Conformational effects on stereoselectivities in electron-transfer and ion-association reactions between metal complexes

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The stereoselectivities in the oxidation of $[Co(pn)_3]^{2+}$ (pn = 1,2-propanediamine) by Δ-$[Co(glyO)(ox)_2]^{2-}$ (glyO = glycinate, ox = oxalate) and in ion-association of (*lel*)$_3$- and (*ob*)$_3$-$[Co(pn)_3]^{3+}$ with the same anionic complex are observed to be dependent on the chelate-ring conformation and are indications of the importance of the electron-transfer step within a precursor assembly in the overall electron-transfer stereoselectivity.

It is recognized that chelate-ring conformation is an important factor in determinating stereoselectivities in both electron-transfer[1] and ion-association reactions.[2] Four conformational isomers are possible for $[Co(pn)_3]^{n+}$; (*lel*)$_3$, (*lel*)$_2$(*ob*), (*lel*)(*ob*)$_2$, and (*ob*)$_3$, where *lel* or *ob* refer to a conformation of the chelate ring in which the C–C bond is either parallel or oblique to the (*pseudo*-) C_3 axis of the complex (Fig. 1). In connection with the specific interactions of the conformational isomers with various anions in solution, although it was predicted from the chromatographic behaviour that the *lel* conformation differs from the *ob* conformation in the direction of the N–H bonds on coordinated nitrogen atoms responsible for the formation of hydrogen bonding between the reactants, a numerical difference in the stereoselective ion-association constants of the conformational isomers has not been reported.[2]

On the other hand, outer-sphere electron-transfer reactions are generally envisaged to occur in two steps: (*i*) the formation of a precursor assembly and (*ii*) electron transfer within this assembly. Little, however, is known about the relative contribution to the overall stereoselectivity of the two steps in electron-transfer reactions between metal complexes.[3] Thus, in order to gain an understanding of stereoselectivity in the formation of a precursor assembly, we tried to determine the stereoselective ion-association constants for the pairs, (*lel*)$_3$- and (*ob*)$_3$-$[Co(pn)_3]^{3+}$ with $[Co(glyO)(ox)_2]^{2-}$, using the isostructural non-redox active analogues, and to examine the influence of chelate-ring conformation on the overall electron-transfer stereoselectivity. $[Co(glyO)(ox)_2]^{2-}$ has been selected because this complex was already revealed to be an effective stereoselective oxidant for $[Co(en)_3]^{2+}$ (ref. 4) and $[Co(phen)_3]^{2+}$ (ref. 5) (phen = 1, 10-phenanthroline) and to have a high ability for chiral discrimination in ion-association with $[Co(en)_3]^{3+}$.[6]

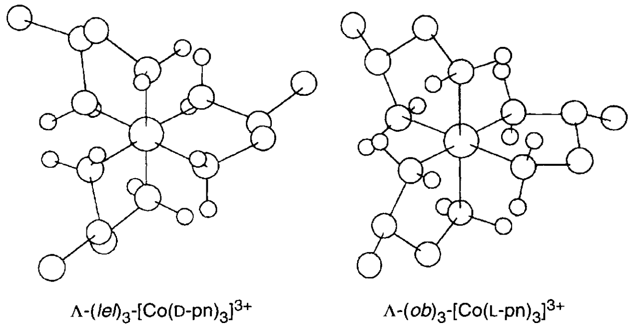
Λ-(*lel*)$_3$-$[Co(D\text{-}pn)_3]^{3+}$ Λ-(*ob*)$_3$-$[Co(L\text{-}pn)_3]^{3+}$

Fig. 1 Conformational isomers of $[Co(pn)_3]^{3+}$ with Λ configuration of *mer* species

To estimate quantitatively the ion-association stereoselectivity, the conductometric method which was previously confirmed to be useful for determining the stereoselective ion-association constants between metal complexes[6,7] has been employed. Fig. 2 shows the deviations of the observed conductivities, |Δκ|, from the sum of the conductivities of component electrolytes as a function of the volume fraction, *x*, of the cationic complex for Δ-(*lel*)$_3$-$[Co(L\text{-}pn)_3]^{3+}$–Δ-$[Co(glyO)(ox)_2]^{2-}$ and Λ-(*lel*)$_3$-$[Co(D\text{-}pn)_3]^{3+}$–Δ-[Co(glyO)-

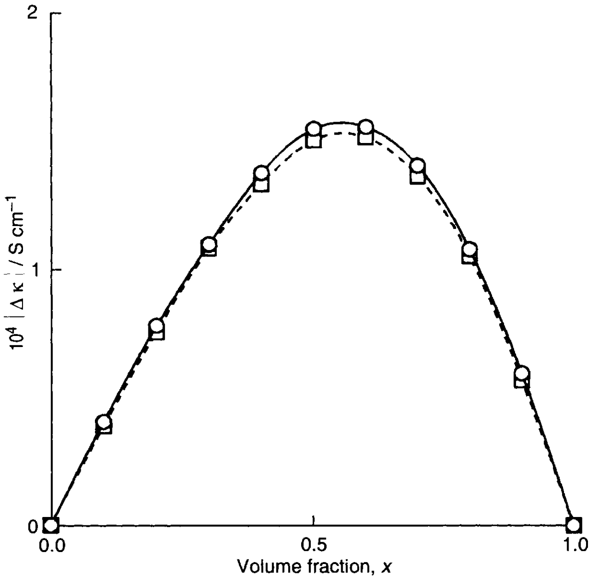

Fig. 2 Deviations, |Δκ|, of the observed conductivity from additivity as a function of the volume fraction of the cationic complex, *x*, for Δ-(*lel*)$_3$-$[Co(L\text{-}pn)_3]^{3+}$–Δ-$[Co(glyO)(ox)_2]^{2-}$ (○) and Λ-(*lel*)$_3$-$[Co(D\text{-}pn)_3]^{3+}$–Δ-$[Co(glyO)(ox)_2]^{2-}$ (□) pairs at 25 °C, I = 0.02

Table 1 Enantiomeric excesses and isomer distributions of conformational isomers in electron-transfer reactions of $[Co(pn)_3]^{2+}$ and ion-association constants of (*lel*)$_3$ and (*ob*)$_3$ isomers of $[Co(pn)_3]^{3+}$ with Δ-$[Co(glyO)(ox)_2]^{2-}$ at 25 °C

	Product in electron-transfer[b]		Ion-association constants[c]	
Conformational isomer[a]	% ee	Isomer distribution (%)	K_A (ΔΔ)/ dm^3 mol^{-1}	K_A (ΛΔ)[d]/ dm^3 mol^{-1}
(*lel*)$_3$	15.9 ΔΔ	34	277 ± 13	262 ± 12
(*lel*)$_2$(*ob*)	0.9 ΔΔ	44		
(*lel*)(*ob*)$_2$	1.6 ΔΛ[e]	18		
(*ob*)$_3$	4.1 ΔΔ	4	277 ± 19	276 ± 19

[a] These isomers are mixtures of *mer* and *fac* species. [b] Ionic strength I = 0.1 (KCl). [c] I = 0.02. [d] K_A (ΛΔ) denotes ion-association constant between Λ-cationic and Δ-anionic complexes. [e] ΔΛ means a Λ preference in % ee of the product when oxidized by Δ-oxidant complex.

Table 2 Comparisons of $k(\Delta\Delta)/k(\Delta\Lambda)$ in electron-transfer reactions with $K(\Delta\Delta)/K(\Delta\Lambda)$ in ion-association reactions in $(lel)_3$- and $(ob)_3$-$[\mathrm{Co(pn)_3}]^{n+}$–$[\mathrm{Co(glyO)(ox)_2}]^{2-}$ systems at 25 °C

Cation–anion pair	Electron-transfer[a] $k(\Delta\Delta)/k(\Delta\Lambda)$[b]	Ion-association[c] $K(\Delta\Delta)/K(\Lambda\Delta)$[d]
$(lel)_3$-$[\mathrm{Co(pn)_3}]^{n+}$ [e]–$[\mathrm{Co(glyO)(ox)_2}]^{2-}$	1.38	1.06 ± 0.02
$(ob)_3$-$[\mathrm{Co(pn)_3}]^{n+}$ [e]–$[\mathrm{Co(glyO)(ox)_2}]^{2-}$	1.09	1.00 ± 0.01

[a] Ionic strength $I = 0.1$ (KCl). [b] Calculated by $k(\Delta\Delta)/k(\Delta\Lambda) = (100 + \%\ \mathrm{ee})/(100 - \%\ \mathrm{ee})$. [c] $I = 0.02$. [d] Standard deviations were calculated using the equation given in the footnote of Table 2 in ref. 7. The ρ values were 0.952 and 0.966 for the $(lel)_3$ and $(ob)_3$ systems, respectively. [e] $n = 2$ and 3 for electron-transfer and ion-association reactions, respectively. Δ and Λ enantiomers of the $(lel)_3$ isomer are Δ-$(lel)_3$-$[\mathrm{Co(L\text{-}pn)_3}]^{n+}$ and Λ-$(lel)_3$-$[\mathrm{Co(D\text{-}pn)_3}]^{n+}$ and Δ and Λ enantiomers of $(\mathrm{ob})_3$ isomer are Δ-$(ob)_3$-$[\mathrm{Co(D\text{-}pn)_3}]^{n+}$ and Λ-$(ob)_3$-$[\mathrm{Co(L\text{-}pn)_3}]^{n+}$, respectively.

$\mathrm{(ox)_2]^{2-}}$ pairs at a stoichiometrically constant ionic strength ($I = 0.02$) and 25 °C.

The values of $|\Delta\kappa|$, with the assumption made by Katayama and Tamamuchi,[8] were related to the concentration of the ion pairs. The ion-association constants were analysed in the same way as previously reported,[6,7] and are given in Table 1 together with the results for Δ-$(ob)_3$-$[\mathrm{Co(D\text{-}pn)_3}]^{3+}$ and Λ-$(ob)_3$-$[\mathrm{Co(L\text{-}pn)_3}]^{3+}$ isomers. It can be seen that the Δ enantiomer of the $(lel)_3$ isomer forms more favourably with Δ-$[\mathrm{Co(glyO)(ox)_2}]^{2-}$ than does the Λ enantiomer, with a discrimination factor of 1.06 ± 0.02, but the Δ- and Λ-enantiomers of the $(ob)_3$ isomer scarcely discriminate the chirality of $[\mathrm{Co(glyO)(ox)_2}]^{2-}$.

Oxidation of $[\mathrm{Co(pn)_3}]^{2+}$ by Δ-$[\mathrm{Co(glyO)(ox)_2}]^{2-}$ is a rapid reaction similar to that of $[\mathrm{Co(en)_3}]^{2+}$ which proceeds by the outer-sphere mechanism. To the mixture of $\mathrm{Co^{II}}$ (2.5×10^{-2} mol dm^{-3}) and racemic propane-1,2-diamine (2.5×10^{-1} mol dm^{-3}) in KCl (1.0×10^{-1} mol dm^{-3}) solution was added Δ-$[\mathrm{Co(glyO)(ox)_2}]^{2-}$ (2.5×10^{-3} mol dm^{-3}) at 25 °C under a nitrogen atmosphere. Four conformational isomers of the oxidation product $[\mathrm{Co(pn)_3}]^{3+}$ were separated on an SP-Sephadex C-25 column (45 × 2.9 cm) using 0.15 mol dm^{-3} $\mathrm{Na_3PO_4}$ as eluent. The percentage enantiomeric excess (% ee) and the isomer distribution (%) which were determined from the absorption and the circular dichroism spectra of each conformational isomer are given in Table 1. The isomer distributions are very similar to those reported; $(lel)_3$: 35.0%, $(lel)_2(ob)$: 41.1%, $(lel)(ob)_2$: 18.0%, and $(ob)_3$: 4.0% for $[\mathrm{Co(pn)_3}]^{3+}$ equilibrated in the presence of charcoal at 100 °C,[9] suggesting that the isomer distributions of electron-transfer products depend not only on differences in the isomer distributions of $[\mathrm{Co(pn)_3}]^{2+}$ which were shown by molecular mechanics calculations[10] to be different from those of $[\mathrm{Co(pn)_3}]^{3+}$, but also on differences in the electron-transfer reactivities of the conformational isomers.

While the electron-transfer stereoselectivities of $(lel)_3$, $(lel)_2(ob)$, and $(lel)(ob)_2$ isomers show a trend from ΔΔ to ΔΛ with an increase in the number of *ob* conformers in a similar manner to those in the oxidation of $[\mathrm{Co(chxn)_3}]^{2+}$ (chxn = *trans*-1,2-diaminocyclohexane) and $[\mathrm{Co(bn)_3}]^{2+}$ (bn = 2,3-diaminobutane) by Δ-$[\mathrm{Co(edta)}]^{-}$,[1a,b] that of $(ob)_3$ isomer deviates from this trend (Table 1). The $(lel)_2(ob)$ and $(lel)(ob)_2$ isomers show very low selectivity with the opposite sense to each other, whereas the $(lel)_3$ and $(ob)_3$ isomers show significantly high selectivity with the same sense of a ΔΔ preference. For the $(lel)_3$ and $(ob)_3$ isomers, the electron-transfer stereoselectivities expressed as relative rates, $k(\Delta\Delta)/k(\Lambda\Delta)$, and the ion-association ones, $K(\Delta\Delta)/K(\Lambda\Delta)$, are summarized in Table 2. The overall stereoselectivity in electron-transfer reactions is generally considered to depend on the stereoselectivity in the formation of a precursor assembly. Lappin *et al.* explained the conformational dependence of stereoselectivity in the oxidation of $[\mathrm{Co(chxn)_3}]^{2+}$ by $[\mathrm{Co(edta)}]^{-}$ in terms of the changes in the ion-pairing interaction mode of $[\mathrm{Co(chxn)_3}]^{3+}$ isomers.[1a,b]

In the $(lel)_3$ isomer, the stereoselectivities in electron-transfer and ion-association reactions in the present study were ΔΔ in the same manner as that in the case of the chxn complex,[1a,b] consistent with a C_3C_3 interaction. It is noteworthy that the $k(\Delta\Delta)/k(\Lambda\Delta)$ value is significantly larger than the $K(\Delta\Delta)/K(\Lambda\Delta)$ value (Table 2), suggesting that the electron-transfer process within a precursor assembly contributes largely to the overall stereoselectivity though the influence of a decrease in the charge on the pn complex which forms a precursor assembly is not clear.

In the $(ob)_3$ isomer, the $K(\Delta\Delta)/K(\Lambda\Delta)$ value indicates virtually no stereoselectivity in the ion-association of $[\mathrm{Co(pn)_3}]^{3+}$ with $[\mathrm{Co(glyO)(ox)_2}]^{2-}$, unlike that between $[\mathrm{Co(chxn)_3}]^{3+}$ and $[\mathrm{Co(edta)}]^{-}$ with a ΛΔ preference. On the other hand, the $k(\Delta\Delta)/k(\Lambda\Delta)$ value shows that the electron-transfer reaction of the $(ob)_3$-$[\mathrm{Co(pn)_3}]^{2+}$ proceeds stereoselectively, but judging from the absence of ion-association stereoselectivity of the isostructural $(ob)_3$-$[\mathrm{Co(pn)_3}]^{3+}$, when $(ob)_3$-$[\mathrm{Co(pn)_3}]^{2+}$ forms a precursor assembly with $[\mathrm{Co(glyO)(ox)_2}]^{2-}$, the occurrence of stereoselectivity can not be expected. Thus, these indicate that at least in the $(ob)_3$ isomer, the overall electron-transfer stereoselectivity is not induced by the formation process of a precursor assembly, but exclusively by the electron-transfer process within the assembly. A similar importance of the electron-transfer process has been also shown for the stereoselectivity in the oxidation of $[\mathrm{Co(phen)_3}]^{2+}$ by $[\mathrm{Co(ox)_3}]^{3-}$.[11]

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