

## New Photoreduction Catalysis by $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$ ( $\text{N-N} = 2,9\text{-Dimethyl-1,10-phenanthroline}$ or $4,4',6,6'\text{-Tetramethyl-2,2'-bipyridine}$ ) and Its Application to Cobalt(III) Complexes

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The copper(I) complexes  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  [ $\text{N-N} = 2,9\text{-dimethyl-1,10-phenanthroline}$  (dmphen) or  $4,4',6,6'\text{-tetramethyl-2,2'-bipyridine}$  (tmbipy)] photocatalytically reduce cobalt(III) complexes such as  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ ,  $[\text{Co}(\text{edta})]^-$  (edta = ethylenediaminetetra-acetate), and  $[\text{Co}(\text{acac})_3]$  (acac = acetylacetonate), upon irradiation with near-u.v. light corresponding to the metal-to-ligand charge-transfer absorption band (about 360 nm) of the copper(I) complex. This is a new type of photocatalytic reduction by copper(I) complexes. The photosensitizing mechanism is discussed on the basis of the Stern-Volmer relationship. The dmphen complex has a higher activity than that of the tmbipy analogue, and the reactivity of the cobalt(III) complexes decreases in the order  $[\text{CoCl}(\text{NH}_3)_5]^{2+} > [\text{Co}(\text{edta})]^- > [\text{Co}(\text{acac})_3]$ . The results are discussed in terms of the lifetime of the excited copper(I) complex and the reduction potentials of the cobalt(III) complexes.

There has been growing interest in the photochemistry of transition-metal complexes.<sup>1</sup> Recent investigations have concentrated on the photocatalysis by  $[\text{Ru}(\text{bipy})_3]^{2+}$  (bipy = 2,2'-bipyridine), because this complex can reduce  $\text{H}^+$  (leading to  $\text{H}_2$  evolution) upon irradiation with visible light.<sup>2</sup> Many photochemical reactions are known for copper(I) complexes.<sup>1</sup> For example, several  $2\pi + 2\pi$  type cycloadditions<sup>3</sup> and *trans*  $\rightleftharpoons$  *cis* isomerizations of olefins are catalysed by copper(I) complexes upon irradiation with u.v. or visible light.<sup>4</sup> Also, copper(I) complexes undergo two kinds of photoinduced electron-transfer reactions; one is the photoreduction of cobalt(III) complexes by  $[\text{Cu}(\text{dmphen})_2]^+$  (dmphen = 2,9-dimethyl-1,10-phenanthroline) upon irradiation with visible light,<sup>5</sup> and the other is the reduction of  $\text{H}^+$  (*i.e.*  $\text{H}_2$  evolution) by  $[\text{CuCl}_3]^{2-}$  upon irradiation with u.v. light.<sup>6</sup> Unfortunately, however, these photoreductions are not catalytic but stoichiometric.

The above-mentioned photoreactions of copper(I) complexes seem to result from the fact that such complexes have the metal-to-ligand charge-transfer (m.l.c.t.) excited state as the lowest excited state. This situation is similar to that of  $[\text{Ru}(\text{bipy})_3]^{2+}$ , and it is therefore worthwhile to investigate the photochemistry of copper(I) complexes with the aim of finding new catalytic systems. In this work, the photocatalytic reduction of several cobalt(III) complexes has been examined. The catalysts chosen were  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  ( $\text{N-N} = \text{dmphen}$  or  $4,4',6,6'\text{-tetramethyl-2,2'-bipyridine}$  (tmbipy)), for the following reasons: (i) though the excited state of  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  has been well investigated,<sup>7</sup> their photochemical reactions have not yet been reported; (ii) because of the reducing ability of  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  in its excited state,<sup>7a</sup> this complex is expected to be useful for the photoreduction of various substrates. The copper(I) complexes examined can reduce catalytically several cobalt(III) complexes upon irradiation with near-u.v. light. This system is a new type of a photoreduction catalyst involving copper(I) complexes. The photosensitizing mechanism is discussed on the basis of the Stern-Volmer relationship.

### Experimental

**Chemicals.**—The complexes  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]\text{NO}_3$  ( $\text{N-N} = \text{dmphen}$  or tmbipy) were prepared from  $[\text{Cu}(\text{PPh}_3)_2]\text{NO}_3$ ,<sup>8</sup> according to a previous method<sup>9</sup> with slight modi-

fications as described by McMillin and co-workers.<sup>7a</sup> Their purity was ascertained by elemental analysis. The complex  $[\text{Co}(\text{acac})_3]$  (acac = acetylacetonate) was purchased from Nakarai Co. and used after recrystallization from benzene-light petroleum (b.p. 40–100 °C) solution. The salts  $[\text{Co}(\text{edta})]$  (edta = ethylenediaminetetra-acetate) and  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$  were prepared by literature methods.<sup>10</sup> Their purity was ascertained by elemental analysis and u.v.–visible spectroscopy.

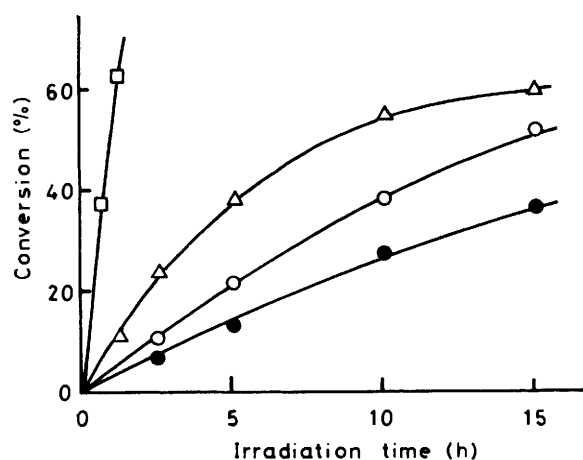
**Photoreactions.**—In typical runs, the copper(I) complex ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>), cobalt(III) complex ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>), and  $\text{PPh}_3$  ( $4 \times 10^{-3}$  mol dm<sup>-3</sup>) were dissolved in 60 vol. % ethanol-water solution and irradiated at 30 °C in a 1-cm Pyrex cell under nitrogen atmosphere by using a 400-W high-pressure mercury arc lamp (Toshiba H-400P). The  $\text{PPh}_3$  was added to the solution to suppress the dissociation of  $\text{PPh}_3$  from  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$ . The incident light (360–400 nm), corresponding to the m.l.c.t. absorption band of  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$ , was selected using a combination of cut-off filters (Toshiba UV 35  $\times$  2 and UV-D35). The light intensity absorbed by the reaction system was measured as the difference in the light intensity transmitted by the reaction and the reference cells by using Reineck's chemical actinometry.<sup>11</sup> The concentration of cobalt(II) ion, the reduction product of the cobalt(III) complexes, was measured by spectrophotometric determination (at 625 nm) of its thiocyanate complex in isobutyl methyl ketone,<sup>12</sup> with the aid of a calibration curve. Thiourea was added to mask the copper(II) ion. For the  $[\text{Co}(\text{edta})]^-$  reduction only, the decrease in  $[\text{Co}(\text{edta})]^-$  concentration was measured by observing its *d-d* band (at 539 nm) spectrophotometrically, because edta co-ordinates to  $\text{Co}^{\text{II}}$  thereby interfering with the thiocyanate complex formation.

**Measurements.**—A Hitachi UV 200-10 spectrophotometer was used in the measurements of u.v.–visible spectra. The emission spectra were measured by using a JASCO FP 550A spectrofluorometer at 30 °C, the deoxygenation of samples being carried out by several freeze-pump-thaw cycles. Methanol was used as solvent after careful rectification. The emission spectra of  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  and its tmbipy analogue were obtained by excitation at 395 and 350 nm, respectively, and the emission intensity was measured at 520 and 515 nm, respectively.

**Table.** Photoreduction of cobalt(III) complexes catalysed by  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  (N-N = dmphen or tmbipy)

Catalyst	Substrates	$10^2\Phi^a$	Intercept <sup>b</sup>	Slope <sup>b</sup>	$k_d/k_r$	$k_r^c$
$[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$	$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	11.1	0.7	$8.0 \times 10^{-3}$	$1.1 \times 10^{-2}$	1
	$[\text{Co}(\text{edta})]^-$	2.8	15	$1.9 \times 10^{-2}$	$1.3 \times 10^{-3}$	8
	$[\text{Co}(\text{acac})_3]$	1.2	59	$2.7 \times 10^{-2}$	$4.6 \times 10^{-4}$	24
$[\text{Cu}(\text{tmbipy})(\text{PPh}_3)_2]^+$	$[\text{Co}(\text{acac})_3]$	0.83	43	$7.3 \times 10^{-2}$	$1.7 \times 10^{-3}$	—

<sup>a</sup> The quantum yield for cobalt(III) reduction. <sup>b</sup> Defined in the text. <sup>c</sup> The value of  $k_r$  relative to system  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+ - [\text{CoCl}(\text{NH}_3)_5]^{2+}$ .



**Figure 1.** Reduction of several cobalt(III) complexes photocatalysed by  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  (N-N = dmphen or tmbipy) as a function of time: (□)  $[\text{CoCl}(\text{NH}_3)_5]^{2+} - [\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$ ; (△)  $[\text{Co}(\text{edta})]^- - [\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$ ; (○)  $[\text{Co}(\text{acac})_3] - [\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$ ; (●)  $[\text{Co}(\text{acac})_3] - [\text{Cu}(\text{tmbipy})(\text{PPh}_3)_2]^+$

## Results and Discussion

The cobalt(III) complexes, examined here, are efficiently photoreduced by copper(I) complexes, as shown in Figure 1. Their reactivity decreases in the order  $[\text{CoCl}(\text{NH}_3)_5]^{2+} > [\text{Co}(\text{edta})]^- > [\text{Co}(\text{acac})_3]$ , and the catalytic activity of  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  is higher than that of the tmbipy analogue, as will be discussed in more detail later. To examine whether the photoreduction is catalytic or stoichiometric, several runs, in which the concentration of cobalt(III) complexes was five times that of the copper(I) complex, were carried out. For the reduction of  $[\text{Co}(\text{edta})]^-$  by  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$ , the turnover number was 2.3 after 5 h, for the  $[\text{Co}(\text{acac})_3]$  reduction, 1.8 after 20 h, and for the  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  reduction, 2.8 after 3 h.† These results mean that the photoreduction is not stoichiometric but catalytic. After the reaction, addition of 2,4-dinitrophenylhydrazine to the solution yielded a yellow precipitate, suggesting the presence of acetaldehyde. No triphenylphosphine oxide was observed by i.r. measurement of the evaporated reaction solution. Further, the photochemical reduction of  $[\text{Cu}(\text{dmphen})_2]^{2+}$  by ethanol has been previously reported.<sup>13</sup> Thus, a conceivable picture of the

catalytic cycle emerges as shown in Scheme 1, where the oxidized  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^{2+}$  is photochemically reduced to  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  by ethanol. In other words,  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  plays the role of electron carrier, supplying an electron to the cobalt(III) complex and abstracting an electron from ethanol.

A reaction mechanism for the initial stage of the reaction is shown in Scheme 2, where  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  is transformed into its m.l.c.t. excited state by absorption of near-u.v. light, then forms an encounter complex with the cobalt(III) complex, and the reduction of the latter proceeds in the encounter complex. A similar reaction mechanism has been reported for the stoichiometric photoinduced electron transfer from  $[\text{Cu}(\text{dmphen})_2]^+$  to a cobalt(III) complex.<sup>5b</sup> Application to this reaction mechanism of the Stern-Volmer relation yields equation (1),<sup>5c</sup> where the steady-state approximation is assumed

$$\Phi^{-1} = \eta^{-1}(k_p + k_b)/k_p\{(k_d/k_r)[\text{Co}^{\text{III}}]^{-1} + 1\} \quad (1)$$

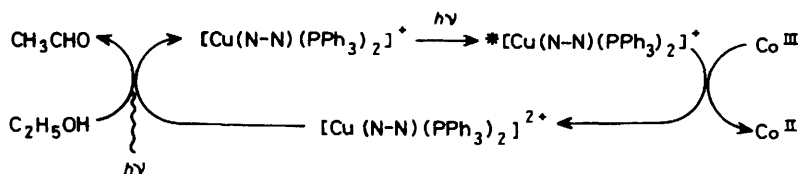
for the excited state  $^*[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  and its encounter complex with cobalt(III). Here  $\Phi$  is the quantum yield for the cobalt(III) reduction. Of course, this relation is not valid over the whole reaction, but only for the initial stage, because the oxidized  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^{2+}$  would absorb incident light and be reduced to the copper(I) form. In the kinetic study, therefore, the reaction is stopped after a few percent conversion. The  $\Phi^{-1}$  values, obtained in such experiments, are plotted against  $[\text{Co}^{\text{III}}]^{-1}$  in Figure 2. The good linear relationships obtained support the reaction mechanism in Scheme 2.

The  $\Phi$  values for various reaction systems are listed in the Table. Those with  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  are larger than with  $[\text{Cu}(\text{tmbipy})(\text{PPh}_3)_2]^+$ . According to equation (1), the intercept of the plots in Figure 2 are given by  $\eta^{-1}(k_p + k_b)/k_p$  and the slope by  $[\eta^{-1}(k_p + k_b)/k_p](k_d/k_r)$ , i.e. intercept  $\times (k_d/k_r)$ . The complex  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  and its tmbipy analogue give similar values for the intercept, but considerably different slopes, suggesting that the difference in their activity does not result mainly from the  $\eta^{-1}(k_p + k_b)/k_p$  but from the  $(k_d/k_r)$  term. The rate constant for decay of the excited copper(I) complex,  $k_d$ , and the lifetime of the excited state  $^*[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$ , corresponding to  $k_d^{-1}$ , might vary in parallel with intensity of the emission spectrum.‡ The emission spectra of  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  and its tmbipy analogue were observed at 520 and 515 nm, respectively;§ the spectrum of the former complex has ca. 5.6 times the intensity of

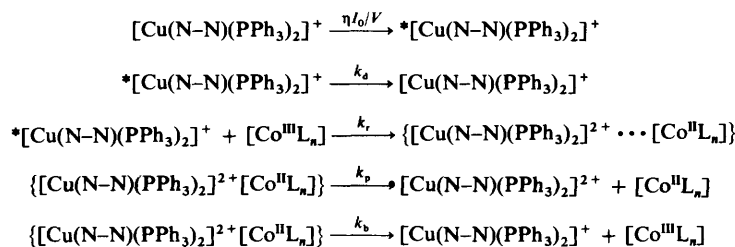
† After reaction of  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  for a long time a brownish white precipitate was observed. Unfortunately, this could not be identified because of the small amount available. Although the characteristics of the precipitate cannot be known, the incident light would be scattered by such a precipitate which suppresses the photoreaction. Thus, the turnover numbers of the  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  reduction would be lower than expected on the basis of its high reactivity. A precipitate was not found in the short time of the  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  reduction and even in the long reactions of  $[\text{Co}(\text{edta})]^-$  and  $[\text{Co}(\text{acac})_3]$ . It is not clear why the precipitate was found only in the long reaction of  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ . Further detailed investigation should be carried out.

‡ The intensity of the emission spectrum depends on  $\eta k_r k_d^{-1}$ , where  $k_r$  is the emission rate constant and  $k_d$  is given by the sum of  $k_f$  and the non-radiative deactivation rate constant,  $k_{nd}$ . The photoreactive state is considered to be a triplet, and therefore the  $\eta$  and  $k_r$  values are closely related with the spin-orbit coupling interaction. This interaction mainly arises from heavy atoms such as Cu and P. Because both  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$  and its tmbipy analogue have one Cu atom and two P atoms, the corresponding  $\eta$  and  $k_r$  values should not be very different for the two complexes. Thus, the intensity of the emission spectrum would depend on the lifetime of the excited state.

§ Uncorrected values.



Scheme 1.



Scheme 2.  $V$  = Photolyte volume,  $\eta$  = quantum efficiency with which the reactive excited state is formed from the Franck-Condon state reached upon excitation,  $I_0$  = number of photons per second absorbed by copper; see ref. 5c.

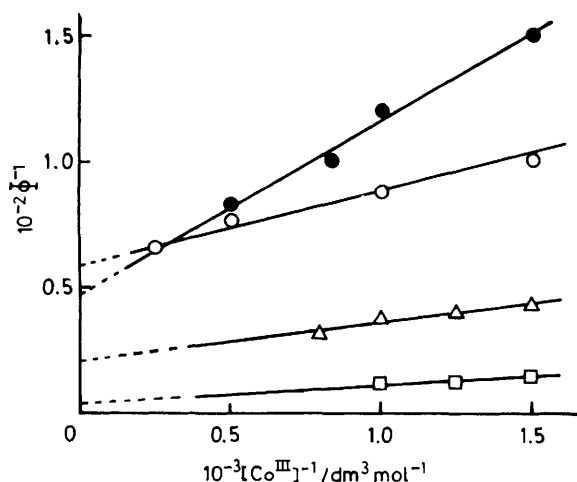


Figure 2. The relation between the quantum yield for cobalt(III) reduction,  $\Phi$ , and the concentration of cobalt(III) complex in the photo-reduction catalysed by  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$ . Details as in Figure 1

that of the latter. From the relative values of the lifetime and  $k_d/k_r$  (Table), the  $k_r$  value of the tmbipy complex is estimated to be about 1.9 times that of the dmphen complex. Thus, the higher activity of  $[\text{Cu}(\text{dmphen})(\text{PPh}_3)_2]^+$ , corresponding to the lower  $k_d/k_r$  value, does not result from the fast  $k_r$  process but from the slow  $k_d$  process, *i.e.* the long lifetime of its excited state.

Of the cobalt(III) complexes,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  has the highest reactivity, as shown in Figure 1 and the Table, and  $[\text{Co}(\text{acac})_3]$  has the lowest reactivity. From the slopes and intercepts of the plots in Figure 2, the relative value of  $k_r$  can be estimated for various cobalt(III) complexes examined, because  $k_d$  does not depend on the nature of the cobalt(III) complexes but only on the copper(I) complex. As seen in the Table, the relative value of  $k_r$  decreases in the order  $[\text{Co}(\text{acac})_3] > [\text{Co}(\text{edta})^-] > [\text{CoCl}(\text{NH}_3)_5]^{2+}$ . This order does not coincide with the decreasing order of the reactivity of the cobalt(III) complexes, and further, the most reactive,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ , has the lowest  $k_r$  value. These results suggest that the reactivity

of the cobalt(III) complexes does not depend on the  $k_r$  process, *i.e.* the formation of the encounter complex, but on some other factors. The most plausible candidate for such a factor is the  $k_p$  process. In fact, the intercept, which is closely related with this process, decreases with increasing reactivity of the cobalt(III) complexes, as shown in Figure 2. The intercept has been proposed to depend on the reduction potential of the cobalt(III) complexes.<sup>5c</sup> The high reduction potential of  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  [ $E_1 = 0.53$  V vs. standard hydrogen electrode (s.h.e.)]<sup>14a</sup> would result in a higher  $k_p$  value relative to the  $k_b$  process, leading to a lower value for the intercept and higher reactivity. The lower reactivity of  $[\text{Co}(\text{edta})^-]$  can be attributed to its low reduction potential ( $E_1 = 0.38$  V vs. s.h.e.)<sup>14b</sup> Though the reduction potential of  $[\text{Co}(\text{acac})_3]$  is not known, we infer that it is lower than that of  $[\text{Co}(\text{edta})^-]$ , because a higher intercept value is observed for the  $[\text{Co}(\text{acac})_3]$  reduction.

In conclusion, the photoreduction catalysis by  $[\text{Cu}(\text{N-N})(\text{PPh}_3)_2]^+$  is demonstrated. This system uses ethanol as a reductant to complete the catalytic cycle, which is inexpensive compared with the edta and triethylamine used with the  $[\text{Ru}(\text{bipy})_3]^{2+}$  catalyst. Thus, it is worthwhile applying this catalytic system to various photoreduction reactions.

### Acknowledgements

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