonium perchlorate + 0.1 mmol/dm^3 $HClO_4$) produces another very wide band in the near-infrared region (Figure 6). Further oxidation leads to the complete disappearance of this band.

3. Electrochemistry of the Mononuclear and Binuclear Compounds. Redox potentials of the ruthenium(II) compounds were obtained as shown in Table II. Oxidation potentials were measured as $E_{1/2}$ values by means of differential-pulse voltammetry (Figure 7). The reduction processes of the $dpimbH_2$-coordinated compounds were irreversible so that the potentials were not determined. Without 0.1 mmol/dm^3 $HClO_4$, the mononuclear compound exhibits one irreversible oxidation wave at 0.92 V vs $Fc^{\bullet+}/Fc$. This suggests that the NH imino protons are easily deprotonated after the oxidation.

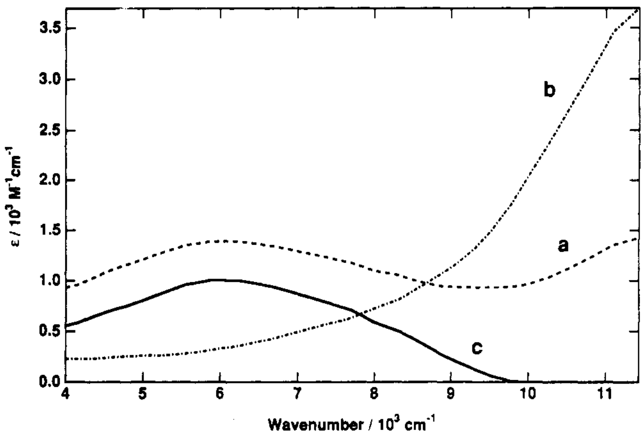


Figure 6. Changes of the absorption spectrum of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ with stepwise oxidation: (a) Ru(II)–Ru(III); (b) Ru(III)–Ru(III). Curve c was obtained by substracting half of (b) from (a) and was assigned to the Ru(II)-to-Ru(III) CT transition.

Table II. Redox Potentials of Ruthenium(II) Compounds vs $Fc^{•+}/Fc$ in CH_3CN Containing 0.1 M Tetraethylammonium Perchlorate

	$E_{1/2}$(Ru(III)/Ru(II))/mV	$E_{1/2}(L/L^{•-})$/mV
$Ru(bpy)_3^{2+}$	875	−1724, −1913, −2167
$Ru(bpy)_2(dpimbH_3)^{3+}$	802	
$Ru(bpy)_2(dpimbH_4)^{4+}$	817[a]	−830[a]
$[Ru(bpy)_2]_2(dpimbH_2)^{4+}$	750, 830	

[a] Reference 19.

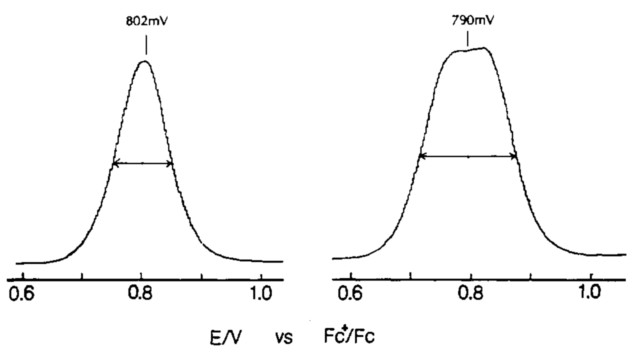


Figure 7. Differential-pulse voltammograms of $Ru(bpy)_2(dpimbH_3)^{3+}$ (left) and $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ (right) in 10 mmol/dm³ $HClO_4$ in CH_3CN at ambient temperature.

4. Transient Absorption (TA) Spectra of the Photoexcited Ru(II) Compounds. A transient absorption (TA) spectrum at ambient temperature was obtained 100 ns after the laser excitation of $Ru(bpy)_2(dpimbH_2)^{2+}$ in neutral CH_3CN, as is shown in Figure 2b. Figures 2c and 3c show the TA spectra of $Ru(bpy)_2$-$(dpimbH_2)^{2+}$ and its monoprotonated species, respectively, at 90 K in a mixture of methanol and ethanol (1:4 by volume). The TA decayed with the same rate as the phosphorescence monitored at 15.2×10^3 cm^{-1}. The TA, therefore, is ascribed to the formation of the lowest excited CT state. The lifetimes of the TA at 90 and 300 K are listed in Table I.

The difference in molar absorption coefficient between the ground state and the excited state, $\Delta\epsilon$, was determined by utilizing a bimolecular energy-transfer process. The electronic excitation of the Ru(II) compound was transferred to DCA, whose triplet-state production was spectrophotometrically determined. The rate constants for the Ru(II)-to-DCA energy-transfer processes are close to the diffusion-controlled ones.

A TA spectrum of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ at 300 K was similarly obtained in the presence of 1 mM $HClO_4$ (Figure 4b). Addition of 50 mM pyridine, which enhanced deprotonation from the NH groups of $dpimbH_2$, shifted the TA peak to higher energy, as shown in Figure 5b. The lifetime of the TA was as short as 30 ns at 286 K and 101 ns at 171 K.

An addition of an electron donor, phenothiazine (0.8 mM), quenched the TA of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ to produce another transient absorption spectrum (Figure 4c).

Discussion

1. Assignments of Absorption and Emission. The lowest excited state of RuL_3^{2+} (L = bpy, phen, etc.) is well characterized as a Ru(II)-to-L charge-transfer (CT) state.[9–13] The energy of the Ru(II)-to-L CT excited state of a ruthenium compound can be expressed to a first-order approximation by

$$h\nu = -[E^\circ(L/L^{•-}) - E^\circ(Ru(III)/Ru(II))] + EE + \Delta Sol \qquad (1)$$

where E°, EE, and ΔSol represent the redox potential, the sum of electrostatic energy and electronic exchange energy between Ru(III) and a reduced ligand, and the solvation energy change of the redox reaction $[L + Ru(II) \rightarrow L^{•-} + Ru(III)]$, respectively. In the mixed-ligand complex $RuL_2L'^{\,2+}$, the excited electron resides on L for which $E^\circ(L/L^{•-})$ is less negative, provided that EE and ΔSol are constant irrespective of the ligands. The reduced ligand cannot be assigned by applying eq 1 to these compounds because $E^\circ(L/L^{•-})$ values for the Ru(II)–$dpimbH_2$ compounds are unknown.

$Ru(bpy)_2(dpimbH_2)^{2+}$ exhibits a poorly resolved absorption spectrum at 90 K. The Ru(II)-to-ligand CT band, however, is decomposed to three peaks at 20×10^3, 2.13×10^3, and 23.2×10^3 cm^{-1}. The first two peaks are lower in energy than the lowest peak of $Ru(bpy)_3^{2+}$ (22.1×10^3 cm^{-1}) or Ru(2-(2-pyridyl)-imidazole)$_3^{2+}$ (22.8×10^3 cm^{-1}).[18] The other bands at 26.5×10^3, 28.1×10^3, 29.0×10^3, 30.5×10^3, and 34.8×10^3 cm^{-1} are assigned to a π–π^* transition of either $dpimbH_2$ or bpy. The unresolved CT band at 90 K, which is not characteristic of Ru-to-bpy CT, suggests an overlap of Ru-to-bpy CT and Ru-to-$dpimbH_2$ CT bands.

The emission energy of $Ru(bpy)_2(dpimbH_2)^{2+}$ is lower by 110 meV than that[8] of $Ru(bpy)_3^{2+}$. The emission shift can be accounted for in terms of oxidation potential, which mostly depends on the d_π-orbital energy of Ru(III). Though the oxidation potential of $Ru(bpy)_2(dpimbH_2)^{2+}$ was not determined, it is estimated to be less positive than those of $Ru(bpy)_2(dpimbH_3)^{3+}$ and $Ru(bpy)_2(dpimbH_4)^{4+}$ because of its less positive charge. Since the oxidation potential (802 mV) of the monoprotonated species, $Ru(bpy)_2(dpimbH_3)^{3+}$, is less positive by 15 mV than that of the diprotonated species, the oxidation potential of Ru-$(bpy)_2(dpimbH_2)^{2+}$ is inferred to be as positive as 787 mV. It turns out that the difference in oxidation potential between Ru-$(bpy)_2(dpimbH_2)^{2+}$ and $Ru(bpy)_3^{2+}$ is close to the difference in emission energy between them.

Monoprotonation and diprotonation of the uncoordinating nitrogens of $dpimbH_2$ reduced the emission energy by 27 and 110 meV,[19] respectively. The phosphorescence shift to lower energy with the protonation indicates that the reduced ligand in the excited CT state is $dpimbH_3^+$ or $dpimbH_4^{2+}$. Assignments of the reduced ligand in the excited CT state of $Ru(bpy)_2(dpimbH_2)^{2+}$ can be inferred from the TA spectrum.

The CT emission energy of the binuclear compound, [Ru-$(bpy)_2]_2(dpimbH_2)^{4+}$, was 58 meV lower than that of the mononuclear compound. The increased stabilization of both the π^*-level of $dpimbH_2$ and the d_π-level of Ru(III) in the excited binuclear compound can be responsible for the emission shift. The coordination of the second Ru(II) ion to $dpimbH_2$ is likely to stabilize the π^*-level of $dpimbH_2$ as much as the protonation

(18) Orellana, G.; Quiroga, M. L.; Braun, A. M. *Helv. Chim. Acta* **1987**, *70*, 2073–86.
(19) Nozaki, K.; Ohno, T. To be submitted for publication.

of the mononuclear compound. The stabilization of the d_π-orbital of the excited binuclear compound is assessed from the redox data. The oxidation potential of the binuclear compound is estimated to be 750 mV from an analysis of the large width of the voltammogram (Figure 7) following Taube and Richardson.[20] The increase in stabilization of Ru(III) in the binuclear compound is estimated to be ~40 meV from the difference in oxidation potential between the mononuclear and the binuclear compound. A part of the stabilization can be brought about by superexchange interaction of the d_π-orbitals of Ru(III) with those of Ru(II). The extent of the superexchange interaction in the mixed-valence compound, $[Ru(bpy)_2](dpimbH_2)^{5+}$, is estimated from the intensity of Ru(II)-to-Ru(III) CT to be 5 meV (vide infra). Since the superexchange interaction through the negatively charged bridging ligand ($bpbimH^{\bullet-}$) in $[Ru(bpy)_2]_2(bpbimH)^{3+}$ is much larger than that through the neutral bridging ligand ($bpbimH_2$),[21] the excited electron residing on $dpimbH_2$ of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ seems to substantially enhance the superexchange interaction. The presence of two equivalent metal sites in the symmetrical binuclear compound further stabilizes Ru(III) by $k_BT \ln 2$ (5 meV).

On the other hand, electrostatic repulsion between Ru(III) and Ru(II) in the binuclear compound slightly destabilizes the CT state of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$.

2. Identification of a Reduced Ligand in the Excited Ru(II)-to-Ligand CT State. $Ru(bpy)_2(dpimH_2)^{2+}$. The TA spectra of $Ru(bpy)_2(dpimbH_2)^{2+}$ subjected to laser excitation (Figure 2b,c) are very different from that of $Ru(bpy)_3^{2+}$, which is composed of a π–π^* band of $bpy^{\bullet-}$ at 27×10^3 cm^{-1} [10,22,23] ($\Delta\epsilon = 17 \times 10^3$ M^{-1} cm^{-1}),[16] a weak and broad band in the red region ($\epsilon = 1500$ M^{-1} cm^{-1}),[16,22f] and a π–π^* band of bpy coordinated to Ru(III) at 32×10^3 cm^{-1} ($\Delta\epsilon = 13.8 \times 10^3$ M^{-1} cm^{-1}).[24] A positive TA band at 24×10^3 cm^{-1} (16×10^3 M^{-1} cm^{-1}) will be assigned to the π–π^* transition of $dpimbH_2^{\bullet-}$ in the following section. A broad TA band in the lower energy region can be ascribed to the π–π^* transition of $dpimbH_2^{\bullet-}$ or $dpimbH_2^{\bullet-}$-to-Ru(III) CT, because the band ($\epsilon = 9 \times 10^3$ M^{-1} cm^{-1}) is much stronger than that of $bpy^{\bullet-}$. The strong bleaching of π–π^* bands of $dpimbH_2$ at 26.5×10^3 and 28.1×10^3 cm^{-1} is consistent with the formation of $dpimbH_2^{\bullet-}$.

The TA spectrum of the protonated species of $Ru(bpy)_2(dpimbH_2)^{2+}$ is similar to that of $Ru(bpy)_2(dpimbH_2)^{2+}$ with the exception of the reduced intensity of the red band. The strongly bleached bands at 27×10^3 and 28.6×10^3 cm^{-1} suggest the reduction of $dpimbH_3^+$. Since the protonation of $dpimbH_2$ raises the electron affinity of $dpimbH_2$, it is more probably that the positive band at 24.7×10^3 cm^{-1} is ascribed to the reduction of $dpimbH_3^+$ in the CT state. The reduced intensity of the red band (9000 → 5200 M^{-1} cm^{-1}) indicates that the red band originates from either the π–π^* of transition $dpimbH_3$ or $dpimbH_3$-to-Ru(III) CT.

(20) Richardson, D. F.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278–85.
(21) Haga, M.; Ano, T.; Kano, K.; Yamabe, S. *Inorg. Chem.* **1991**, *30*, 3843–9.
(22) (a) Bensasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 3722–4. (b) Lachish, U.; Infelta, P. P.; Gratzel, M. *Chem. Phys. Lett.* **1979**, *62*, 317–9. (c) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M. Y.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309–19. (d) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801–3. (e) Milder, S. J.; Gold, J. S.; Kliger, D. S. *J. Phys. Chem.* **1986**, *90*, 548–50. (f) Hauser, A.; Krausz, E. *Chem. Phys. Lett.* **1987**, *138*, 355–60.
(23) (a) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6384–5. (b) Mulazzani, Q. C.; Emmi, S.; Fuochi, P. G.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1978**, *100*, 982–3. (c) Hearh, G.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287–9. (d) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519–26.
(24) Oxidation of $Ru(bpy)_3^{2+}$ gives rise to the similarly strong band at 32×10^3 cm^{-1} with a vibronic structure in the absorption spectrum, which was indistinct in the absorption spectrum of $Ru(bpy)_3^{3+}$ reported by: Mason, S. F. *J. Chem. Soc. A* **1969**, 1428–47.

The π–π^* band of bpy at 34.8×10^3 cm^{-1} was partially bleached ($\Delta\epsilon = -32 \times 10^3$ M^{-1} cm^{-1}). The bleaching of the π–π^* band of bpy, however, does not imply the formation of $bpy^{\bullet-}$ in the excited state but the formation of Ru(III), because the formation of Ru(III) shifts the strong π–π^* transition of bpy to lower energy, losing its intensity at 34.8×10^3 cm^{-1} ($\Delta\epsilon = -30 \times 10^3$ M^{-1} cm^{-1}), as shown in Figure 3b.

$[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ and $[Ru(bpy)_2]_2(dpimbH)^{3+}$. $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ in CH_3CN (Figure 4b) displays a TA spectrum similar to that of the protonated mononuclear compound. The TA band at 23.8×10^3 cm^{-1} is assigned to the π–π^* transition of $dpimbH_2^{\bullet-}$, because the one-electron-reduced species of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$, produced in the quenching of the CT state by phenothiazine (0.8 mM), exhibits a similar absorption band at 23.3×10^3 cm^{-1}. On the other hand, the broad TA of the CT excited state in the energy region lower than 16×10^3 cm^{-1} is lacking for the reduced species ($[Ru(bpy)_2]_2(dpimbH_2)^{3+}$). Therefore, the broad TA band cannot be assigned to the π–π^* transition of $dpimbH_2^{\bullet-}$ but to $dpimbH_2^{\bullet-}$-to-Ru(III) CT. A TA band of the electron-transfer products at 19.2×10^3 cm^{-1} is assigned to the cation radical of phenothiazine.[25]

A photoexcited deprotonated species, $[Ru(bpy)_2]_2(dpimbH)^{3+}$, exhibited bleaching of the wide CT band and a moderate intensity band at 28×10^3 cm^{-1} at 170 K, which were recovered within 1 μs. The TA of $[Ru(bpy)_2]_2(dpimbH)^{3+}$ does not show both the wide band around 23×10^3 cm^{-1} and the bleached π–π^* band of dpimbH at 25.6×10^3 and 27×10^3 cm^{-1} any longer. The TA spectrum is characteristic of the Ru-to-bpy CT state, which has been seen in the cases of $Ru(bpy)_3^{2+}$, $Ru(bpy)_2(imidazole)_2^{2+}$, etc.[10] This interconversion of the lowest CT excited state might be accounted for by a more negative value for $E_{1/2}(dpimbH^-/dpimbH^{\bullet 2-})$ than for $E_{1/2}(dpimbH_2/dpimbH_2^{\bullet-})$ due to a negative charge on the anionic ligand. The short life of the CT excited state is associated with proximity to the d–d phosphorescent state, which is lowered in energy by the coordination of an anionic ligand.

3. Interaction between Ruthenium(II) Sites of Excited Binuclear Compounds. Chromophore–chromophore electronic interaction in the CT state of $[Ru(bpy)_2]_2(dpimbH_2)^{4+}$ allows delocalization of the excited CT state through the whole binuclear compound. The excited electron, which mainly resides on a part of $dpimbH_2$ close to the Ru(III) ion, may move to another part of $dpimbH_2$ provided that the hole on the one metal site moves to the other metal site. The rate of the CT excitation energy transfer between the metal sites depends on the extent of electronic exchange interaction between the excited (Ru(III)) site and the unexcited (Ru(II)) site, because the Ru(III)–Ru(II) interaction is small compared with the intraligand interaction.

The d_π-electrons of the Ru(III) ion undergo superexchange interaction with the d_π-electrons of Ru(II), the extent of which can be estimated from a Ru(II)-to-Ru(III) CT transition of the mixed-valence compound. From Hush theoretical treatments for symmetric mixed-valence compounds,[26] the bandwidth at half-intensity, $\Delta\bar{\nu}_{1/2}$, and the degree of electronic coupling between the metal centers, H_{AB}, can be calculated from

$$\Delta\bar{\nu}_{1/2} = (2310\epsilon_{max})^{1/2}\ (\text{cm}^{-1})$$

$$H_{AB} = 2.05 \times 10^{-2}(\epsilon_{max}\Delta\bar{\nu}_{1/2}/\bar{\nu}_{max})^{1/2}\bar{\nu}_{max}/r\ (\text{cm}^{-1})$$

where $\bar{\nu}_{max}$, ϵ_{max}, and r are the band maximum, the molar absorption coefficient (M^{-1} cm^{-1}) at the band maximum, and the separation between the metal centers. The value of the metal–

(25) Hanson, P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 264–71.
(26) (a) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357–90. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–445. (c) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (d) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135–57.

metal distance, $r = 0.8$ nm, was used on the basis of the molecular model. The observed bandwidth (4340 cm^{-1}) is a little broader than the calculated one (3780 cm^{-1}). H_{AB} is estimated to be 470 cm^{-1} (58 meV). The stabilization energy of the mixed-valence state is estimated to be 5 meV ($H_{AB}^2/\bar{\nu}_{max}$) at the bottom of potential energy by assuming a two-states-model from the extent of electronic coupling and the CT transition energy ($\bar{\nu}_{max} = 6100$ cm^{-1}). Assuming that metal-to-ligand CT completely occurs in the CT excited state, the CT excited binuclear compound is stabilized by the same amount (5 meV) as the mixed-valence compound is. The negative charge on $dpimbH_2$ of the excited electron may enhance the superexchange interaction between the metal sites, which causes the excited state to be delocalized through the metal sites.

Acknowledgment. M.H. gratefully acknowledges financial support from the Ministry of Education of Japan for a Grant-in-Aid for Scientific Research (No. 02640474) and the Okasan-Kato Foundation. We thank Prof. T. Yamagishi and Dr. M. Yamaguchi of Tokyo Metropolitan University for the FAB mass spectra.