Chiral Induction in the Reduction of $[Co(glyO)(ox)_2]^{2-}$ by $[Co(phen)_3]^{2+}$ (glyO = glycinate, ox = oxalate, phen = 1,10-phenanthroline)

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Oxidation of $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) by $[Co(glyO)(ox)_2]^{2-}$ (glyO = glycinate, ox = oxalate) has been found to be an outer-sphere reaction with a second-order rate constant of 0.14 $dm^3\ mol^{-1}\ s^{-1}$ at 25 °C and 0.01 mol dm^{-3} ionic strength. Chiral induction amounting to a 37% enantiomeric excess of the Δ isomer in the $[Co(phen)_3]^{3+}$ product was detected when Δ-$[Co(glyO)(ox)_2]^{2-}$ was used as oxidant.

Systematic studies involving changes in reactant structure and charge have been used to pinpoint features which are important in determining chiral induction in electron-transfer reactions involving metal-ion complexes.[1,2] Chiral induction in outer-sphere reactions between $[Co(en)_3]^{2+}$ (en = 1,2-diaminoethane) and the three oxidants $[Co(ox)_3]^{3-}$ [ox = oxalate(2−)], $[Co(glyO)(ox)_2]^{2-}$ [glyO = glycinate(1−)] and $[Co(edta)]^-$ [edta = 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetraacetate(4−)] gives rise to an enantiomeric excess of 10 ± 2% of the Λ enantiomer when the Δ form of the oxidant is used, a 10% ΔΛ stereoselectivity. In contrast, the induction with $[Co(en)(ox)_2]^-$ as oxidant is much smaller, amounting to 2 ± 2% ΔΛ stereoselectivity. The difference is the presence, in the former series of reagents, of a pseudo-C_3 carboxylate motif, in which none of the edges is subtended by a chelate ring. This motif is capable of forming a key hydrogen-bonding interaction with the reductant and plays an important role in determining the stereoselectivity.[2]

Recently, interest has focused on reactions of $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) as an example of a reductant which is not capable of hydrogen bonding. In the reaction with $[Co(ox)_3]^{3-}$ a 25 ± 1% enantiomeric excess of the Δ enantiomer of $[Co(phen)_3]^{3+}$ is formed when Δ-$[Co(ox)_3]^{3-}$ is used.[3] Investigations of stereoselectivity in reactions of the related reagents $[Co(glyO)(ox)_2]^{2-}$, $[Co(edta)]^-$ and $[Co(en)(ox)_2]^-$ are of interest to discover if the C_3 carboxylate motif has an important effect on this set of reactions. However, there is an added complication. In the presence of $[Co(phen)_3]^{2+}$ the optically active product $[Co(phen)_3]^{3+}$ undergoes racemization by a self-exchange mechanism much more rapidly than the corresponding process with $[Co(en)_3]^{3+}$.[4,5] Detection of chiral induction requires that conditions be found where the rate of electron transfer is faster than, or comparable with, the succeeding racemization of the products. Among the oxidants of interest, only $[Co(glyO)(ox)_2]^{2-}$ meets these conditions in the oxidation of $[Co(phen)_3]^{2+}$, and studies of this reaction are reported in this paper.

Experimental

The complexes $Na[Co(edta)]\cdot 2H_2O$,[6] $Na[\Delta\text{-}(+)_{546}\text{-}Co(edta)]\cdot 4H_2O$ (ε_{535} = 331 $dm^3\ mol^{-1}\ cm^{-1}$, $\Delta\varepsilon_{575}$ = −1.79 $dm^3\ mol^{-1}\ cm^{-1}$),[7] $Na_2[Co(glyO)(ox)_2]\cdot 1.5H_2O$,[8] $Na_2[\Delta\text{-}(+)_{546}\text{-}Co(glyO)(ox)_2]\cdot H_2O$ (ε_{565} = 138, $\Delta\varepsilon_{581}$ = −3.08 $dm^3\ mol^{-1}\ cm^{-1}$),[2,8] $Na[Co(en)(ox)_2]\cdot H_2O$,[9] $Na[\Delta\text{-}(+)_{546}\text{-}Co(en)(ox)_2]\cdot 3.5H_2O$,[10] $[Co(phen)_3][ClO_4]_3\cdot 2H_2O$,[4] and $\Lambda\text{-}(+)_{589}\text{-}[Co(phen)_3][ClO_4]_3\cdot 2H_2O$ (ε_{455} = 99, $\Delta\varepsilon_{490}$ = +1.189 $dm^3\ mol^{-1}\ cm^{-1}$)[11–13] were prepared by literature methods. Solutions of $[Co(phen)_3]^{2+}$, $[Co(4,7\text{-}dmphen)_3]^{2+}$ (4,7-dmphen = 4,7-dimethyl-1,10-phenanthroline) and $[Co(5,6\text{-}dmphen)_3]^{2+}$ (5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline) were prepared and used under an atmosphere of argon gas as described earlier.[4,14]

The kinetics of reduction of $[Co(glyO)(ox)_2]^{2-}$ by $[Co(phen)_3]^{2+}$ and the methylated derivatives $[Co(4,7\text{-}dmphen)_3]^{2+}$ and $[Co(5,6\text{-}dmphen)_3]^{2+}$ were investigated under pseudo-first-order conditions at 25.0 ± 0.2 °C, 0.010 mol dm^{-3} ionic strength (KNO_3) and pH 6.0 (1 × 10^{-3} mol dm^{-3} mes) (mes = 2-morpholinoethanesulfonic acid) by circular dichroism spectroscopy. In a typical experiment, a solution containing 2 × 10^{-4} mol dm^{-3} $Na_2[\Delta\text{-}(+)_{546}\text{-}Co(glyO)(ox)_2]$ was mixed with an equal volume of a solution containing 4 × 10^{-3} mol dm^{-3} reductant under an atmosphere of argon gas. The reaction was monitored at 581 nm where $\Delta\text{-}(+)_{546}[Co(glyO)(ox)_2]^{2-}$ has a maximum signal ($\Delta\varepsilon_{581}$ = −3.08 $dm^3\ mol^{-1}\ cm^{-1}$)[8] and the oxidized phenanthroline complexes have negligible signal. Plots of $\ln(\varphi - \varphi_\infty)$, where φ is the ellipticity, were generally linear for at least three half-lives, and pseudo-first-order rate constants, k_{obs}, were calculated from the slopes by least-squares analysis. Stereoselectivity in the reactions was determined by measuring the transient circular dichroism at the maximum for the reaction products, 487 nm for $[Co(phen)_3]^{3+}$ and 480 nm for $[Co(4,7\text{-}dmphen)_3]^{3+}$ and $[Co(5,6\text{-}dmphen)_3]^{3+}$. At these wavelengths $\Delta\text{-}(+)_{546}[Co(glyO)(ox)_2]^{2-}$ has a small signal ($\Delta\varepsilon_{487}$ = −0.18, $\Delta\varepsilon_{480}$ = −0.12 $dm^3\ mol^{-1}\ cm^{-1}$). Absorption measurements were made on a Varian Instruments Cary 3 spectrophotometer, and circular dichroism measurements on an Aviv model 60DS or 62DS spectrometer.

Results

The reductions of $[Co(glyO)(ox)_2]^{2-}$ by $[Co(phen)_3]^{2+}$ and its methylated derivatives, equation (1), were examined at

$$[Co(glyO)(ox)_2]^{2-} + [Co(phen)_3]^{2+} \xrightarrow{k_{so}} [Co(glyO)(ox)_2]^{3-} + [Co(phen)_3]^{3+} \quad (1)$$

0.010 mol dm^{-3} ionic strength (KNO_3) and 25.0 °C. Pseudo-first-order rate constants, k_{obs}, are collected in Table 1. The reaction is first order in the concentrations of both reagents, and second-order rate constants, k_{so}, are 0.14 ± 0.01 $dm^3\ mol^{-1}\ s^{-1}$ for $[Co(phen)_3]^{2+}$, 6.5 ± 0.5 $dm^3\ mol^{-1}\ s^{-1}$ for [Co(4,7-

Table 1 Second-order rate constants and stereoselectivity results for the reduction of Δ-(+)$_{546}$[Co(glyO)(ox)$_2$]$^{2-}$ with [Co(phen)$_3$]$^{2+}$ and derivatives at 25.0 ± 0.2 °C and 0.010 mol dm^{-3} ionic strength (KNO$_3$)

Reductant	10^4[Co^{II}]/mol dm^{-3}	10^4[Co^{III}]/mol dm^{-3}	k_{so}/dm^3 mol^{-1} s^{-1}	k_{ex}/dm^3 mol^{-1} s^{-1}	Stereoselectivity (e.e.), % $\Delta\Delta$
[Co(phen)$_3$]$^{2+}$	21.5	1.0	0.14		
	10.8	1.0	0.15		
	21.5	1.0	0.14	2.6	34 ± 9
	10.8	1.0	0.14	2.6	41 ± 9
[Co(4,7-dmphen)$_3$]$^{2+}$	21.5	1.0	6.1		
	10.8	1.0	6.8		
	21.5	1.0	6.1	26	79 ± 4
	10.8	1.0	6.7	26	78 ± 3
[Co(5,6-dmphen)$_3$]$^{2+}$	21.5	1.0	2.2		
	10.8	1.0	2.3		
	21.5	1.0	2.2	64	63 ± 8
	10.8	1.0	2.3	63	56 ± 8

dmphen)$_3$]$^{2+}$, and 2.3 ± 0.1 dm^3 mol^{-1} s^{-1} for [Co(5,6-dmphen)$_3$]$^{2+}$. The circular dichroism response at 480 nm for the reaction of 1.0 × 10^{-4} mol dm^{-3} Δ-(+)$_{546}$[Co(glyO)(ox)$_2$]$^{2-}$ with 1.08 × 10^{-3} mol dm^{-3} [Co(4,7-dmphen)$_3$]$^{2+}$ at 25.0 °C in 0.010 mol dm^{-3} KNO$_3$ is shown in Fig. 1. This is a composite trace with contributions from the loss of optical activity due to reduction of Δ-[Co(glyO)(ox)$_2$]$^{2-}$, the concomitant increase in optical activity for Δ-[Co(4,7-dmphen)$_3$]$^{3+}$, equation (2), and the subsequent racemization of Δ-[Co(4,7-dmphen)$_3$]$^{3+}$ by a self-exchange mechanism in the presence of [Co(4,7-dmphen)$_3$]$^{2+}$, equation (3).

$$\Delta\text{-[Co(glyO)(ox)}_2]^{2-} + [\text{Co(4,7-dmphen)}_3]^{2+} \xrightarrow{k_{so}} [\text{Co(glyO)(ox)}_2]^{3-} + \Delta\text{-[Co(4,7-dmphen)}_3]^{3+} \quad (2)$$

$$\Delta\text{-[Co(4,7-dmphen)}_3]^{3+} + [\text{Co(4,7-dmphen)}_3]^{2+} \xrightarrow{k_{ex}} [\text{Co(4,7-dmphen)}_3]^{2+} + [\text{Co(4,7-dmphen)}_3]^{3+} \quad (3)$$

Detection of the transient circular dichroism for the product is limited by the rate of racemization of the product relative to the rate of the initial electron-transfer reaction. Conditions of low ionic strength were chosen in an effort to enhance the former and retard the latter. Both processes are under pseudo-first-order conditions, and an analytical expression for the trace, equation (4), can be derived with the use of a consecutive first-order reaction treatment.[15] In this expression, l is the pathlength, $\Delta\varepsilon_{ox}$ is $\Delta\varepsilon$ for the Δ-[Co(glyO)(ox)$_2$]$^{2-}$ at 480 nm, and $\Delta\varepsilon_{app}$ is the apparent $\Delta\varepsilon$ for the product, [Co(4,7-dmphen)$_3$]$^{3+}$, at this wavelength. A fit to the experimental data obtained by holding independently determined values for k_{so} and $\Delta\varepsilon_{ox}$ invariant and optimizing the fit with k_{ex} and $\Delta\varepsilon_{app}$ is illustrated in Fig. 1. The stereoselectivity is $\Delta\varepsilon_{app}/\Delta\varepsilon$, the apparent optical purity (enantiomeric excess, e.e.) of the product. Rate constants k_{so} and k_{ex} and stereoselectivities are presented in Table 1 for this reaction and also for reductions by [Co(phen)$_3$]$^{2+}$ and [Co(5,6-dmphen)$_3$]$^{2+}$. It should be noted that $\Delta\varepsilon$ values for [Co(5,6-dmphen)$_3$]$^{2+}$ and [Co(4,7-dmphen)$_3$]$^{2+}$ are not accurately known and are estimates based on the better defined values for [Co(phen)$_3$]$^{2+}$.[4] In all cases, $k_{ex} > k_{so}$, and the values for k_{ex} are in good agreement with those determined previously.[4]

$$\frac{\varphi}{3300l} = \left(\Delta\varepsilon_{app}\frac{k_{so}}{k_{ex}-k_{so}}\{\exp(-k_{so}[\text{Co}^{\text{II}}]_t) - \exp(-k_{ex}[\text{Co}^{\text{II}}]_t)\} + \Delta\varepsilon_{ox}\exp(-k_{so}[\text{Co}^{\text{II}}]_t)\right)[\text{Co}^{\text{III}}] \quad (4)$$

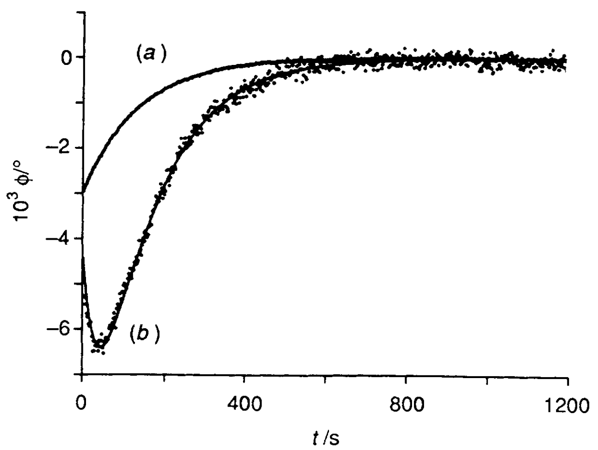

Fig. 1 Circular dichroism responses at 581 (*a*) and 480 nm (*b*) for the reaction of 1.0 × 10^{-4} mol dm^{-3} Δ-(+)$_{546}$[Co(glyO)(ox)$_2$]$^{2-}$ with 1.08 × 10^{-3} mol dm^{-3} [Co(4,7-dmphen)$_3$]$^{2+}$ at 25.0 °C in 0.010 mol dm^{-3} KNO$_3$. The response at 581 nm has been normalized to show the component for decay of Δ-(+)$_{546}$[Co(glyO)(ox)$_2$]$^{2-}$ in trace (*b*). The solid line in trace (*b*) is a fit of the data in Table 1 with equation (4)

Discussion

The rates and products of the reaction of [Co(glyO)(ox)$_2$]$^{2-}$ with [Co(phen)$_3$]$^{2+}$ and its derivatives are consistent with outer-sphere mechanisms. Reduction potential and self-exchange rate data for [Co(glyO)(ox)$_2$]$^{2-/3-}$ are not available but, for the reaction with [Co(phen)$_3$]$^{2+}$, a rate intermediate between the rates for [Co(edta)]$^-$ (7.1 × 10^{-3}) and [Co(ox)$_3$]$^{3-}$ (15.8 dm^3 mol^{-1} s^{-1}) is expected for an outer-sphere mechanism.[2] Inner-sphere reactions of [Co(glyO)(ox)$_2$]$^{2-}$ have been noted previously[3] and the expected product of this process [Co(ox)(phen)$_2$]$^+$, is not observed. Conditions of low [phen] were employed in an attempt to induce an inner-sphere reaction but complications from precipitation precluded a detailed investigation.

Detection of stereoselectivity in these reactions illustrates clearly a problem which commonly limits the detection of stereoselectivity in electron-transfer reactions: the racemization of the optically active products by self-exchange processes.[16] An excess of reductant is desirable in the reduction of Δ-[Co(glyO)(ox)$_2$]$^{2-}$ by [Co(phen)$_3$]$^{2+}$ since the rate of racemization of [Co(phen)$_3$]$^{2+}$ (6.9 s^{-1}),[17] and presumably also of [Co(4,7-dmphen)$_3$]$^{2+}$ and [Co(5,6-dmphen)$_3$]$^{2+}$, is not particularly fast and the continuous regeneration of the racemate is necessary for detection of stereoselectivity.[3,16] A consequence of these conditions is that the optically active [Co(phen)$_3$]$^{3+}$ product undergoes racemization catalysed by self exchange with the excess of [Co(phen)$_3$]$^{2+}$ [4] With all three of the reductants the self-exchange rate, k_{ex}, is larger than the initial electron-transfer rate, k_{so}, and consequently the optically active transient is formed in amounts which are far from stoichiometric. In particular, with $[Co(phen)_3]^{2+}$ as reductant, the transient is formed in near-steady-state amounts and is difficult to detect. These observations can be contrasted with those for reduction of $[Co(ox)_3]^{3-}$ where $k_{so} > k_{ex}$.[3]

Detection of stereoselectivity by this technique in reactions of $[Co(phen)_3]^{2+}$ and derivatives with less-reactive oxidants such as $[Co(edta)]^-$ and $[Co(en)(ox)_2]^-$ was attempted but did not prove possible since the rates of electron transfer are not competitive with the more rapid self-exchange processes. Interestingly, however, induction can be detected in the reaction of $[Co(phen)_3]^{3+}$ with $[Co(edta)]^{2-}$ where the enantiomeric excess is 20% with a ΔΔ preference.[13] Although thermodynamic effects on stereoselectivity are believed to be smaller than the kinetic values determined here,[18] they cannot be excluded, and it is difficult to infer a stereoselectivity for the reaction of $[Co(edta)]^-$ with $[Co(phen)_3]^{2+}$ from this result.

Stereoselectivity in the reaction of $[Co(glyO)(ox)_2]^{2-}$ with $[Co(phen)_3]^{2+}$ is moderately high, 37% ΔΔ. Absolute values for $\Delta\varepsilon$ for the $[Co(4,7\text{-dmphen})_3]^{3+}$ and $[Co(5,6\text{-dmphen})_3]^{3+}$ derivatives are not accurately known, but stereoselectivities estimated at 79 and 60% ΔΔ respectively are high in those reactions also. The former value corresponds to a discrimination factor $k_{\Delta\Delta}/k_{\Delta\Lambda} = 8.5$ which is among the largest values detected for outer-sphere stereoselectivity.[1] Comparison of the corresponding values for $[Co(ox)_3]^{3-}$ as oxidant,[3] 25 (phen), 43 (4,7-dmphen), and 19% ΔΔ (5,6-dmphen), indicates that the $[Co(glyO)(ox)_2]^{2-}$ reagent is capable of better discrimination than the more symmetric $[Co(ox)_3]^{3-}$ with all three reductants. The stereoselectivities are all in the same sense but vary considerably in magnitude, suggesting that the mechanism for chiral discrimination is quite different from that found for $[Co(en)_3]^{2+}$ as reductant.

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