Polyhedron Vol. 6, No. 3, pp. 651–654, 1987
Printed in Great Britain

0277–5387/87 $3.00+.00
Pergamon Journals Ltd

COMMUNICATION

LIGAND SUBSTITUTION REACTIONS OF (BIDENTATO-*O*,*O* and -*O*,*N*) BIS(ETHYLENEDIAMINE)COBALT(III) COMPLEXES WITH ETHYLENEDIAMINE CATALYZED BY PHOTOEXCITED TRIS(2,2′-BIPYRIDINE)RUTHENIUM(II) COMPLEX: THE ROLE OF CIRCULARLY POLARIZED LIGHT IN PHOTOIRRADIATION

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

(*Received* 4 *July* 1986; *accepted* 27 *October* 1986)

Abstract—The substitution reactions with ethylenediamine of the bidentato-*O*,*O* ligand of (bidentato-*O*,*O*)bis(ethylenediamine)cobalt(III) complex have been studied in a weakly alkaline aqueous solution in the presence of tris(2,2′-bipyridine)ruthenium(II) complex under photoirradiation. The reaction was catalyzed by the photoexcited ruthenium(II) complex. Enhanced generation of the photoexcited ruthenium(II) complex and acceleration of the reaction of the bidentato-*O*,*N* ligand of (bidentato-*O*,*N*)bis(ethylenediamine)cobalt(III) complex were noticed when the optically active isomer of the ruthenium(II) complex was irradiated by the corresponding circularly polarized light.

It has been reported that the ligand substitution reaction of glycinato ligand in bis(ethylenediamine)glycinatocobalt(III), $[Co(gly)(en)_2]^{2+}$, with ethylenediamine does not proceed at room temperature (25°C) but does proceed at an elevated temperature (60–70°C)[1] or in the presence of triplet state excited tris(2,2′-bipyridine)ruthenium(II), $*[Ru(bpy)_3]^{2+}$, even at room temperature.[2] The $*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction mechanism has been explained in terms of labilization of $[Co(gly)(en)_2]^{2+}$ by a charge-transfer process between $*[Ru(bpy)_3]^{2+}$ and $[Co(gly)(en)_2]^{2+}$.[2]

Further investigation of the role of $*[Ru(bpy)_3]^{2+}$ on the ligand substitution reaction of carbonatobis(ethylenediamine)cobalt(III), $[Co(CO_3)(en)_2]^+$, and bis(ethylenediamine)oxalatocobalt(III), $[Co(ox)(en)_2]^+$, with ethylenediamine suggested that the mechanism is general for the (bidentato-*O*,*O* and -*O*,*N*) bis (ethylenediamine) cobalt(III) complexes. Furthermore, it was found that the catalytic role of $*[Ru(bpy)_3]^{2+}$ could be enhanced for $[Co(gly)(en)_2]^{2+}$ by using the optically active isomer of $[Ru(bpy)_3]^{2+}$, and by exciting with irradiation by the corresponding circularly polarized light. The present article relates to these investigations.

EXPERIMENTAL

$[Co(CO_3)(en)_2]Cl$ and $[Co(ox)(en)_2]Cl\cdot H_2O$ were prepared and resolved into optically active isomers according to procedures given in the literature.[3,4] All other complexes and reagents used have been described elsewhere.[2]

The $*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction was followed by procedures given in a

---

†Author to whom correspondence should be addressed.

previous paper.[2] In addition, excitation of $[Ru(bpy)_3]^{2+}$ at 452 nm by irradiation by left and right circularly polarized light was made by using Polaroid Circular Polarizers, Nos HNCP37L-4 and HNCP37R-4, which were attached in front of the sample holder of the photoirradiation system.[2] Other experimental procedures, including fluorescence quenching of $^*[Ru(bpy)_3]^{2+}$, determination of hydroxide ion concentration etc., have been carried out as described elsewhere.[1,2]

RESULTS AND DISCUSSION

Investigation by liquid chromatography [SP-Sephadex C-25 column (Na^+ form); eluant, 0.05 mol dm^{-3} aqueous NaCl] of the photoirradiation reaction solution {initial conditions: 1.00×10^{-2} mol dm^{-3} $[Co(CO_3)(en)_2]^+$, 1.00×10^{-3} mol dm^{-3} $[Ru(bpy)_3]^{2+}$, 2.00 mol dm^{-3} ethylenediamine, pH 12.0 (buffered), room temperature (25°C)}, revealed that $[Co(CO_3)(en)_2]^+$ changed uniquely to $[Co(en)_3]^{3+}$. The amount of $[Co(CO_3)(en)_2]^+$ was decreased linearly with increasing photoirradiation time. Furthermore, no evidence was noticed of the formation of $[Co(en)_3]^{3+}$ in the absence of $[Ru(bpy)_3]^{2+}$. When $[Co(ox)(en)_2]^+$ was used in place of $[Co(CO_3)(en)_2]^+$, a stoichiometric change of $[Co(ox)(en)_2]^+$ to $[Co(en)_3]^{3+}$ by $^*[Ru(bpy)_3]^{2+}$ was also found. However, the relation between the decreased amount of $[Co(ox)(en)_2]^+$ and the photoirradiation time [cf. Fig. 1 (for CD data), curves 5 and 6] showed a deviation from linearity. This deviation can be ascribed to the photodecomposition process of $[Co(ox)(en)_2]^+$ (cf. Fig. 1, curve 7).† Hence it is deduced that the ligand substitution reaction of $[Co(bidentato\text{-}O,O)(en)_2]^+$ with ethylenediamine is catalyzed by $^*[Ru(bpy)_3]^{2+}$, as in the case of $[Co(gly)(en)_2]^{2+}$.[2]

Stern–Volmer plots were taken at 25°C by monitoring fluorescence intensities at 607 nm of 1.00×10^{-3} mol dm^{-3} $[Ru(bpy)_3]^{2+}$ in relation to concentration (0–2.00×10^{-2} mol dm^{-3}) of $[Co(bidentato\text{-}O,O)(en)_2]^+$. Linear relations with an intercept of unity were obtained for $[Co(CO_3)(en)_2]^+$ and $[Co(ox)(en)_2]^+$ with Stern–Volmer constants of 0.54×10^2 and 0.50×10^2 mol^{-1} dm^3, which can be converted by applying a lifetime of $^*[Ru(bpy)_3]^{2+}$ in water at 25°C of 0.6 μs[6,7] to quenching rate constants (k_q) of 0.90×10^8 and 0.83×10^8 mol^{-1} dm^3 s^{-1}, respectively. These data compare well with the rate constant of $[Co(gly)(en)_2]^{2+}$ (1.25×10^8 mol^{-1} dm^3 s^{-1}),[2] corresponding to a diffusion-controlled, outer-sphere charge-transfer between $^*[Ru(bpy)_3]^{2+}$ and $[Co(gly)(en)_2]^{2+}$. It should be noted that the Stern–Volmer constant decreases slightly in the following order; $[Co(gly)(en)_2]^{2+} > [Co(CO_3)(en)_2]^+ > [Co(ox)(en)_2]^+$.

The yield for the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction of $[Co(bidentato\text{-}O,O)(en)_2]^+$ with ethylenediamine against $^*[Ru(bpy)_3]^{2+}$ generated, Φ^{sub} $\{= (-d[[Co(bidentato\text{-}O,O)(en)_2]^+]/dt)/I_a\Phi^o$, where $I_a\Phi^o$ corresponds to the formation rate of $^*[Ru(bpy)_3]^{2+}\}$,[2] was determined on both racemates as well as optically active isomers, and the data are summarized in Table 1. The yield does not depend on the stereochemistries of both the ruthenium(II) and the cobalt(III) complexes; the values are about the same magnitude with, however, a slight decrease in the following order; $[Co(gly)(en)_2]^{2+}$,[2] $> [Co(CO_3)(en)_2]^+ \fallingdotseq [Co(ox)(en)_2]^+$.

From the evidence given above, it is concluded that the mechanism of the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction of $[Co(bidentato\text{-}O,O)(en)_2]^+$ with ethylenediamine is the same as that of $[Co(gly)(en)_2]^{2+}$.[2]

According to the discussion above, there remains an interesting point left unsolved on the role of circularly polarized light on the generation of $^*[Ru(bpy)_3]^{2+}$. The $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction was followed under irradiation by left or right circularly polarized light at 452 nm of the optically active isomers of both $[Ru(bpy)_3]^{2+}$ and $[Co(bidentato\text{-}O,O)(en)_2]^+$ as well as $[Co(gly)(en)_2]^{2+}$ (cf. Fig. 1). Figure 1 demonstrates that $[Co(gly)(en)_2]^{2+}$ clearly shows the effect of irradiation by circularly polarized light; the rate of the decrease in $[Co(gly)(en)_2]^{2+}$ is enhanced by irradiation by right circularly polarized light on a solution containing $\Delta\text{-}(-)_{589}\text{-}[Ru(bpy)_3]^{2+}$ irrespective of the optical isomerism of $[Co(gly)(en)_2]^{2+}$. This effect can be explained in terms of an enhanced excitation of $\Delta\text{-}(-)_{589}\text{-}[Ru(bpy)_3]^{2+}$ by right circularly polarized light because this isomer shows a negative CD sign at 452 nm. Furthermore, this finding supports our conclusion on the mechanism of the $^*[Ru(bpy)_3]^{2+}$-catalyzed ligand substitution reaction of $[Co(gly)(en)_2]^{2+}$,[2] that the overall rate of the reaction is governed by the photoexcitation step of $[Ru(bpy)_3]^{2+}$. We could not obtain any definite indication of the irradiation effect of circularly polarized light on $[Co(bidentato\text{-}O,O)(en)_2]^+$ within our experimental uncertainties. The reason is not clear at present, but we can safely state that the effect may be less pronounced $\{[Co(CO_3)(en)_2]^+\}$ or may be influenced by the

---

†$[Co(ox)(en)_2]^+$ has been reported not to racemize on photoirradiation.[5]

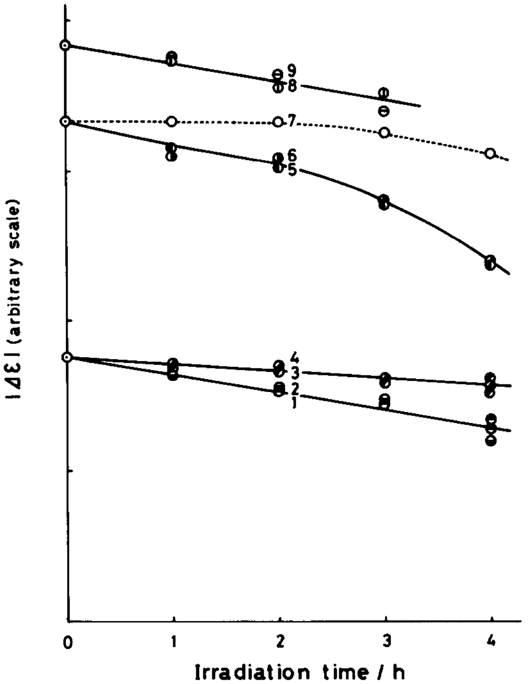

Fig. 1. CD intensity changes of cobalt(III) complexes with irradiation time of circularly polarized light in relation to the coexisting optically active ruthenium(II) complex. $[[\mathrm{Co(bidentato}\text{-}O,O\ \mathrm{or}\ \text{-}O,N)(\mathrm{en})_2]^{+\,\mathrm{or}\,2+}]$, $1.00 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ (initial state); $[[\mathrm{Ru(bpy)_3}]^{2+}]$, $1.00 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$; [en], $2.00\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{OH^-}]$, $1.58 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ (buffered); and $[\mathrm{Cl^-}]$, $1.0\ \mathrm{mol\,dm^{-3}}$. T(°C), 25. Excitation wavelength of circularly polarized light (nm), 452. Wavelength of CD intensity measurement (nm), 509 $\{[\mathrm{Co(gly)(en)_2}]^{2+}\}$, 520 $\{[\mathrm{Co(ox)(en)_2}]^{+}\}$, and 530 $\{[\mathrm{Co(CO_3)(en)_2}]^{+}\}$. Notation is as follows:

	$[\mathrm{Co(gly)(en)_2}]^{2+}$		$[\mathrm{Co(ox)(en)_2}]^{+}$	$[\mathrm{Co(CO_3)(en)_2}]^{+}$
	Δ-$(-)_{589}$-	Λ-$(+)_{589}$-	Λ-$(+)_{589}$-	Λ-$(+)_{589}$-
Right CPL	1	2	5	9
Left CPL	3	4	6	8

CPL = circularly polarized light. Δ-$(-)_{589}$-$[\mathrm{Ru(bpy)_3}]^{2+}$ was used throughout the runs. Curve 7 is a blank run for Λ-$(+)_{589}$-$[\mathrm{Co(ox)(en)_2}]^{+}$ in the absence of Δ-$(-)_{589}$-$[\mathrm{Ru(bpy)_3}]^{2+}$.

Table 1. Yield for ligand substitution reaction against $^*[\mathrm{Ru(bpy)_3}]^{2+}$ generated as determined by the circular dichroism spectral method at 25°C

	$\Phi^{\mathrm{sub}\,a}$					
	$[\mathrm{Co(ox)(en)_2}]^{+}$		$[\mathrm{Co(CO_3)(en)_2}]^{+}$		$[\mathrm{Co(gly)(en)_2}]^{2+}$	
	Δ-$(-)_{589}$-	Λ-$(+)_{589}$-	Δ-$(-)_{589}$-	Λ-$(+)_{589}$-	Δ-$(-)_{589}$-	Λ-$(+)_{589}$-
$[\mathrm{Ru(bpy)_3}]^{2+}$	0.33	0.31	0.34	0.35	0.55[b]	0.55[b]
Δ-$(-)_{589}$-$[\mathrm{Ru(bpy)_3}]^{2+}$	0.33	0.31	0.35	0.34	0.52[b]	0.55[b]

[a] $\Phi^{\mathrm{sub}} = \{-\mathrm{d}[[\mathrm{Co(bidentato}\text{-}O,O\ \mathrm{or}\ \text{-}O,N)(\mathrm{en})_2]^{+\ \mathrm{or}\ 2+}]/\mathrm{d}t\}/I_a\Phi^{o}$ (consult the text).

[b] Reference 2. $[[\mathrm{Co(bidentato}\text{-}O,O\ \mathrm{or}\ \text{-}O,N)(\mathrm{en})_2]^{+\,\mathrm{or}\,2+}]$, $1.00 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ (initial state); $[[\mathrm{Ru(bpy)_3}]^{2+}]$, $1.00 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$; [en], $2.00\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{OH^-}]$, $1.58 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ (buffered); and $[\mathrm{Cl^-}]$, $1.0\ \mathrm{mol\,dm^{-3}}$.

photosensitivity of the cobalt(III) complex $\{[\mathrm{Co(ox)(en)_2}]^{+}\}$.

REFERENCES

1. M. Ishikawa, K. Okamoto, J. Hidaka and H. Einaga, *Polyhedron* 1986, **5**, 1345.
2. M. Ishikawa, K. Okamoto, J. Hidaka and H. Einaga, *Helv. Chim. Acta* 1985, **68**, 2015.
3. H. Fushimi, K. Okamoto, J. Hidaka and H. Einaga, *Inorg. Chim. Acta* 1985, **98**, 47.
4. F. P. Dwyer, I. K. Reid and F. L. Garvan, *J. Am. Chem. Soc.* 1961, **83**, 1285.
5. S. T. Speeds and A. W. Adamson, *Inorg. Chem.* 1962, **1**, 531.
6. J. van Houten and R. J. Watts, *J. Am. Chem. Soc.* 1976, **98**, 4853.

7. M. S. Wrighton (Ed.), *Inorganic and Organometallic Photochemistry*, Chap. 1. American Chemical Society, Washington D.C. (1978).

8. Absolute configurations of the complexes are designated by the IUPAC tentative rule. *Inorg. Chem.* 1970, **9**, 1.