211. Ligand Substitution Reaction of Bis(ethylenediamine)glycinatocobalt(III) Complex with Ethylenediamine Catalyzed by the Photo-excited Tris(2,2′-bipyridine)ruthenium(II) Complex

by **Masahiko Ishikawa, Ken-ichi Okamoto**, and **Jinsai Hidaka**

Department of Chemistry, University of Tsukuba, Niihari, Ibaraki 305, Japan

and **Hisahiko Einaga***

Institute of Materials Science, University of Tsukuba, Niihari, Ibaraki 305, Japan

(5.VII.85)

Substitution reaction with ethylenediamine of coordinated glycinate ligand in bis(ethylenediamine)-glycinatocobalt(III) complex has been studied in the presence of photo-excited tris(2,2′-bipyridine)ruthenium(II) complex in alkaline aqueous solution (buffered around pH 12) containing 1.0M chloride ion at 25 °C. VIS absorption and CD spectra were used for the racemate and the optically active isomers of the Co(III) complexes, respectively. The reaction was catalyzed by the excited Ru(II) complex to give tris(ethylenediamine)cobalt(III) complex. Mechanism of the ligand-substitution reaction and role of the excited Ru(II) complex were discussed.

Introduction. – Co(III) complexes are characteristic in that they are intrinsically substitution-inert for their coordinated ligands (*e.g.* [1]). This substitution-inertness has been interpreted in terms of an electronic structure of the central metal atom, *i.e.*, $(t_{2g})^6$ state for Co(III) in an octahedral or pseudo-octahedral coordination. Such being the case, the ligand-substitution reaction of the Co(III) complexes can be made labile by changing temporarily the electronic structure of the metal atom from $(t_{2g})^6$ to $(t_{2g})^5(e_g)^1$ state by excitation or to $(t_{2g})^5(e_g)^2$ state by charge transfer by means of any appropriate methods. Of course, final conversion from the $(t_{2g})^5(e_g)^1$ or $(t_{2g})^5(e_g)^2$ state to the $(t_{2g})^6$ ground state is prerequisite after the ligand substitution processes.

It was found that the coordinated glycinate ligand in bis(ethylenediamine)-glycinatocobalt(III) complex ($[Co(gly)(en)_2]^{2+}$, where gly and en denote glycinate and ethylenediamine, respectively) is made labile and is substituted by en in the presence of photo-excited tris(2,2′-bipyridine)ruthenium(II) complex ($*[Ru(bpy)_3]^{2+}$, where bpy denotes 2,2′-bipyridine) to give tris(ethylenediamine)cobalt(III) complex ($[Co(en)_3]^{3+}$) even at room temperature. At this temperature, no thermal ligand-substitution reaction proceeds at all. The ligand-substitution reaction of $[Co(gly)(en)_2]^{2+}$ with en was studied in the present investigation under the coexistence of $*[Ru(bpy)_3]^{2+}$ in alkaline aqueous solution (buffered around pH 12) containing 1.0M chloride ion at 25 °C under the pseudo-first-order kinetic condition with respect to en. The reaction mechanism and role of $*[Ru(bpy)_3]^{2+}$ in the reaction will be discussed.

Results. – The ligand substitution reaction did not proceed when $[Co(gly)(en)_2]^{2+}$ was directly photo-excited at the first absorption band ($^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$) in the d–d transi-

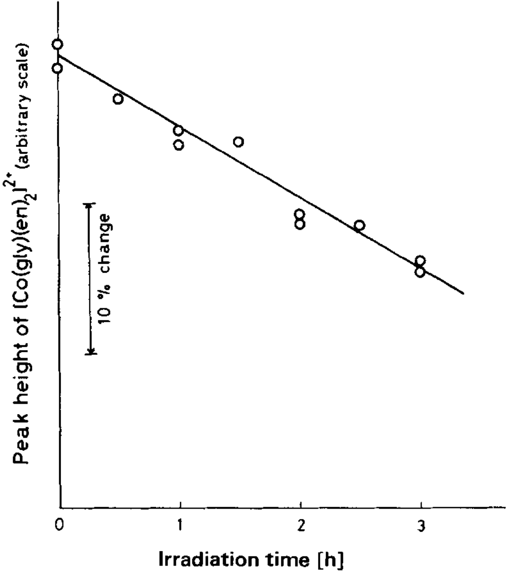

Fig. 1. *Change in amount of* $[Co(gly)(en)_2]^{2+}$ *determined by HPLC with photo-irradiation time in the presence of* $[Ru(bpy)_3]^{2+}$. $[[Co(gly)(en)_2]^{2+}] = 1.00 \times 10^{-2}$ M (initial state); $[[Ru(bpy)_3]^{2+}] = 1.00 \times 10^{-3}$ M; [en] = 2.00 M; $[OH^-] = 1.58 \times 10^{-2}$ M (buffered); $[Cl^-] = 1.0$ M; 25°. Irradiation wavelength, 452 nm. No change in amount of $[Co(gly)(en)_2]^{2+}$ was noticed in the absence of $[Ru(bpy)_3]^{2+}$.

tion but it did proceed when $[Ru(bpy)_3]^{2+}$ was coexisted and photo-excited at the charge-transfer band (452 nm). Further, no photo-irradiation on a solution containing both $[Co(gly)(en)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ gave no progress of the reaction. Hence, we can expect the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction.

Separation by HPLC and characterization by UV/VIS absorption spectra were carried out on the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction product of $[Co(gly)(en)_2]^{2+}$ under the large excess of en. The product was composed of $[Co(en)_3]^{3+}$ with no noticeable quantities of $[Co(en)_3]^{2+}$ and other types of Co(II) and Co(III) complexes. *Fig. 1* shows that the amount of $[Co(gly)(en)_2]^{2+}$ decreases linearly with increase in the photo-irradiation time for the generation of $^*[Ru(bpy)_3]^{2+}$. Furthermore, the amount of $[Co(en)_3]^{3+}$ formed was found to increase linearly with increase in the irradiation time just in compensation for the decrease of $[Co(gly)(en)_2]^{2+}$. Yield for the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction of $[Co(gly)(en)_2]^{2+}$ against $^*[Ru(bpy)_3]^{2+}$ generated, Φ^{sub}, was obtained from $-d[[Co(gly)(en)_2]^{2+}]/dt$ by HPLC based on the relation,

$$\Phi^{sub} = (-d[[Co(gly)(en)_2]^{2+}]/dt) / I_a\Phi^{\circ} \qquad (1)$$

where $I_a\Phi^{\circ}$ corresponds to the formation rate of $^*[Ru(bpy)_3]^{2+}$ (this will be discussed later). The yield is summarized in the *Table*. It should be noted that the yield does not depend on the $[Ru(bpy)_3]^{2+}$ concentration.

The yield was also determined on the optically active isomers, Λ-$(+)_{589}$- and Δ-$(-)_{589}$-$[Co(gly)(en)_2]^{2+}$[1]), in the presence of racemic $[Ru(bpy)_3]^{2+}$ by following CD spectral

---

[1]) Absolute configuration of the complexes are indicated according to the IUPAC tentative rule: *Inorg. Chem.* **1970**, *9*, 1.

Table. *Yield for Ligand-Substitution Reaction* vs. **$[Ru(bpy)_3]^{2+}$ Generated*

	Φ^{sub} [a])		
	$[Co(gly)(en)_2]^{2+}$	Λ-(+)$_{589}$-$[Co(gly)(en)_2]^{2+}$	Δ-(−)$_{589}$-$[Co(gly)(en)_2]^{2+}$
$[Ru(bpy)_3]^{2+}$	0.45[b]), 0.41[c])	0.55[d]), 0.56[e]), 0.54[f])	0.55[d])
Δ-(−)$_{589}$-$[Ru(bpy)_3]^{2+}$	–	0.55[d])	0.52[d])

[a]) $\Phi^{sub} = (-d[[Co(gly)(en)_2]^{2+}]/dt)/I_a\Phi°$ (*cf.* the text). [b]) [c]) By HPLC. [d])–[f]) By CD. Relative error by HPLC was ±20% and that by CD was ±5%. $[[Co(gly)(en)_2]^{2+}] = 1.00 \times 10^{-2}$M. $[[Ru(bpy)_3]^{2+}]$ [b]) = 1.00×10^{-2}; [c]) = 1.00×10^{-3}; [d]) = 1.00×10^{-5}; [e]) = 2.00×10^{-5}; [f]) = 5.00×10^{-5}M. [en] = 2.00M. $[OH^-] = 1.58 \times 10^{-2}$M (buffered). $[Cl^-]$ = 1.0M; 25°.

change with the photo-irradiation time. The CD intensities of these isomers in the d–d transition ($^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$) region decreased linearly with increase in the irradiation time with no change in the spectral pattern (*cf. Fig. 2* for the Λ-(+)$_{589}$ isomer). This means that these optically active isomers change to racemic $[Co(en)_3]^{3+}$ by the *$[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction. The yield for these isomers, as given in the *Table*, agrees with that for racemic $[Co(gly)(en)_2]^{2+}$ when experimental errors by HPLC and CD are taken into consideration.

Likewise, the yield was determined on the optically active isomers of $[Co(gly)(en)_2]^{2+}$ in the presence of the optically active isomer of the Ru(II) complex, Δ-(−)$_{589}$-$[Ru(bpy)_3]^{2+}$, by following the CD-intensity changes of the former with the photo-irradiation time of the latter. (No photoracemization of the optically active isomers of $[Ru(bpy)_3]^{2+}$ was ascertained by the CD spectra during the irradiation at 452 nm under the experimental condition.) The yield, which is also given in the *Table*, agrees well with that obtained above. Hence, it is concluded that in the *$[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction there are no specific and stereochemical interactions between *$[Ru(bpy)_3]^{2+}$ and $[Co(gly)(en)_2]^{2+}$, except charge or energy transfer between them. ($[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ are inert in the thermal substitution of the coordinated ligand [2]).

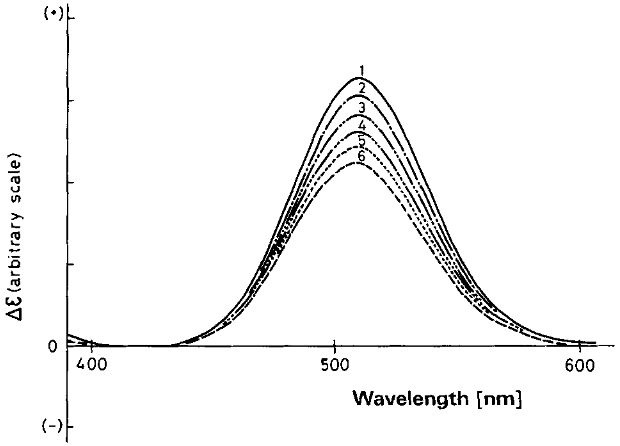

Fig. 2. *CD-spectral change with photo-irradiation time of optically active isomer* (Λ-(+)$_{589}$-$[Co(gly)(en)_2]^{2+}$) *in the presence of racemic* $[Ru(bpy)_3]^{2+}$. $[[Co(gly)(en)_2]^{2+}] = 1.00 \times 10^{-2}$M; $[[Ru(bpy)_3]^{2+}] = 1.00 \times 10^{-5}$M; [en] = 2.00M; $[OH^-] = 1.58 \times 10^{-2}$M (buffered); $[Cl^-]$ = 1.0M; 25°. Irradiation wavelength, 452 nm. Irradiation time, 1:0; 2:60; 3:120; 4:180; 5:240; and 6:300 min. No change in CD spectra was noticed in the absence of $[Ru(bpy)_3]^{2+}$.

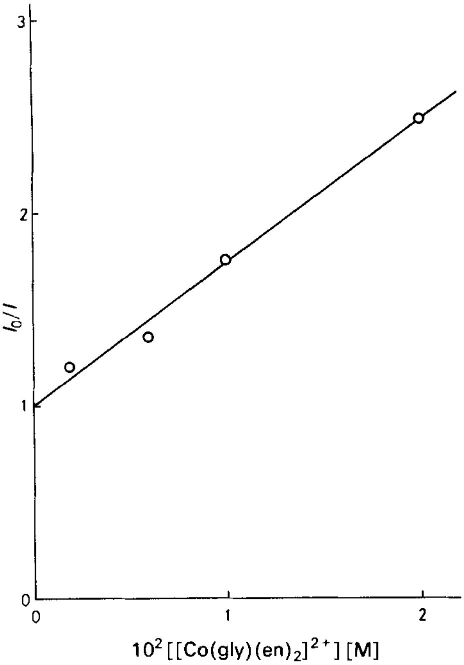

Fig. 3. Stern-Volmer *plots for the quenching of fluorescence intensity of* $[Ru(bpy)_3]^{2+}$ *by* $[Co(gly)(en)_2]^{2+}$. $[[Ru(bpy)_3]^{2+}] = 1.00 \times 10^{-3}$ M; 25°. Excitation wavelength, 452 nm. Fluorescence wavelength, 607 nm.

Fluorescence quenching of $^*[Ru(bpy)_3]^{2+}$ was determined in relation to concentration of $[Co(gly)(en)_2]^{2+}$ by monitoring the fluorescence intensity at 607 nm. *Fig. 3* shows the *Stern-Volmer* plots.

$$I_0/I = 1 + K_{sv}[[Co(gly)(en)_2]^{2+}] \qquad (2)$$

Here, I_0 and I are the fluorescence intensities of $^*[Ru(bpy)_3]^{2+}$ in the absence and presence of $[Co(gly)(en)_2]^{2+}$, respectively, and K_{sv} is the *Stern-Volmer* constant. A linear relation with an intercept of unity was obtained between I_0/I and $[[Co(gly)(en)_2]^{2+}]$ with K_{sv} of 0.75×10^2 M^{-1}.

Discussion. – In the present ligand-substitution reaction, $^*[Ru(bpy)_3]^{2+}$ can take either of two possible functions: a charge transfer or an energy transfer to change electronic structure of the central metal atom of the Co(III) complex. Photochemical characteristics of $[Ru(bpy)_3]^{2+}$ have recently been well reviewed by *Watts* [2]: $[Ru(bpy)_3]^{2+}$ is excited at *ca.* 450 nm with metal-to-ligand charge transfer characteristics [3] to a lowest singlet excited state (^{1}CT $^*[Ru(bpy)_3]^{2+}$), which changes rapidly to the lowest triplet excited state (^{3}CT $^*[Ru(bpy)_3]^{2+}$) with an intersystem crossing quantum yield of unity [2]. The latter then gives an emission band at 590 nm [3] (lifetime: 0.6 µs (aqueous solution at 25°) [4] [5]), and it behaves as an electron donor or acceptor according to the redox properties of the coexisting reaction partner ($[Ru(bpy)_3]^{3+} + e \rightarrow {}^3$CT $^*[Ru(bpy)_3]^{2+}$, $E° = -0.84$ V; ^{3}CT $^*[Ru(bpy)_3]^{2+} + e \rightarrow [Ru(bpy)_3]^+$, $E° = +0.82$ V; $[Ru(bpy)_3]^{3+} + e \rightarrow [Ru(bpy)_3]^{2+}$, $E° = +1.26$ V; and $[Ru(bpy)_3]^{2+} + e \rightarrow [Ru(bpy)_3]^+$, $E° = -1.28$ V (*vs.* SHE) [2]). If charge transfer is the case, then ^{3}CT $^*[Ru(bpy)_3]^{2+}$ should behave as an electron donor to $[Co(gly)(en)_2]^{2+}$, because the latter has the formal redox potential, $E° = -0.36$ V (*vs.* SHE)

($[Co(gly)(en)_2]^{2+}$ + e$\rightarrow[Co(gly)(en)_2]^{+}$ [6]). Likewise, if energy transfer [7] is the case, then the process, ^{3}CT $*[Ru(bpy)_3]^{2+} + [Co(gly)(en)_2]^{2+} \rightarrow [Ru(bpy)_3]^{2+} + *[Co(gly)(en)_2]^{2+}$, should take place to generate $*[Co(gly)(en)_2]^{2+}$ with electronic structure of $^1T_{1g}(O_h)$ $((t_{2g})^5(e_g)^1)$ or $^3T_{1g}(O_h)((t_{2g})^5(e_g)^1)$ in analogy with that for $[Co(NH_3)_6]^{3+}$ [8] [9]. (*Wilson* and *Solomon* [8] reported that the potential energy surfaces at the excited and the ground states of $[Co(NH_3)_6]^{3+}$ are in the following order:

$$^1T_{1g}((t_{2g})^5(e_g)^1) > {}^3T_{1g}((t_{2g})^5(e_g)^1) > {}^5T_{2g}((t_{2g})^4(e_g)^2) > {}^1A_{1g}((t_{2g})^6).)$$

The *Stern-Volmer* constant, K_{sv}, of the quenching of ^{3}CT $*[Ru(bpy)_3]^{2+}$ with $[Co(gly)(en)_2]^{2+}$ gives us the quenching rate constant, k_q, of 1.25×10^8 $M^{-1}s^{-1}$ by using the lifetime of ^{3}CT $*[Ru(bpy)_3]^{2+}$, τ_0 ($= K_{sv}/k_q$), of 0.6 µs [4] [5]. This quenching rate constant is of the same magnitude as that for such quenchers as $[Co(en)_3]^{3+}$ (k_q, 2.0×10^7 $M^{-1}s^{-1}$; 0.1M H_2SO_4, air equilibrated; *ca.* 22° [10]), $[Co(OAc)(NH_3)_5]^{2+}$ (k_q, 2.1×10^8 $M^{-1}s^{-1}$; 0.10M $LiClO_4$, pH 5.8; 25°; AcO denotes acetate [11]), *etc.*, where the central metal atom of the quencher is reduced to bivalent state. These rate constants can be well compared with the rate constant (10^8–10^9 $M^{-1}s^{-1}$) at an infinite dilution of the diffusion-controlled reaction in aqueous solution estimated by the *Debye* equation[2]) and with rate constants for the electron transfer processes in the $*[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ couple of *ca.* 10^8 $M^{-1}s^{-1}$ [2]. These rate constants are also in line with those by the electron-transfer quenching process[2]) [10] [11]. Furthermore, direct excitation of $[Co(gly)(en)_2]^{2+}$ in the d–d transition region caused no ligand-substitution reaction in the present investigation. Hence, it can be concluded that ^{3}CT $*[Ru(bpy)_3]^{2+}$ plays as the electron donor to $[Co(gly)(en)_2]^{2+}$, and the charge transfer takes place *via* an outer sphere, diffusion-controlled mechanism to give $[Ru(bpy)_3]^{3+}$ and substitution-labile $[Co(gly)(en)_2]^{+}$. This charge-transfer process proceeds without any stereoselectivity because the yield for the ligand-substitution reaction does not depend on stereochemistry of the Ru(II) as well as the Co(III) complex *(cf. Table)*.

The fact that the yield does not depend on the stereochemistry of both complexes indicates further that the overall rate of the reaction is limited by the photo-excitation step of $[Ru(bpy)_3]^{2+}$ and that the racemization of the starting optically active isomers of $[Co(gly)(en)_2]^{2+}$ takes place in the succeeding rapid step, to which the substitution-labile $[Co(gly)(en)_2]^{+}$ is directly related.

On the basis of the reaction mechanism deduced above, the following kinetic equations can be derived:

$$d[[Co(en)_3]^{3+}]/dt = k_{el}[[Co(en)_3]^{2+}][[Ru(bpy)_3]^{3+}] \tag{3}$$

$$d[[Co(en)_3]^{2+}]/dt = k_{sub}[[Co(gly)(en)_2]^{+}][en] - k_{el}[[Co(en)_3]^{2+}][[Ru(bpy)_3]^{3+}] \tag{4}$$

$$d[[Co(gly)(en)_2]^{+}]/dt = k_q[[Co(gly)(en)_2]^{2+}][*[Ru(bpy)_3]^{2+}] - k_{sub}[[Co(gly)(en)_2]^{+}][en] \tag{5}$$

$$d[*[Ru(bpy)_3]^{2+}]/dt = I_a\Phi^\circ - \{(k_{em} + k_{th}) + k_q[[Co(gly)(en)_2]^{2+}]\}[*[Ru(bpy)_3]^{2+}] \tag{6}$$

$$-d[[Co(gly)(en)_2]^{2+}]/dt = d[[Co(en)_3]^{3+}]/dt \tag{7}$$

---

[2]) *Lay et al.* [12] and *Mok et al.* [13] pointed out that the quenching of some caged complexes, $[Co(cage)]^{3+}$, proceeds through the parallel electron transfer ((1–10) × 10^8 $M^{-1}s^{-1}$ [13]) and energy transfer (1 × 10^8 $M^{-1}s^{-1}$ [13]) pathways based simply on kinetic aspect of the reaction mechanism.

Here, k_{el}, k_{sub}, k_q, k_{em} and k_{th} denote the rate constants for the electron transfer between $[Co(en)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$, for the ligand-substitution process of $[Co(gly)(en)_2]^+$ with en and for the quenching by $[Co(gly)(en)_2]^{2+}$, emission and radiationless transition of $*[Ru(bpy)_3]^{2+}$, respectively; I_a is the intensity of the irradiating light and $\Phi°$ is the yield for the generation of $*[Ru(bpy)_3]^{2+}$. Under the assumption that the steady-states hold for $[Co(en)_3]^{2+}$, $[Co(gly)(en)_2]^+$ and $*[Ru(bpy)_3]^{2+}$, *Eqn. 8* can be derived from *Eqns. 3–7* to give the relation between the observed rate, $-d[[Co(gly)(en)_2]^{2+}]/dt$, and concentration of $[Co(gly)(en)_2]^{2+}$:

$$I_a\Phi°/\{I_a\Phi° - (-d[[Co(gly)(en)_2]^{2+}]/dt)\} = 1 + \{k_q/(k_{em} + k_{th})\}[[Co(gly)(en)_2]^{2+}] \quad (8)$$

Eqn. 8 is a type of the *Stern-Volmer* relation corresponding to the usual expression of

$$I_0/I = 1 + \{k_q/(k_{em} + k_{th})\}[[Co(gly)(en)_2]^{2+}] \quad (9)$$

with the *Stern-Volmer* constant, K_{sv} ($= k_q\tau_0$), being equal to $k_q/(k_{em} + k_{th})$ *(cf. Eqn. 2)*. In the *Table*, the yield for the ligand-substitution reaction is given against $*[Ru(bpy)_3]^{2+}$ generated, as has been defined by *Eqn. 1*.

In summary, the $*[Ru(bpy)_3]^{2+}$-catalyzed ligand-substitution reaction proceeds according to the following mechanism: $[Co(gly)(en)_2]^{2+}$ is reduced by ^3CT $*[Ru(bpy)_3]^{2+}$ to give $[Ru(bpy)_3]^{3+}$ and $[Co(gly)(en)_2]^+$. This substitution-labile $[Co(gly)(en)_2]^+$ complex then plays a rapid ligand-substitution with en to form $[Co(en)_3]^{2+}$, which interacts with $[Ru(bpy)_3]^{3+}$ to give finally $[Co(en)_3]^{3+}$ and $[Ru(bpy)_3]^{2+}$.

Experimental. – $[Co(gly)(en)_2]Cl_2$ was prepared from *trans*-$[CoCl_2(en)_2]Cl$ and glycine [14] [15]. Its optical resolution was carried out by using $K_2[Sb_2(d\text{-}(+)\text{-tart})_2]\cdot H_2O$, where tart denotes tartrate, according to [15]. $[Ru(bpy)_3]Cl_2\cdot 6\,H_2O$ was synthesized from $RuCl_3$ and 2,2′-bipyridine in DMF as reported in [16]. The complex was resolved into enantiomers by using $(NH_4)_2(d\text{-}(+)\text{-tart})$ based on procedure in [17]. All the complexes and their optically active isomers were characterized by elemental analysis and UV/VIS-absorption and CD spectra. Ethylenediamine (en) of anal. grade was used and it was purified when necessary by distillation under reduced pressure before use. All other reagents used were of anal. grade.

UV/VIS and CD spectra were recorded on *JASCO* spectrophotometers, models *UVIDEC-1* and *-610 C*, and on *JASCO* spectropolarimeters, models *J-20* and *-500 C*, respectively. pH of the soln. was measured with a *Horiba* glass electrode pH meter, model *F7-SS*. The pH meter reading was converted to $[OH^-]$ by defining $-\log[OH^-]$ of a soln. containing 0.0100M NaOH and 0.9900M NaCl to be 2.00.

Runs in the presence of $*[Ru(bpy)_3]^{2+}$ were carried out at 25° in an alkaline aq. soln. containing 1.0M Cl^- and large excess of en over $[Co(gly)(en)_2]^{2+}$ so that the pseudo-first-order kinetic condition with respect to en holds. The soln. was highly buffered for $[OH^-]$ owing to large [en]; no other buffer systems were necessary for its control. $*[Ru(bpy)_3]^{2+}$ was generated by using maximum absorption wavelength at 452 nm of $[Ru(bpy)_3]^{2+}$ with the irradiation of visible light from a Xe lamp (150 W) with a UV filter *(Kenko SL-39)* and a *JASCO* grating monochromator, model *CT-25*, so that any other excitation processes of $[Ru(bpy)_3]^{2+}$ could be avoided. Intensity of the light source was checked when necessary by potassium tris(oxalato)ferrate(III) chemical actinometry [18] [19]. Concentrations of $[Co(gly)(en)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ were 1.00×10^{-2}M and 1.00×10^{-5}–1.00×10^{-2}M, respectively; light absorption by the former could be neglected except the case for very low concentration of the latter, where correction was made on the light absorption by using molar absorption coefficients of the complexes. It was ascertained by UV/VIS spectra and HPLC that neither photodecomposition nor ligand substitution of $[Ru(bpy)_3]^{2+}$ proceeded under the photo-irradiation condition. After the regular intervals of the irradiation time, the sample soln. was taken out for the HPLC analysis of the product in the case of the racemate or for the CD spectral measurements in the case of the optically active isomers. HPLC with a *JASCO* high-performance liquid chromatograph, model *FAMILIC-100*, to which a spectrophotometer, model *UVIDEC-100*, was attached, with a column of *SP-Sephadex C-25* (Na^+ form) and elution with 0.1–0.5M aq. NaCl soln. (programmed concentration) as an eluent afforded us good separation of $[Ru(bpy)_3]^{2+}$, $[Co(gly)(en)_2]^{2+}$ and $[Co(en)_3]^{3+}$ one another.

Fluorescence quantum yield for the *Stern-Volmer* plots of $^*[Ru(bpy)_3]^{2+}$ in the presence of $[Co(gly)(en)_2]^{2+}$ was determined on a deoxygenated soln. at 25° by monitoring the fluorescence intensity at 607 nm under excitation at 452 nm with a hand-made spectrofluorometer, which was composed of *JASCO* grating monochromators, model *CT-25* for the excitation and model *CT-10 C* for the emission. The yield was corrected by using quinine in H_2SO_4 soln. as a standard [20].

REFERENCES

[1] a) F. Basolo, R.G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, 2nd edn., 1967, pp. 124–350; b) R.G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes', Allyn & Bacon, Boston, 1974, pp. 181–251, pp. 377–381.
[2] R.J. Watts, *J. Chem. Educ.* **1983,** *60,* 834.
[3] P.C. Ford, R.E. Hintze, J.D. Petersen, in 'Concepts of Inorganic Photochemistry', Ed. A.W. Adamson and P.D. Fleischauer, Wiley, New York, 1975, pp. 203–267.
[4] J. van Houten, R.J. Watts, *J. Am. Chem. Soc.* **1976,** *98,* 4853.
[5] N. Sutin, C. Creutz, in 'Inorganic and Organometallic Photochemistry', Ed. M.S. Wrighton, Am. Chem. Soc., Washington D.C., 1978, pp. 1–27.
[6] N. Maki, Y. Shimura, R. Tsuchida, *Bull. Chem. Soc. Jpn.* **1957,** *30,* 909.
[7] F. Scandola, V. Balzani, *J. Chem. Educ.* **1983,** *60,* 814.
[8] R.B. Wilson, E.I. Solomon, *J. Am. Chem. Soc.* **1980,** *102,* 4085.
[9] A.W. Adamson, in 'Concepts of Inorganic Photochemistry', Ed. A.W. Adamson and P.D. Fleischauer, Wiley, New York, 1975, pp. 413–431.
[10] D. Sandrini, M.T. Gandolfi, M. Maestri, F. Bolletta, V. Balzani, *Inorg. Chem.* **1984,** *23,* 3017.
[11] W. Böttcher, A. Haim, *J. Am. Chem. Soc.* **1980,** *102,* 1564.
[12] P.A. Lay, A.W.H. Mau, W.H.F. Sasse, I.I. Creaser, L.R. Gahan, A.M. Sargeson, *Inorg. Chem.* **1983,** *22,* 2347.
[13] C.-Y. Mok, A.W. Zanella, C. Creutz, N. Sutin, *Inorg. Chem.* **1984,** *23,* 2891.
[14] J. Meisenheimer, *Ann.* **1924,** *438,* 217.
[15] C.T. Liu, B.E. Douglas, *Inorg. Chem.* **1964,** *3,* 1356.
[16] L.N. Braddock, T.J. Meyer, *J. Am. Chem. Soc.* **1937,** *59,* 3158.
[17] F.H. Burstall, *J. Chem. Soc.* **1936,** 173.
[18] C.G. Hatchard, C.A. Parker, *Proc. R. Soc [London], Ser. A* **1956,** *235,* 518.
[19] E.E. Wagner, A.W. Adamson, *J. Am. Chem. Soc.* **1966,** *88,* 394.
[20] W.H. Melhuish, *J. Phys. Chem.* **1960,** *64,* 762.