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Isomer Distribution and Stereoselectivity in Electron Transfer Reactions of $[Co(dien)_2]^{2+}$ with Anionic Cobalt(III) Complexes

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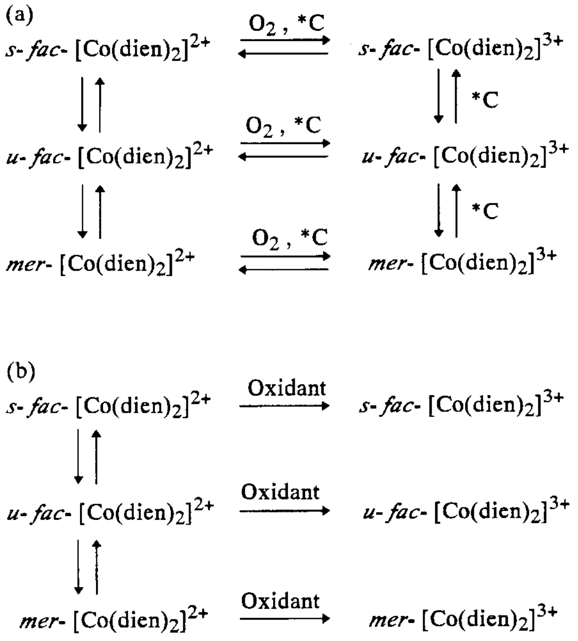
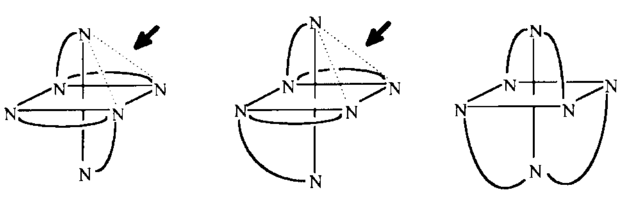
The product distribution of the three geometrical isomers and the stereoselectivity of the *u-fac* isomer in the oxidation of $[Co(dien)_2]^{2+}$ (dien = diethylenetriamine) by optically active anionic cobalt(III) complexes were significantly influenced by the geometrical arragement of the coordinated atoms in the oxidants, reflecting the differences in the stabilization of the precursor assemblies due to the hydrogen bonding interactions between the reactants. Solvent effects on the isomer proportions and the stereoselectivity were examined in water, methanol, ethanol, formamide, dimethylformamide, and dimethyl sulfoxide. The results are explained in terms of the differences in the degree of oxidant-solvent interactions depending on acceptor number of solvents.

The tridentate ligand, dien, can bind to metal ions in three ways: *s-fac*, *u-fac*, and *mer* isomers (Chart 1). It is known that when the aerial oxidation products of $[Co(dien)_2]^{2+}$ are equilibrated in the presence of charcoal, the isomer proportions of $[Co(dien)_2]^{3+}$ are profoundly influenced by many factors such as added anion, solvent, and temperature.[1] However, in the absence of charcoal, the effects of different oxidants are not known. The isomer proportions and the stereoselectivity of the oxidation products in the absence of charcoal are expected to be significantly different from those in the presence of charcoal because charcoal catalyzes racemization and isomer interconversions not only between the Co(II)–Co(III) redox couples but also between the isomers of Co(III) complex (Scheme 1).

Thus, it should be helpful in understanding the effective interactions between metal complexes in the electron transfer reaction to obtain information on the stereoselectivity of the *u-fac* isomer as well as on the geometrical selectivity in the oxidation of $[Co(dien)_2]^{2+}$ by various anionic cobalt(III) complexes. Many investigations on the stereoselective interactions between metal complexes in solution have been made. Among them, Miyoshi and Yoneda noted that interionic hydrogen bonds play a major role in stereoselective ion association. They proposed the association models represented as the C_3–C_3, C_3–C_2, and C_2–C_2 interaction modes in which chiral discrimination between the cationic and anionic complexes is effected along either the (*pseudo*-)C_3 or the (*pseudo*-)C_2 axis of the respective complexes.[2] We previously studied the stereoselective electron transfer reactions of $[Co(en)_3]^{2+}$ (en = ethylenediamine) with various kinds of oxidant cobalt(III) complexes.[3] The stereoselectivity in the reactions was shown to be less sensitive to the changes in charge on the oxidants from −3 to −1, although the rates of these reactions span three orders of the magnitude in the rate



Scheme 1. (a) Aerial oxidation of $[Co(dien)_2]^{2+}$ in the presence of charcoal. (b) Oxidation of $[Co(dien)_2]^{2+}$ by anionic Co(III) complexes in the absence of charcoal.



s-fac *u-fac* *mer*

Chart 1. Geometrical isomers of $[Co(dien)_2]^{2+/3+}$. *s-fac* (left) and *u-fac* (center) are shown to have the unhindered three NH groups along the *pseudo*-C_3 axis.

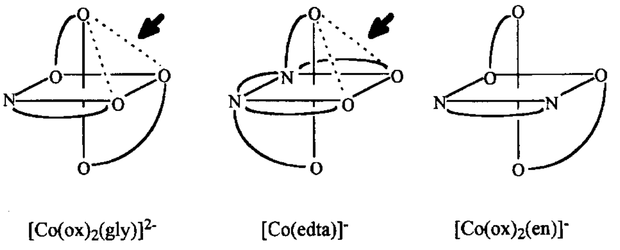
constants. The temperature effect on the stereoselectivity revealed that the reactions proceed through two different types of activated complexes, depending on whether or not the oxidant possesses sterically unhindered *pseudo*-C_3 carboxylate face available for hydrogen bonding (Chart 2).[4] Further, it was shown that the degree of stereoselectivity in the oxidations of $[Co(en)_3]^{2+}$ by $[Co(ox)_2(gly)]^{2-}$ (ox = oxalate, gly = glycinate) and $[Co(ox)_2(en)]^-$ was strongly solvent dependent and showed quite different behavior for variations in solvent.[5] In the present study, to clarify the role of hydrogen bonding interactions between the solvent and the reactant as well as between the reactants, effects of the geometry in reductants and of the unhindered *pseudo*-C_3 carboxylate face in oxidants on the isomer proportions and the stereoselectivities of $[Co(dien)_2]^{3+}$ products are investigated. Their solvent effects are examined using the oxidants of $[Co(ox)_2(gly)]^{2-}$, $[Co(edta)]^-$ (edta = ethylenediaminetetraacetate), and $[Co(ox)_2(en)]^-$, and are compared with the results of the oxidation of $[Co(en)_3]^{2+}$.

Experimental

Preparation of Complexes. Sodium or potassium salts of Δ isomer of anionic cobalt(III) complexes were prepared by literature methods and were used as oxidants in the electron transfer reactions with $[Co(dien)_2]^{2+}$ after their purities were ascertained by the absorption and circular dichroism (CD) spectra; $[Co(ox)_3]^{3-}$,[6] $[Co(ox)_2(gly)]^{2-}$,[7] $[Co(edta)]^-$,[8] C_1-*cis*(*N*)-, C_2-*cis*(*N*)-, and *trans*(*N*)-$[Co(ox)(gly)_2]^-$,[9] and $[Co(ox)_2(en)]^-$.[10] Commercially-available diethylenetriamine (Wako Pure Chemical Industries, Ltd.) was distilled under reduced pressure and kept in a refrigerator to use as the need arose. The three geometrical isomers of $[Co(dien)_2]^{3+}$ were prepared by literature methods.[11,12] Their molar extinction coefficients in 1.5 M HCl (1 M = 1 mol dm^{-3}) were determined for use in evaluation of isomer proportions in electron transfer experiments (ε_{459} = 68 for *s-fac*, ε_{468} = 96 for *u-fac*, ε_{466} = 143 M^{-1} cm^{-1} for *mer* isomer). Resolution of *u-fac*-$[Co(dien)_2]^{3+}$ ($\Delta\varepsilon_{503}$ = +0.98 M^{-1} cm^{-1} for Λ isomer) was carried out on SP-Sephadex C-25 column with 0.15 M $Na_2[Sb_2(d\text{-tart})_2]$ (*d*-tart = (+)$_{589}$-tartrate(4−)) as eluent,[11] and the CD value was used to calculate the enantiomeric excesses of *u-fac*-$[Co(dien)_2]^{3+}$ products.

Electron Transfer Experiments. Isomer proportions and stereoselectivities in the reactions of $[Co(dien)_2]^{2+}$ with optically active cobalt(III) complexes at 25 °C and ionic strength of 0.18 M under an atmosphere of nitrogen were determined. All solutions were purged with N_2 gas for 15 min prior to use. In a typical run, 20 cm^3 of 0.165 M diethylenetriamine, 5 cm^3 of 0.33 M HCl, 5 cm^3 of 0.30 M $CoCl_2$, and 25 cm^3 of 0.30 M KCl were mixed. To the mixture, 20 cm^3 of 7.5×10^{-3} M Δ-oxidant was added. After complete disappearance of the color of the oxidant (5—45 min), the reaction was quenched with 10 cm^3 of 3 M HCl. Separation of the geometrical isomers in the resulting mixtures was carried out on an SP-Sephadex C-25 column (Φ 1.9×45 cm) using 0.3 M Na_2HPO_4 as an eluent. The column showed three bands of *s-fac*, *u-fac*, and *mer* isomers in the order of elution. After each isomer was readsorpted on another SP-Sephadex C-25 short column and washed with water, it was collected in a 50 cm^3 volumetric flask by eluting with 1.5 M HCl. Absorption spectra were measured for the three isomers on a Shimadzu UV-3100 spectrophotometer to obtain their concentrations, and CD spectra for *u-fac* isomer were measured on a JASCO J-500 spectropolarimeter. Stereoselectivity of the *u-fac* isomer products was expressed in terms of percent enantiomeric excess (%ee) on the basis of the optical purity determined by comparison with an optical pure sample of Λ-*u-fac*-$[Co(dien)_2]^{3+}$. Although *mer*-$[Co(dien)_2]^{3+}$ can exist in two optical forms resulting from the so-called N–H chiral effect,[11,12] no optical activity can be detected for all *mer* isomer products in this study owing to no or much smaller stereoselectivity. Electron transfer experiments in organic solvents were carried out using Δ-$(Me_4N)_2[Co(ox)_2(gly)]\cdot2H_2O$ (Me = methyl group), Δ-(Et_4N)-$[Co(ox)_2(en)]\cdot H_2O$ (Et = ethyl group), and Δ-(Et_4N)-$[Co(edta)]\cdot2H_2O$ as oxidants. Δ-$(Me_4N)_2[Co(ox)_2(gly)]\cdot2H_2O$ was prepared by addition of Me_4NI to diastereomer $[\Delta\text{-}Co(ox)(en)_2]_2[\Delta\text{-}Co(ox)_2(gly)]$ to precipitate insoluble Δ-$[Co(ox)(en)_2]$-I, followed by crystallization from the filtrate. Δ-$(Et_4N)[Co(ox)_2(en)]\cdot H_2O$ and Δ-$(Et_4N)[Co(edta)]\cdot2H_2O$ were prepared by a similar manner to that for Δ-$(Me_4N)_2[Co(ox)_2(gly)]\cdot2H_2O$ described above. To avoid the production of precipitate, lower concentrations than in aqueous media were usually used in organic solvents, holding the concentration ratio of the reagents constant. $Co(CF_3SO_3)_2$ was prepared from $CoCO_3$ and CF_3SO_3H and was used in the place of $CoCl_2$. LiCl was used in the place of KCl in solvents other than DMF, in which $LiCF_3SO_3$ was used. All of the solvents were dried over molecular sieves. Methanol (MeOH) and ethanol (EtOH) were distilled at atmospheric pressure, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were distilled under reduced pressure, and formamide (FA) was used without further purification.

Favorable Pairs by Chromatography. Determination of favorable pairs between Λ-*u-fac*-$[Co(dien)_2]^{3+}$ and oxidant complexes in ion pair formation was made in essentially the same manner as in the previous studies.[2,13] A column (Φ 1.0×55 cm) of SP-Sephadex C-25 cation exchanger, which was saturated with Λ-*u-fac*-$[Co(dien)_2]^{3+}$, was prepared. When a racemic anionic complex (3 cm^3 in 15 mM) was passed through the column with 30% aqueous ethanol, a partial resolution of the anionic complex took place. The enantiomer of the anionic complex which interacts favorably with Λ-*u-fac*-$[Co(dien)_2]^{3+}$ adsorbed to the ion exchanger can be expected to be eluted later from the column. Thus, favorable pairs between Λ-*u-fac*-$[Co(dien)_2]^{3+}$ and the oxidant complexes were chromatographically determined by observing the late-eluted enantiomer.



$[Co(ox)_2(gly)]^{2-}$ $[Co(edta)]^-$ $[Co(ox)_2(en)]^-$

Chart 2. $[Co(ox)_2(gly)]^{2-}$ and $[Co(edta)]^-$ having the unhindered *pseudo*-C_3 carboxylate face and $[Co(ox)_2(en)]^-$ having no such a carboxylate face.

Results and Discussion

Effects of Different Oxidants. Table 1 collects the reaction product data in aqueous solution and the favorable pairs of *u-fac*-$[Co(dien)_2]^{3+}$ with the oxidants. All isomer proportions were always in the order *s-fac* < *u-fac* ≪ *mer*, but closer examination reveals that there are significant varia-

Table 1. Reaction Product Data in the Oxidation of $[Co(dien)_2]^{2+}$ by Anionic Cobalt(III) Complexes at 25 °C and Ionic Strength of 0.18 M, and Favorable Pairs between Δ Oxidant and *u-fac*-$[Co(dien)_2]^{3+}$

Oxidant	Isomer proportions/% *s-fac*	*u-fac*	*mer*	Recovery of product[a)]	%ee of *u-fac*[b)]	Favorable pair[c)]
$\Delta\,[Co(ox)_3]^{3-}$	5	16	79	1.04	4.3%$\Delta\Lambda$	[d)]
$\Delta\,[Co(ox)_2(gly)]^{2-}$	5	18	77	0.97	4.6%$\Delta\Lambda$	$\Delta\Lambda$
	(5	19	76	0.94	3.7%$\Delta\Lambda$)[e)]	
$\Delta\,[Co(edta)]^{-}$	5	20	75	0.92	3.0%$\Delta\Lambda$	$\Delta\Lambda$
$[Co(ox)(gly)_2]^{-}$						
Δ-C_1-*cis*(*N*)	3	23	74	0.99	3.1%$\Delta\Lambda$	$\Delta\Lambda$
Δ-C_2-*cis*(*N*)	2	14	84	0.87	1.1%$\Delta\Lambda$	$\Delta\Delta$
Δ-*trans*(*N*)	2	15	83	0.83	ca. 0	$\Delta\Delta$
$\Delta\,[Co(ox)_2(en)]^{-}$	3	15	82	0.92	2.8%$\Delta\Lambda$	$\Delta\Delta$
	(3	20	77	0.97	2.2%$\Delta\Lambda$)[e)]	
O_2 (air)[f)]	1	6	93			
O_2 (air)[g)]	7	28	65			
O_2 (air)[h)]	(55	25	20)			

a) Ratio of molar quantity of the recovered product to that of the oxidant. b) %ee $\Delta\Lambda$ denotes that Δ oxidant yields an excess of Λ-*u-fac*-$[Co(dien)_2]^{3+}$ product. c) Determined chromatographically using an SP-Sephadex C-25 column in Λ-*u-fac*-$[Co(dien)_2]^{3+}$ form. Given as the favorable pair for Δ oxidant. d) Precipitation. e) In 0.08 M Na_3PO_4 at 25 °C in the absence of charcoal. f) In 0.1 M KCl at 25 °C in the absence of charcoal. g) In 2 M KCl at 18 °C in the presence of charcoal, taken from Ref. 1. h) In 0.08 M Na_3PO_4 at 18 °C in the presence of charcoal, taken from Ref. 1.

tions in their values with kinds of oxidants; that is, in the case of oxidants $[Co(ox)_3]^{3-}$, $[Co(ox)_2(gly)]^{2-}$, $[Co(edta)]^{-}$, and C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, the proportions of *s-fac* and, particularly of *u-fac* isomer, show a trend to increase at the expense of *mer* isomer compared with those in the case of oxidants C_2-*cis*(*N*)- and *trans*(*N*)-$[Co(ox)(gly)_2]^{-}$ and $[Co(ox)_2(en)]^{-}$, as can be seen in Fig. 1a. This observation may be correlated with the structural characteristic that the former group of oxidants possess the unhindered *pseudo*-C_3 carboxylate face, whereas the latter group of oxidants do not possess such a carboxylate face (Chart 2). The unhindered *pseudo*-C_3 carboxylate face will lead to the increased stabilization of the precursor assembly through hydrogen bondings which are triply formed between three coordinated oxygen atoms of oxidant and three N–H protons of reductant.[3,4] Such arrangements of N–H groups are unhindered by the ligand backbone for approach of the oxidant along the *pseudo*-C_3 axis of the reductant and thus are possible only in *s-fac* and *u-fac* isomers (Chart 1).

To confirm the preference for this C_3–C_3 interaction, we recently have determined the ion association constants between the three geometrical isomers of $[Co(dien)_2]^{3+}$ and $[Co(ox)_2(gly\ or\ \beta\text{-}ala)]^{2-}$ (β-ala = β-alaninate) by a conductometic method.[14] The ion association constants, K_A, were observed to be in the order *s-fac* ($471\pm13\ M^{-1}$) > *u-fac* ($439\pm13\ M^{-1}$) > *mer* ($357\pm14\ M^{-1}$) for $[Co(dien)_2]^{3+}\cdot[Co(ox)_2(gly)]^{2-}$ pair and *s-fac* ($598\pm22\ M^{-1}$) > *u-fac* ($535\pm22\ M^{-1}$) > *mer* ($453\pm20\ M^{-1}$) for $[Co(dien)_2]^{3+}\cdot[Co(ox)_2(\beta\text{-}ala)]^{2-}$ pair at 25 °C and ionic strength of 0.01 M. These values suggest that the C_3–C_3 interaction plays an important role in the increase in ion association constants of *s-fac* and *u-fac* isomers. Similar effects of the geometry of $[Co(dien)_2]^{2+}$ reductant can be also expected upon the formation of precursor assemblies in electron transfer reaction and are, therefore, supposed to contribute to the increase in the products of *s-fac* and *u-fac* isomers. However, the isomer proportions of the oxidation products (*s-fac* < *u-fac* ≪ *mer*) are in the reverse order to the magnitude of ion association of $[Co(dien)_2]^{3+}$ isomers. This suggests that the isomer proportions of the products are primarily controlled by those of the reductants before reacting and undergo relatively small changes due to the differences in the stabilization of precursor assemblies through hydrogen bondings. The isomer proportions of $[Co(dien)_2]^{2+}$ may be deduced from the aerial oxidation products in the absence of charcoal in this study (Table 1). The observed proportions (*s-fac* : *u-fac* : *mer* = 1 : 6 : 93 in KCl medium) are in good agreement with the values obtained by polarographic study (*s-fac* : *u-fac* : *mer* = 1 : 4 : 95 in acetone)[15] if one takes into consideration the difference in medium, showing the higher preference for *mer* isomer of $[Co(dien)_2]^{2+}$ when compared with the equilibrium isomer proportions reported for $[Co(dien)_2]^{3+}$ in the presence of charcoal (*s-fac* : *u-fac* : *mer* = 7 : 28 : 65 in KCl medium).[1] In this regard, Bond and co-workers reported on the basis of the detailed molecular mechanics' calculations for $[Co(dien)_2]^{n+}$ (n = 2, 3) that the major change in isomer distribution on going from Co(III) to Co(II) state was an increase in the degree of preference for *mer* isomer.[16] This preference for the *mer* isomer of $[Co(dien)_2]^{2+}$ may be a significant reason for bringing about the increased *mer* isomer proportions in all the oxidation products in the absence of charcoal studied here. Thus, the *mer* isomer proportions of products by the oxidants such as $[Co(ox)_2(en)]^{-}$ or C_2-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, for which the C_3–C_3 interaction is not possible, reflect the higher preference for *mer* isomer of $[Co(dien)_2]^{2+}$, whereas the oxidants such as $[Co(ox)_2(gly)]^{2-}$ or C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, for which the C_3–C_3 interaction is possible and contributes to the greater formation of precursor assemblies

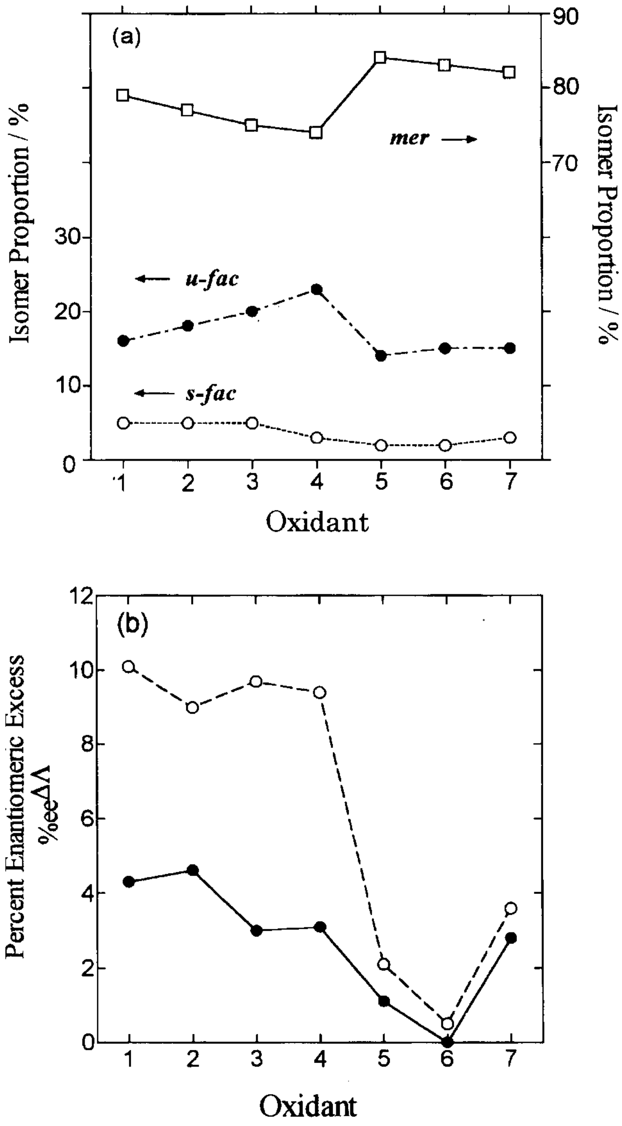


Fig. 1. (a) Isomer proportions in the oxidations of $[Co(dien)_2]^{2+}$; *s-fac* (○), *u-fac* (●), and *mer* (□) isomer products, and (b) Percent enantiomeric excesses (%ee) of *u-fac*-$[Co(dien)_2]^{3+}$ product (●) and $[Co(en)_3]^{3+}$ product (○) in the oxidations of $[Co(dien)_2]^{2+}$ and $[Co(en)_3]^{2+}$, respectively, by various oxidants at 25 °C and ionic strength of 0.18 M. The numbering of oxidants; 1: Δ-$[Co(ox)_3]^{3-}$, 2: Δ-$[Co(ox)_2(gly)]^{2-}$, 3: Δ-$[Co(edta)]^{-}$, 4: Δ-C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, 5: Δ-C_2-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, 6: Δ-*trans*(*N*)-$[Co(ox)(gly)_2]^{-}$, 7: Δ-$[Co(ox)_2(en)]^{-}$.

of *s-fac* and *u-fac* isomers, produce larger proportions of *s-fac* and *u-fac* isomers and, as a result, a smaller proportion of *mer* isomer than the former oxidants (Fig. 1a). Owing to the specific effects of added anions, the charcoal-catalyzed isomer proportions in the preparation of $[Co(dien)_2]^{3+}$ were shown to be markedly affected in Na_3PO_4 medium from *s-fac* : *u-fac* : *mer* = 7 : 28 : 65 in KCl medium to 55 : 25 : 20.[1] However, the isomer proportions in the oxidation of $[Co(dien)_2]^{2+}$ by $[Co(ox)_2(gly)]^{2-}$ and $[Co(ox)_2(en)]^{-}$ were not so greatly affected by the addition of $PO_4{}^{3-}$ as the equilibrium proportions of isomers in the presence of charcoal, and the effect of $PO_4{}^{3-}$ on the stereoselectivity also was small. Thus, it is worth noting that, although oxoanions such as $PO_4{}^{3-}$ in the presence of charcoal lead to a marked increase in a particular isomer, both by the catalytic action of charcoal for Co(III) complexes and by the specific ion association effects, such phenomena occur only slightly in the oxidation of $[Co(dien)_2]^{2+}$ by cobalt(III) complexes in the absence of charcoal.

Electron-transfer stereoselectivities of *u-fac*-$[Co(dien)_2]^{2+}$ showed invariably a $\Delta\Lambda$ preference regardless of kinds of oxidants (Table 1). As shown in Fig. 1b, although the magnitudes of selectivity were, on the whole, considerably smaller than that in the case of $[Co(en)_3]^{2+}$,[3,4] the sense of the stereoselectivities was quite the same as that of $[Co(en)_3]^{3+}$ products. This small stereoselectivity may be ascribed to the decrease in Λ character (for example, for optical isomers specified as Λ) of Λ-*u-fac*-$[Co(dien)_2]^{2+}$ having a $\Lambda\Lambda\Delta$ combination of chelate rings according to the ring-paired method in comparison with Λ-$[Co(en)_3]^{2+}$ having a $\Lambda\Lambda\Lambda$ combination. Comparison between the electron-transfer and the ion-pairing stereoselectivities reveals that, while Δ-oxidants such as C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$, which has an unhindered *pseudo*-C_3 carboxylate face and forms a favorable pair of $\Delta\Lambda$ with *u-fac*-$[Co(dien)_2]^{3+}$, yielded relatively large enantiomeric excess (3—5% Λ), Δ-oxidants such as C_2-*cis*(*N*)-$[Co(ox)(gly)_2]^{-}$ and $[Co(ox)_2(en)]^{-}$, which have no such a *pseudo*-C_3 carboxylate face and form a favorable pair of $\Delta\Delta$ with *u-fac*-$[Co(dien)_2]^{3+}$, yielded smaller enantiomeric excess (0—3% Λ). This classification of oxidants was quite the same as that based on the isomer proportions. Thus, the C_3–C_3 interaction between reactants leads to the enhanced stereoselectivity as well as to the increasing isomer proportions. The mechanism proposed for electron transfer reactions is expressed in terms of Eqs. 1, 2, and 3 for $[Co(ox)_2(en)]^{-}$, where K_o is a precursor ion pair formation constant and k_{et} represents the rate of electron transfer within the precursor ion pair.[5]

$$[Co(dien)_2]^{2+} + [Co(ox)_2(en)]^{-} \xrightleftharpoons{K_o} \{[Co(dien)_2]^{2+}\cdot[Co(ox)_2(en)]^{-}\} \quad (1)$$

$$\{[Co(dien)_2]^{2+}\cdot[Co(ox)_2(en)]^{-}\} \xrightarrow{k_{et}} \{[Co(dien)_2]^{3+}\cdot[Co(ox)_2(en)]^{2-}\} \quad (2)$$

$$\{[Co(dien)_2]^{3+}\cdot[Co(ox)_2(en)]^{2-}\} \xrightarrow{\text{fast}} [Co(dien)_2]^{3+} + [Co(ox)_2(en)]^{2-} \quad (3)$$

In the electron transfer reactions between reactants incapable of the C_3–C_3 interaction, since the observed electron-transfer stereoselectivity ($\Delta\Lambda$) is opposite to the ion-pairing stereoselectivity ($\Delta\Delta$) as shown in Table 1, it should be noted that the electron-transfer step (k_{et}) within the precursor assembly rather than the precursor formation step (K_o) must contribute predominantly to the overall electron-transfer stereoselectivity; that is, this indicates that the value of $k_{\mathrm{et}}(\Delta\Lambda)/k_{\mathrm{et}}(\Delta\Delta)$ is significantly larger than that of $K_{\mathrm{o}}(\Delta\Delta)/K_{\mathrm{o}}(\Delta\Lambda)$.[17] A similar importance of the electron-transfer step within precursor assembly has been also shown for the stereoselective oxidation of $[\mathrm{Co(phen)_3}]^{2+}$ (phen = 1, 10-phenanthroline) by $[\mathrm{Co(ox)_3}]^{3-}$[19] and for conformational effects on the stereoselectivity in the reaction of $[\mathrm{Co(pn)_3}]^{2+}$ (pn = 1,2-propanediamine) with $[\mathrm{Co(ox)_2(gly)}]^{2-}$.[20]

Effects of Solvents. Studies of solvent dependence of electron transfer reactions between metal complexes are expected to give useful information about specific interactions of complex with solvent. The observed isomer proportions and stereoselectivities in the oxidations of $[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$, $[\mathrm{Co(edta)}]^{-}$, and $[\mathrm{Co(ox)_2(en)}]^{-}$ in six solvents are summarized in Table 2. The isomer proportions and the stereoselectivities are significantly dependent on the solvent. Such behavior should be due to solvation effects for the reactants. Since each isomer of $[\mathrm{Co(dien)_2}]^{2+}$ is not greatly polar, specific cation–solvent interactions would not be large. Therefore we paid attention to solvation effects for anions rather than for cations. For various kinds of anionic Co(III) and Cr(III) complexes, it was reported that there exists a fairly good linear correlation between the ligand field absorption band maxima and the acceptor numbers of the solvents.[5,21] Thus, the acceptor number (AN) was selected as an indication of the solvating powers of solvents for anions. The geometrical isomer proportions as a function of acceptor number are shown for $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ oxidants (Fig. 2a) and for $[\mathrm{Co(ox)_2(en)}]^{-}$ oxidant (Fig. 2b). The oxidations of $[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ having the unhindered *pseudo*-C_3 carboxylate face gave the closely similar isomer proportions for variations in AN. In these cases, as the acceptor number of solvent increases, the proportion of the *mer* isomer increased at the expense of the *s-fac* isomer, with the *u-fac* proportion remaining nearly constant. The oxidants $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ are more polar than $[\mathrm{Co(ox)_2(en)}]^{-}$ and hence are expected to be solvated more strongly through hydrogen bonds mainly at the *pseudo*-C_3 carboxylate face. The strong interactions of the oxidant with the solvent will interfere with the reactions between the oxidant and the reductant. With increasing acceptor number, the carboxylate faces in the oxidant are more strongly blocked by solvents, so that it can be considered that the weakened C_3–C_3 interactions of the oxidant with the reductant led to the decrease in the *s-fac* proportion and, as a result, brought about the increase in the *mer* proportion (Fig. 2a). In contrast, in the case of $[\mathrm{Co(ox)_2(en)}]^{-}$ oxidation, almost invariably large proportions of the *mer* products except for that in EtOH were observed (Fig. 2b). Presumably they are due primarily to the fact that the *mer* form in the Co(II) state is favored over the *s-fac* and *u-fac* forms as described previously. The less polar $[\mathrm{Co(ox)_2(en)}]^{-}$, having no unhindered *pseudo*-C_3 carboxylate face, can not interact strongly with *s-fac* and *u-fac*-$[\mathrm{Co(dien)_2}]^{2+}$ through C_3–C_3 interactions and, therefore, seems not to have given the largely increased proportions of the *s-fac* and the *u-fac* products, compared with the cases of $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ oxidations. Moreover, each of the three isomer proportions of products showed only a slight change for variations in acceptor number (Fig. 2b), indicating that $[\mathrm{Co(ox)_2(en)}]^{-}$ is poorly solvated.

The solvent dependence on the enantiomeric excesses of *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$ products are shown in Fig. 3a. The oxidations of $[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ again gave the closely similar enantiomeric excesses for variations in solvent. These enantiomeric excesses were relatively large and decreased in the order DMF > DMSO > FA > EtOH > MeOH > H_2O, indicating that the stereoselectivity decreases effectively with increasing acceptor number of solvent. The formation of hydrogen bonds between the solvent and the oxidants will obstruct the hydrogen bonding between the oxidants and the reductants. Therefore, the increase in the strength of oxidant–solvent

Table 2. Isomer Proportions and Percent Enantiomeric Excesses of *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$ in the Oxidation of $[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$, $[\mathrm{Co(edta)}]^{-}$, and $[\mathrm{Co(ox)_2(en)}]^{-}$ in Different Solvents at 25 °C and Ionic Strength of 0.12—0.18 M

Solvent	AN	$[\mathrm{Co(ox)_2(gly)}]^{2-}$ Isomer proportion /%				$[\mathrm{Co(edta)}]^{-}$ Isomer proportion /%				$[\mathrm{Co(ox)_2(en)}]^{-}$ Isomer proportion /%			
		s-fac	*u-fac*	*mer*	%ee of *u-fac*	*s-fac*	*u-fac*	*mer*	%ee of *u-fac*	*s-fac*	*u-fac*	*mer*	%ee of *u-fac*
DMF	16.0	30	21	49	20% $\Delta\Lambda$	26	26	49	18.7% $\Delta\Lambda$	9	11	80	1.5% $\Delta\Lambda$
DMSO	19.3	25	21	54	16% $\Delta\Lambda$	26	24	51	15.1% $\Delta\Lambda$	11	15	73	0.3% $\Delta\Lambda$
EtOH	37.1	15	31	54	5.9% $\Delta\Lambda$	13	17	70	7.7% $\Delta\Lambda$	18	24	58	2.0% $\Delta\Lambda$
FA	39.8	9	25	67	10% $\Delta\Lambda$	10	27	63	8.1% $\Delta\Lambda$	5	20	76	0.8% $\Delta\Lambda$
MeOH	41.3	15	23	62	5.4% $\Delta\Lambda$	8	17	75	5.2% $\Delta\Lambda$	9	15	76	2.5% $\Delta\Lambda$
H_2O	54.8	5	18	77	4.6% $\Delta\Lambda$	6	22	73	3.2% $\Delta\Lambda$	3	15	82	3.2% $\Delta\Lambda$

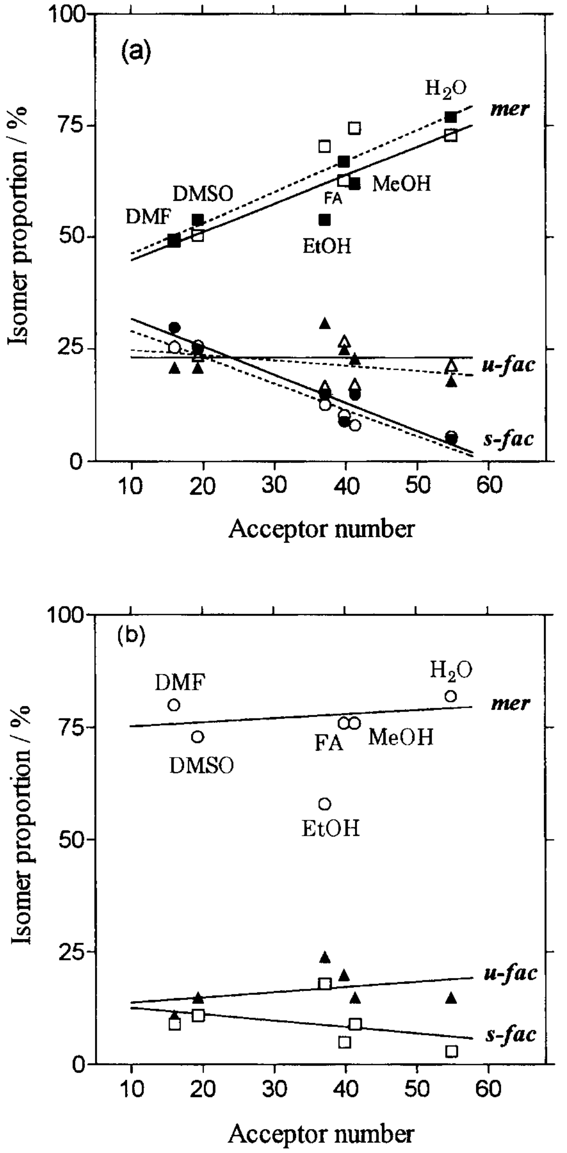


Fig. 2. Solvent effects on isomer proportions in the oxidations of $[Co(dien)_2]^{2+}$ by (a) Δ-$[Co(ox)_2(gly)]^{2-}$ and Δ-$[Co(edta)]^-$ shown as a function of acceptor number; *s-fac* (●), *u-fac* (▲), and *mer* (■) for Δ-$[Co(ox)_2(gly)]^{2-}$; *s-fac* (○), *u-fac* (△), and *mer* (□) for Δ-$[Co(edta)]^-$, and by (b) Δ-$[Co(ox)_2(en)]^-$; *s-fac* (□), *u-fac* (▲), and *mer* (○).

hydrogen bonding must have diminished the differences in energy between the diastereomeric transition states.

On the other hand, the enantiomeric excesses in $[Co(ox)_2(en)]^-$ oxidation were very much smaller than those in $[Co(ox)_2(gly)]^{2-}$ and $[Co(edta)]^-$ oxidations and showed a slight increase with increasing acceptor number. The order of stereoselectivity, DMSO < FA $\leq$ DMF < EtOH < MeOH < H_2O, was virtually the reverse of that in $[Co(ox)_2(gly)]^{2-}$ and $[Co(edta)]^-$ oxidations. Such small changes in stereoselectivity seem to be due to both the essentially weak interaction of $[Co(ox)_2(en)]^-$ with *u-fac*-$[Co(dien)_2]^{2+}$ and the weak solvent effects of poorly solvated $[Co(ox)_2(en)]^-$. Thus, in the oxidations of $[Co(dien)_2]^{2+}$ by two types of oxidants, the trends in the stereoselectivity in solvent also were quite different. For comparison, the solvent dependence on stereoselectivities in the oxidation of $[Co(en)_3]^{2+}$ is shown in Fig. 3b. The solvent dependence in the *u-fac*-$[Co(dien)_2]^{2+}$ system was similar to that in the $[Co(en)_3]^{2+}$ system, although the magnitudes of stereoselectivities in the former were considerably smaller than those in the latter as a whole (Fig. 3a). Taube and co-workers reported that, for the oxidation of $[Co(en)_3]^{2+}$ by $[Co(edta)]^-$, the reactions in more protic solvents show lower stereoselectivities than those in the less protic solvents.[22] This describes the importance of hydrogen bondings between the oxidant and the solvent, but we have no clear quantitative measure of the protic property of solvent, and this reduces the usefulness of this explanation. Recently we have come to be able to express the stereoselectivities

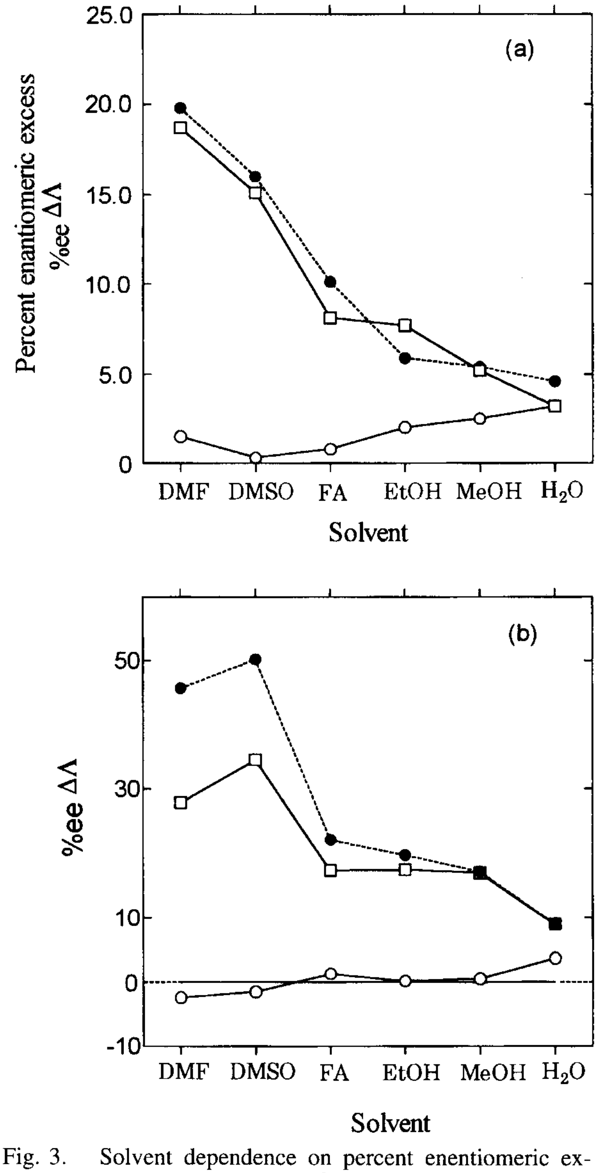


Fig. 3. Solvent dependence on percent enentiomeric excesses of (a) *u-fac*-$[Co(dien)_2]^{3+}$ products in the oxidations of $[Co(dien)_2]^{2+}$ (I = 0.12—0.18 M) and of (b) $[Co(en)_3]^{3+}$ products in the oxidation of $[Co(en)_3]^{2+}$ (I = 0.14 M) by Δ-$Co(ox)_2(gly)^{2-}$ (●), Δ-$[Co(edta)]^-$ (□), and Δ-$[Co(ox)_2(en)]^-$ (○).

Table 3. Donor Number (DN) and Acceptor Number (AN) Description of the Solvent Effect on Stereoselectivities

	$\log(k_{\Delta\Lambda}/k_{\Delta\Delta})=\alpha\mathrm{DN}+\beta\mathrm{AN}+Q_o$			
Oxidant	$\alpha(\bar{\alpha})$[a)]	$\beta(\bar{\beta})$[a)]	Q_o	r
$[\mathrm{Co(ox)_2(gly)}]^{2-}$	0.00476 (41)	−0.00220 (59)	0.0576	0.940
$[\mathrm{Co(edta)}]^{-}$	0.00139 (12)	−0.00311 (88)	0.160	0.973

a) Percentage contribution from DN and AN given by $\overline{\alpha} = 100\alpha'/(\alpha'+\beta')$ and $\overline{\beta} = 100 \times\beta'/(\alpha'+\beta')$, where α' and β' are the partial regression coefficients; $\alpha' = |\alpha|[\sum(\mathrm{DN}_i-\overline{\mathrm{DN}})^2/\sum\{(\log(k_{\Delta\Lambda}/k_{\Delta\Delta}))_i-\overline{\log(k_{\Delta\Lambda}/k_{\Delta\Delta})}\}^2]^{1/2}$ and $\beta' = |\beta|[\sum(\mathrm{AN}_i-\overline{\mathrm{AN}})^2/\sum\{(\log(k_{\Delta\Lambda}/k_{\Delta\Delta}))_i-\overline{\log(k_{\Delta\Lambda}/k_{\Delta\Delta})}\}^2]^{1/2}$.

in the oxidation of $[\mathrm{Co(en)_3}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$, $[\mathrm{Co(edta)}]^{-}$, and $[\mathrm{Co(ox)_2(en)}]^{-}$ as a linear function of donor number (DN) and acceptor number (AN).[5] So, similar approaches were tried for the oxidation of *u-fac*-$[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$. The stereoselectivity was expressed in terms of a rate ratio, $k_{\Delta\Lambda}/k_{\Delta\Delta}$, using the relation, $k_{\Delta\Lambda}/k_{\Delta\Delta} = (100+\%\mathrm{ee})/(100-\%\mathrm{ee})$, and the observed $\log(k_{\Delta\Lambda}/k_{\Delta\Delta})$ values in various solvents were fitted to the following Eq. 4;

$$\log(k_{\Delta\Lambda}/k_{\Delta\Delta}) = \alpha\mathrm{DN}+\beta\mathrm{AN}+Q_o, \qquad (4)$$

where α and β are regression coefficients and Q_o is a constant independent on solvent. The best fit parameters of the stereoselectivity data as oxidized by $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ are presented in Table 3, and plots of $\log(k_{\Delta\Lambda}/k_{\Delta\Delta})_{\mathrm{obs}}$ against $\log(k_{\Delta\Lambda}/k_{\Delta\Delta})_{\mathrm{calc}}$ are shown in Fig. 4, indicating a good fit of the data to Eq. 4 with correlation coefficients 0.940 and 0.973, respectively. The percentage contribution of DN and AN to the solvent effect is given by $\overline{\alpha}$ and $\overline{\beta}$, respectively (Table 3). The values of $\overline{\alpha}$ and $\overline{\beta}$ obtained here were 41% and 59%, respectively, for $[\mathrm{Co(ox)_2(gly)}]^{2-}$, and 12% and 88%, respectively, for $[\mathrm{Co(edta)}]^{-}$. These values indicate that the most important contributions to the solvent effects result from interactions of the solvent as an acceptor with the oxidant, particularly with $[\mathrm{Co(edta)}]^{-}$, supporting a convenient interpretation made by the simplified assumption that acceptor number exclusively plays an important role in the solvent effect (Fig. 3a). Although the difference in $\overline{\beta}$ between $[\mathrm{Co(ox)_2(gly)}]^{2-}$ and $[\mathrm{Co(edta)}]^{-}$ can probably be attributed to the difference in the hydrogen-bond acceptor properties of these two anions, further details are not clear. However, Figure 4 may be useful for predicting the magnitudes of stereoselectivity in different solvents. For the oxidation of *u-fac*-$[\mathrm{Co(dien)_2}]^{2+}$ by $[\mathrm{Co(ox)_2(en)}]^{-}$ the variations in the stereoselectivities in solvents were too small to be analyzed meaningfully, and therefore attempts to evaluate the contributions of DN and AN were unfruitful.

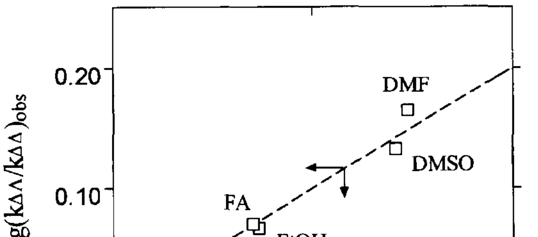


Fig. 4. Plots of $\log(k_{\Delta\Lambda}/k_{\Delta\Delta})_{\mathrm{obs}}$ against $\log(k_{\Delta\Lambda}/k_{\Delta\Delta})_{\mathrm{calc}}$ evaluated from Eq. 4 for the oxidations of $[\mathrm{Co(dien)_2}]^{2+}$ by Δ-$[\mathrm{Co(ox)_2(gly)}]^{2-}$ (●) and Δ-$[\mathrm{Co(edta)}]^{-}$ (□).

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17 The second-order rate constant for an outer-sphere electron-transfer reaction, k, is assumed to be expressed in terms of the equation, $k = k_{et} K_o$. This equation based on the relation, $1 \gg K_o[[Co(en)_3]^{2+}]$, was kinetically confirmed in the $[Co(en)_3]^{2+}$ system,[5] but not in the present $[Co(dien)_2]^{2+}$ system. However, ion association constants[14] of $[Co(dien)_2]^{3+}$ with $[Co(ox)_2(gly)]^{2-}$ were comparable for *s-fac* isomer and somewhat smaller for *u-fac* and *mer* isomers compared with that of $[Co(en)_3]^{3+}$ with the same anion.[18] Therefore in the oxidation of $[Co(dien)_2]^{2+}$ also, it is reasonable to presume a similar relation, $1 \gg K_o[[Co(dien)_2]^{2+}]$, and hence the equation, $k = k_{et} K_o$, can be expected to hold.

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