Coordination Chemistry Reviews, 132 (1994) 215–222

Intramolecular Electron Transfer within Mixed–valence Diruthenium Complexes

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Abstract

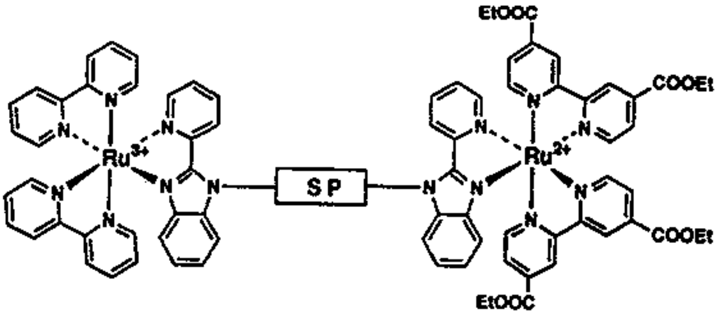
Mixed–valence diruthenium complexes, $[(bpy)_2Ru^{III}(L–SP–L)Ru^{II}(decbpy)_2]^{5+}$ [where bpy=2,2'–bipyridine, decbpy=4,4'–diethoxycarbonyl–2,2'–bipyridine, L=2–(2'–pyridyl)benzimidazolyl, SP=–$(CH_2)_n$– (Cn, n=1–5, 10) or –$CH_2C_6H_4CH_2$– (Xy)] have been prepared in butyronitrile. The mixed–valence isomer state was formed via quenching of a metal–to–ligand charge–transfer state of the $Ru^{II}(decbpy)_2$ moiety by the $Ru^{III}(bpy)_2$ moiety in the complex bridged with C4, C5, C10 or Xy. Arrhenius plots of intramolecular electron transfer rates between the ruthenium ions were obtained by monitoring the decay of the isomer state. The distance dependence of the electronic coupling between the dπ orbitals was determined (β=0.7 $Å^{-1}$).

Introduction

Electron transfer (ET) processes between metal complexes[1,2] and metallocenes[3] have been studied intensively and played important roles in constructing electron transfer theories. Electronic coupling[4–7], its dependence of separation distance[8], nuclear tunneling[9,10], and solvent dynamics[11,12] have been recent subjects on ET. Evaluation of these problems requires the precise examination of intramolecular ET in chemically linked donor–accepter systems where no diffusion processes are involved[13–16]. In this point of view, thermal ET within mixed–valence complexes such as $L_2Ru^{II}–Ru^{III}L_2'$ has been considered attractive. Such an asymmetric mixed–valence complex has the thermally unstable mixed–valence isomer state and intramolecular ET will be observed by monitoring the change of this state into the ground state. The generation of the isomer state can be achieved by some photochemical techniques. Direct excitation of a metal–to–metal charge–transfer (MMCT) band gives the isomer state when the electronic states of metal sites are strongly coupled[17,18]. Another method is to form the isomer state via intramolecular ET quenching of an excited state of one of the moieties by the other. Although the observation of the fast recovery of the ground state upon excitation have been reported for few complexes[19,20] with the latter method, no spectroscopic evidence for generation of unstable isomer states have been given so far.

To examine the intramolecular ET between ruthenium ions we have prepared a series of asymmetric mixed–valence diruthenium complexes,

0010-8545/94/$26.00
SSDI 0010-8545 (94) 02026–F



$[(bpy)_2Ru^{III}(L\text{-}SP\text{-}L)Ru^{II}(decbpy)_2]^{5+}$

Cn complex: SP=$-(CH_2)_n-$ (n=1-5, 10)

Xy complex: SP=$-CH_2C_6H_4CH_2-$

Figure 1 Asymmetric diruthenium mixed-valence complexes examined.

$[(bpy)_2Ru^{III}(L\text{-}SP\text{-}L)Ru^{II}(decbpy)_2]^{5+}$, where the following abbreviations are used: bpy for 2,2'-bipyridine, decbpy for 4,4'-diethoxycarbonyl-2,2'-bipyridine, L-SP-L for a tetradentate bridging ligand, L for 2-(2'-pyridyl)benzimidazolyl, SP for $-(CH_2)_n-$ (Cn, n=1-5, 10) or $-CH_2C_6H_4CH_2-$ (Xy) (Figure 1). The separation distance between ruthenium ions in a stretching form varies from 10 to 22 Å with increase in the number of the methylene groups. The redox potential of the two ruthenium ions are different by 0.2 V. Hereafter, we will call these mixed-valence complexes bridged with Cn and Xy, Cn complex and Xy complex, respectively.

Experimental Section

Materials. Butyronitrile was purified by distillation over P_2O_5 under a reduced pressure. Tetra-n-butylammonium perchlorate (TBAP) was recrystallized from ethanol/water.

Preparation. *Tetradentate bridging ligands (L-SP-L).* A bridging ligand was synthesized by coupling 2-(2'-pyridyl)benzimidazole with dibromoalkane or α,α'-dibromo-*p*-xylene in dry *N,N*-dimethylformamide in the presence of CaH_2. The ligand was recrystallized from ethylacetate.

Mononuclear complex $[Ru(bpy)_2(L\text{-}SP\text{-}L)](ClO_4)_2$. A mixture of $Ru(bpy)_2Cl_2$ and a bridging ligand in ethanol/water mixture was refluxed for 4 h. The product was purified with a SP-Sephadex cation-exchange column using a mixture of acetonitrile and the Britton-Robinson buffer of pH 4.6 (1:1 v/v). The complex was recrystallized from ethanol/water.

Asymmetric diruthenium complex [Ru(bpy)$_2$(L–SP–L)Ru(decbpy)$_2$](PF$_6$)$_4$. A mixture of Ru(decbpy)$_2$Cl$_2$ and [Ru(bpy)$_2$(L–SP–L)](ClO$_4$)$_2$ in ethanol/water mixture was refluxed for 7 h. The product was purified with a CM–Sephadex cation–exchange column using a mixture of acetonitrile and the buffer of pH 5.7 (1:1 v/v) containing 20 mM NH$_4$PF$_6$. The complex was recrystallized from ethanol/water.

Apparatus. The nano–sec laser photolysis system used here was described previously[13].

Electrochemical oxidation of ruthenium complexes. Electrochemical oxidation was performed using a flow–electrolysis method with a Pt column electrode[21]. A solution of diruthenium complex in butyronitrile containing 0.05 M TBAP was passed through the column electrode at the flow rate of 0.5 ml/min. The solution was electrolyzed quantitatively in the column in which lots of fine Pt wires were packed tightly and then transferred into a quartz cell. Since lifetimes of mixed–valence states was only a few hours, laser flush photolysis was carried out immediately after the oxidation.

Results

Figures 2a and 2b show the absorption spectra of [Ru(bpy)$_2$(L–C5–L)]$^{n+}$ and

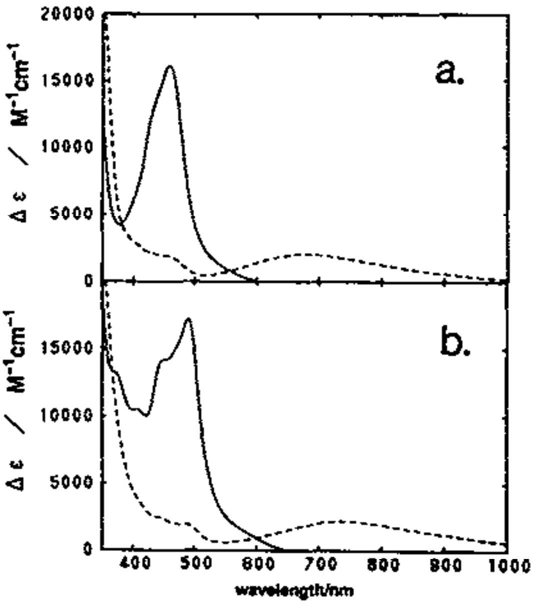


Figure 2 Absorption spectra of [(bpy)$_2$Ru(L–C5–L)]$^{n+}$ (a) and [(decbpy)$_2$Ru(L–C5–L)]$^{n+}$ (b) in acetonitrile with n=2 (solid line) and n=3 (broken line).

[Ru(decbpy)$_2$(L–C5–L)]$^{n+}$ (n=2, 3), respectively. An absorption band of the Ru(II) state in the 400–500 nm region is a metal-to-ligand charge-transfer (MLCT) band. After oxidation the MLCT band disappeared and a broad ligand-to-metal charge-transfer (LMCT) band appeared in a lower energy region. The MLCT band for [Ru(bpy)$_2$(L–C5–L)Ru(decbpy)$_2$]$^{4+}$ was the sum of those of each Ru(II) moieties. After one-electron oxidation, the MLCT band due to the Ru^{II}(decbpy)$_2$ moiety remained, showing the formation of [Ru^{III}(bpy)$_2$(L–C5–L)Ru^{II}(decbpy)$_2$]$^{5+}$.

When [Ru(bpy)$_2$(L–C5–L)Ru(decbpy)$_2$]$^{4+}$ is irradiated with a 532 nm laser pulse, the decay of the MLCT state of the Ru^{II}(decbpy)$_2$ moiety was observed with the lifetime of 500 ns in acetonitrile at room temperature. However, the MLCT state in the mixed-valence complex decayed within 10 ns, showing that the excited state was quenched by the remote Ru^{III}(bpy)$_2$ moiety. A characteristics bleaching was observed at 490 nm in the transient absorption spectrum measured at 20 ns after excitation in butyronitrile at 213 K (Figure 3a). The difference spectrum is identical to that obtained by simulation provided that the mixed-valence isomer state [Ru^{II}(bpy)$_2$(L–C5–L)Ru^{III}(decbpy)$_2$]$^{5+}$ is generated (Figure 3b), indicating that ET occurs from the MLCT state of the Ru^{II}(decbpy)$_2$ moiety to the Ru^{III}(bpy)$_2$ moiety to give the isomer state. The strong bleaching at 490 nm is due to the difference in the

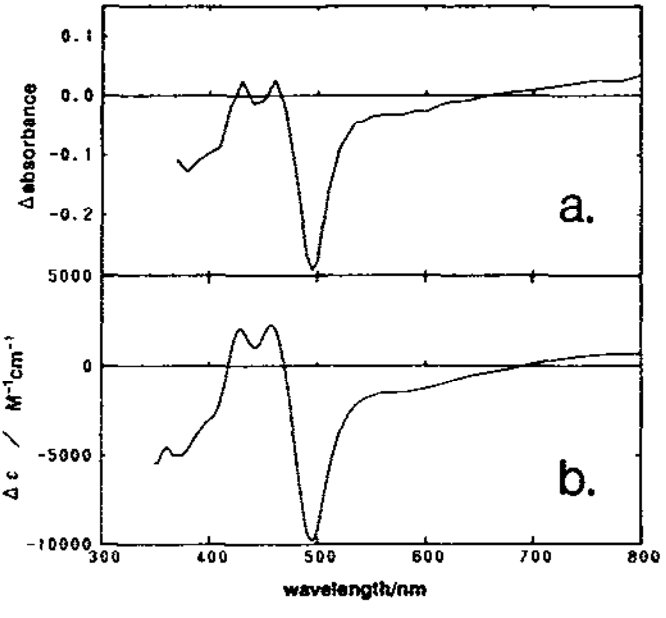


Figure 3 Transient absorption spectrum observed at 20 ns after the excitation of [(bpy)$_2$Ru^{III}(L–C5–L)Ru^{II}(decbpy)$_2$]$^{5+}$ with 532 nm at 213K in butyronitrile (a) and the difference spectrum simulated for generation of the mixed-valence isomer state (b).

MLCT band between two Ru(II) moieties (Figures 2a and 2b).

The isomer state was observed for the complex linked with a long spacer such as C4, C5, C10 and Xy, but the transient absorption for the complex with a short spacer such as C1, C2, nor C3 showed only a rapid decay of the MLCT state over the temperatures examined (170–300 K).

For further study on faster decay of the excited state followed by the generation of the isomer state, picosecond resolved transient absorption spectra were measured for C5 complex. The MLCT state decayed with the lifetime of 550 ps, which was accompanied by the generation of the characteristic bleaching at 490 nm. The quantum yield of the production of the isomer state is 0.47. The energy transfer to the low-lying LMCT state of the $Ru^{III}(bpy)_2$ moiety is a possible process competing with the ET quenching.

On the other hand, the isomer state was not observed though the decay of the excited state was observed for C1 and C2 complex (lifetime: 77 ps (C1), 120 ps (C2)). Two possible mechanisms are proposed. In the first mechanism, the energy transfer was so fast compared to the ET quenching that the quantum yield of production of the isomer state was quite low. In the second one, the isomer state was formed but the back ET to regenerate the grand state was so fast compared to its generation that it could not be detected. Further information is needed for determination which mechanism is dominant.

The rates of the back ET were determined by monitoring the recovery of the characteristic bleaching at 490 nm. These rates showed relatively large temperature dependence. It is interesting that the C4, C5 and Xy complexes have almost the same activation energy (0.13 eV) while the C10 complex has large activation energy (0.19 eV). It should be noted that the isomer states of the C5 and Xy complexes with the same separation distance decayed with almost the same rates over a wide temperature range.

The weak MMCT bands (ε<50 $M^{-1}cm^{-1}$) were observed for the symmetric mixed-valence complexes, $[(bpy)_2Ru^{III}(L\text{-}SP\text{-}L)Ru^{II}(bpy)_2]^{5+}$ (SP=C1 and C2)[13], in acetonitrile around 1200 nm though not observed for the asymmetric complexes due to the overlapping with the LMCT bands. Although the excitation of the asymmetric complex bridged with C2, C3, or C4 spacer using the fundamental wave of the YAG laser (1064 nm, 100 mJ) was attempted for direct formation of the isomer state, no detectable transient signals were observed.

Discussion

When electronic exchange interaction between a donor and an acceptor is weak, ET rates are dominated by both the Frank–Condon factor and the extent of electronic coupling (matrix element, H_{rp}). However, when the electronic coupling is strong ET rates depend not on H_{rp} but on a longitudinal and a rotational relaxation time of the solvent. Such an adiabatic process has been often observed for ET reactions lying in the normal region[11–13]. The frequency factor for the adiabatic ET in butyronitrile was calculated to be $4x10^{11}$ s^{-1} using a current solvent-controlled ET theory[13]. Since all of the frequency factors obtained for the ET processes examined here are smaller than the adiabatic value, these processes are regarded as nonadiabatic processes. Accordingly, *Hrp* and reorganization energy(λ) for each complexes were determined by simulating the temperature dependence of the rates using the rate equation for nonadiabatic ET[1],

$$k = \frac{H_{rp}{}^{2}}{\hbar} \sqrt{\frac{\pi}{\lambda RT}} \exp\left[-\frac{(\Delta G^{\circ}+\lambda)^{2}}{4\lambda RT} \right] \qquad (1)$$

where ΔG° is a free energy change.

In the case that ET involves considerable extent of ΔS° this factor is very important factor in evaluating the temperature dependence of ET rates[14]. However, ΔS° for these ET was estimated to be less than 5×10^{-5} eV/K from electrochemical measurements and thus we neglected ΔS°.

Although no information on intramolecular reorganization energy (λ_{in}) has not been obtained for these ruthenium complexes, the changes of nuclear position on ET in such polypyridine-like ruthenium complexes is expected to be little [22]. Therefore, the simulation was done under the assumption that outersphere reorganization energy λ_{out} is dominant in λ.

The temperature variation of λ_{out} in butyronitrile was corrected using Eq.2[13],

$$\frac{1}{\lambda_{out}} \frac{d\lambda_{out}}{dT} = 3.5 \times 10^{-4}\ \mathrm{K}^{-1} \qquad (2)$$

The kinetic parameters are summarized in Table together with *Hrp* and λ obtained

Table Parameters for intramolecular ET within the mixed-valence complexes in butyronitrile.

SP	ΔG^{0} eV	*k* at 298K s^{-1}	*Ea* eV	*A* s^{-1}	H_{rp} meV	$\lambda^{b)}$ eV	d_{M-M} Å
C_1	−0.19	--	--	--	$(9)^{a)}$	$(0.92)^{a)}$	10
C_2	−0.19	--	--	--	$(8)^{a)}$	$(0.96)^{a)}$	11.5
C_3	−0.18	--	--	--	--	--	12.5
C_4	−0.18	$19\ \ x10^{7}$	0.124	$2.3x10^{10}$	2.6	0.94	14
C_5	−0.18	$7.9x10^{7}$	0.130	$1.3x10^{10}$	2.0	0.97	15
Xy	−0.19	$6.8x10^{7}$	0.133	$1.2x10^{10}$	1.9	1.01	15
C_{10}	−0.18	$1.9x10^{7}$	0.190	$3.0x10^{10}$	3.9	1.25	22

a. Evaluated from the Hush treatment of the MMCT bands for $[(bpy)_2Ru^{III}(L\text{-}SP\text{-}L)Ru^{II}(bpy)_2]^{5+}$ in acetonitrile.

from the Hush treatment of the MMCT band for the symmetric diruthenium complexes with C_1 and C_2 in acetonitrile. The H_{Tp} values for these ET processes represents the resonance energy between the dπ orbitals of the ruthenium ions.

The rates at 298 K decreases with the increase of the separation distance, showing an usual distance dependence of ET rates. While H_{Tp} decreases as the length of the methylene chain increases from C_1 to C_5, one for the C_{10} complex is bigger than those of the C_4 and C_5 complexes. When two ruthenium complexes are connected with a flexible spacer such as C_{10}, the separation distance between them is controlled by both electrostatic repulsion and thermal energy. Therefore, as temperature increases the mean distance decreases and thus the ET becomes faster than that of the stretching form. Moreover, some molecular motions such as folding of the methylene chain are anticipated to enhance the ET rates and the contribution of this effect becomes important with decreasing the ET rate at the stretching form. Since both thermal effects make activation energy larger than that expected for the ET process of the stretching diruthenium complex, the temperature dependence for the C_{10} complex must be treated by considering such chain motions to determine the precise parameters.

On the other hand, such effects seem to be less important for the C_4 and C_5 complexes because these activation energy are almost the same as that for Xy complex bridged with a less flexible spacer. These results imply the absence of additional activation energy due to the flexibility of the spacer.

The plot of 2 ln(H_{Tp}) against the separation distance (R) ranging from 10 to 15 angstroms shows a linear relationship as has been expected for the distance dependence of electronic coupling (Eq. 3),

$$H_{Tp}^2 \propto \exp[-\beta R] \qquad (3)$$

The β value was determined to be 0.7 Å^{-1}. The β value for d^5–d^6 metal complexes bridged with methylene groups has not been reported. It is of interest that the methylene-bridged system showed a distance dependence similar to those bridged with a saturated hydrocarbon such as dithiaspiro ring-bridged diruthenium complexes (0.8 Å^{-1})[24] and polyproline-bridged Ru–Os complexes (0.6 Å^{-1})[8]. These β values are much bigger than that for a conjugated system as polyene-bridged diruthenium complexes (0.2 Å^{-1})[25].

We reported here that it is possible to observe ET processes in mixed-valence complexes when the electronic coupling is not strong. There will be possibility of the observation of intramolecular ET also for the other mixed-valence complexes such as diosmium complexes, dirhenium complexes as well as bisporphyrin compounds. Key parameters for these ET processes can be accumulated by using the technique described here.

Acknowledgement

We thank Dr. Yoshinori Hirata of Osaka University for his help with measurements of pico-sec laser photolysis.

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23 Eq. 2 was derived from the dielectric continuum model[1],

$$\Lambda_{out} \propto \frac{1}{n^2} - \frac{1}{\epsilon_s}$$

where n is a refractive index and ε_s is a static dielectric constant of butyronitrile and using $dn/dT=-0.00043\ K^{-1}$. The value of $(1/\varepsilon_s)(d\varepsilon_s/dT)$ is assumed to equal to that of acetonitrile ($-0.0055\ K^{-1}$).
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