Synthesis of a new chiral copper(I) complex and its application to stereoselective photoreduction of $[Co(edta)]^-$ (H_4edta = ethylenedinitrilotetraacetic acid)

Shigeyoshi Sakaki,* Hiroyuki Ishikura, Ko-ichi Kuraki, Ko-jyoh Tanaka, Takashi Satoh, Toru Arai and Taisuke Hamada

Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860, Japan

A chiral bipyridine derivative, 4,4′-6,6′-tetramethyl-5,5′-bis[(*S*)-(−)-1-phenylethylcarbamoyl]-2,2′-bipyridine (L), was newly synthesized. Using its copper(I) complex, $[CuL(PPh_3)_2]^+$, $[Co(edta)]^-$ (H_4edta = ethylenedinitrilotetraacetic acid) was stereoselectively photoreduced upon irradiation with near-UV light (360–400 nm) corresponding to the metal-to-ligand charge transfer absorption band of the copper(I) complex, where the Λ enantiomer of $[Co(edta)]^-$ was preferentially reduced. The stereoselectivity of 42% enantiomeric excess was observed at 10% conversion, where the solvent was EtOH–water (75:25 v/v). This $[Co(edta)]^-$ photoreduction by $[CuL(PPh_3)_2]^+$ proceeds through both static and dynamic quenching mechanisms. Quenching experiments with the optical isomers, Δ- and Λ-$[Co(edta)]^-$, clearly indicated that quenching takes place with little stereoselectivity, but charge separation and/or a reverse electron transfer occur stereoselectively.

Stereoselective photoinduced electron-transfer reactions between transition-metal complexes are attractive subjects of research for the following reasons: (1) the stereoselectivity is interesting in itself, since the photoinduced electron-transfer reaction is a typical outer-sphere electron transfer which proceeds *via* a weak contact between a photosensitizer and a reactant; (2) the photoinduced electron-transfer reaction involves several elementary processes such as encounter-complex formation, charge separation and reverse electron transfer, but it has not been clarified which step mainly determines the stereoselectivity and (3) the stereoselectivity would be influenced by many factors such as the redox potentials of the photosensitizer at the excited and ground states, the redox potential of the reactant, the charges of the photosensitizer and reactant and the nature of the solvent, but it is still ambiguous as to what extent.

However, only a few studies have been carried out on stereoselective photoinduced electron transfer.[1–4] One of the reasons is that excellent chiral photosensitizers are sparse. For instance, Δ- and Λ-$[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) which were previously used as photosensitizers for stereoselective photoreduction of chiral viologen (4,4′-bipyridinium)[1] and cobalt(III) complexes[2] easily cause photoracemization, and therefore $[Ru(bipy)_3]^{2+}$ is not very useful for the detailed investigation of stereoselective photoreaction. Recently, Ohkubo, Hamada and their co-workers[4] reported excellent chiral photosensitizers of a ruthenium(II) complex, which do not cause photoracemization. These photosensitizers were successfully applied to stereoselective photoreduction of $[Co(acac)_3]$ (acac = acetylacetonate) and $[Co(edta)]^-$ (H_4edta = ethylenedinitrilotetraacetic acid) and stereoselective photosynthesis of $[Co(acac)_3]$ from $[Co(acac)_2]$. Besides the ruthenium(II) complex, the copper(I) complexes of such conjugated ligands as bipy and 1,10-phenanthroline (phen) are expected to be efficient photosensitizers since their lowest-energy excited state is the triplet metal-to-ligand charge-transfer (m.l.c.t.) state like that of $[Ru(bipy)_3]^{2+}$. Many photoreactions involving copper(I) complexes have been reported by McMillan,[5] Sauvage and co-workers[6] and us.[3,7] Those findings encouraged us to synthesize a chiral conjugated compound which would be useful for the copper(I) photosensitizer. It should be remembered that such conjugated compounds as bipy and phen should have alkyl or aryl substituents at the positions neighbouring the N atom, because they are believed to lengthen the excited-state lifetime of the copper(I) complex by inhibiting approach of a quencher to it.[5h,6a]

In this work we synthesized 4,4′,6,6′-tetramethyl-5,5′-bis[(*S*)-(−)-1-phenylethylcarbamoyl]-2,2′-bipyridine (L, see Scheme 1) which has two chiral (*S*)-(−)-1-phenylethylcarbamoyl groups at the 5 and 5′ positions and two methyl groups at the 6 and 6′ positions neighbouring the N atom. It has two additional methyl groups at the 4 and 4′ positions which would be useful to orientate the chiral groups perpendicularly to the bipyridine plane. Using its copper(I) complex, $[CuL(PPh_3)_2]^+$ we tried to perform stereoselective photoreduction of $[Co(edta)]^-$. Our purposes were (1) to achieve highly stereoselective photoreduction, (2) to elucidate whether the photoreduction of $[Co(edta)]^-$ proceeds through a dynamic quenching or static quenching mechanism, (3) to clarify an elementary step at which the stereoselectivity is determined and (4) to investigate solvent effects on the stereoselectivity.

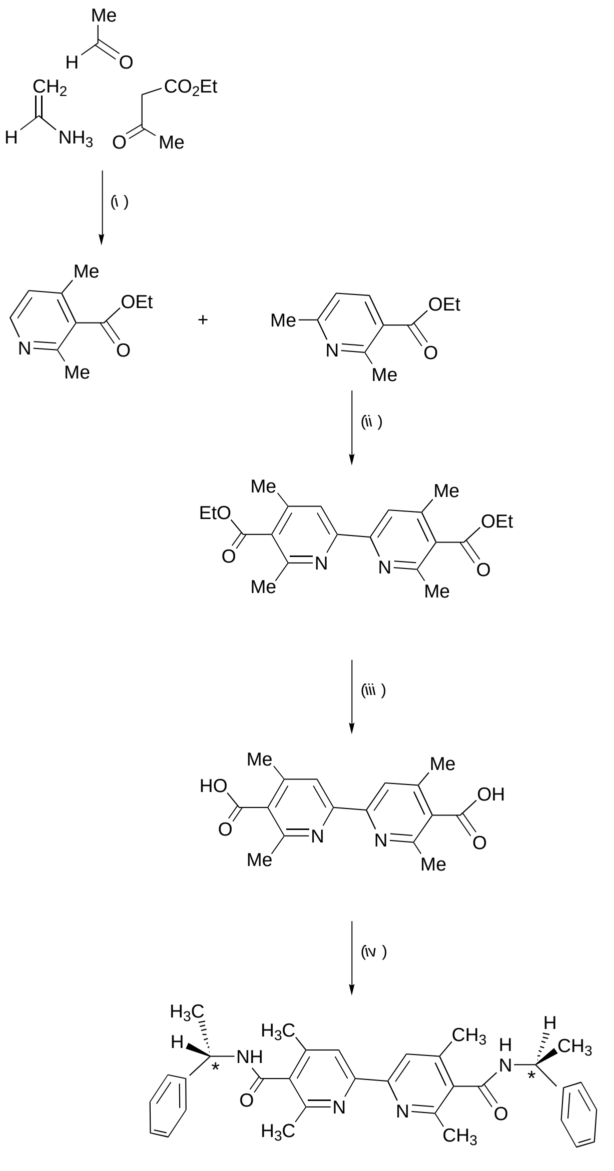
Experimental

Syntheses

The compound L was synthesized according to Scheme 1. Details of each step are described.

3-Ethoxycarbonyl-2,4-dimethylpyridine. According to Ohno *et al.*,[8] cyclodehydrogenation of $CH_2{=}CHNH_3$ (141 g, 2.8 mol), ethyl acetoacetate (292 cm^3, 2.3 mol), and acetaldehyde (162 cm^3, 2.8 mol) was carried out at 75–85 °C for 3 d to afford 3-ethoxycarbonyl-2,4-dimethylpyridine and 3-ethoxycarbonyl-2,6-dimethylpyridine as an orange solution. These two compounds were separated as described in ref. 8. The first was immediately used for the next step. Yield 80 g (15% relative to $CH_2{=}CHNH_3$).

5,5′-Bis(ethoxycarbonyl)-4,4′,6,6′-tetramethyl-2,2′-bipyridine. 3-Ethoxycarbonyl-2,4-dimethylpyridine was subjected to Pd/C-catalysed coupling at 180 °C for 6 d, where 5% Pd/C (10 g) was used.[9] Then, acetone (50 cm^3) was added and Pd/C filtered off. The filtrate was evaporated, followed by cool-



L

Scheme 1 (*i*) 75–85 °C, 3 d; (*ii*) Pd/C (5%), 180 °C, 6 d; (*iii*) NaOH, 70 °C, 1 d; (*iv*) dcc, 1-hydroxybenzotriazole, PhCH(Me)NH_2

ing in a refrigerator overnight, to afford the required compound as a crude precipitate. It was purified by recrystallization from methanol. Yield: 6.3 g [1.3% relative to CH_2=$CHNH_3$ (141 g, 2.8 mol)] (Found: C, 67.1; H, 6.95; N, 7.6. Calc. for $C_{20}H_{12}N_2O$: C, 67.4; H, 6.95; N, 7.85%).

4,4′,6,6′-Tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid. The above compound (3 g, 8.42 mmol) was hydrolysed with NaOH (3 g) in acetone–ethanol–water (1.5 : 1 : 1 v/v, 210 cm_3), and then the solution was acidified to pH 3 with HCl (1.2 mol dm^{-3}), to produce the dicarboxylic acid as a white precipitate. Yield: 2.0 g (6.66 mmol, 79.1%) (Found: C, 63.75; H, 5.4; N, 9.25. Calc. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.35; N, 9.35%).

4,4′,6,6′-Tetramethyl-5,5′-bis[(*S*)-(−)-1-phenylethylcarbamoyl]-2,2′-bipyridine. Dicyclohexylcarbodiimide (dcc, 0.45 g, 2.08 mmol) and 1-hydroxybenzotriazole (0.25 g, 1.85 mmol) were added to a dimethylformamide solution (16 cm^3) containing the above compounds (0.3 g, 1.0 mmol) and (*S*)-(−)-1-phenylethylamine (0.25 g, 2.06 mmol) at 0 °C. The solution was stirred at 0 °C for 2 h and then at a room temperature for 14 h. After removal of a precipitate of dicyclohexylurea, evaporation of the filtrate left a pale yellow precipitate. This was dissolved in chloroform and washed with an aqueous solution of sodium hydrogencarbonate. Evaporation of the organic phase yielded white crystalline L. This was purified by recrystallization from chloroform–diethyl ether. Its optical purity was checked by NMR measurement (in $CDCl_3$): δ 5.557 (NH) in the presence of (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyl tartrate and δ 5.552 (NH) in the presence of the (2*S*,3*S*)-(+) enantiomer. Yield: 0.35 g (0.70 mmol, 70%). CD spectrum: λ/nm 318, $\Delta\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ (EtOH) 0.146, m.p. >300 °C (Found: C, 75.7; H, 6.7; N, 11.05. Calc. for $C_{32}H_{32}N_4O_2$: C, 75.9; H, 6.75; N, 11.05%). δ_H(400 MHz, $CDCl_3$) 1.63 (3 H, m, CH_3), 2.3 (3 H, s, CH_3 of py), 2.5 (3 H, s, CH_3 of py), 5.37–5.41 (1 H, m, CH), 6.25 (1 H, br, NH), 7.30–7.40 (5 H, m, C_6H_5) and 8.02 (1 H, s, H of py).

Chiral [CuL(PPh_3)$_2$]ClO_4 1. Complex **1** was synthesized according to previous reports.[7] An ethanol solution (40 cm^3) of tetrakis(acetonitrile)copper(I) perchlorate (0.082 g, 0.25 mmol), L (0.127 g, 0.25 mmol), and 2 molar equivalents of PPh_3 (0.132 g) was stirred at room temperature for 1 h. This solution was evaporated to dryness at low temperature (about 0 °C), to produce a pale yellow precipitate. The latter was washed three times with cold ether. Yield: 0.21 g (0.175 mmol, 70%) (Found: C, 68.2; H, 5.75; N, 4.25. Calc. for $C_{68}H_{62}ClCuN_4O_6P_2$: C, 68.4; H, 5.4; N, 4.7%).

Measurements

The absorption spectrum of complex **1** was measured with a Hitachi spectrophotometer (model 150-20). Its emission spectrum was recorded at 30 °C with a Hitachi fluorescence spectrometer (model F3010), where **1** was irradiated with light corresponding to its m.l.c.t. absorption maximum (352 nm). The CD spectra were recorded with a JASCO J-500C circular dichroism spectropolarimeter.† The excited-state lifetime of **1** was measured with a Horiba NAES-550 time-resolved fluorometer, in which the incident light was selected by a band-path filter (Toshiba U-360) and the intensity of the emission spectrum was monitored at the λ_{max}. In these measurements the sample solution was deaerated by five freeze–pump–thaw cycles.

Photoreactions

In a typical run an ethanol–water (60 : 40 v/v) solution containing complex **1** (1.0 mmol dm^{-3}), [Co(edta)]$^-$ (1.0 mmol dm^{-3}) and phosphine (1.0–5.0 mmol dm^{-3}, five-fold excess relative to Cu^I) was prepared under a nitrogen atmosphere, and then placed in a flask equipped with a Pyrex square cuvette (inside diameter 10 mm). The excess of phosphine was used in order to suppress dissociation of phosphine from **1**.‡ The solution was deaerated by five freeze–pump–thaw cycles, transferred to a Pyrex cuvette, and then irradiated with a 400 W high-pressure mercury-arc lamp (Toshiba H-400P) at 25 °C, where the incident light ($360 < \lambda < 400$ nm) was isolated with a combination of cut-off filters (Toshiba UV-35 and UV-D35 glass).

The concentration of [Co(edta)]$^-$ was spectrophotometrically monitored at λ_{max}/nm (EtOH–water) 538 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 323). The light intensity absorbed by the reaction solution was measured as the difference between the light intensities transmitted through reaction and reference cells, using a Reineckate chemical actinometer, K[Cr(NH_3)$_2$(NCS)$_4$].[10] The

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† Since the enantiomeric excess (e.e.) was rather low in several experiments, the measurement of the CD spectrum was repeated eight times. The resulting spectra were accumulated and averaged. The e.e. values reported seem reliable.

‡ If excess of phosphine was not added the solution of [CuL(PPh_3)$_2$]$^+$ exhibited a small absorption around 440 nm besides a large absorption at 360 nm. The small absorption appears when PPh_3 dissociates from [CuL(PPh_3)$_2$]$^+$.[5f,h,m,p,7] When the excess is added the absorption at 360 nm increases and the small absorption at 440 nm decreases. It was ascertained that the small absorption at 440 nm disappeared upon addition of a five-fold excess relative to **1** and that further addition of phosphine resulted in little change in the UV/VIS spectrum of the [CuL(PPh_3)$_2$]$^+$ solution.

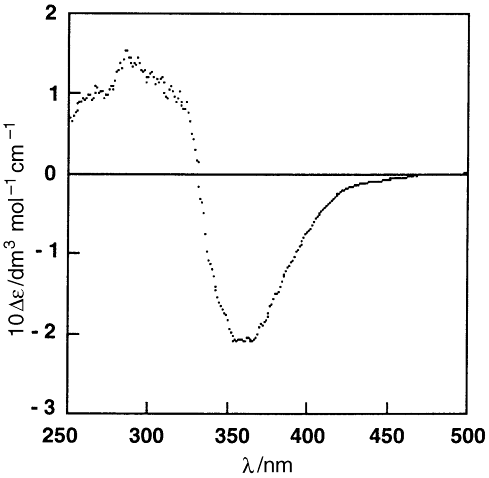

Fig. 1 The CD spectrum of $[CuL(PPh_3)_2]^+$ **1** in EtOH

quantum yield $\Phi(Co^{II})$ was defined as the decrease in $[Co(edta)]^-$ divided by the number of quanta absorbed by the copper complex. The quantum yield for the $[Co(edta)]^-$ photoreduction was measured in the early stage of the reaction (less than 10% conversion), in order to avoid the influence of the change in concentration of $[Co(edta)]^-$.

Quenching reactions

An EtOH–water (60:40 or 75:25 v/v) solution containing the photosensitizer **1** (0.10 mmol dm^{-3}) and the quencher, Δ- or Λ-$[Co(edta)]^-$ (0.10–3.0 mmol dm^{-3}), was placed in a Pyrex cell, and then deaerated through five freeze–pump–thaw cycles. The emission intensity and the excited-state lifetime of the copper(I) complex were measured at 30 °C, under irradiation of light corresponding to the absorption maximum of **1** (352 nm). In a quenching experiment, the emission intensity was corrected by the method of Demas and Adamson[11] because the emission spectrum of the photosensitizer **1** overlaps with the absorption spectrum of $[Co(edta)]^-$.

Results and Discussion

Photochemical properties of $[CuL(PPh_3)_2]^+$ 1

The m.l.c.t. absorption band of complex **1** is observed at λ_{max}/nm (EtOH) 352 (ε/dm³ mol^{-1} cm^{-1} 1910), and its emission occurs at λ_{max}/nm [EtOH–water (60:40 v/v)] 550. The complex shows a CD spectrum around 250–430 nm [λ_{max}/nm (EtOH) 360 (Δε/dm³ mol^{-1} cm^{-1} −0.21)], Fig. 1, whereas the (*S*)-(−)-1-phenylethylamide group does not have any absorption around 360 nm. This means that this chiral group induces enantiomeric effects in the m.l.c.t. absorption of **1**. The CD spectrum of **1** has no absorption at wavelenghts longer than 450 nm. Since $[Co(edta)]^-$ exhibits a characteristic CD spectrum around 450–650 nm, it can be measured without any disturbance from the CD spectrum of **1**. The CD spectrum of **1** changes little upon irradiation with near-UV light, indicating that no racemization of **1** occurs. The excited state of **1** is long-lived, as expected; for instance, its excited-state lifetime is 256 ns in EtOH–water (60:40 v/v) and 265 ns in EtOH–water (75:25 v/v).

Stereoselective photoreduction of $[Co(edta)]^-$ by complex 1

Racemic $[Co(edta)]^-$ was smoothly reduced by complex **1** under irradiation with near-UV light (360–400 nm), while the photoreaction was almost inhibited in EtOH–water (80:20 v/v), as shown in Fig. 2(*a*). The quantum yield for $[Co(edta)]^-$ reduction was rather low: 1.46×10^{-2} in EtOH–water (60:40 v/v) and 0.38×10^{-2} in EtOH–water (75:25 v/v). The excess of phosphine was added to the reaction solution as described in the Experimental section. However, it was experimentally ascertained here that free phosphine does not participate in the $[Co(edta)]^-$ photoreduction even under photoirradiation. Of course, this photoreduction cannot occur without **1**. Interestingly, the reactivity significantly depends on the solvent system, as shown in Fig. 2(*b*); the reaction becomes faster in the order Pr^iOH–water < EtOH–water < MeOH–water.

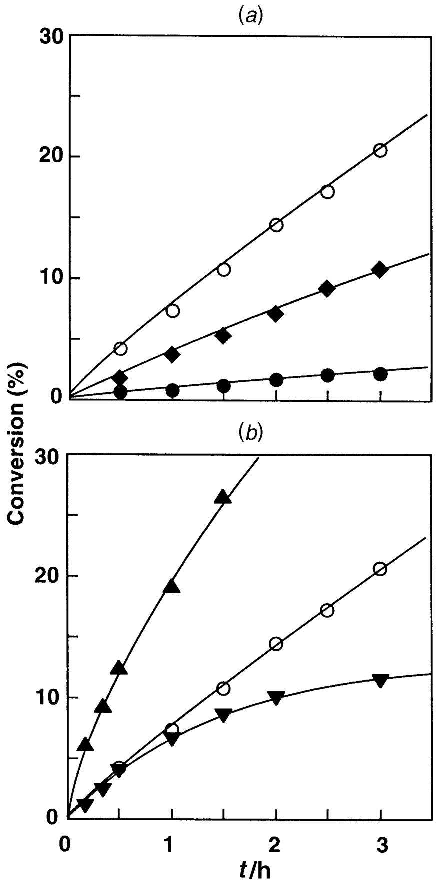

Fig. 2 Time curves of $[Co(edta)]^-$ photoreduction by $[CuL(PPh_3)_2]^+$ **1** in (*a*) EtOH–water = [60:40 (○), 70:30 (◆) and 80:20 (v/v) (●)] and (*b*) MeOH–water (60:40) (▲), EtOH–water (60:40) (○) and Pr^iOH–water (60:40) (▼) at 25 °C. Conversion based on $[Cu^I]$. Reaction conditions: [**1**] = 1.0 mmol dm^{-3}, $[Co(edta)^-]$ = 1.0 mmol dm^{-3}, excess of phosphine = 5.0 mmol dm^{-3}

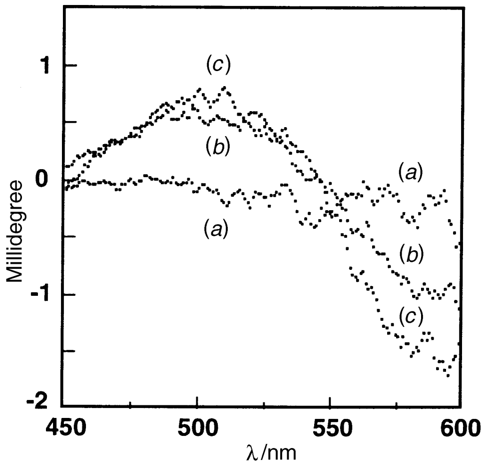

Fig. 3 The CD spectra of the reaction solution at 0 (*a*), 10 (*b*) and 20% conversion (*c*). Conditions: EtOH–water (60:40 v/v). See Fig. 2 for the other conditions

As the reaction proceeds the CD spectra of the reaction solution change, as shown in Fig. 3; the positive peak and negative one appear at λ/nm 515 and 590 respectively, and increase in intensity. This spectral change indicates that Δ-$[Co(edta)]^-$ exists in excess after the reaction, in other words the Λ enan-

Table 1 Stereoselectivity in the $[Co(edta)]^-$ photoreduction* by $[CuL(PPh_3)_2]^+$

Solvent	% v/v	e.e. (%)	τ_0/ns
EtOH–water	60:40	30	256
	75:25	42	265
Pr^iOH–water	60:40	14	208
	75:25	15	212
MeOH–water	60:40	33	279
	75:25	40	285

* Λ-$[Co(edta)]^-$ is preferentially reduced. The selectivity at 10% conversion is given; e.e. calculated from equation (1), experimental errors within ±3%.

tiomer is preferentially reduced by **1** than the Δ enantiomer. The enantiomeric excess of reduced $[Co(edta)]^-$ was estimated from the CD spectra as in equation (1). In this work the e.e. (%)

$$\text{e.e. (\%)} = \frac{\Delta\text{-}[Co(edta)]^-_{\mathbf{reduced}} - \Lambda\text{-}[Co(edta)]^-_{\mathbf{reduced}}}{\text{total } [Co(edta)]^-_{\mathbf{reduced}}} \times 100 \quad (1)$$

values at 10% conversion are given, where the 10% conversion was rather arbitrarily taken (note that the e.e. depends on the conversion). If **1** is oxidized to the corresponding copper(II) complex ($\mathbf{1_{oxid}}$) we must take into consideration the possibility that $\mathbf{1_{oxid}}$ shows a CD spectrum in the visible region. However, the UV/VIS spectrum of **1** changed little in the photoreaction, indicating that $\mathbf{1_{oxid}}$ would be photoreduced to **1** by ethanol involved in the solvent, as reported previously.[7]

Complex **1** gives a considerably high e.e. value of 30% at EtOH–water (60:40 v/v) and a much higher value of 42% at EtOH–water (75:25 v/v), as shown in Table 1. These values are much higher than those previously reported in the $[Co(edta)]^-$ photoreduction by $[Cu(dmphen)\{(R,R)\text{-diop}\}]^+$ {dmphen = 2,9-dimethyl-1,10-phenanthroline, diop = 3,4-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane},[3] and the value of 42% e.e. observed in EtOH–water (75:25 v/v) exceeds the highest value previously reported in the $[Co(edta)]^-$ photoreduction by a chiral ruthenium(II) complex.§,[4c] The e.e. value, as well as the conversion, also significantly depends on the solvent system. As shown in Table 1 the e.e. value increases in the order Pr^iOH–water < EtOH–water ≈ MeOH–water and in the order alcohol–water (60:40 v/v) < alcohol–water (75:25 v/v). Solvent effects on reactivity and stereoselectivity will be discussed below.

Reaction mechanism

The photoinduced electron-transfer reaction is considered to proceed *via* either the dynamic quenching mechanism [equations (2)–(6)] or the static quenching mechanism

$$Cu^I \xrightarrow{\eta h\nu} {}^*Cu^I \quad (2)$$

$$^*Cu^I \xrightarrow{k_d} Cu^I \quad (3)$$

$$^*Cu^I + Co^{III} \xrightarrow{k_r} [Cu^{II}\cdots Co^{II}] \quad (4)$$

$$[Cu^{II}\cdots Co^{II}] \xrightarrow{k_p} Cu^{II} + Co^{II} \quad (5)$$

$$[Cu^{II}\cdots Co^{II}] \xrightarrow{k_b} Cu^{I} + Co^{III} \quad (6)$$

[equations (8)–(13)]. The Stern–Volmer equation (7) is derived

$$I_0/I = \tau_0/\tau = 1 + k_r\tau_0[Co^{III}] \quad (7)$$

$$Cu^I + Co^{III} \underset{}{\overset{K}{\rightleftharpoons}} [Cu^I\cdots Co^{III}] \quad (8)$$

$$[Cu^I\cdots Co^{III}] \xrightarrow{\eta h\nu} [^*Cu^I\cdots Co^{III}] \quad (9)$$

$$[^*Cu^I\cdots Co^{III}] \xrightarrow{k_d'} [Cu^I\cdots Co^{III}] \quad (10)$$

$$[^*Cu^I\cdots Co^{III}] \xrightarrow{k_r'} [Cu^{II}\cdots Co^{II}] \quad (11)$$

$$[Cu^{II}\cdots Co^{II}] \xrightarrow{k_p'} Cu^{II} + Co^{II} \quad (12)$$

$$[Cu^{II}\cdots Co^{II}] \xrightarrow{k_b'} Cu^{I} + Co^{III} \quad (13)$$

from the dynamic quenching reaction, where τ and *I* are the excited-state lifetime and the emission intensity respectively, the subscript '0' represents the absence of quencher and $[Co^{III}]$ is the concentration of the quencher, $[Co(edta)]^-$.

On the other hand, equation (14) is derived from the static

$$I_0/I = 1 + K[Co^{III}] \quad (14)$$

quenching mechanism. Even in this mechanism some part of the copper(I) complex remains free from the adduct, because the latter is in general weak. The free complex contributes to the lifetime of the excited state. This means that the Stern–Volmer equation for the lifetime is given by (15) for this mechanism.

$$\tau_0/\tau = 1 + k_r\tau_0[Co^{III}] \quad (15)$$

Thus, the I_0/I value differs from the τ_0/τ value in the static quenching mechanism, unlike in the dynamic quenching mechanism.

As shown in Fig. 4, τ_0/τ is linearly dependent on the quencher concentration, as expected. It should be noted here that the slope of I_0/I is about three times greater than that of τ_0/τ (Fig. 4 and Table 2). From these results, it can reasonably be concluded that the $[Co(edta)]^-$ photoreduction by **1** proceeds through both static and dynamic quenching mechanisms. The driving force of the static quenching mechanism would be an electrostatic attraction between the negatively charged $[Co(edta)]^-$ and the positively charged **1**.

Elementary process determining the stereoselectivity

Both dynamic and static quenching mechanisms consist of several elementary steps. To clarify which step determines the stereoselectivity we carried out the quenching reaction using the optical isomers Δ- and Λ-$[Co(edta)]^-$. The quenching reaction of complex **1** provides the equilibrium constant *K* for the adduct formation, since the slope of I_0/I is the same as *K* in the static quenching mechanism [see equation (14)]. As clearly shown in Fig. 4(*a*) and Table 2, the slope of I_0/I_Δ (*i.e.* K_Δ) is only slightly larger than that of I_0/I_Λ (*i.e.* K_Λ), where the subscript Δ (or Λ) indicates that Δ-$[Co(edta)]^-$ {or Λ-$[Co(edta)]^-$} is used as a quencher. This means that the adduct formation occurs stereoselectively only to a small extent, and furthermore its stereoselectivity is the reverse of the selectivity of the whole photoreduction.

Then, we measured the excited-state lifetime τ of $[CuL(PPh_3)_2]^+$ in the presence of Δ- or Λ-$[Co(edta)]^-$. The τ_0/τ_Δ and τ_0/τ_Λ values are shown as a function of the concentration of Δ- and Λ-$[Co(edta)]^-$, respectively [Fig. 4(*b*)], where τ_Δ and τ_Λ are the excited-state lifetimes of the copper(I) complex in the presence of Δ- and Λ-$[Co(edta)]^-$, respectively. Apparently, both τ_0/τ_Δ and τ_0/τ_Λ values linearly increase with an increase of the concentration of Δ- and Λ-$[Co(edta)]^-$, respectively. The slopes of these linear relationships correspond to k_r/k_d

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§ In ref. 4*c* k_Δ/k_Λ was reported to be 1.90. From this value, the e.e. of reduced $[Co(edta)]^-$ is estimated to be 33% at 10% conversion.

Table 2 Quenching experiments and the rate constant for encounter-complex formation of $[CuL(PPh_3)_2]^+$

EtOH–water (% v/v)	Slope for I_0/I		Slope for τ_0/τ		$10^{-6}\ k_r{}^c$/dm^3 mol^{-1} s^{-1}	
	Λ^a	Δ^b	Λ^a	Λ^b	Λ	Δ
60:40	1.17 ± 0.09^d	1.17 ± 0.09^d (1.00)^e	4.24 ± 0.08	4.20 ± 0.08 (1.01)^e	16.6	16.4
75:25	1.20 ± 0.09^d	1.21 ± 0.09^d (0.09)^e	5.13 ± 0.08	5.12 ± 0.08 (1.00)^e	20.0	20.0

[a] Λ-$[Co(edta)]^-$ used as a quencher. [b] Δ-$[Co(edta)]^-$ used as a quencher. [c] Estimated using τ_0 given in Table 1. [d] Corresponding to K (dm^3 mol^{-1}) [equation (8)]. [e] Slope (Λ)/slope (Δ).

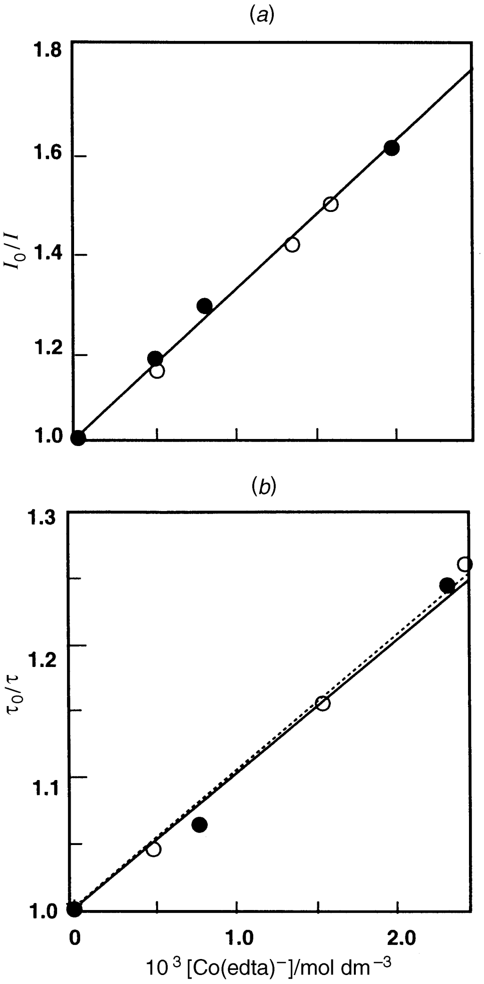

Fig. 4 Stern–Volmer plots for the quenching of $[CuL(PPh_3)_2]^+$ **1** by Δ-$[Co(edta)]^-$ (●) or Λ-$[Co(edta)]^-$ (○). Reaction conditions: [**1**] = 0.10 mmol dm^{-3}, $[Co(edta)]^-$ = 0.10–0.30 mmol dm^{-3}, in EtOH–water (60:40 v/v) at 30 °C

[equations (7) and (15)] where k_d is the reciprocal of the excited-state lifetime τ_0 in the absence of quencher, which can be independently measured, as shown in Table 1. Thus, the k_r value can be estimated from the slope and τ_0. It should be noted that the $k_{r(\Delta)}$ value is almost the same as $k_{r(\Lambda)}$, as clearly shown in Table 2. This means that the formation of encounter complex also occurs stereoselectively only to a small extent.

From the above results, it can be concluded that the stereoselectivity is not determined at the quenching step but at the charge-separation and/or reverse electron-transfer step.

Solvent effects on Φ(Co^{II}) and the stereoselectivity

Since the stereoselectivity appears at the charge-separation and/or reverse-electron-transfer step in both static and dynamic quenching mechanisms, one of the important factors is the contact between Cu^{II} and $[Co^{II}(edta)]^{2-}$ in the adduct (*i.e.* the encounter complex) which is formed after the one-electron transfer from **1** to $[Co(edta)]^-$. This adduct is represented here as [**1**$_{oxid}\cdots$Co(edta)$^{2-}$], to distinguish it from the ground-state adduct, [**1**$\cdots$Co(edta)$^-$]. The strength of the contact would be significantly influenced by the solvent, since the charged species, **1**$_{oxid}$ and $[Co(edta)]^{2-}$, form the ion-pair adduct [**1**$_{oxid}\cdots$Co(edta)$^{2-}$] in a solvent cage through electrostatic interaction. Thus, the solvent effects on reactivity and stereoselectivity are of considerable interest.

In the EtOH–water mixed solvent the stereoselectivity increases as the ethanol content increases, as shown in Table 1. When the ethanol content increases from 60:40 to 75:25 (v/v) the relative permittivity (ε_r) decreases from 42.4 to 34.4. On the other hand, the stereoselectivity increases in the order Pr^{i}OH–water < EtOH–water ≈ MeOH–water (see Table 1), while the relative permittivity increases in the order Pr^{i}OH–water < EtOH–water < MeOH–water. These results indicate that the solvent effects on stereoselectivity do not arise from the solvent polarity. Although a clear understanding of these effects is not easy, one plausible picture might emerge by remembering that the selective solvation occurs in the mixed solvent; for instance, the nickel cation is solvated by water in MeOH–water.[12] In our system $[Co(edta)]^-$ would be mainly solvated by water but **1** would be mainly solvated by ethanol, since the former is hydrophilic and the latter cannot be dissolved in water. If the solvation of **1** and $[Co(edta)]^-$ weaken, the contact between **1** and $[Co(edta)]^-$ would strengthen in the adduct [**1**$_{oxid}\cdots$Co(edta)$^{2-}$], leading to an increase in stereoselectivity. The solvation of **1** would weaken in the order Pr^{i}OH–water < EtOH–water < MeOH–water, while the solvation of $[Co(edta)]^-$ would be little different in Pr^{i}OH–water, EtOH–water and MeOH–water. This would be a reason that the stereoselectivity increases in the order Pr^{i}OH–water < EtOH–water ≈ MeOH–water. When the ethanol content increases in EtOH–water the solvation of **1** strengthens but the solvation of $[Co(edta)]^-$ weakens. This result might be understood if the water solvation of $[Co(edta)]^-$ decreases the stereoselectivity more than does the alcohol solvation of **1**. Although this is one of the most plausible proposals, a more detailed examination is necessary.

The extent of conversion increases with a decrease in ethanol content, and at the same time increases in the order Pr^{i}OH–water < EtOH–water < MeOH–water (see Fig. 2), *i.e.* in the order of increasing solvent polarity. The lifetime of the excited copper(I) complex is not responsible for these results, since it does not differ very much in these solvent systems, as shown in Table 1. One conceivable reason is that the charge-separation step becomes easy in the polar solvent because the products, edta anion and cobalt(II) cation, become stable in this solvent.

Conclusion

The stereoselective photoreduction of $[Co(edta)]^-$ was successfully performed with a new chiral copper(I) complex, **1**, and quenching experiments were carried out to shed some light on the reaction mechanism and the elementary step which determines the stereoselectivity. Important findings are as follows: (1) considerably high stereoselectivity of 42% e.e. was observed in EtOH–water (75:25 v/v), (2) photoreduction proceeds through both static and dynamic quenching mechanisms, (3) the stereoselectvity is not determined at the quenching step but at the charge-separation and/or reverse electron-transfer step, (4) the stereoselectivity increases with a decrease in the solvent polarity and (5) the solvent effects on stereoselectivity are interpreted in terms of the solvation of **1** and [Co(edta)]$^-$.

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