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# Reduction of Macrocyclic Cobalt(III) Complex Photosensitized by Tris(2,2′-bipyridine)ruthenium(II)

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**Synopsis.** The photosensitized reduction of macrocyclic cobalt(III) complex, $[Co(N_4)(OH_2)_2]^{3+}$ ($N_4$=$Me_6$[14]-4,11-diene$N_4$), occurs rapidly in an anaerobic $[Ru(bpy)_3]^{2+}$/$[Co(N_4)(OH_2)_2]^{3+}$/triethanolamine solution. The mechanistic implications of the photosensitized reaction are discussed.

Several studies have been carried out on the electron-transfer quenching of the excited state of $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine), $*[Ru(bpy)_3]^{2+}$, by several quenchers.[1] However, very little attention[2] seems to have been paid to the "net" reduction of the metal complex which gives the product having a potentially high redox power and reversible redox property. It may be important to find efficient charge-separation systems as a prototype model for solar energy conversion.

In this paper the $[Ru(bpy)_3]^{2+}$ photosensitized reduction of macrocyclic cobalt(III) complex is described.

## Experimental

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$[3] and $[Co(N_4)(OH_2)_2](ClO_4)_3$[4] ($N_4$= 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene which is usually abbreviated as $Me_6$[14]4,11-diene$N_4$) were synthesized in a manner similar to that described elsewhere. Reactant solutions of the cobalt(III) complex were prepared under nitrogen atmosphere shortly before use. Solution of the reduced species of the cobalt(III) complex, $[Co(N_4)(OH_2)_2]^{2+}$, was prepared by the reduction of the cobalt(III) complex by excess of ascorbate in an anaerobic solution at pH 6. The hydrogen ion concentration in the reactant solutions was adjusted using dilute perchloric acid and/or dilute sodium hydroxide solution without buffer reagents because the absorption spectra of the cobalt(III) and cobalt(II) complexes were found to be affected by both the pH and the concentration of the dissolved salts such as acetate and phosphate. Acid dissociation constants of $[Co(N_4)(OH_2)_2]^{3+}$ were determined by pH titration using a Hitachi-Horiba Model F-5 pH meter. Steady state irradiation was carried out using 150-W slide projector with UV cut-off filter (Kenko Skylight L-40, UV). The solution in the photometer cell (10 mm × 10 mm) in a cell holder (25±0.2 °C) was deoxygenated by introducing pure nitrogen prior to the photolysis. Development of the photoproduct was monitored by taking absorption spectra on Hitachi Model 320 spectrophotometer. Comparison measurements were carried out on the same day.

## Results and Discussion

The acid dissociation constants of $[Co(N_4)(OH_2)_2]^{3+}$ defined by $K_1=[Co(N_4)(OH_2)(OH)^{2+}][H^+]/[Co(N_4)(OH_2)_2{}^{3+}]$ and $K_2=[Co(N_4)(OH)_2{}^{+}][H^+]/[Co(N_4)(OH_2)(OH)^{2+}]$ were determined to be $10^{-3.95}$ and $10^{-8.85}$ respectively ($\mu$=0.3, 25 °C). The molar absorptivity ($\varepsilon$) of $[Co(N_4)(OH_2)_2]^{2+}$ was determined from the slope of the straight line of the absorbance *vs.* $[Co^{II}]$ plot: $\lambda_{max}$ 442 nm ($\varepsilon$=78 $M^{-1}$ $cm^{-1}$, 1 M=1 mol $dm^{-3}$) at pH 6.3.

The photosensitized reduction of the cobalt(III) complex was carried out at pH 6.3 and $\mu$=0.25 ($NaClO_4$), At this pH, predominant cobalt(III) species and the donor species are $[Co(N_4)(OH_2)(OH)]^{2+}$ (*ca.* above 99%) and the monoprotonated species of triethanolamine (above *ca.* 98%, p$K_a$ 7.90[5]) respectively. A typical example of the spectral change (Fig. 1) shows an increase in the absorption band intensity due to the cobalt(II) complex ($\lambda_{max}$ 442 nm) with the irradiation time. The concentration of the cobalt(II) in the irradiated solution was determined using an equation: $[Co^{II}]=(A_0-A_t)/(\varepsilon_3-\varepsilon_2)$ where $A_0$ is the absorbance at time 0, $A_t$, that at time $t$, and $\varepsilon_3$ (46 $M^{-1}$ $cm^{-1}$) and $\varepsilon_2$ (16 $M^{-1}$ $cm^{-1}$) are the molar absoptivities of the cobalt(III) and cobalt(II) complexes respectively at 530 nm. The reduction rates of the cobalt(III) were determined from the slopes of $[Co^{II}]$ *vs.* irradiation time plots in the initial stages. A plot of the reduction rate *vs.* [TEOA] (TEOA=triethanolamine) showed that the rate almost levelled at above $2\times10^{-2}$ M TEOA. It was also found that the rate increases as $[Co^{III}]$ increases ($[Co^{III}]\lesssim7.0\times10^{-3}$ M).

The main feature of the photosensensitized reduction of the cobalt(III) complex are rationalized by Eqs. 1—5:

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\nu} *[Ru(bpy)_3]^{2+}, \tag{1}$$

$$*[Ru(bpy)_3]^{2+} \xrightarrow{k_2} [Ru(bpy)_3]^{2+} + h\nu' + \Delta, \tag{2}$$

$$*[Ru(bpy)_3]^{2+} + [Co(N_4)(OH_2)(OH)]^{2+} \xrightarrow{k_3} [Ru(bpy)_3]^{3+} + Co^{II}, \tag{3}$$

$$[Ru(bpy)_3]^{3+} + Co^{II} \xrightarrow{k_4} [Ru(bpy)_3]^{2+} + [Co(N_4)(OH_2)(OH)]^{2+}, \tag{4}$$

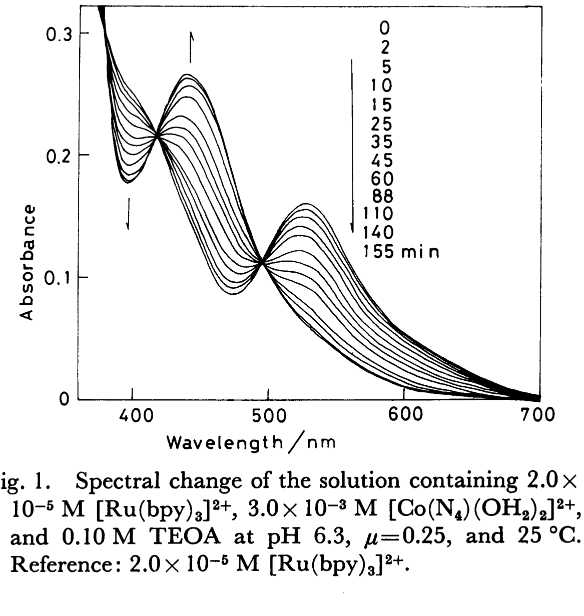

Fig. 1. Spectral change of the solution containing $2.0\times10^{-5}$ M $[Ru(bpy)_3]^{2+}$, $3.0\times10^{-3}$ M $[Co(N_4)(OH_2)_2]^{2+}$, and 0.10 M TEOA at pH 6.3, $\mu$=0.25, and 25 °C. Reference: $2.0\times10^{-5}$ M $[Ru(bpy)_3]^{2+}$.

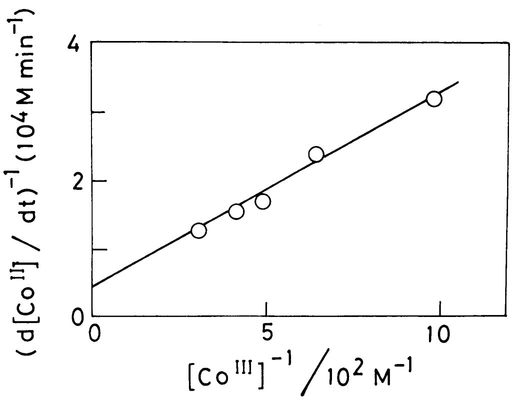

Fig. 2. A plot of $(d[Co^{II}(N_4)]/dt)^{-1}$ *vs.* $([Co(N_4)(OH_2)(OH)]^{2+})^{-1}$. $2.0\times10^{-5}$ M $[Ru(bpy)_3]^{2+}$, 0.10 M TEOA

$$[Ru(bpy)_3]^{3+} + TEOA \xrightarrow{k_5} [Ru(bpy)_3]^{2+} + TEOA_{ox}, \qquad (5)$$

where $TEOA_{ox}$ is the oxidized species of TEOA.

The rate equation resulting from this mechanism, assuming a steady-state concentrations for $*[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$, is given by

$$\frac{d[Co^{II}]}{dt} = \left(\frac{\phi I_{abs}k_3[Co^{III}]}{k_2+k_3[Co^{III}]}\right)\left(\frac{k_5[TEOA]}{k_4[Co^{II}]+k_5[TEOA]}\right), \qquad (6)$$

where $\phi$ is the quantum yield for generation of cobalt(II); $I_{abs}$, the light intensity absorbed by $[Ru(bpy)_3]^{2+}$ in the system; $k_2$, $k_3$, $k_4$, and $k_5$ are the rate constants for the corresponding reactions. The rate constant $k_3$ is given by $k_3=k_qF$ where $k_q$ is the rate constant for the quenching of $*[Ru(bpy)_3]^{2+}$ by $[Co(N_4)(OH_2)(OH)]^{2+}$ and $F$, a portion of the reduction of the cobalt(III) in the quenching process. It may be resonable to assume that $F=1$[6] and $k_4\,[Co^{II}] \ll k_5[TEOA]$[8] for a sufficient excess of TEOA and at the initial stage of the reaction. Thus, we obtain

$$\frac{d[Co^{II}]}{dt} = \frac{\phi I_{abs}k_3[Co^{III}]}{k_2+k_3[Co^{III}]}, \qquad (7)$$

which after rearrangement will give

$$\left\{\frac{d[Co^{II}]}{dt}\right\}^{-1} = \frac{1}{\phi I_{abs}}\left(1+\frac{k_2}{k_3[Co^{III}]}\right). \qquad (8)$$

A plot of $(d[Co^{II}]/dt)^{-1}$ *vs.* $[Co^{III}]^{-1}$ gives a straight line (Fig. 2). The value of $k_2/k_3$ $(=6.1\times10^{-3}$ M) can be calculated from the slope/intercept value of the plot. Using $k_2=1.7\times10^6$ s$^{-1}$,[1a] we obtain $k_3=2.7\times10^8$ M$^{-1}$ s$^{-1}$.

When the irradiated solution ($2.0\times10^{-5}$ M $[Ru(bpy)_3^{2+}]$, $3.0\times10^{-3}$ M cobalt(III), 0.10 M TEOA, 50 min) was flushed with oxygen, the resulting spectrum became similar to that of the initial solution, suggesting that the cobalt(II) species generated by the irradiation were reoxidized to the initial species. Such a complex as $[Co(N_4)(OH_2)_2]^{3+}$ having a reversible redox property and relatively high reducing power may be important for making efficient charge separation system for solar energy conversion.

## References

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6) It has been demonstrated that there is ample evidence for electron-transfer quenching of $*[Ru(bpy)_3]^{2+}$ by several cobalt(III) complexes.[7]

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8) Under the conditions employed ($2.0\times10^{-5}$ M $[Ru(bpy)_3]^{2+}$, $3.0\times10^{-3}$ M cobalt(III), and 0.10 M TEOA), the "back-reaction" may be ignored because the curve for the plot of the rate *vs.* [TEOA] levels off above *ca.* 0.05 M TEOA.