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Effects of Six-Membered Chelate Rings in the Oxidant Cobalt(III) Complexes on the Stereoselective Oxidation of $[Co(en)_3]^{2+}$

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Synopsis. The stereoselectivities in the oxidation of $[Co(en)_3]^{2+}$ by chiral cobalt(III) complexes containing six-membered chelate ligands, such as malonate, β-alaninate, and acetylacetonate ions, were examined. All of the oxidant complexes with the Δ-configuration studied here, like the corresponding oxalato and glycinato complexes containing five-membered chelate rings, led to an excess of Λ-$[Co(en)_3]^{3+}$, with the exception of Δ-$[Co(ox)(acac)_2]^-$.

There have been some studies on stereoselective electron-transfer reactions between cobalt(II) and cobalt(III) complexes.1—4) Most of them, however, were limited to the oxidation of cobalt(II) amine complexes by $[Co(edta)]^-$ and its derivatives. Then, as shown for the $[Co(en)_3]^{2+}$–$[Co(edta)]^-$ system (en=ethylenediamine and edta=ethylenediaminetetraacetate ion), it was thought that the ion-pairing stereoselectivity must play a dominant role in the electron-transfer stereoselectivity. Recently, we reported that even the Δ-$[Co(ox)_2(en)]^-$, Δ-C_2-*cis(N)*- and Δ-*trans(N)*-$[Co(ox)(gly)_2]^-$ (ox=oxalate ion and gly=glycinate ion), which form favorable pairs with Δ-$[Co(en)_3]^{3+}$, oxidized $[Co(en)_3]^{2+}$ to produce an excess of Λ-$[Co(en)_3]^{3+}$.5) This indicates that there exist systems in which the observed stereoselectivity in the electron-transfer reaction is different from the ion-pairing stereoselectivity. Thus, in order to obtain more detailed information about the stereoselective reaction mechanisms, it is important to know what kinds of factors affect the electron-transfer stereoselectivity between metal complexes. In this paper, the influence of six-membered chelate rings in the chiral oxidant cobalt(III) complexes are examined.

Experimental

Preparation of Complexes. $K_3[Co(mal)_3]\cdot 3H_2O$ (mal=malonate ion) was prepared and resolved according to a method by Butler and Snow,6) with Λ-lel$_3$-$[Co(+pn)_3]Cl_3$ (+pn=(S)-1,2-propanediamine) used as a resolving agent. Several Δ anionic complexes ($[Co(mal)_2(gly)]^{2-}$,7) $[Co(mal)_2(\beta\text{-ala})]^{2-}$,7) $[Co(ox)_2(\beta\text{-ala})]^{2-}$,7) $[Co(ox)_2(acac)]^{2-}$,8) $[Co(ox)(acac)_2]^-$,8) $[Co(mal)_2(en)]^-$,9) and C_1-*cis(N)*-,10) C_2-*cis(N)*-,10) and *trans(N)*-11)$[Co(ox)(\beta\text{-ala})_2]^-$ (β-ala=β-alaninate ion and acac=acetylacetonate ion)) were prepared according to methods described in the literature, and were isolated as their sodium or potassium salts. *fac*-12) and *mer*-13)$[Co(\beta\text{-ala})_3]$ were resolved by the chromatographic methods of Yoneda and co-workers. All of the complexes presently obtained were confirmed by the absorption and circular dichroism (CD) spectra, and were then used as the oxidant in electron-transfer reactions with $[Co(en)_3]^{2+}$.

Electron-Transfer Stereoselectivity. Measurements of electron-transfer stereoselectivity were made in the same manner as in a previous study.5) The maximum absorbance and CD spectrum in the first absorption region of the $[Co(en)_3]^{3+}$ product collected in 1.5 M HCl (1 M=1 mol dm^{-3}) were measured by a Jasco Uvidec-320 spectrophotometer and a Jasco J-500 spectropolarimeter, respectively, using 2 cm cells. The stereoselectivity was expressed in terms of enantiomeric excess (%ee) by evaluating the optical purity of the $[Co(en)_3]^{3+}$ product. Each standard deviation of %ee in this study was smaller than ±0.2%ee for at least triplicate runs.

Ion-Pairing Stereoslectivity. A column (ϕ 1.0 cm×55 cm) of SP-Sephadex C-25 cation exchanger, saturated with chiral $[Co(en)_3]^{3+}$, was prepared. When the anionic or neutral complex (3 cm^3 of 10—15 mmol dm^{-3}) was passed through the column with water, a partial resolution took place. The enantiomer which interacts favorably with the chiral $[Co(en)_3]^{3+}$ anchored to the ion exchanger can be expected to be eluted later from the column. Thus, favorable pairs between $[Co(en)_3]^{3+}$ and the complexes used as the oxidant were chromatographically determined by examining the late-eluted enantiomer.

Results and Discussion

In Table 1 are summarized the enantiomeric excesses of $[Co(en)_3]^{3+}$ produced by electron-transfer reactions of $[Co(en)_3]^{2+}$ with Δ-anionic or neutral complexes containing six-membered chelate rings and the enantiomers of $[Co(en)_3]^{3+}$ which form favorable pairs with the Δ-oxidant complexes, together with previous results for complex systems containing the corresponding five-membered chelate rings. It has been pointed out that the oxidation of $[Co(en)_3]^{2+}$ by chiral $[Co(mal)_3]^{3-}$ leads to a much lower stereoselectivity than that by chiral $[Co(ox)_3]^{3-}$.4,5) A similar trend has been observed for bis(malonato) complexes such as $[Co(mal)_2gly]^{2-}$ and $[Co(mal)_2(\beta\text{-ala})]^{2-}$, although the differences in magnitude of stereoselectivity between bis(malonato) and the corresponding bis(oxalato) complexes are considerably smaller than that between the tris complexes. The complexes of the type $[Co(\text{ox or mal})_2(\text{gly or }\beta\text{-ala})]^{2-}$ possess a pseudo-C_3 carboxylate face capable of forming hydrogen bonds with N–H protons of $[Co(en)_3]^{3+}$ and, therefore, were classified as the C_3^- group by Miyoshi and Yoneda.14) This group of anionic complexes shows the same stereoselectivity in the electron-transfer reaction as that in ion-pairing reaction ($\Delta\Delta$ preference). On the other hand, $[Co(mal)_2en]^-$ showed a more enhanced electron-transfer stereoselectivity than did $[Co(ox)_2en]^-$, and the electron-transfer ($\Lambda\Delta$ preference) and the ion-pairing stereoselectivities ($\Delta\Delta$ preference) by $[Co(mal)_2en]^-$ were opposite to each other, unlike the above C_3^- group complexes, in direction in the same manner as those by $[Co(ox)_2en]^-$. These anionic complexes were expected to interact with $[Co(en)_3]^{3+}$ along their C_2 axes and, thus, were classified as the C_2^- group;14) the above results, therefore, indicate that bis(malonato) chelates lead to either a lower or higher electron-transfer stereoselectivity than do the corresponding bis(oxalato) chelates according as they belong

Table 1. Electron-Transfer and Ion-Pairing Stereoselectivities

Oxidant	$[Co(en)_3]^{3+}$ %ee	$[Co(en)_3]^{3+}$ Favorable pair[a]	Oxidant	$[Co(en)_3]^{3+}$ %ee[b]	$[Co(en)_3]^{3+}$ Favorable pair[a,b]
Δ-$[Co(mal)_3]^{3-}$	1.9Λ, 0.6Λ[c]	Λ	Δ-$[Co(ox)_3]^{3-}$	10.0Λ, 7.6Λ[c]	—[d]
Δ-$[Co(mal)_2gly]^{2-}$	6.2Λ	Λ	Δ-$[Co(ox)_2gly]^{2-}$	9.0Λ	Λ[g]
Δ-$[Co(mal)_2(\beta\text{-ala})]^{2-}$	4.3Λ	Λ			
Δ-$[Co(ox)_2(\beta\text{-ala})]^{2-}$	8.7Λ	Λ			
Δ-$[Co(mal)_2en]^{-}$	5.6Λ	Δ[e]	Δ-$[Co(ox)_2en]^{-}$	3.6Λ	Δ[g]
Δ-$[Co(ox)(\beta\text{-ala})_2]^{-}$			Δ-$[Co(ox)(gly)_2]^{-}$		
C_1-*cis(N)*	10.5Λ	Λ	C_1-*cis(N)*	9.4Λ	Λ[g]
C_2-*cis(N)*	10.0Λ	Λ	C_2-*cis(N)*	2.1Λ	Δ[g]
trans(N)	—[f]	—[f]	*trans(N)*	0.5Λ	Δ
Δ-$[Co(\beta\text{-ala})_3]$					
fac	7.9Λ	Δ[g]			
mer	3.6Λ	Δ[e]			
Δ-$[Co(ox)_2acac]^{2-}$	2.6Λ	Λ[g]			
Δ-$[Co(ox)(acac)_2]^{-}$	3.1Δ	Λ			

a) The enantiomer of $[Co(en)_3]^{3+}$ which forms favorable pair with Δ-complexes used as the oxidant. b) Ref. 5. c) Ref. 4. d) Precipitation (less soluble diastereomer is a Δ–Δ pair). Erroneously given in Ref. 5 and thus corrected here. e) Very small stereoselectivity. f) Virtually no detectable stereoselectivity. g) Also reported in Ref. 14.

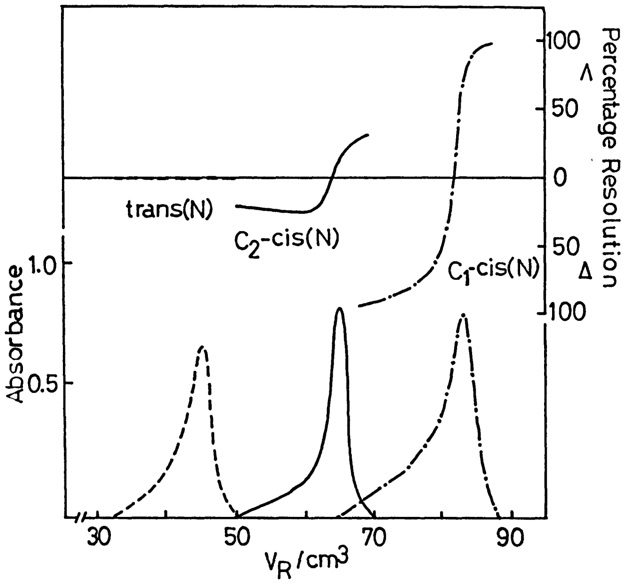

Fig. 1. Elution curves and percentage resolutions for *trans(N)*-, C_2-*cis(N)*-, and C_1-*cis(N)*-$[Co(ox)(\beta\text{-ala})_2]^-$ by Δ-$[Co(en)_3]^{3+}$ form SP-Sephadex column using H_2O as an eluent.

to either the C_3¯or C_2^- group. This suggests that the interaction mode of malonato complexes with $[Co(en)_3]^{2+}$ plays an important role regarding the magnitude of electron-transfer stereoselectivity.

For β-alaninato complexes, apart from *trans(N)*-$[Co(ox)(\beta\text{-ala})_2]^-$, which show virtually no detectable stereoselectivities in both the electron-transfer and the ion-pairing reactions (Fig. 1), all of the β-alaninato complexes with the Δ-configuration used here produced excess Λ-$[Co(en)_3]^{3+}$, although the electron-transfer and ion-pairing stereoselectivities by tris(β-alaninato) complexes were inverted in same manner as those by $[Co(ox)_2en]^-$ and $[Co(mal)_2en]^-$. Thus, in spite of large size and conformational lability of the six-membered chelate ring, it may be concluded that the observed electron-transfer stereoselectivity by the malonato and β-alaninato complexes was the same in direction as that by the corresponding oxalato and glycinato complexes containing five-membered chelate rings.

Finally, for the acetylacetonato complexes, the mono(acetylacetonato) complex, $[Co(ox)_2(acac)]^{2-}$ showed essentialy the same electron-transfer stereoselectivity as did $[Co(ox)_2gly]^{2-}$ and $[Co(ox)_2(\beta\text{-ala})]^{2-}$. However, the bis(acetylacetonato) complex, Δ-$[Co(ox)(acac)_2]^-$, was the only oxidant complex which produced an excess of Δ-$[Co(en)_3]^{3+}$ in the present study. The favorable ion pair of $[Co(en)_3]^{3+}$ with $[Co(ox)(acac)_2]^-$ was $\Lambda\Delta$, similar to that with $[Co(ox)_2\text{-}acac)]^{2-}$. At present, it is difficult to explain the unique phenomenon caused by $[Co(ox)(acac)_2]^-$. The selectivities in the oxidation reactions by various acetylacetonato complexes need to be examined further.

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