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Novel photo-induced deracemization of $[Co(acac)_3]$ (acac = acetylacetonate) with a chiral ruthenium(II) complex, Δ-$[Ru(menbpy)_3]^{2+}$ (menbpy = 4,4′-bis{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine). Reaction mechanism and significant effects of solvent and anion†

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Deracemization of a racemic mixture of Δ- and Λ-$[Co(acac)_3]$ (acac = acetylacetonate) took place with a chiral ruthenium(II) complex, Δ-$[Ru(menbpy)_3]^{2+}$ (menbpy = 4,4′-bis{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine), under visible light ($420 < \lambda < 470$ nm) irradiation in the presence of either triethylamine or NaOH. The enantiomeric excess (e.e.) of Λ-$[Co(acac)_3]$ was 28% in acetonitrile–water (7 : 3 v/v; ionic strength (I) = 0.1 mol dm^{-3} (KCl)) without acetylacetone and 38% with acetylacetone (50 mmol dm^{-3}) added to the solution. Quenching experiments on Δ-*$[Ru(menbpy)_3]^{2+}$ led to the conclusion that this deracemization occurs through combination of the preferential photo-reduction of Δ-$[Co(acac)_3]$ by Δ-*$[Ru(menbpy)_3]^{2+}$ to afford $[Co(acac)_2]$ and the thermal oxidation of $[Co(acac)_2]$ by Δ-$[Ru(menbpy)_3]^{3+}$ to afford preferentially Λ-$[Co(acac)_3]$. The selectivity of deracemization remarkably depends on the solvent; the e.e. value is 51% in acetone–water (7 : 3 v/v), 38% in ethanol–water (7 : 3 v/v), and 37% in DMF–water (7 : 3 v/v). The e.e. value significantly decreases to 33% from 51% in acetone–water (7 : 3 v/v) when the KCl concentration is increased to 0.3 mol dm^{-3} from 0.1 mol dm^{-3}. When either KF or CH_3CO_2K is added to acetone–water (7 : 3 v/v) instead of KCl the deracemization proceeds much more rapidly without decrease of the e.e. value (≈50%). These counter anion effects are interpreted in terms that the reduction potential of $[Co(acac)_3]$ becomes more negative by addition of either F^- or $CH_3CO_2^-$.

Introduction

Enantioselectivity in thermal[1,2] and photo-induced[3–8] electron transfer (ET) reactions of transition metal complexes has received considerable attention in the last two decades because it is still a challenge to achieve a highly enantioselective ET reaction. Also, one can expect that the latter would be applied to obtain optically active transition metal complexes. One example is optical resolution of a racemic mixture in which one enantiomer is decomposed to a greater extent than the other. However, there are several problems; for instance, the enantioselectivities reported are not high[3–8] and the enantiomer to be obtained as the desired product is also consumed in the reaction. Another example is photo-asymmetric synthesis of one enantiomer from achiral substrates.[9,10] Though this reaction is interesting, only a few examples have been reported and the enantiomeric excess is not high.[9,10]

Deracemization of a racemic mixture is considered a good method to obtain optically active compounds, where deracemization means that one enantiomer in a racemic mixture isomerizes to the other one without change in the total concentration of the enantiomers. Recently, thermal deracemization of $[Fe(4,4'\text{-}Me_2bpy)_3]^{2+}$ (4,4′-Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) was carried out with a chiral anion, (*P*)-tris{tetrachlorobenzene-1,2-dioxy}phosphate ((*P*)-TRIPHAT),[11] where *P* means a plus screw arrangement along the C_3 axis. The enantiomeric excess (e.e.) was extremely high (over 96%). However, application of this deracemization technique seems to be limited to a labile transition metal complex with positive charge. In inert transition metal complexes ligand dissociation from a central metal would not be induced by formation of an ion pair adduct. Also, neutral or negatively charged transition metal complexes cannot form an ion pair adduct with (*P*)-TRIPHAT. On the other hand, transition metal complexes are expected to become labile in either an excited state or a one-electron reduced state which is produced by photo-induced ET reaction, even if they are inert in the ground state or in a usual oxidation state. This suggests that photo-deracemization could be applied to inert transition metal complexes. However, only a few studies of photo-deracemization have been reported and the observed e.e. values were very small; for instance, tris(oxalato)chromate(III)[12] and tris(acetylacetonato)chromium(III)[13] undergo photo-deracemization by circularly polarized light with the e.e. value being only 0.68 and 4.3%, respectively.

One of the present authors (TH) reported highly enantioselective photo-reduction of $[Co(acac)_3]$ (acac = acetylacetonate) with a chiral ruthenium(II) complex, Δ-$[Ru(menbpy)_3]^{2+}$ (menbpy = 4,4′-bis-{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine).[14,15] He also succeeded in photo-induced asymmetric synthesis[9,10] of $[Co(acac)_3]$ from $[Co(acac)_2]$ and $acac^-$ with Δ-$[Ru(menbpy)_3]^{2+}$. When investigating the reductant effects in photo-reduction of $[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^{2+}$, we unexpectedly observed that photo-deracemization of $[Co(acac)_3]$ occurred under visible light irradiation in acetonitrile–water, as reported preliminarily.[16] However, the e.e. value (38%) was not high and the details of this deracemization were not clarified. In this paper we report a considerable improvement of

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† Electronic supplementary information (ESI) available: absorption and CD spectral changes of the reaction solution. See http://www.rsc.org/suppdata/dt/b0/b009124n/

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the e.e. value, significantly large solvent effects and surprising anion effects in this photo-deracemization, and present the reaction mechanism of the photo-deracemization.

Experimental

Materials and preparation

Δ-[Ru(menbpy)$_3$]Cl$_2$ was prepared as reported previously.[14b–d] Calc. for [Ru(menbpy)$_3$]Cl$_2$·5H$_2$O : $C_{96}H_{142}Cl_2N_6O_{17}Ru$: C, 63.21; H, 7.85; N, 4.61%. Found: C, 63.79; H, 7.81; N, 4.38%. Its optical purity was also ascertained with the CD spectrum; $\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1} (λ/nm) = −31.9 (485) and +37.3 (432).[17] A racemic mixture of Δ- and Λ-[Co(acac)$_3$] (*rac*-[Co(acac)$_3$]) was purchased from Nakarai chemical Co. Ltd. (guaranteed grade) and used after recrystallization from ethanol–hexane.[18] All the solvents were distilled before use.

Photoreaction

In a typical run, an acetonitrile–water (7 : 3 v/v) solution containing Δ-[Ru(menbpy)$_3$]Cl$_2$ (32 μmol dm^{-3}), *rac*-[Co(acac)$_3$] (5.0 mmol dm^{-3}), triethylamine (TEA; 0.50 mmol dm^{-3}), and Hacac (0.05 mol dm^{-3}) was prepared, where the ionic strength was adjusted to 0.10 mol dm^{-3} with KCl. This solution was put in a Pyrex cuvette after deaeration through five freeze–pump–thaw cycles, and then irradiated with visible light ($420 < \lambda < 470$ nm) from a 500 W xenon lamp (USHIO UXL-500D) at 25 °C, where the incident light was isolated with a combination of cut-off filters (Toshiba L-42 + KL-46). This incident light corresponds to the metal to ligand charge transfer (MLCT) absorption band of Δ-[Ru(menbpy)$_3$]$^{2+}$ ($\lambda_{max} = 466$ nm and $\varepsilon = 26600$ dm^{-3} mol^{-1} cm^{-1}).[14b–d] Absorption and circular dichroism (CD) spectra were measured with a Hitachi 150–20 spectrophotometer and JASCO J-500 spectropolarimeter, respectively. From these spectra, the concentrations of Δ- and Λ-[Co(acac)$_3$] were evaluated, where molar absorption coefficient (ε) and $\Delta\varepsilon$ values of Δ-[Co(acac)$_3$] were taken from the literature; $\varepsilon = 133$ dm^3 mol^{-1} cm^{-1} [11] and $\Delta\varepsilon = +2.88$ and −8.11 dm^3 mol^{-1} cm^{-1} at 647 and 574 nm,[18] respectively.

Quenching experiment

An acetonitrile–water (7 : 3 v/v) solution containing Δ-[Ru(menbpy)$_3$]Cl$_2$ (0.10 mmol dm^{-3}), KCl (0.10 mol dm^{-3}), and a quencher such as [Co(acac)$_3$], [Co(acac)$_2$], acac$^-$, or TEA (0.10–3.0 mmol dm^{-3}) was put in a Pyrex cell after deaeration through five freeze–pump–thaw cycles. The lifetime of Δ-[Ru(menbpy)$_3$]$^{2+}$ was measured with a time-resolved fluorometer, Horiba NAES-700D, at 25 °C, where the incident light ($410 < \lambda < 500$ nm) was isolated with a combination of cut-off filters (Toshiba L-42 + U390).

CV Measurements

The cyclic voltammogram of [Co(acac)$_3$] was recorded at room temperature under an argon atmosphere with an electroanalyzer (ALS model 600A). A glassy carbon electrode was used as a working electrode. A sample solution was prepared by dissolving [Co(acac)$_3$] (0.5 mmol dm^{-3}) in acetone–water, acetonitrile–water, DMF–water, or EtOH–water mixed solvent, where tetra-n-buthylammonium hexafluorophosphate (0.1 mol dm^{-3}) and tetra-n-butylammonium perchlorate (0.1 mol dm^{-3}) were added to the first three solvents and the last one, respectively. Tetra-n-butylammonium perchlorate was used in EtOH–water solvent because NBu$^n_4$PF$_6$ could not be dissolved in this solvent.

Results and discussion

Effects of triethylamine concentration on the enantioselectivity of photo-deracemization of [Co(acac)$_3$]

As reported in our preliminary communication,[16] the absorption spectrum of [Co(acac)$_3$] and Δ-[Ru(menbpy)$_3$]Cl$_2$ in acetonitrile–water changed little upon visible light irradiation in the presence of TEA (0.50 mmol dm^{-3}), but the CD spectrum corresponding to Λ-[Co(acac)$_3$] appeared. These spectra are given as ESI. From these spectra the concentrations of Δ- and Λ-[Co(acac)$_3$] were evaluated. As shown in Fig. 1, the concentration of Δ-[Co(acac)$_3$] decreased and that of Λ-[Co(acac)$_3$] increased after a few hours of induction. Their concentration changes stopped after 50 h and the reaction reached a stationary state. The e.e. value at the stationary state (after 50 h) was 28%, where about 10% of [Co(acac)$_3$] was decomposed (see entry 3 of Table 1). From these results it can clearly be concluded that deracemization of [Co(acac)$_3$] occurs photo-chemically.

Table 1 The enantiomeric excess of Λ-[Co(acac)$_3$] and consumption of [Co(acac)$_3$] in the photo-reaction of [Co(acac)$_3$] with Δ-[Ru(menbpy)$_3$]$^{2+}$ at the stationary state[a]

Entry	[TEA]/ mmol dm^{-3}	e.e. (%)	Consumption of [Co(acac)$_3$] (%)	TSS[b]/ h
1	0	6	3	102
2	0.25	20	5	127
3	0.50	28	10	50
4	1.0	32	19	26
5	2.0	31	26	6
6	5.0	31	47	1.8

[a] [Δ-Ru(menbpy)$_3$]$^{2+}$ = 32 μmol dm^{-3}, [Co(acac)$_3$] = 5.0 mmol dm^{-3}, [KCl] = 0.10 mol dm^{-3} in acetonitrile–water (7 : 3 v/v). [b] Time to reach the stationary state.

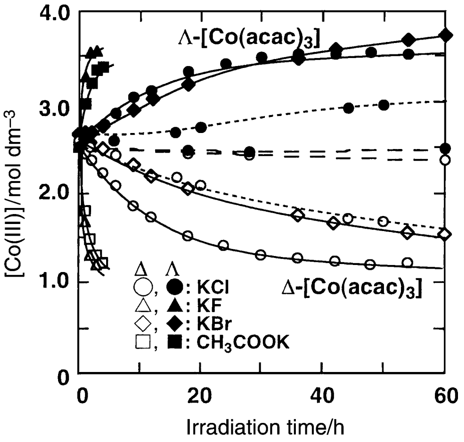


Fig. 1 The concentration changes of Δ- and Λ-[Co(acac)$_3$] in acetonitrile–water (7 : 3 v/v) at 25 °C. Δ-[Ru(menbpy)$_3$]$^{2+}$ = 32 μmol dm^{-3}, [Co(acac)$_3$] = 5.0 mmol dm^{-3}, [Hacac] = 50 mmol dm^{-3}, [TEA] = 0.5 mmol dm^{-3}. Broken lines (---) represent the reaction in the absence of both Hacac and TEA, dotted lines (······) that in the absence of Hacac.

When TEA was not added to the solution the deracemization hardly occurred, as shown by entry 1 of Table 1. Even after 102 h irradiation the e.e. value and the consumption of [Co(acac)$_3$] were only 6 and 3%, respectively. However, the e.e. value at the stationary state moderately increased to 32 and 31% at [TEA] = 1.0 and 2.0 mmol dm^{-3}, respectively. It is also noted that the reaction reached the stationary state earlier and more [Co(acac)$_3$] was consumed, as the TEA concentration was increased (entries 2–5 of Table 1); for instance, the time necessary to reach the stationary state (TSS) was only 6 h and 26% of [Co(acac)$_3$] was decomposed at [TEA] = 2.0 mmol dm^{-3}. When the TEA concentration was high (5.0 mmol dm^{-3}) the reaction reached the stationary state in 1.8 h, while 47% of [Co(acac)$_3$] was decomposed. These results indicate that deracemization can occur when the TEA concentration is appropriate but the usual catalytic photo-reduction of [Co(acac)$_3$] preferentially occurs when the TEA concentration is high.

Table 2 Hacac and NaOH concentration effects in the photo-deracemization of [Co(acac)$_3$][a]

Entry	[TEA]/ mmol dm^{-3}	[Hacac]/ mol dm^{-3}	[NaOH]/ mmol dm^{-3}	e.e.[b] (%)	Consumption of [Co(acac)$_3$][b] (%)	TSS/h
7	0.5	0.050	0	38	1.7	32
8	0	0.050	0	5.7	3	24
9	0	0.050	0.1	13	1.0	24[c]
10	0	0.050	0.5	38	5.5	24
11	0	0.15	0.5	38	3.7	18
12	0	0.25	0.5	39	5.2	24

[a] Δ-[Ru(menbpy)$_3$]$^{2+}$ = 32 μmol dm^{-3}, [Co(acac)$_3$] = 5.0 mmol dm^{-3}, [KCl] = 0.10 mol dm^{-3} in acetonitrile–water (7 : 3 v/v). [b] At the stationary state. [c] The reaction did not reach the stationary state in this run.

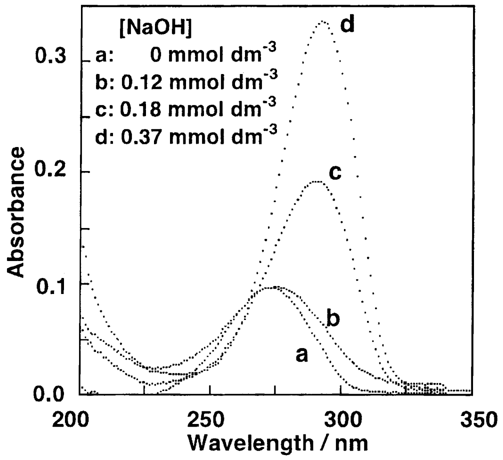
When acetylacetone (50 mmol dm^{-3}) was added to the reaction solution with TEA (0.50 mmol dm^{-3}) the concentration of Λ-[Co(acac)$_3$] increased immediately without an induction period, and the reaction reached the stationary state earlier (see entry 7 of Table 2 and Fig. 1). Furthermore, the e.e. increased to 38 from 28%, and decomposition of [Co(acac)$_3$] was suppressed to 1.7% by addition of Hacac. In the absence of TEA (entry 8 of Table 2) the deracemization hardly occurred even in the presence of Hacac (50 mmol dm^{-3}), where the e.e. value (5.7%) was very small. From these results it is clearly concluded that not only TEA but also Hacac is necessary for this photo-deracemization.

TEA is a well known reductant, while it also plays a role of Lewis base. In order to investigate which role TEA plays the reaction was carried out with NaOH instead of TEA. When NaOH (0.5 mmol dm^{-3}) was added to the solution the deracemization proceeded well and an e.e. value of 38% was observed (entries 10–12 of Table 2). This e.e. value was the same as that observed in the reaction carried out with TEA (0.5 mmol dm^{-3}). Upon addition of either NaOH or TEA the absorption maximum (λ_{max}) of Hacac shifted to longer wavelength and became significantly large, as shown in Fig. 2(A). We plotted the λ_{max} value against the concentrations of TEA and NaOH, as shown in Fig. 2(B). We also examined plots of the molar absorption coefficient against the concentrations of TEA and NaOH. These plots are almost the same as those of Fig. 2(B). These results clearly indicate that deprotonation of Hacac occurs upon addition of NaOH and TEA. The plots of λ_{max} against the concentration of NaOH and TEA [Fig. 2(B)] show that Hacac completely converts into acac$^-$ by addition of 0.50 mmol dm^{-3} of NaOH and 5.0 mmol dm^{-3} of TEA. From these results, it can reasonably be concluded that TEA plays a role of Lewis base in this photo-deracemization and that acac$^-$ is indispensable for this reaction.

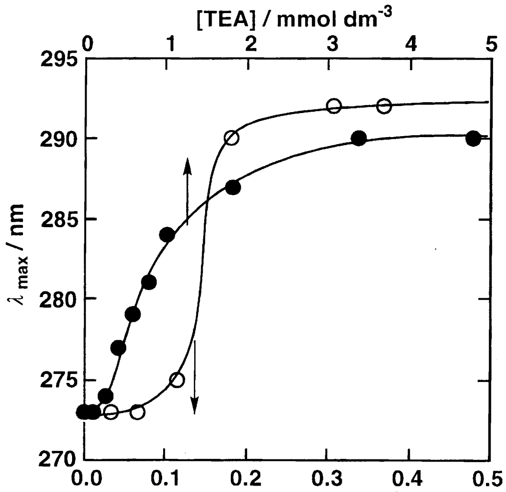
Solvent effects

The photo-deracemization remarkably depends on the solvent, as shown in Table 3. The best e.e. value of 51% was observed in acetone–water (7 : 3 v/v) and the e.e. value decreased in the order acetone–water (7 : 3 v/v) ≫ acetonitrile–water (7 : 3 v/v) ≈ EtOH–water (7 : 3 v/v) ≈ DMF–water (7 : 3 v/v). TSS becomes longer in the order EtOH–water (7 : 3 v/v) < DMF–water (7 : 3 v/v) < acetonitrile–water (7 : 3 v/v) < acetone–water (7 : 3 v/v) (see entries 13–15 and 18). Though TSS in EtOH–water (7 : 3 v/v) was the shortest, decomposition of [Co(acac)$_3$] to [Co^{II}(acac)$_2$] was considerable (28%) in this solvent (entry 13 of Table 3). This is because EtOH plays a role of reductant to convert ruthenium(III) into ruthenium(II).[14b–d] Also, a considerable amount of [Co(acac)$_3$] was consumed in DMF–water (7 : 3 v/v). On the other hand, decomposition of [Co(acac)$_3$] was significantly suppressed in acetonitrile– and acetone–water (7 : 3 v/v), 1.7 and 6.5% respectively. Thus, these are good solvents for deracemization but EtOH–water is not. DMF–water is intermediate.

Since the acetone–water solvent provides the large e.e. value without consumption of [Co(acac)$_3$], we varied the solvent composition in this mixed solvent. When the acetone content was increased to 90% the TSS became short with little change of the e.e. value, as shown in Table 3 (entry 17). On the other hand, when it was decreased to 50% the e.e. value became smaller (43%) with little change of TSS (see entry 19 in Table 3). However, when the acetonitrile content was decreased to 50% in acetonitrile–water solvent the e.e. value changed little (see entries 10 and 16 in Tables 2 and 3). The above results will be discussed below in more detail after discussion of the reaction mechanism.



(A) Absorption spectral change of acetylacetone



(B) Absorption maximum (λ_{max}) *vs*. base concentration

Fig. 2 (A) Absorption spectral changes of acetylacetone (16 μmol dm^{-3}) in acetonitrile–water (7 : 3 v/v) with addition of NaOH. (B) Absorption maximum change of acetylacetone in the presence of NaOH (○) and TEA (●) in acetonitrile–water (7 : 3 v/v).

Table 3 Solvent effects in the photo-deracemization of $[Co(acac)_3]$[a]

Entry	Solvent	[TEA]/ mmol dm^{-3}	e.e[b] (%)	Consumption of $[Co(acac)_3]$[b] (%)	TSS/h
13	EtOH–water 7 : 3	0.5	38	28	18
14	DMF–water 7 : 3	0.5	37	11	30
15	Acetonitrile–water 7 : 3	0.5	38	1.7	32
16	5 : 5	1.0	38	7	50
17	Acetone–water 9 : 1	0.5	50	9.8	24
18	7 : 3	0.5	51	6.5	54
19	5 : 5	0.5	43	8.2	54

[a] Δ-$[Ru(menbpy)_3]^{2+}$ = 32 μmol dm^{-3}, $[Co(acac)_3]$ = 5.0 mmol dm^{-3}, [Hacac] = 0.05 mol dm^{-3}, [KCl] = 0.10 mol dm^{-3} at the stationary state. [b] At the stationary state.

Table 4 Salt effects on the e.e. value and consumption of $[Co(acac)_3]$ in the photo-deracemization[a]

Entry	Salt	[Salt]/ mol dm^{-3}	e.e.[b] (%)	Consumption of $[Co(acac)_3]$[b]	TSS/h
20	KCl	0.00	51	6.5	54
21	KCl	0.01	49	13	48
22	KCl	0.05	50	7.6	54
23	KCl	0.10	51	6.5	54
24	KCl	0.20	45	1.6	48
25	KCl	0.30	33	0.0	60
26	KF	0.01	50	8.5	8
27	KF	0.05	51	9.4	3
28	KF	0.10	50	10	3
29	KF	0.15	49	14	2
30	KBr	0.10	43	8.2	54
31	CH_3CO_2K	0.10	47	8.0	4

[a] Δ-$[Ru(menbpy)_3]^{2+}$ = 32 μmol dm^{-3}, $[Co(acac)_3]$ = 5.0 mmol dm^{-3}, [Hacac] = 0.050 mol dm^{-3}, [TEA] = 0.50 mmol dm^{-3} in acetone–water (7 : 3 v/v) at 25 °C. [b] At the stationary state.

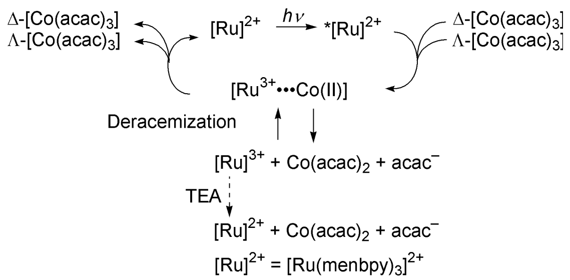
Salt effects

Since $[Ru(menbpy)_3]^{2+}$ is positively charged its adduct formation with $[Co(acac)_3]$ would be influenced by a co-existing anion. Actually, the e.e. value significantly depends on the KCl concentration, as shown in Table 4. Though the e.e. value changed little when the KCl concentration was decreased to 0.01 mol dm^{-3} from 0.1 mol dm^{-3}, the e.e. value decreased sharply to 33 from 51% when the KCl concentration was increased to 0.3 mol dm^{-3} from 0.1 mol dm^{-3} in acetone–water (7 : 3 v/v) (see entries 20–25 of Table 4). This is probably because $[Ru(menbpy)_3]^{2+}$ forms an ion pair adduct with Cl^- at the high concentration of KCl and the contact between $[Ru(menbpy)_3]^{2+}$ and $[Co(acac)_3]$ is weakened by Cl^-. Similar behaviour was previously presented in the enantioselective quenching reaction of Δ-*$[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) by $[Co(edta)]^-$ ($edta^{4-}$ = ethylenediaminetetraacetate).[5]

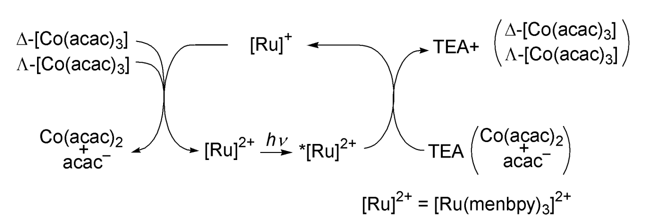
In order to investigate the salt effects in more detail, various salts such as KF, KBr, and CH_3CO_2K were applied to the reaction. Although the e.e. value was little influenced, the reaction proceeded very rapidly when KF and CH_3CO_2K were used, as shown in Fig. 1. The reduction potential of $[Co(acac)_3]$ was measured in the presence of these salts. Interestingly, it is most positive in the presence of CH_3CO_2K and next in KF. Since the explanation is deeply related to the reaction mechanism the details will be presented after discussion of the reaction mechanism.

Reaction mechanism

Two types of reaction mechanism are considered possible in this photo-deracemization, as shown in Schemes 1 and 2; in one (Scheme 1) the photo-excited *$[Ru(menbpy)_3]^{2+}$ is oxidatively quenched by $[Co(acac)_3]$ to form an exciplex with $[Co(acac)_3]$ followed by electron transfer to $[Co(acac)_3]$ from *$[Ru(menbpy)_3]^{2+}$, leading to a successor complex, $[Ru^{III}(menbpy)_3{}^{3+}\cdots Co^{II}(acac)_3{}^-]$. This successor complex dissociates to $[Ru^{III}(menbpy)_3]^{3+}$, $[Co(acac)_2]$, and $acac^-$. Part of $[Ru^{III}(menbpy)_3]^{3+}$ is reduced to $[Ru^{II}(menbpy)_3]^{2+}$ by TEA, if TEA is used in the reaction. Remaining $[Ru^{III}(menbpy)_3]^{3+}$ undergoes the reverse reaction with $[Co(acac)_2]$ and $acac^-$ to form $[Co(acac)_3]$ and $[Ru(menbpy)_3]^{2+}$. This reaction is considered to proceed through an encounter complex, $[Ru^{III}(menbpy)_3{}^{3+}\cdots Co^{II}(acac)_3{}^-]$. If the reduction of $[Co(acac)_3]$ by Δ-*$[Ru(menbpy)_3]^{2+}$ occurs enantioselectively and the oxidation of $[Co(acac)_2]$ to $[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^{3+}$ also with the opposite enantioselectivity, deracemization takes place. Actually, our previous experiments clearly showed that Δ-$[Co(acac)_3]$ was more rapidly photo-reduced by Δ-$[Ru(menbpy)_3]^{2+}$ than Λ-$[Co(acac)_3]$ in EtOH–water under visible light irradiation[14b–d] and that Λ-$[Co(acac)_3]$ was preferentially



Scheme 1



Scheme 2

Table 5 The rate constant of the quenching reaction of Δ-[Ru(menbpy)$_3$]$^{2+}$ by various quenchers[a]

Quencher	k_q/dm^3 mol^{-1} s^{-1}
Δ-[Co(acac)$_3$)]	(1.62 ± 0.02) × 10^8
Λ-[Co(acac)$_3$]	(1.45 ± 0.02) × 10^8
Co(acac)$_2$	(6.90 ± 0.32) × 10^7
acac[b]	(1.80 ± 0.02) × 10^7
TEA	(3.80 ± 0.21) × 10^7

[a] [Ru(menbpy)$_3$]$^{2+}$ = 32 μmol dm^{-3}, [Co(acac)$_3$] = 5.0 mmol dm^{-3}. In acetonitrile–water (7 : 3 v/v) at 25 °C. [b] In the presence of [NaOH] (1.5 × 10^{-1} mol dm^{-3}).

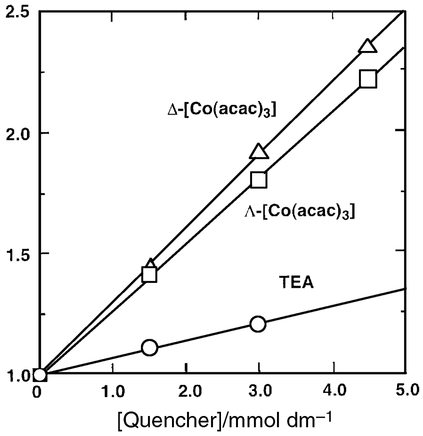


Fig. 3 Stern–Volmer plots for the quenching of Δ-[Ru(menbpy)$_3$]$^{2+}$ by Δ-[Co(acac)$_3$] (△), Λ-[Co(acac)$_3$] (□), and TEA (○) in acetonitrile–water (7 : 3 v/v) at 25 °C.

produced from [Co(acac)$_2$] and Hacac by [Ru(menbpy)$_3$]$^{2+}$ under visible light irradiation in the presence of O_2.[9] These results are consistent with the enantioselectivity of the photo-deracemization.

In the other mechanism (Scheme 2), Δ-*[Ru(menbpy)$_3$]$^{2+}$ is reductively quenched by either TEA or the reduction products, [Co(acac)$_2$] and acac$^-$, to afford one electron reduced Δ-[Ru(menbpy)$_3$]$^+$. Our pulse radiolysis experiment of Δ-[Ru(menbpy)$_3$]$^{2+}$ revealed that Δ-[Ru(menbpy)$_3$]$^+$ enantioselectively reduced [Co(acac)$_3$] with the selectivity of 2.7 (k_Δ/k_Λ) in 85% EtOH–water.[17] If [Co(acac)$_3$] is formed enantioselectively through reductive quenching of Δ-*[Ru(menbpy)$_3$]$^{2+}$ by [Co(acac)$_2$], deracemization should take place.

To clarify through which mechanism the photo-deracemization occurs, we investigated the quenching reaction of *[Ru(menbpy)$_3$]$^{2+}$ with [Co(acac)$_3$] and TEA. The τ_0/τ value linearly increases as the concentration of the quencher ([Co(acac)$_3$] or TEA) increases, as shown in Fig. 3, where τ and τ_0 are the lifetime in the presence of the quencher and that in the absence of the quencher, respectively. The τ_0/τ value is represented with the usual Stern–Volmer equation (1), where [Q] is

$$\tau_0/\tau = 1 + k_q\tau_0[\mathrm{Q}] \qquad (1)$$

the concentration of quencher. From this relation the quenching rate constant (k_q) can easily be estimated. The estimated oxidative quenching rate constant (1.62 ± 0.02) × 10^8 dm^3 mol^{-1} s^{-1}, by Δ-[Co(acac)$_3$] is somewhat larger than that, (1.45 ± 0.02) × 10^8 dm^3 mol^{-1} s^{-1} by Λ-[Co(acac)$_3$], as shown in Table 5. It should be noted that the oxidative quenching by [Co(acac)$_3$] occurs much more rapidly than reductive quenching by [Co(acac)$_2$], acac$^-$ and TEA (see Table 5). However, the quenching of Δ-*[Ru(menbpy)$_3$]$^{2+}$ by [Co(acac)$_3$] occurs not only through electron transfer but also through energy transfer in EtOH–water (85 : 15 v/v).[17] Since the above mentioned quenching rate constants are not significantly different between [Co(acac)$_3$] and TEA, it is still ambiguous through which reaction mechanism the photo-deracemization occurs.

If the photo-deracemization takes place through the mechanism of Scheme 2, *[Ru(menbpy)$_3$]$^{2+}$ is reduced by [Co(acac)$_2$], acac$^-$ and/or TEA. The k_q value with [Co(acac)$_2$] is about 2 to 4 times larger than those with TEA and acac$^-$. However, the concentration of [Co(acac)$_2$] is reasonably considered to be much lower than that of acac$^-$, because the concentration of acac$^-$ is 10 times as large as that of [Co(acac)$_3$] (see the reaction conditions). The concentration of TEA (0.5 mmol dm^{-3}) is also much lower than that of acac$^-$ (0.05 mol dm^{-3}). Thus, the quenching by TEA and [Co(acac)$_2$] can be neglected and the quenching by acac$^-$ would occur mainly by the reductive quenching mechanism. If so, [Ru(menbpy)$_3$]$^+$ is produced by acac$^-$ and then reduces [Co(acac)$_3$] to [Co(acac)$_2$], which leads to accumulation of [Co(acac)$_2$] in the solution. Even if the concentration of [Co(acac)$_2$] was the same as that of acac$^-$, about 25% of [Ru(menbpy)$_3$]$^+$ was produced by acac$^-$ and about 75% of [Ru(menbpy)$_3$]$^+$ by [Co(acac)$_2$] (note that the k_q value with acac$^-$ is about one-fourth of that with [Co(acac)$_2$]); in other words, [Co(acac)$_2$] was produced by [Ru(menbpy)$_3$]$^+$ and thereby accumulated in the reaction. This is against the experimental result that [Co(acac)$_2$] is little observed. From these results, it is reasonably concluded that the photo-induced deracemization occurs through the reaction mechanism of Scheme 1 which involves oxidative quenching of *[Ru(menbpy)$_3$]$^{2+}$ by [Co(acac)$_3$]. It should also be noted that the enantioselectivity in the oxidative quenching is much smaller than that of the deracemization. This suggests that the enantioselectivity of the deracemization would mainly result from the re-oxidation process.

At the end of this section we wish to mention that the enantioselectivity in the oxidative quenching is reverse to that in the re-oxidation processes. As reported previously, oxidative quenching occurs faster for the homochiral pair, Δ-[Ru(menbpy)$_3$]$^{2+}$ and Δ-[Co(acac)$_3$], than that for the heterochiral one, Δ-[Ru(menbpy)$_3$]$^{2+}$ and Λ-[Co(acac)$_3$]. This suggests that the homochiral adduct $\mathbf{A}_{\Delta\text{-}\Delta}$, Δ-[Ru(menbpy)$_3$]$^{3+}$ ··· Δ-[Co(acac)$_3$]$^-$, is more stable than the heterochiral adduct $\mathbf{A}_{\Delta\text{-}\Lambda}$, Δ-[Ru(menbpy)$_3$]$^{3+}$ ··· Λ-[Co(acac)$_3$]$^-$, as shown in Scheme 3, where we use "adduct **A**" and "adduct **B**" for [Ru(menbpy)$_3$]$^{3+}$ ··· [Co(acac)$_3$]$^-$ and [Ru(menbpy)$_3$]$^{2+}$ ··· [Co(acac)$_3$], respectively.‡ The energy difference between the homochiral and heterochiral adducts is reasonably considered smaller in the adduct **B** than that in **A**, because the electrostatic attraction between two ions increases the contact in adduct **A**. Hence, the energy difference in the transition state between homochiral and heterochiral reactions would be smaller than the energy difference in the adduct **A**, which leads to a larger activation energy in the re-oxidation of the homochiral adduct $\mathbf{A}_{\Delta\text{-}\Delta}$ than that in re-oxidation of the heterochiral adduct $\mathbf{A}_{\Delta\text{-}\Lambda}$, as shown in Scheme 3. Thus, the enantioselectivity of the re-oxidation reaction is reverse to that of the oxidative quenching reaction.

Origins of solvent and anion effects

Anion effects on the TSS will be discussed here based on the mechanism shown in Scheme 1. The reduction potential of [Co(acac)$_3$] in acetone depends on the anion, as follows: the $E_{1/2}$(Co$^{\text{III/II}}$) value is −0.35 V (*vs.* SCE) in the presence of KBr, −0.39 V in the presence of KCl, −0.41 V in the absence of any anion, −0.44 V in the presence of KF, and −0.46 V in the presence of CH_3CO_2K. Since the TSS is short in the presence of

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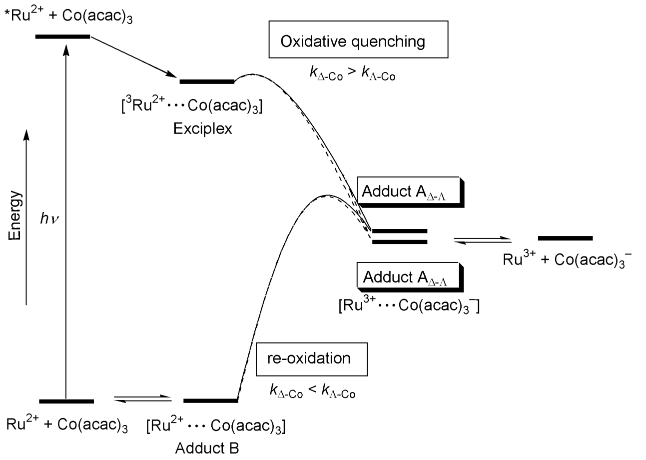
‡ Δ-[Ru(menbpy)$_3$]$^{3+}$ ··· Δ-[Co(acac)$_3$]$^-$ is named a successor complex in the oxidative quenching reaction, but an encounter complex in the re-oxidation of Co(acac)$_2$ by [Ru(menbpy)$_3$]$^{3+}$. To avoid the confusion, we refer to [Ru(menbpy)$_3$]$^{3+}$ ··· [Co(acac)$_3$]$^-$ as adduct **A** and [Ru(menbpy)$_3$]$^{2+}$ ··· [Co(acac)$_3$] as adduct **B**.



Scheme 3

KF and CH_3CO_2K, as discussed above, it is reasonably concluded that deracemization rapidly occurs when reduction of [Co(acac)$_3$] to [Co(acac)$_3$]$^-$ is difficult, in other words when re-oxidation of [Co(acac)$_3$]$^-$ to [Co(acac)$_3$] occurs easily. This means that the rate-determinating step of this deracemization is the oxidation of [Co(acac)$_2$] by Δ-[Ru(menbpy)$_3$]$^{3+}$ to afford [Co(acac)$_3$].

Here, let us compare the e.e. values in DMF–water, acetonitrile–water, and acetone–water, the EtOH–water solvent being excluded from the comparisons because reduction of [Co(acac)$_3$] occurs considerably in this solvent. The relative permittivity (dielectric constant) at 25 °C decreases in the order DMF (37.8) ≈ acetonitrile (37.5) > acetone (20.3),[19] and the e.e. value increases in the order DMF–water < acetonitrile–water < acetone–water, where the values in parentheses are the dielectric constants at 25 °C.[19] These results suggest that the use of a less polar solvent leads to the larger e.e. value.

However, we must remember that the e.e. value little changes in acetonitrile–water upon increase of the water content from 30 to 50 vol%. In acetone–water the e.e. value also changes little upon decrease of the water content from 30 to 10 vol%, while it decreases upon increase of the water content from 30 to 50 vol%. Though these results do not seem consistent with the above discussion about the relationship between the solvent polarity and e.e. value, the water content effects can reasonably be understood, as follows: [Ru(menbpy)$_3$]$^{2+}$, [Co(acac)$_3$], and [Co(acac)$_2$] tend to be solvated by organic solvent, because of their hydrophobicity. As a result, only when the water content is sufficiently high would these complexes be solvated with water, and the reaction proceed in a polar atmosphere. Thus, the e.e. value is very sensitive to the water content.

The next question is why the less polar solvent is favorable for the deracemization. The e.e. value would increase when *[Ru(menbpy)$_3$]$^{2+}$ more closely contacts with [Co(acac)$_3$] in the exciplex and the transition state of the oxidative quenching process, and/or when [Ru(menbpy)$_3$]$^{3+}$ more closely contacts with [Co(acac)$_3$]$^-$ in the ion-pair adduct and the transition state of the re-oxidation processes. Since the contact between [Ru(menbpy)$_3$]$^{3+}$ and [Co(acac)$_3$]$^-$ is considered to be closer than that between [Ru(menbpy)$_3$]$^{2+}$ and [Co(acac)$_3$] due to the electrostatic attraction (see above), it is reasonably suggested that the enantiomeric excess would mainly depend on the contact between [Ru(menbpy)$_3$]$^{3+}$ and [Co(acac)$_3$]$^-$. This suggestion is consistent with the above discussion that the enantioselectivity mainly results from the re-oxidation process. The solvent polarity significantly influences the contact between [Ru(menbpy)$_3$]$^{3+}$ and [Co(acac)$_3$]$^-$, as follows: since the polar solvent strongly solvates the charged species it results in looser contact between the reactant ions, [Ru(menbpy)$_3$]$^{3+}$ and [Co(acac)$_3$]$^-$, in the ion pair and/or the transition state of the re-oxidation process, which leads to decrease of the e.e. value. On the other hand, the less polar solvent provides closer contact between the ions than does the polar solvent, which leads to increase of the e.e. value.

Conclusion

In this work we investigated the photo-induced deracemization of [Co(acac)$_3$] with the chiral photo-sensitizer Δ-[Ru(menbpy)$_3$]$^{2+}$. The e.e. value of 51% observed in acetone–water (7 : 3 v/v; $I = 0.1$ mol dm^{-3}) is much higher than that reported previously in photo-deracemization of tris(oxalato)chromate (0.68%) and tris(acetylacetonate)chromium (4.3%). The e.e. value remarkably depends on the solvent system, and the best solvent is acetone–water. It also considerably depends on the ionic strength (I) and decreases to 37% upon increase of I to 0.30 mol dm^{-3} in acetone–water (7 : 3 v/v).

Two reaction mechanisms are considered possible: in one *[Ru(menbpy)$_3$]$^{2+}$ is oxidatively quenched by [Co(acac)$_3$], to yield [Co(acac)$_2$] and acac$^-$, followed by oxidation of [Co(acac)$_2$] by [Ru(menbpy)$_3$]$^{3+}$ to regenerate [Co(acac)$_3$]. In the other *[Ru(menbpy)$_3$]$^{2+}$ is reductively quenched by TEA, [Co(acac)$_2$], and acac$^-$, to afford one-electron reduced Δ-[Ru(menbpy)$_3$]$^+$, which enantioselectively reduces [Co(acac)$_3$] to [Co(acac)$_2$] and acac$^-$, concomitantly with regeneration of [Ru(menbpy)$_3$]$^{2+}$. From the rate constants for reductive quenching by [Co(acac)$_2$] and acac$^-$, it is reasonably concluded that photo-deracemization occurs through enantioselective reduction of [Co(acac)$_3$] by Δ-*[Ru(menbpy)$_3$]$^{2+}$ and enantioselective oxidation of [Co(acac)$_2$] by Δ-[Ru(menbpy)$_3$]$^{3+}$.

The essence of this deracemization is interesting: [Co(acac)$_3$] can be reduced by photo-excited Δ-*[Ru(menbpy)$_3$]$^{2+}$ to yield [Co(acac)$_2$] and acac$^-$, since Δ-*[Ru(menbpy)$_3$]$^{2+}$ has a more negative redox potential than that of [Co(acac)$_3$]. Δ-[Ru(menbpy)$_3$]$^{3+}$ can oxidize [Co(acac)$_2$] to afford [Co(acac)$_3$] since Δ-[Ru(menbpy)$_3$]$^{3+}$ has a more positive redox potential than that of [Co(acac)$_2$]. In other words, the negative redox potential of the photo-excited *[Ru(menbpy)$_3$]$^{2+}$ and the positive redox potential of the one-electron oxidized species, [Ru(menbpy)$_3$]$^{3+}$ are skilfully utilized in this deracemization. This is expected to provide us with new applications of photochemical reactions by transition metal complexes.

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