an increase in $\nu_l$ fundamentals and characterize a more rigidly bound hydrogen-bonded complex. The strengths of the $H_2S$--HF and $H_2Se$--HF hydrogen bonds are similar on the basis of almost equal values of $\Delta\nu_s$, but the 30-$cm^{-1}$ decrease in $\nu_l$ modes for the $H_2Se$ complex relative to $H_2S$ characterizes a less rigidly bound complex. The same trend of decreasing complex rigidity for hydrogen bonds of similar strengths has been observed for the HF complexes of the increasingly heavier $CH_3Cl$, $CH_3Br$, and $CH_3I$ bases.[19] The trend of increasing stability of the reverse complexes HF--HAH for A = O, S, and Se on the basis of displacement of the $\nu$(H–F) fundamental follows the strength of the HAH acids as determined by proton affinities[14] of $AH^-$ but is not in accord with calculated dimerization energies[16] for this series of reverse complexes. It is possible that larger basis sets will be required for more accurate calculations involving $H_2S$ and $H_2Se$.

The separation between the $\nu_s$(H–F) stretching mode of the 1:1 complexes (**1**) and the $\nu(H_a$–F) stretching mode of the 1:2 complex (**2**) decreases in the order $H_2O$ (295 $cm^{-1}$)[4] > $H_2S$ (89 $cm^{-1}$ > $H_2Se$ (60 $cm^{-1}$). The difference is most significant between $H_2S$--HF and $H_2Se$--HF because of the equally strong 1:1 complex hydrogen bonds of these complexes. We would expect equal displacements of the $H_a$–F modes due to the fluoride ion affinity of the $H_b$–F submolecule in a chainlike complex. The displacement of $H_a$–F depends on the strength of the base--$H_a$ hydrogen bond that in turn depends on the distance between the base and the $H_a$ atom. This implies a decrease in the polarizing strength of proton $H_a$ in $H_a$–F when confronted by the more diffuse lone pairs of the heavier bases.

## Conclusions

The cocondensation of Ar/$H_2S$ or Ar/$H_2Se$ with Ar/HF samples at 12 K has revealed several different hydrogen-bonded complexes. The 1:1 $H_2S$--HF complex is characterized by a strong $\nu_s$(H–F) stretching mode at 3652 $cm^{-1}$ and two librational modes at 508 and 481 $cm^{-1}$. The 3655-$cm^{-1}$ value of $\nu_s$ for $H_2Se$--HF indicates an equally strong hydrogen bond, which is expected on the basis of gas-phase proton affinities. Low $2\nu_l/\nu_l$ ratios and decreasing librational fundamentals for $H_2S$--HF and $H_2Se$--HF indicate decreasing complex rigidity and anharmonic librational potential functions. A sharp absorption at 3799 $cm^{-1}$, which increased on matrix annealing, characterizes a stable HF--HSH reverse complex. Several other complexes, including a 1:2 $H_2S$--$(HF)_2$ chainlike complex and a 2:1 $H_2S$--H-F--HSH complex, have been identified.

**Acknowledgment.** We gratefully acknowledge support from NSF Grant CHE 82-17749 and assistance from our inorganic colleagues on the synthesis of hydrogen selenide.

**Registry No.** $H_2S$, 7783-06-4; $H_2Se$, 7783-07-5; HF, 7664-39-3.

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Nara Women's University, Nara 630, Japan

# Light-Induced Ligand-Substitution Reactions. Reaction between the Chloropentaamminecobalt(III) Ion and Ethylenediaminetetraacetate by Irradiation with Visible Light of Aqueous Solutions Containing the Tris(2,2'-bipyridine)ruthenium(II) Ion

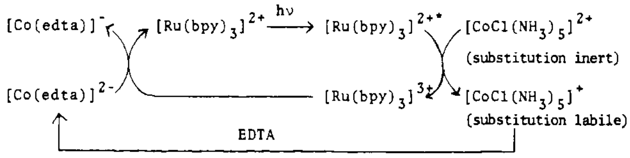
MASARU KIMURA,* MARI YAMASHITA, and SUZUKO NISHIDA

*Received July 5, 1984*

The ligand-substitution reaction between the chloropentaamminecobalt(III) ion, $[CoCl(NH_3)_3]^{2+}$, and ethylenediaminetetraacetate, which denotes all the forms of edta, i.e., $edta^{4-}$, $Hedta^{3-}$, $H_2edta^{2-}$, etc., was induced by irradiation with visible light of aqueous solutions of acetate buffer (pH 4.75) containing the tris(2,2'-bipyridine)ruthenium(II) ion, $[Ru(bpy)_3]^{2+}$, and $[Co(edta)]^-$ was efficiently produced, where $[Ru(bpy)_3]^{2+}$ acts as an inductor and as a photocatalyst. The ligand-substitution reaction constitutes a chain reaction containing a cycle of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$, where the reaction is initiated by the reaction between the photoexcited complex $[Ru(bpy)_3]^{2+*}$ and $[CoCl(NH_3)_5]^{2+}$. The rate of the formation of $[Co(edta)]^-$ is described essentially by a rate law of $d[[Co(edta)]^-]/dt = I_a\Phi k_q[[CoCl(NH_3)_5]^{2+}]/\{k_0 + k_q[[CoCl(NH_3)_5]^{2+}]\}$, where $I_a\Phi$ corresponds to the formation rate of $[Ru(bpy)_3]^{2+*}$, $k_q$ is the quenching rate constant of $[Ru(bpy)_3]^{2+*}$ by $[CoCl(NH_3)_5]^{2+}$, and $k_0$, the quenching constant of $[Ru(bpy)_3]^{2+*}$ due to the light emission and to the thermal energy loss. The reaction mechanisms and the rate law are verified by the results obtained. The bimolecular quenching constants $k_q$ are determined by means of the kinetic experiments for the light-induced ligand-substitution reaction and are compared to the $k_q$ values that are obtained by measurements of luminescence of $[Ru(bpy)_3]^{2+*}$.

Although the abbreviation EDTA is generally for ethylenediaminetetraacetic acid, i.e., $H_4edta$, we use, throughout this paper, EDTA for all the forms of $H_4edta$, $H_3edta^-$, $H_2edta^{2-}$, $Hedta^{3-}$, and $edta^{4-}$. It is known that the oxidative quenching of the photoexcited ruthenium(II) complex $[Ru(bpy)_3]^{2+*}$ (bpy = 2,2'-bipyridine) by $[CoCl(NH_3)_5]^{2+}$ produces $[Ru(bpy)_3]^{3+}$ and $[CoCl(NH_3)_5]^+$, and that the latter species dissociates rapidly to $Co^{2+}_{aq}$, $Cl^-$, and $NH_3$ (or $NH_4^+$),[1-3] in which $Co^{2+}_{aq}$ could form $[Co(edta)]^{2-}$ rapidly in an aqueous solution with acetate buffer (pH 4.75) if EDTA is present in the reaction mixture. The $[Ru(bpy)_3]^{3+}$ ion is so a strong oxidant as to oxidize $[Co(edta)]^{2-}$ to $[Co(edta)]^-$. Therefore, we could design an experiment for the light-induced substitution reaction between $[CoCl(NH_3)_5]^{2+}$ and EDTA by employing $[Ru(bpy)_3]^{2+}$ as a catalyst. This reaction can be briefly described as shown in Scheme I. In this paper we demonstrate that the proposed scheme operates well in an acetate buffer soluiton of pH 4.75, and the operation mechanisms are discussed.

**Scheme I**



## Experimental Section

**Chemicals.** $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ was prepared as described in the literature[4] and recrystallized twice. $[CoCl(NH_3)_5]Cl_2$ was prepared as described in the literature[5] and recrystallized twice. Disodium di-

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(1) Neumann-Spallart, M.; Kalyanasundaram, K. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 704.

(2) Kalyanasundaram, K.; Gräzel, M. *Helv. Chim. Acta* **1980**, *63*, 478.

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(4) Tachibana, T., Nakahara, M., Shibata, M., Eds. "Shin Jikken-Kagaku Koza 8"; Japan Chemical Society: Maruzen, 1975; p 1475. Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 964. Fujita, I.; Kobayashi, H. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 115.

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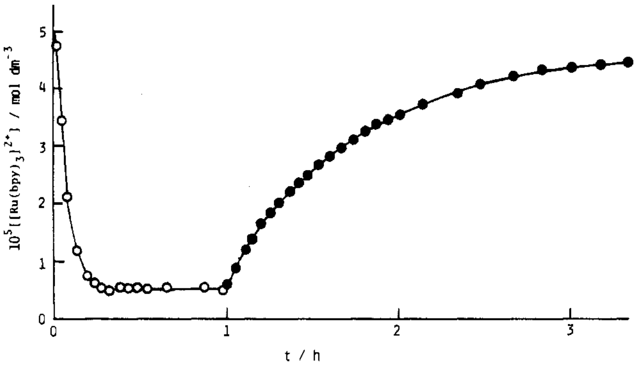

**Figure 1.** Variation of the $[Ru(bpy)_3]^{2+}$ ion concentration in the absence of EDTA. Conditions: 5 × $10^{-5}$ mol dm$^{-3}$ in $[Ru(bpy)_3]Cl_2$, 5 × $10^{-3}$ mol dm$^{-3}$ in $[CoCl(NH_3)_3]Cl_2$, 0.05 mol dm$^{-3}$ for each acetic acid and sodium acetate (pH 4.75), nitrogen saturated, 25 °C. Plots ○ indicate the results with irradiation of visible light by four 100-W tungsten lamps, and plots ● indicate the results obtained when the reaction mixture stood in the dark after irradiation for 1 h. The plots follow the rate law of $-d[[Ru(bpy)_3]^{3+}]/dt = k[[Ru(bpy)_3]^{3+}]$ with $k = 3.2 \times 10^{-4}$ s$^{-1}$ in ●.

hydrogen ethylenediaminetetraacetate ($Na_2H_2edta$) and other chemicals used were of guaranteed-reagent grade. Deionized water was further distilled with and without addition of permanganate in a glass still.

**Procedure.** The oxygen dissolved in solutions was removed by the saturation of nitrogen gas bubbling through the reaction solution. The pH of solution was maintained constant at pH 4.75 with acetate buffer of 0.05 mol dm$^{-3}$ for each acetic acid and sodium acetate. The reaction vessel was a colorless glas bottle (5 dL; diameter 80 mm, thickness 1 mm, with 10-mm neck) and was placed in thermostated water in a cubic bath of colorless glass (2 × 2 × 3 dm$^3$; thickness 6 mm). Unless otherwise stated, the sample of 3 dL was irradiated with light from four 100-W tungsten lamps that were placed 3 dm to the right- and left-hand sides to the center of the reaction vessel. The irradiation of light continued throughout the reaction. Aliquot samples of 5 mL were withdrawn at appropriate times and mixed with cation-exchange resin (1 g) (Dowex 50W-X8, 200–400 mesh, hydrogen form of the Wako Pure Chemical Co., washed with distilled water) in order to remove the $[Ru(bpy)_3]^{2+}$ and $[CoCl(NH_3)_5]^{2+}$ ions from the reacting solution and to stop the reaction. After filtration, the concnetration of the $[Co(edta)]^-$ formed was determined spectrophotometrically by using the maximum molar absorption coefficient 295 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 536 nm. The concentrations of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{3+}$, and $[CoCl(NH_3)_5]^{2+}$ in the reacting solution in the absence of EDTA in the case of Figure 1 were determined by the measurement of absorbance for the reaction mixture (see ref 6).

## Results and Discussion

As seen in Figure 1, when the solution containing the $[Ru(bpy)_3]^{2+}$ and $[CoCl(NH_3)_5]^{2+}$ ions in the absence of EDTA was irradiated with visible light, the $[Ru(bpy)_3]^{2+}$ ion was oxidized to the $[Ru(bpy)_3]^{3+}$ ion by the bimolecular quenching reaction with the photoexcited species $[Ru(bpy)_3]^{2+*}$; this corresponds to the reaction of eq 2 (v.i). When the solution which had once reached the steady-state concentrations with respect to $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ was placed in the dark, the latter was reduced slowly by the medium water and returned to the former.

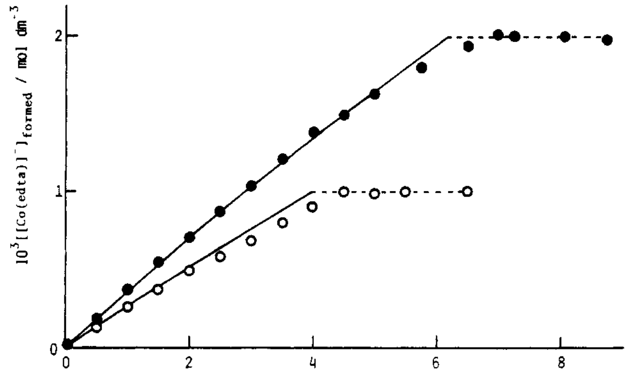

**Figure 2.** Examples of plots of $[[Co(edta)]^-]_{formed}$ vs. *t*. For plots ●, the initial concentrations of EDTA and $[CoCl(NH_3)_5]^{2+}$ are 2.0 × $10^{-3}$ and 1 × $10^{-2}$ mol dm$^{-3}$, respectively, and for plots ○, they are 1.0 × $10^{-3}$ and 5 × $10^{-3}$ mol cm$^{-3}$, respectively. The other conditions are the same as those in Figure 1 with irradiation of light by four lamps. Both plots ● and ○ indicate the results obtained experimentally, and the solid lines indicate the curves calculated by using eq 9′ with $I_a\Phi = 1.5 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$, $k_q = 3 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, and $k_q' = 5 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.

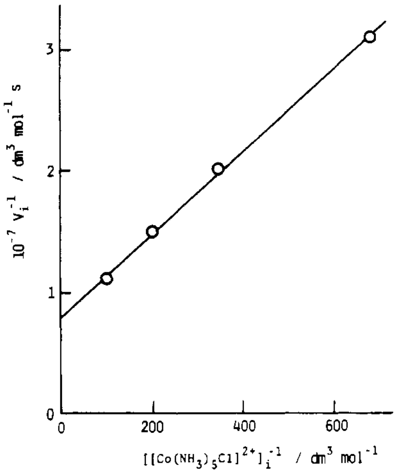

**Figure 3.** An example of plots of $V_i^{-1}$ vs. $[[CoCl(NH_3)_5]^{2+}]_i^{-1}$ (eq 10). Conditions are the same as those for the plots ● in Figure 2, except for the various concentrations of $[CoCl(NH_3)_5]^{2+}$.

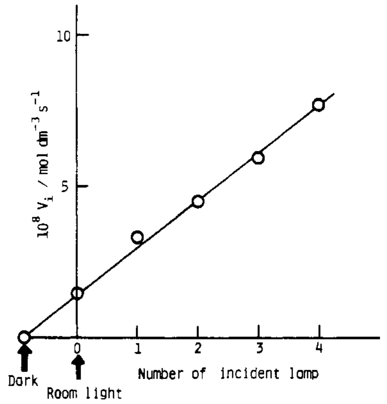

**Figure 4.** Effect of intensity of incident light. Conditions are as in Figure 3, except for 5 × $10^{-3}$ mol dm$^{-3}$ in $[CoCl(NH_3)_5]Cl_2$ and for various intensities of the incident light.

On the other hand, in the presence of EDTA in the reaction mixture, the $[Ru(bpy)_3]^{2+}$ ion concentration did not decrease and did not change at all during the irradiation of light, and $[Co(edta)]^-$ was produced in proportion to the irradiation time (*t*) at least for the initial stages of reaction (see Figure 2). This fact indicates that $[Ru(bpy)_3]^{3+}$ once formed is reduced rapidly to $[Ru(bpy)_3]^{2+}$ by the $[Co(edta)]^{2-}$ ion, which is produced by the reaction between EDTA and $Co^{2+}_{aq}$ or $[CoCl(NH_3)_5]^+$. The latter

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(5) Yamazaki, K., Ed. "Jikken-Kagaku Koza 11"; Japan Chemical Society: Marzen, 1972; p 21. Hynes, W. A.; Yanowsky, K.; Schiller, M. *J. Am. Chem. Soc.* **1938**, *60*, 3253.

(6) The following equations hold for the case:

$$A_{420} = \epsilon_{1a}[[Ru(bpy)_3]^{2+}] + \epsilon_{2a}[[Ru(bpy)_3]^{3+}] + \epsilon_{3a}[[CoCl(NH_3)_5]^{2+}]$$

$$A_{452} = \epsilon_{1b}[[Ru(bpy)_3]^{2+}] + \epsilon_{2b}[[Ru(bpy)_3]^{3+}] + \epsilon_{3b}[[CoCl(NH_3)_5]^{2+}]$$

$$A_{534} = \epsilon_{1c}[[Ru(bpy)_3]^{2+}] + \epsilon_{2c}[[Ru(bpy)_3]^{3+}] + \epsilon_{3c}[[CoCl(NH_3)_5]^{2+}]$$

where $A_{420}$, $A_{452}$, and $A_{534}$ indicate the absorbance of the reaction mixture at 420, 452, and 534 nm, respectively, and they correspond to the absorption maximum for each species of $[Ru(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{2+}$, and $[CoCl(NH_3)_5]^{2+}$, respectively. $\epsilon_{1a}$, $\epsilon_{2a}$, and $\epsilon_{3a}$ are 1.1 × $10^4$, 3.3 × $10^3$, and 9.9 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively; $\epsilon_{1b}$, $\epsilon_{2b}$, and $\epsilon_{3b}$ are 1.4 × $10^4$, 2.8 × $10^2$, and 22.3 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively; $\epsilon_{1c}$, $\epsilon_{2c}$, and $\epsilon_{3c}$ are 7.7 × $10^2$, 95.4, and 51.3 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively.

**Table I.** Values of $I_a\Phi$, $k_q/k_0$, and $k_q$ under Various Conditions[a]

| temp/ °C | ionic strength/ mol dm$^{-3}$ | $10^7 I_a\Phi$/ mol dm$^{-3}$ s$^{-1}$ | $(k_q/k_0)$/ dm$^3$ mol$^{-1}$ | $10^{-8} k_q$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 5 | 0.07 | 1.7 | 117 | |
| 15 | 0.07 | 1.5 | 147 | |
| 25 | 0.07 | 1.4 | 196 | 3.0 |
| 35 | 0.07 | 1.5 | 231 | |
| 25 | 0.03 | | | 2.2[b] |
| 25 | 0.04 | 1.4 | 182 | 2.8 |
| 25 | 0.05 | | | 3.4[b] |
| 25 | 0.1 | 1.5 | 871 | 13 |
| 25 | 0.2 | | | 8.2[b] |
| 25 | 0.22 | 1.7 | 902 | 14 |
| | | av 1.5 ± 0.2 | | |

[a] Conditions are as in Figure 3, except for 0.024 mol dm$^{-3}$ of each acetic acid and sodium acetate for the experiments of ionic strengths 0.04, 0.1, and 0.22 mol dm$^{-3}$ at 25 °C. [b] Values were obtained by the measurements of luminescence of $[Ru(bpy)_3]^{2+*}$, which is quenched by $[CoCl(NH_3)_5]^{2+}$; the Stern–Volmer constants $K_{sv}$ were 144, 225, and 539 dm$^3$ mol$^{-1}$ for ionic strengths 0.03, 0.05, and 0.2 mol dm$^{-3}$, respectively.

species could be formed first by the quenching reaction of $[Ru(bpy)_3]^{2+*}$ with $[CoCl(NH_3)_5]^{2+}$ and dissociates rapidly to $Co^{2+}{}_{aq}$, $Cl^-$, and $NH_3$ or $NH_4^+$ (refer to eq 2). The concentration of $[Co(edta)]^-$ formed up to the expiration time of the uncomplexed EDTA was equivalent to the EDTA concentration at the initial time of reaction. Therefore, it is concluded that no decomposition of EDTA occurs during occurrence of the light-induced ligand-substitution reaction.

**Dependence of Reaction Rate on the $[CoCl(NH_3)_5]^{2+}$ Ion Concentration.** The initial rate of the formation of $[Co(edta)]^-$ ($V_i$ in eq 10) was determined from plots such as in Figure 2, and the reciprocal $V_i$ was plotted against the reciprocal concentrations of $[CoCl(NH_3)_5]^{2+}$ at the initial time of reaction. As seen in Figure 3, the plots $V_i^{-1}$ vs. $[[CoCl(NH_3)_5]^{2+}]_i^{-1}$ showed a straight line with an intercept. The intercept was hardly dependent on temperature as well as on ionic strength, but the slope was dependent on both of them (see Table I).

**Effect of Light Intensity on Formation of $[Co(edta)]^-$.** Results are given in Figure 4. No formation of $[Co(edta)]^-$ was found in the dark, and the rate of formation of $[Co(edta)]^-$ was proportional to the numbers of the lamps used for irradiation.

**Mechanisms of Reaction.** Before further results are presented, the reaction mechanism is proposed to account for the results obtained:

$$[Ru(bpy)_3]^{2+} + h\nu \xrightarrow{I_a} [Ru(bpy)_3]^{2+*} \xrightarrow{k_0} \begin{cases} [Ru(bpy)_3]^{2+} + h\nu' \\ [Ru(bpy)_3]^{2+} + \Delta \end{cases} \qquad (1)$$

$$[CoCl(NH_3)_5]^{2+} + [Ru(bpy)_3]^{2+*} \xrightarrow{k_q} [Ru(bpy)_3]^{3+} + Co^{2+}{}_{aq} + Cl^- + 5(NH_3 \overset{H^+}{\rightleftarrows} NH_4^+) \qquad (2)$$

$$Co^{2+}{}_{aq} + EDTA \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Co(edta)]^{2-} \qquad (3)$$

$$[Co(edta)]^{2-} + [Ru(bpy)_3]^{3+} \xrightarrow{k_2} [Co(edta)]^- + [Ru(bpy)_3]^{2+} \qquad (4)$$

$$EDTA + [Ru(bpy)_3]^{3+} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} EDTA^{+\cdot} + [Ru(bpy)_3]^{2+} \qquad (5)$$

$$Co^{2+}{}_{aq} + EDTA^{+\cdot} \xrightarrow{k_4} [Co(edta)]^- \qquad (6)$$

$$[Co(edta)]^{2-} + EDTA^{+\cdot} \xrightarrow{k_5} [Co(edta)]^- + EDTA \qquad (7)$$

$$[Co(edta)]^- + [Ru(bpy)_3]^{2+*} \xrightarrow{k_q'} [Co(edta)]^{2-} + [Ru(bpy)_3]^{3+} \qquad (8)$$

The assumption of the steady-state concentrations of $[Ru(bpy)_3]^{2+*}$, $[Ru(bpy)_3]^{3+}$, $EDTA^{+\cdot}$, and $[Co(edta)]^{2-}$ leads to the following rate law (see ref 7):

$$\frac{d[[Co(edta)]^-]}{dt} = \frac{I_a\Phi k_q[[CoCl(NH_3)_5]^{2+}]}{k_0 + k_q[[CoCl(NH_3)_5]^{2+}] + k_q'[[Co(edta)]^-]} \qquad (9)$$

where $I_a$ indicates the amount of light absorbed, $\Phi$ indicates the quantum yield for the excited species $[Ru(bpy)_3]^{2+*}$, and thus, the $I_a\Phi$ corresponds to the formation rate of the excited species. Since reaction 8 would be negligible at least for the initial period of reaction, the term $k_q'[[Co(edta)]^-]$ in eq 9 could be neglected. Consequently, the following rate law could hold under such conditions:

$$V_i^{-1} = \frac{1}{I_a\Phi} + \frac{k_0}{I_a\Phi k_q}[[CoCl(NH_3)_5]^{2+}]_i^{-1} \qquad (10)$$

Equation 10 is in agreement with the results obtained, and the intercept and slope in Figure 3 are $1/I_a\Phi$ and $k_0/(I_a\Phi k_q)$, respectively.

**Determination of Bimolecular Quenching Constant $k_q$.** From plots such as in Figure 3 for eq 10, we can evaluate the $k_q$ values by using the $k_0$ value where $k_0 = \tau_0^{-1} = 1.52 \times 10^6$ s$^{-1}$ and $\tau_0 =$ 660 ns.[8] The $k_q$ values were obtained under various conditions and given in Table I together with values of $I_a\Phi$ and $k_q/k_0$. As seen in Table I, $I_a\Phi$ is independent not only of temperature but also of ionic strength ($\mu$). On the other hand, $k_q/k_0$ is dependent on both of them. From plots of ln $(k_q/k_0)$ vs. $T^{-1}$ by using data in Table I, we obtained the activation energy for $(E_q - E_0)$ to be 16.3 kJ mol$^{-1}$. Such a low energy would be due to the counterbalancing effect on the activation energies for $k_q$ and $k_0$. Plots of log $k_q$ vs. $\mu^{1/2}/(1 + \mu^{1/2})$ using data in Table I were linear with the positive slope of ca. 4, which was expected for the reaction between two ions of like sign. For comparison, the $k_q$ values were determined by the measurements of luminescence of $[Ru(bpy)_3]^{2+*}$ in various concentrations of $[CoCl(NH_3)_5]^{2+}$ with determination of the Stern–Volmer constant $K_{sv}$. The results are given in Table I together with values obtained by using eq 10. They are in good agreement with each other under the given conditions. This also supports the fact that the kinetic treatment using eq 10 is practically correct. The values of $k_q$ and $K_{sv}$ have been reported to be $9.3 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ [1,2] and 100 dm$^3$ mol$^{-1}$.[3] However, the experimental conditions are not given in the literature,[1-3] and thus, they are not simply compared to the values of $k_q$ and $K_{sv}$ in Table I. Our results given in Table I may be the

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(7) The steady-state concentrations with respect to $[Ru(bpy)_3]^{2+*}$, $[Ru(bpy)_3]^{3+}$, $EDTA^{+\cdot}$, and $[Co(edta)]^{2-}$ yield the following relationships, respectively:

$$I_a\Phi = R_0 + R_q + R_q' \qquad (a)$$

$$R_q + R_q' + R_{-3} = R_2 + R_3 \qquad (b)$$

$$R_3 = R_{-3} + R_4 + R_5 \qquad (c)$$

$$R_1 + R_q' = R_{-1} + R_2 + R_5 \qquad (d)$$

where the $R_n$ indicates the rate corresponding to $k_n$ path in the reaction mechanism in text. Equations e and f are obtained by (b) + (c) and from (a), respectively:

$$R_q + R_q' = R_2 + R_4 + R_5 \qquad (e)$$

$$[[Ru(bpy)_3]^{2+*}] = I_a\Phi/\{k_0 + k_q[[CoCl(NH_3)_5]^{2+}] + k_q'[[Co(edta)]^-]\} \qquad (f)$$

From (e) and (f), we derive (g), which is the same as eq 9 in text:

$$d[[Co(edta)]^-]/dt = R_2 + R_4 + R_5 - R_q' = R_q = k_q[[CoCl(NH_3)_5]^{2+}][[Ru(bpy)_3]^{2+*}] = I_a\Phi k_q[[CoCl(NH_3)_5]^{2+}]/\{k_0 + k_q[[CoCl(NH_3)_5]^{2+}] + k_q'[[Co(edta)]^-]\} \qquad (g)$$

(8) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 5195.

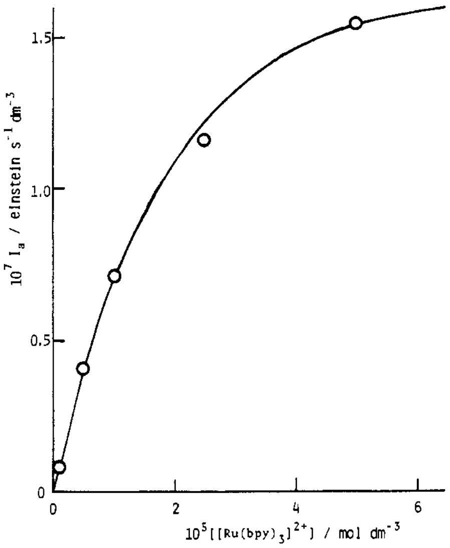

**Figure 5.** Effect of the $[Ru(bpy)_3]^{2+}$ ion concentration. Conditions are as in Figure 3, except for 5 × $10^{-3}$ mol $dm^{-3}$ in $[CoCl(NH_3)_5]Cl_2$ and for various concentrations of the $[Ru(bpy)_3]^{2+}$ ion. Plots ○ indicate the experimental results obtained by using eq 10 where $\Phi$ is assumed to be unity, and the solid line indicates the values calculated by using eq 11 (see text).

most promising, at least this time.

**Effect of the $[Ru(bpy)_3]^{2+}$ Ion Concentration.** The rate of $[Co(edta)]^-$ formation was proportional to the $[Ru(bpy)_3]^{2+}$ ion concentration in the range 0 to ca. 1 × $10^{-5}$ mol $dm^{-3}$ and then deviated from the straight line. This behavior is essentially the same as in Figure 5, because the rate of $[Co(edta)]^-$ formation is proportional to $I_a$ (see eq 9). Such behavior is due to the change of amount of light absorbed according to the change of concentration of $[Ru(bpy)_3]^{2+}$, and is accounted for by the equation

$$I_a = I_0(1 - e^{-\alpha[[Ru(bpy)_3]^{2+}]}) \qquad (11)$$

where $I_0$ indicates amount of light irradiated and $\alpha$ is an empirical constant comprising length of the light path and the molar absorption coefficient of $[Ru(bpy)_3]^{2+}$. It is to be noted that eq 11 is generally applied when the incident light is monochromatic. If $I_0$ and $\alpha$ are assumed to be 1.65 × $10^{-7}$ einstein $s^{-1}$ $dm^{-3}$ and 5.3 × $10^4$ $dm^3$ $mol^{-1}$, respectively, $I_a$ can be calculated by using eq 11. As seen in Figure 5, the calculated values of $I_a$ are in good agreement with the empirical values, which are obtained from measurements of the light-induced reaction rate with a rate law of eq 10, where $\Phi$ is assumed to be 1 mol $einstein^{-1}$.

**Confirmation of Rate Law.** If the concentration of $[CoCl(NH_3)_5]^{2+}$ is in such an excess as to be considered constant during the reaction, eq 9 is integrated as follows:

$$\frac{b}{a}[[Co(edta)]^-] + \frac{k_q'}{2a}[[Co(edta)]^-]^2 = t \qquad (9')$$

where $a = k_q I_a \Phi[[CoCl(NH_3)_5]^{2+}]$ and $b = k_0 + k_q[[CoCl(NH_3)_5]^{2+}]$. In order to examine the validity of the rate law of eq 9, the relationship between concentrations of $[Co(edta)]^-$ formed and $t$ was obtained by using eq 9′. The calculated values are in good agreement with the empirical ones (see Figure 2). It is here noted that $t$ is the reaction time as well as the irradiation time of light.

**Notes on Existence of Reactions 4–8.** When the solution containing $[Ru(bpy)_3]^{2+}$ and $[Co(edta)]^-$ was irradiated with light of four 100-W tungsten lamps for several hours, no appreciable decrease of $[Ru(bpy)_3]^{2+}$ as well as of $[Co(edta)]^-$ was observed. This fact indicates obviously that reaction 4 ($k_2$ path) is occurring rapidly following the occurrence of reaction 8 ($k_q'$ path). We determined separately the rate constant $k_2$ to be 9 × $10^3$ $dm^3$ $mol^{-1}$ $s^{-1}$ in a 0.05 mol $dm^{-1}$ acetate buffer solution of pH 4.75 at 25 °C. The forward reaction of eq 5 ($k_3$ path) has been used by many researchers[9-13] as a sacrificial reaction for model solar-energy conversion systems in which EDTA is used as an electron donor to $[Ru(bpy)_3]^{3+}$, and the rate constant $k_3$ has been reported to be 2 × $10^6$ and 8 × $10^3$ $dm^3$ $mol^{-1}$ $s^{-1}$ at pH 7 and 4, respectively.[9] We also examined separately the reaction rate by using a stopped-flow spectrometer and found that the rate did not simply obey the rate law of $-d[[Ru(bpy)_3]^{3+}]/dt = k_3[EDTA][[Ru(bpy)_3]^{3+}]$ for a whole reaction[14] and that $k_3$ was roughly estimated to be 1 × $10^3$–7 × $10^4$ $dm^3$ $mol^{-1}$ $s^{-1}$ in a 0.05 mol $dm^{-3}$ acetate buffer solution of pH 4.75 at 25 °C. Despite the fact that $k_3$ was as large as $k_2$, no decomposition of EDTA during occurrence of the light-induced reaction was found because the concentration of $[Co(edta)]^-$ formed up to the expiration time of the uncomplexed EDTA was equivalent to that of EDTA added initially (refer to Figure 2). Consequently, we could not help assuming reactions 6 and 7, which might occur before the self-decomposition of $EDTA^{+\cdot}$ as well as before the further oxidation of $EDTA^{+\cdot}$ by $[Ru(bpy)_3]^{3+}$.[14] The contribution of reactions 5–7 should become greater at higher concentrations of EDTA. Thus, we examined the EDTA effect on the rate of the $[Co(edta)]^-$ formation. Under conditions such as in Figure 2 but in 5 × $10^{-3}$ mol $dm^{-3}$ $[CoCl(NH_3)_5]^{2+}$, the formation rate of $[Co(edta)]^-$, i.e. $V_i$, was 8.6 × $10^{-8}$, 7.5 × $10^{-8}$, 7.2 × $10^{-8}$, and 6.1 × $10^{-8}$ $dm^{-3}$ mol $s^{-1}$ in 1, 2, 5, and 10 mmol $dm^{-3}$ of EDTA added, respectively. Because reaction 5 could occur to form $EDTA^{+\cdot}$ to a large extent with increasing EDTA concentration, such a slight decrease of the rate with increasing EDTA concentration may be due to the self-decomposition of $EDTA^{\cdot +}$ and/or to the further oxidation of $EDTA^{+\cdot}$ by the $[Ru(bpy)_3]^{3+}$ ion (refer to ref 14).

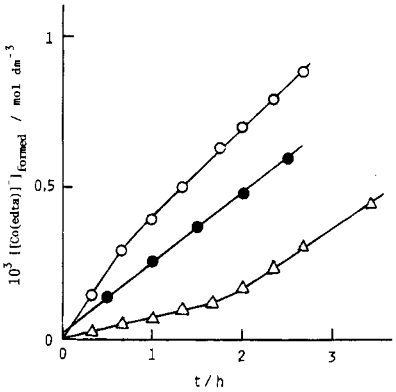

**Figure 6.** Effect of acidity. Conditions are as in Figure 3, except for 5 × $10^{-3}$ mol $dm^{-3}$ in $[CoCl(NH_3)_5]Cl_2$ and for various acidities. Plots ○ indicate results in 0.025 mol $dm^{-3}$ perchloric acid of pH 2, plots ●, those in 0.025 mol $dm^{-3}$ of each acetic acid and sodium acetate (pH 4.75), and plots △, those in 0.025 mol $dm^{-3}$ sodium acetate of pH 6–8, in which the pH value increased with progress of the time $t$.

**Effect of Acidity.** As stated before, the rate constant $k_3$ is greatly dependent on the acidity of solution. Moreover, not only the stability of $EDTA^{+\cdot}$ but also that of $[CoCl(NH_3)_5]^+$, $[Co(edta)]^{2-}$, and $[Co(edta)]^-$ will be dependent on the acidity of the reaction mixture. Thus, the pH effect on this reaction may be extremely complex. We examined the formation rate of $[Co(edta)]^-$ in three different acidities: pH 2 in 0.025 mol $dm^{-3}$ perchloric acid, pH 4.75 in 0.025 mol $dm^{-3}$ acetate buffer, and pH 6–8 in 0.025 mol $dm^{-3}$ sodium acetate. The results are given in Figure 6. As seen in Figure 6, something like an induction

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(14) The kinetic curves for the reaction between EDTA and $[Ru(bpy)_3]^{3+}$ gave two steps of reaction; the first with $k_3$ = 1 × $10^3$–7 × $10^4$ $dm^3$ $mol^{-1}$ $s^{-1}$ may be the one-electron-transfer step to yield $EDTA^{+\cdot}$, and the second with $k$ = 11–200 $dm^3$ $mol^{-1}$ $s^{-1}$ is much slower than the first step and would be the step of the further oxidation of $EDTA^{+\cdot}$ by $[Ru(bpy)_3]^{3+}$. The second step would be much slower than the rate of reactions 6 and 7 as well.

period was found in a solution of pH 6–8, and then, the rate became almost the same as that at pH 4.75. It might be a surprising matter that the rate in a strongly acidic solution of pH 2 was a little faster than that in a solution of the higher pH. It appeared that the formation rate of the $[Co(edta)]^-$ ion by the mechanism of eq 1–8 was not greatly dependent on the acidity at least in the range pH 2–5.

**Concluding Remarks.** We demonstrated that the ligand-substitution reaction between $[CoCl(NH_3)_5]^{2+}$ and EDTA could be induced with irradiation by visible light of an aqueous solution containing a small amount of the $[Ru(bpy)_3]^{2+}$ ion as a photocatalyst. All the results obtained under various conditions were well accounted for by the proposed reaction mechanism. To our knowledge at least this time, this reaction is a new type of photosensitized ligand-substitution reaction for ligand-substitution-inert complexes such as those of cobalt(III). Analogous reaction systems may be successful in other reactions of $[CoX(NH_3)_5]^{2+}$ where X is a ligand other than $Cl^-$ and where a substituting ligand other than EDTA is used.

**Registry No.** $[CoCl(NH_3)_5]^{2+}$, 14970-14-0; edta, 60-00-4; $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Co(edta)]^-$, 15136-66-0.

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# Effects of Applied Pressure on the Emission Lifetimes and Spectroscopic Features of Some Chromium(III) Ammonia and Amine Complex Ions in Aqueous Media

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*Received May 29, 1984*

The emission lifetimes for $[Cr(NH_3)_6]^{3+}$, $[Cr(ND_3)_6]^{3+}$, $[Cr(NH_3)_5(CN)]^{2+}$, $[Cr(NH_3)_5(NCS)]^{2+}$, $[Cr(en)_3]^{3+}$, *trans*-$[Cr(en)_2(NCS)_2]^+$, *trans*-$[Cr(en)_2F_2]^+$, *trans*-$[Cr(cyclam)(CN)_2]^+$, and $[Ru(bpy)_3]^{2+}$, where en, cyclam, and bpy designate ethylenediamine, 1,4,8,11-tetraazacyclotetradecane, and 2,2′-bipyridine ligands, respectively, have been studied in aqueous media under applied pressures of up to 207 MPa. The apparent volumes of activation for the chromium complexes range from +0.1 mL $mol^{-1}$ for *trans*-$[Cr(cyclam)(CN)_2]^+$ to +6.9 mL $mol^{-1}$ for $[Cr(NH_3)_5(NCS)]^{2+}$, and that for $[Ru(bpy)_3]^{2+}$ is −0.65 mL $mol^{-1}$. For $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$, the apparent volumes of activation are found to be independent of temperature (15.1–34.3 °C), and their apparent activation energies (43.5 and 46.0 kJ $mol^{-1}$, respectively) are independent of pressure. For certain of these complex ions, the effects of applied pressure on their ligand field absorption bands in the visible region and also on the doublet-state emission spectrum of $[Cr(NH_3)_6]^{3+}$ have been investigated. In general, the peak maxima of the spin-allowed quartet bands shift to higher wavenumbers on pressurization, and those for the spin-forbidden doublet bands move to lower wavenumbers although the rates of change are much less pronounced for the latter. The implications of the results for the photochemistries of these systems are discussed.

## Introduction

The photochemistry and photophysics of octahedral type chromium(III) complex ions, containing ligands such as ammonia, amines, halogens, and pseudohalogens, have been under active investigation from both experimental and theoretical viewpoints for many years, and a number of reviews and commentaries have recently appeared that cover various facets of their electronic excited-state properties.[1-12] Studies of such complex ions are facilitated by the fact that while they are relatively inert to thermal substitutional processes, they do exhibit on irradiation with near-UV–visible light of their ligand field bands substantial levels of photosubstitution. This is frequently accompanied in room-temperature solutions by emission, generally from the spin-forbidden doublet state(s).

A facet of major and continuing attention has been the identification of the relative extent to which the lowest doublet and quartet levels participate in the photochemistry. For the systems of interest to this report, the results obtained from studies of partial quenching of photochemical reactions and of time-resolved measurements for formation of products indicate in general two stages or levels of reactivity.[13-22] The prompt and usually unquenchable component is attributable to reactions from short-lived quartet states. The longer term stage, the one subject to quenching, occurs with the same lifetime as that for emission from the doublet state(s), and it is this stage that is associated with the major percentage of photoreaction. For example, our results from time-resolved conductivity and emission studies indicate that for $[Cr(NH_3)_6]^{3+}$, $[Cr(NH_3)_5(CN)]^{2+}$, $[Cr(NH_3)_5(NCS)]^{2+}$, and $[Cr(en)_3]^{3+}$ the percentage ranges between 67% and 80% and for *trans*-$[Cr(en)_2F_2]^+$ essentially 100%.[21,22] While it is clear in a

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