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MANGANESE(III) PORPHYRIN

A.C. Maliyackel, J.W. Otvos,
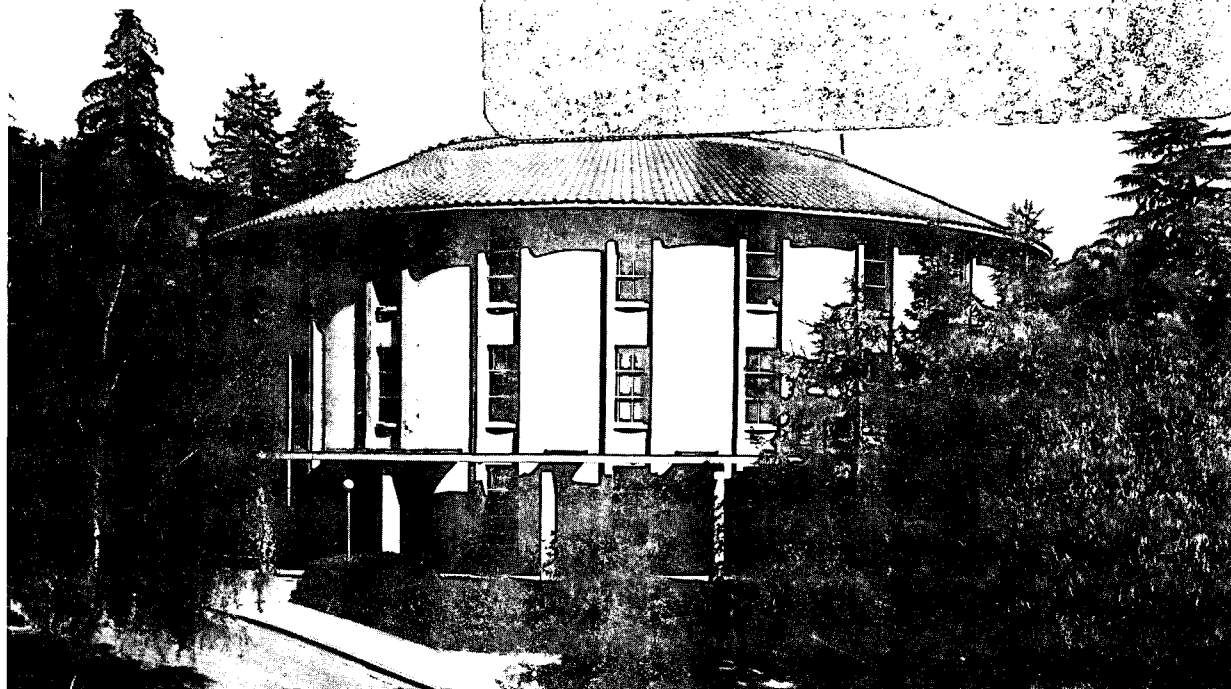L.O. Spreer, and M. Calvin

January 1986

DISCLAIMER

PHOTOINDUCED OXIDATION OF A WATER-SOLUBLE
MANGANESE(III) PORPHYRIN

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ABSTRACT

The photoinduced oxidation of tetra(N-methyl-4-pyridyl)porphyrin manganese(III) has been achieved in homogeneous solution. The manganese porphyrin was used as an electron donor in a three component system with tris(2,2'-bipyridine)ruthenium(II) as the photosensitizer and chloropentaamminecobalt(III) as the electron acceptor. The photooxidized manganese porphyrin is highly reactive, reverting to the starting manganese-(III)porphyrin. The oxidation of manganese(III)porphyrin and the subsequent reduction of the oxidized porphyrin can be cycled repeatedly.

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INTRODUCTION

Much attention has recently been given to the study of photo-chemical generation of hydrogen and oxygen from water as a means of collecting and storing solar energy (1-3). A practical device for such solar energy conversion should be capable of generating hydrogen and oxygen simultaneously. While considerable progress has been made in achieving the photoinduced hydrogen evolution from water (4), only few advances have been made in the photogeneration of oxygen (5-7). The basic reason for the lack of progress in oxygen evolution is that the oxidation of water to oxygen involves four electrons. Nevertheless, photochemical generation of oxygen from water has been reported with the use of heterogeneous catalysts (5-7). In these experiments, tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, was used as a photosensitizer and chloropentaamminecobalt(III), $Co(NH_3)_5Cl^{2+}$, as an electron acceptor. Our work is directed at the development of homogeneous catalysts for the evolution of oxygen.

In photosynthesis, manganese complexes are involved in the oxygen evolution process; the exact nature of these complexes is not yet known (8). Manganese complexes exhibit a rich variety of oxidation states making them promising oxidation catalysts (9), and, in addition, it has recently been reported that manganese porphyrin complexes catalyze the oxidation of olefinic hydrocarbons (10). Therefore, it is of interest to see whether the porphyrin complexes can catalyze the oxidation of water. Since manganese porphyrin complexes with manganese in higher

oxidation states can form dimeric species by bridging two oxygen atoms obtained from water molecules, these complexes might be able to liberate oxygen from water (11). A first and necessary step in the chemical solar energy storing system is the driving of a thermodynamically unfavored reaction by absorption of photons. In the present paper we report the photochemical oxidation of a water-soluble manganese(III)porphyrin, tetra(N-methyl-4-pyridyl)porphyrin manganese(III), $Mn(III)P^+$.

As manganese(III) porphyrin complexes are short-lived in their excited states, use of these complexes as photosensitizers to achieve their oxidation is limited (12,13). The approach taken in the present investigation is to use the manganese porphyrin as an electron donor in a three component system consisting of a photosensitizer, an electron acceptor, and an electron donor. A schematic arrangement of this system is shown in Fig. 1. In this study, $Ru(bpy)_3^{2+}$ is used as photosensitizer and $Co(NH_3)_5Cl^{2+}$ as electron acceptor. By using $Co(NH_3)_5Cl^{2+}$ as an electron acceptor, the back reaction between the oxidized sensitizer and the reduced electron acceptor is prevented as the reduced form of the cobalt complex decomposes rapidly (14).

MATERIALS AND METHODS

Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate was obtained from Strem Chemicals, Inc. and used without further purification. Chloropentaamminecobalt(III) chloride and tetra(N-methyl-4-pyridyl) porphyrin manganese(III) chloride were prepared and purified according to literature methods (15,16). Purity of these compounds was checked from their elemental analyses and their visible and IR spectra.

The water used was purified using a Millipore-Milli Q system. Unless otherwise stated the pH of the solutions was adjusted with phosphate (0.01 M) or acetate (0.01 M) buffers.

Cobalt^{2+} (aq) was determined colorimetrically by converting it to a thiocyanate complex (17). In a typical experiment, 4 ml of the photolyzed solution was equilibrated for about 2 min with equal volumes of freshly prepared 2.5 M ammonium thiocyanate (extracted twice with methyl isobutyl ketone) and methyl isobutyl ketone. Absorption of the organic layer was then measured at 620 nm and the amount of Co^{2+} (aq) was determined from a calibration plot obtained using known concentrations of CoCl$_2$.

Illumination . The illumination of samples was performed in a 1x1 cm glass cuvette equipped with a glass stopcock, a teflon stirring bar, and a septum. Simultaneous illumination and spectrophotometric measurements were performed using a specially designed fiber optics illumination system (18). In this system, the actinic light from a 450 W Xenon lamp was passed through water, copper sulfate solution, and two glass filters (Oriel 5147 and 5430) to give 440 nm light. The emerging light was directed through an optical fiber to impinge directly on the sample. The solutions were constantly stirred during the illumination, and, unless otherwise mentioned, maintained at 25±0.5°C by circulating water through the cuvette holder. The samples were degassed by bubbling deoxygenated argon gas through the solution. The absorption spectra were measured on a Hewlett-Packard 8450A UV/visible spectrophotometer. For the quantum yield measurements, a 1000 W Xenon arc lamp was used as the actinic source; the 440 nm light was obtained as described before. The incident photon flux was (1.2±0.2) x 10^{-8} einstein sec^{-1} cm^{-2} as

determined by ferrioxalate actinometry (19). Luminescence quenching studies were done with a Perkin-Elmer (MPF-2A) fluorescence spectrophotometer equipped with 150 W Xenon arc lamp and a red-sensitive Type R-136 photomultiplier tube.

LUMINESCENCE QUENCHING OF EXCITED $Ru(bpy)_3^{2+}$

In order to examine the susceptibility of excited $Ru(bpy)_3^{2+}$ for deactivation we have studied the quenching of its luminescence by acceptors and donors. Excitation (440 nm) of an aqueous solution containing 0.1 mM $Ru(bpy)_3^{2+}$ at pH 7 gave luminescence with a wavelength maximum at 610 nm. The emission has been attributed to decay of the ligand-to-metal charge transfer excited state of $Ru(bpy)_3^{2+}$ (14). The luminescence intensity, measured at 610 nm, is reduced by the addition of $Mn(III)P^+$ or $Co(NH_3)_5Cl^{2+}$ to the solution. In all these cases, the excitation was carried out at 440 nm where $Mn(III)P^+$ absorption is at a minimum. The measured luminescence intensities were corrected for the absorption by the quenchers (using eq 1) (20) even though the correction was negligible in the case of $Co(NH_3)_5Cl^{2+}$.

$$(Io/I)_{corr} = (Io/I)_{app} \left[\frac{1 - 10^{-(OD_{Ru} + OD_Q)}}{1 - 10^{-OD_{Ru}}} \right] \frac{OD_{Ru}}{OD_{Ru} + OD_Q} \qquad (1)$$

where $(I_0/I)_{app}$ is the measured ratio of emission intensity from an unquenched sample to that of a quenched one. OD_{Ru} and OD_Q are the optical density/cm of $Ru(bpy)_3^{2+}$ and quenchers, respectively, at 440 nm. The luminescence intensity measurements gave excellent Stern-Volmer plots (Fig. 2). From these plots, second-order rate constants k_q = 2.0

x 10^8 and 2.8 x 10^{10} $M^{-1}s^{-1}$ were calculated for the quenching of $*Ru(bpy)_3^{2+}$ by $Co(NH_3)_5Cl^{2+}$ and $Mn(III)P^+$, respectively. A lifetime of 0.6 microseconds for $*Ru(bpy)_3^{2+}$ was used in these calculations (21,22). In 0.5 M sulfuric acid the corresponding quenching constant for $Co(NH_3)_5Cl^{2+}$ is 1.7 x $10^8 M^{-1}s^{-1}$ (14), which is very close to that obtained in the present study. Since the quenching process in sulfuric acid has been shown to involve electron transfer (14), we may reasonably assume that process also in our work.

CONTINUOUS PHOTOLYSIS OF $Ru(bpy)_3^{2+}$ WITH $Co(NH_3)_5Cl^{2+}$

Continuous photolysis (440 nm) of a deaerated aqueous solution containing $Ru(bpy)_3^{2+}$ (0.1 mM) and $Co(NH_3)_5Cl^{2+}$ (1 mM) at pH 4 (acetate buffer) resulted in the formation of $Ru(bpy)_3^{3+}$ (λ_{max} = 420 nm (23)) and Co^{2+} (aq). When photolysis was carried out with an unbuffered solution, the pH of the solution increased from 4 to 7 at the end of 15 min of illumination. The net reaction can be shown as (eq 2):

$$*Ru(bpy)_3^{2+} + Co(NH_3)_5Cl^{2+} \longrightarrow Ru(bpy)_3^{3+} + Co^{2+}(aq) + 5 NH_3 + Cl^- \quad (2)$$
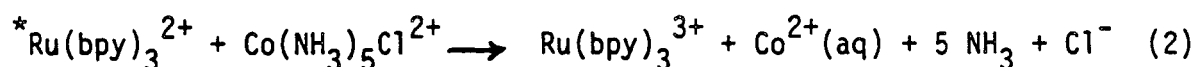
The Co(II) complex formed in the primary quenching process (eq 2) decomposes rapidly to give Co^{2+}(aq) and ammonia (14). Release of ammonia will increase the pH of the solution, as observed.
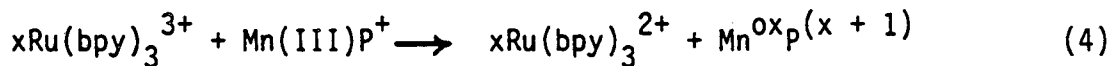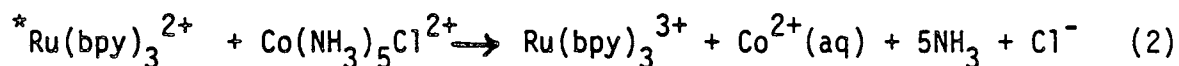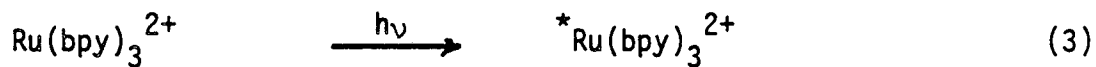
The photochemical yield of Co^{2+}(aq) increased linearly with the time of illumination and with the increase in concentration of $Co(NH_3)_5Cl^{2+}$. A quantum yield of 0.05 was obtained for the formation of

Co^{2+}(aq) in the continuous illumination of 0.1 mM of $Ru(bpy)_3^{2+}$ and 0.5 mM of $Co(NH_3)_5Cl^{2+}$ at pH 4. In these experiments the amount of Co^{2+}(aq) formed in the dark was negligible (< 5%) and this was corrected for in the quantum yield calculations. The $Ru(bpy)_3^{3+}$ formed in the reaction is unstable in the dark and is reduced to $Ru(bpy)_3^{2+}$ (as observed from the absorption spectral changes). The oxidation product accompanying this reduction was not identified. However, the oxidation of water to oxygen by $Ru(bpy)_3^{3+}$ has been reported in the presence of heterogeneous catalysts (5- 7). The decay of $Ru(bpy)_3^{3+}$ at pH 4 followed first-order kinetics. Since the absorption spectrum of $Ru(bpy)_3^{3+}$ is obscured by that of $Ru(bpy)_3^{2+}$, the decay was followed by monitoring the formation of $Ru(bpy)_3^{2+}$. A rate constant of $4.4 \times 10^{-3} s^{-1}$ was calculated from the slope of a plot of log $(A_\infty - A_t)$ vs time. The rate constant was independent of the wavelength used for observation, 424 or 452 nm. The decay of $Ru(bpy)_3^{3+}$ is enhanced significantly with increase in pH of the solution (5). In fact, photolysis of $Ru(bpy)_3^{2+}$ and $Co(NH_3)_5Cl^{2+}$ at pH 7 did not yield a net spectral change of $Ru(bpy)_3^{2+}$. The apparent half-life of $Ru(bpy)_3^{3+}$ was estimated to be less than 10 sec at pH 7. The decay of $Ru(bpy)_3^{3+}$ was also enhanced by the addition of $Mn(III)P^+$ (see below).

PHOTOINDUCED OXIDATION OF Mn(III) PORPHYRIN

Continuous illumination of a degassed solution containing $Ru(bpy)_3^{2+}$ (0.1 mM), $Co(NH_3)_5Cl^{2+}$ (1 mM), and $Mn(III)P^+$ (0.01 mM) at pH 7 (phosphate buffer) resulted in the spectral changes shown in Fig.

3a. The spectra have been corrected for the absorptions of $Ru(bpy)_3^{2+}$ and $Co(NH_3)_5Cl^{2+}$. The appearance of a new absorption band at 424 nm with the concomitant decrease in absorption at 462 nm and the good isobestic points (Fig. 3a) suggests quantitative conversion of $Mn(III)P^+$ to a single, new product. These spectral changes are associated with the oxidation of $Mn(III)P^+$, since in a separate experiment, oxidation of $Mn(III)P^+$ with NaOCl at pH 7 also gave the same new band at 424 nm (Fig. 3a). In the absence of either $Ru(bpy)_3^{2+}$ or $Co(NH_3)_5Cl^{2+}$, the photo-oxidation of $Mn(III)P^+$ was not achieved. Although the photooxidized product of $Mn(III)P^+$ is not fully characterized, we believe it could be a high-valent oxo-type of manganese porphyrin, whose absorption spectrum is reported to be very similar to that shown in Fig. 3a (24-26). In the present discussion we designate this product as $Mn^{OX}P$. A possible pathway for the formation of $Mn^{OX}P$ is shown below:

$$Ru(bpy)_3^{2+} \xrightarrow{\ h\nu\ } {}^*Ru(bpy)_3^{2+} \qquad (3)$$

$$^*Ru(bpy)_3^{2+} + Co(NH_3)_5Cl^{2+} \longrightarrow Ru(bpy)_3^{3+} + Co^{2+}(aq) + 5NH_3 + Cl^- \qquad (2)$$

$$xRu(bpy)_3^{3+} + Mn(III)P^+ \longrightarrow xRu(bpy)_3^{2+} + Mn^{OX}P^{(x + 1)} \qquad (4)$$

As predicted by the above scheme, Co^{2+} was indeed formed in these reactions. The quantum yields of the photoproducts were not measured since the exact amount of the actinic light absorbed by the sensitizer varies with the formation of highly absorbing $Mn^{OX}P$.

The kinetics of the formation of $Mn^{OX}P$ were complex. The formation was completed in 7 minutes under the experimental conditions described in Fig. 3a and in the Materials and Methods section. The $Mn^{OX}P$ formed

is unstable and returns to the original $Mn(III)P^+$ species almost quantitatively. The spectral changes associated with this reduction at pH 7 are shown in Fig. 3b. The reduction followed first-order kinetics over the first 70% of the conversion at wavelengths 424 nm (depletion of $Mn^{OX}P$) and 462 nm (reformation of $Mn(III)P^+$ with a rate constant of 5.3 x $10^{-4}s^{-1}$ at both wavelengths. The same rate constant for the disappearance of $Mn^{OX}P$ and reappearance of $Mn(III)P^+$ is another confirmation of the quantitative interconversion of $Mn(III)P^+$ and $Mn^{OX}P$ as mentioned before. The rate of reduction of $Mn^{OX}P$ increased significantly with the decrease in pH of the solution: k = 5.3 x $10^{-4}s^{-1}$ at pH 7; k = 1.4 x $10^{-3}s^{-1}$ at pH 4.

The formation of $Mn^{OX}P$ and its reduction to $Mn(III)P^+$ can be cycled several times. At least five cycles of the oxidation-reduction of $Mn(III)P^+$ were monitored by the continuous illumination of a solution containing 0.1 mM of $Ru(bpy)_3^{2+}$, 0.01 mM of $Mn(III)P^+$, and 1 mM of $Co(NH_3)_5Cl^{2+}$ at pH 7. At the end of these five cycles, more than 95% of the $Mn(III)P^+$ and 100% of the $Ru(bpy)_3^{2+}$ were regenerated.

CONCLUSION

We have achieved the photoinduced oxidation of manganese(III) porphyrin in aqueous solution by the use of an irreversible electron acceptor in a three component photochemical system. The oxidized manganese porphyrin is highly reactive and is rapidly reduced to the original manganese(III) porphyrin which suggests the possibility that water might be oxidized during this process. While the $Mn^{OX}P$ is found to be more stable at higher pH's, the reverse is true for $Ru(bpy)_3^{3+}$. The

characterization of $Mn^{OX}P$ as well as the identification of the as yet unknown oxidized products are now under investigation.

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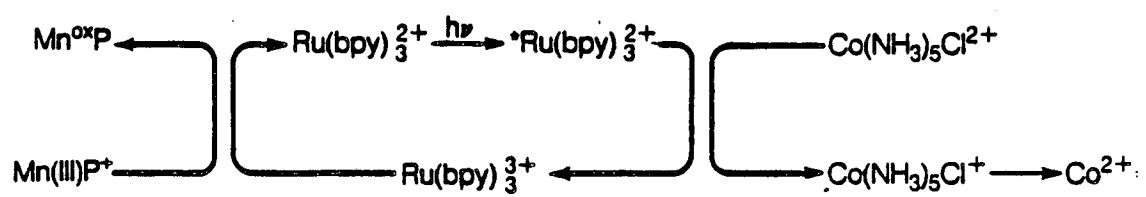
FIGURE CAPTIONS

Figure 1: Schematic diagram of the arrangement used in the photoinduced oxidation of Mn(III) porphyrin in homogeneous solution. $Ru(bpy)_3^{2+}$ is the photosensitizer and $Co(NH_3)_5Cl^{2+}$ is the electron acceptor.
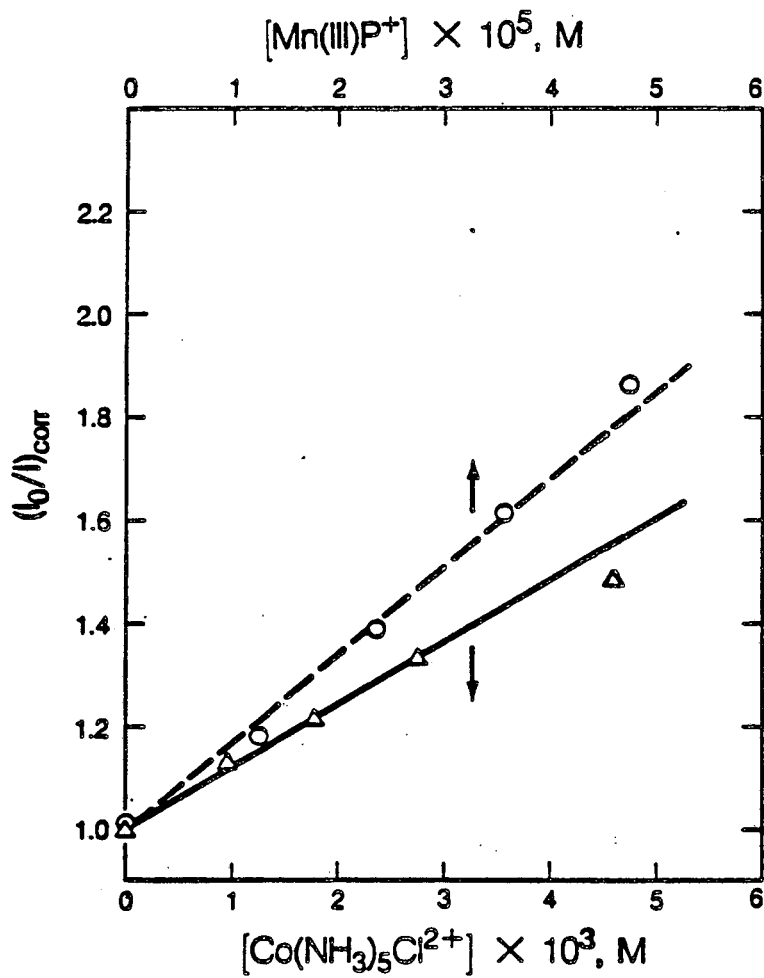
Figure 2: Stern-Volmer plots for the luminescence quenching of $Ru(bpy)_3^{2+}$ (0.1 mM) in homogeneous solution at pH 7 by: (0) Mn(III)P$^+$ ($k_q = 2.8 \times 10^{10} M^{-1}s^{-1}$); (▲) $Co(NH_3)_5Cl^{2+}$ ($k_q = 2.0 \times 10^8 M^{-1}s^{-1}$).

Figure 3: Absorption spectra observed with the time of illumination of a deaerated aqueous solution containing $Ru(bpy)_3^{2+}$ (0.1 mM), $Co(NH_3)_5Cl^{2+}$ (1 mM) and Mn(III)P$^+$ (0.01 mM) at pH 7. The spectra have been corrected for the absorptions of both $Ru(bpy)_3^{2+}$ and $Co(NH_3)_5Cl^{2+}$ and are due only to changes in manganese porphyrin species. The sharp slope change at 400 nm is an instrumental artifact. (a) Formation of Mn^{ox}P (424 nm) and disappearance of Mn(III)P$^+$ (462 nm) at 0, 2, 3, 4 and 7 minutes; (b) decay of Mn^{ox}P and reappearance of Mn(III)P$^+$ at 0, 75 minutes, 4, 8 and 20 hours. See text for kinetic parameters.

$$Mn^{ox}P \longleftarrow \qquad \longrightarrow Ru(bpy)_3^{2+} \xrightarrow{\ h\nu\ } {}^*Ru(bpy)_3^{2+} \qquad \longleftarrow Co(NH_3)_5Cl^{2+}$$

$$Mn(III)P^+ \longleftarrow \qquad Ru(bpy)_3^{3+} \longleftarrow \qquad Co(NH_3)_5Cl^+ \longrightarrow Co^{2+}$$

Figure 1

Figure 2

Figure 3