Induced Circular Dichroism Spectra of Some Racemic *cis*-Bis(ethylenediamine)cobalt(III) Complexes in Aqueous (*R*,*R*)-Tartrate and (*R*,*R*)-Tartratoantimonate(III) Solutions and Their Optical Resolution by Ion-exchange Chromatography

Hiroshi Nakazawa, Chang Eon Oh, Katsuhiko Miyoshi, and Hayami Yoneda*
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730

(Received June 25, 1979)

Synopsis. Induced circular dichroism (induced CD) was measured for some racemic cobalt(III) complexes in aqueous (*R*,*R*)-tartrate and (*R*,*R*)-tartratoantimonate(III) solutions, and correlation was examined between the sign of their induced CD spectra and their elution order in ion-exchange chromatography.

In a previous paper,[1] it was demonstrated that relatively weak circular dichroism (CD) induced in the first d-d transition region for a series of racemic tervalent cobalt(III) complexes of the type *cis*-$[Co(RNH_2)_2(en)_2]^{3+}$ in aqueous (*R*,*R*)-tartrate (*d*-$tart^{2-}$) and (*R*,*R*)-tartratoantimonate(III) (Sb_2d-$tart_2^{2-}$) solutions owes its origin to the differential CD change between the two enantiomers of each complex upon the addition of these chiral anions. It was proposed that the induced CD spectrum serves as a measure of chiral discrimination effected by *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$. An attempt was made to correlate the sign of the induced CD spectrum of a racemic complex with the elution order in its chromatographic resolution on an ion-exchange column with *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$ as an eluent. In the present study, a similar attempt was made for some bi- and univalent bis(ethylenediamine)cobalt(III) complexes whose absolute configurations were established by X-ray diffraction and/or assigned on the basis of their CD spectra.

Experimental

Metal Complexes. Metal complexes $[Co(tn)_3]^{3+}$,[2] $[Co(gly)(en)_2]^{2+}$,[3] $[Co(\beta\text{-ala})(en)_2]^{2+}$,[3] $[Co(acac)(en)_2]^{2+}$,[4] $[Co(ox)(en)_2]^{+}$,[5] $[Co(mal)(en)_2]^{+}$,[5] *cis*-$[Co(CN)_2(en)_2]^{+}$,[6] *cis*-$[Co(NO_2)_2(en)_2]^{+}$,[6,7] *cis*-$[Co(NCS)_2(en)_2]^{+}$,[7] and *cis*-$[Co(N_3)_2(en)_2]^{+}$,[6,7] were prepared as appropriate salts and, when necessary resolved by pertinent methods. They were found to be chromatographically pure and were identified by their absorption and/or CD spectra.

Chromatographic Resolution and Measurements. Chromatographic resolution was carried out in the same way as reported,[1,3] and found incomplete for most of the complexes. Since partial resolution is often attained on an SP-Sephadex column even with achiral eluents owing to the chirality of the resin,[8] Dowex 50W-X2 resin was used to confirm that the resulting elution order was not determined by the chirality of SP-Sephadex resin. Induced CD spectra were recorded for racemic complexes (0.01 mol dm^{-3}) in aqueous solutions containing sodium (*R*,*R*)-tartrate (0.1 mol dm^{-3}) or sodium (*R*,*R*)-tartratoantimonate(III) (0.1 mol dm^{-3}) at ambient temperature.

Results and Discussion

Figure 1 shows the induced CD spectra in the first d-d transition region obtained for all the racemic complexes in aqueous *d*-$tart^{2-}$ and Sb_2d-$tart_2^{2-}$ solutions. Only one CD component is induced for all of the tris-chelate complexes. Their Λ-enantiomers except for $[Co(tn)_3]^{3+}$ have in common a positive main CD component[3–6] in the first d-d transition region, its magnitude being diminished upon the addition of *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$. Thus negative and positive induced CD obtained for these complexes indicates that the Λ- and Δ-enantiomers, respectively, are subjected to a greater CD change upon addition of *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$.[1] The enantiomer for which the eluent has a stronger affinity should be eluted faster in ion-exchange chromatography. It is thus possible to predict the elution order from the sign of the induced CD if stronger interaction of these chiral anions with the complex leads to a greater change in its natural CD spectrum.

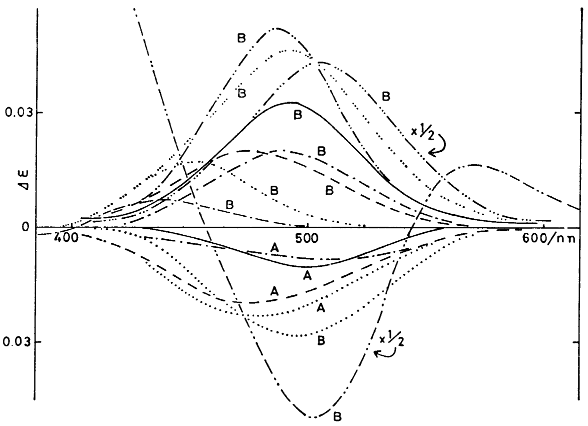

Fig. 1. Induced CD spectra in the first d-d transition region for racemic complexes in aqueous *d*-$tart^{2-}$ (A) and Sb_2d-$tart_2^{2-}$ (B) solutions; $[Co(tn)_3]^{3+}$(———), $[Co(gly)(en)_2]^{2+}$ (…………), $[Co(\beta\text{-ala})(en)_2]^{2+}$ (— — —), $[Co(acac)(en)_2]^{2+}$ (—·—·), $[Co(ox)(en)_2]^{+}$ (—⋯—⋯), $[Co(mal)(en)_2]^{+}$ (—··—··), *cis*-$[Co(CN)_2(en)_2]^{+}$ (——·——), *cis*-$[Co(NO_2)_2(en)_2]^{+}$ (·· ·· ·· ··), *cis*-$[Co(NCS)_2(en)_2]^{+}$ (⋯ ⋯ ⋯ ⋯), and *cis*-$[Co(N_3)_2(en)_2]^{+}$ (——··——).

In Table 1 are summarized the sign of the induced CD spectra and the absolute configurations of the enantiomers for which *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$ is expected to have a greater affinity as judged from the signs of the corresponding induced CD spectra for tris-chelate complexes. Also given in Table 1 are the absolute configurations of the enantiomers eluted faster in ion-exchange chromatography with *d*-$tart^{2-}$ or Sb_2d-$tart_2^{2-}$ as an eluent. It is confirmed that, when *d*-$tart^{2-}$ is used, the elution order[3] is in complete agreement with the prediction from the sign of the induced CD spectrum for all the tris-chelate complexes. On the other hand, when Sb_2d-$tart_2^{2-}$ is used, the induced

TABLE 1. ELUTION ORDER AND SIGN OF INDUCED CD SPECTRA

		Chromatography[a)]	Induced CD	(Affinity)[d)]
Na_2*d*-tart	$[Co(tn)_3]^{3+}$	$(-)_D$-Λ	negative	(Λ)
	$[Co(gly)(en)_2]^{2+}$	$(+)_D$-Λ	negative	(Λ)
	$[Co(\beta\text{-ala})(en)_2]^{2+}$	$(+)_D$-Λ	negative	(Λ)
	$[Co(acac)(en)_2]^{2+}$	$(+)_D$-Λ	negative	(Λ)
	$[Co(ox)(en)_2]^{+}$	$(+)_D$-Λ	negative[e)]	(Λ)
	$[Co(mal)(en)_2]^{+}$	$(+)_D$-Λ	negative[e)]	(Λ)
	cis-$[Co(CN)_2(en)_2]^{+}$	$(+)_D$-Λ	negative[e)]	
	cis-$[Co(NO_2)_2(en)_2]^{+}$	$(+)_D$-Λ	—[f)]	
	cis-$[Co(NCS)_2(en)_2]^{+}$	—[b)]	negative[e)]	
	cis-$[Co(N_3)_2(en)_2]^{+}$	$(+)_D$-Λ[c)]	negative[e)]	
Na_2Sb_2*d*-$tart_2$	$[Co(tn)_3]^{3+}$	$(+)_D$-Δ	positive	(Δ)
	$[Co(gly)(en)_2]^{2+}$	$(+)_D$-Λ	negative	(Λ)
	$[Co(\beta\text{-ala})(en)_2]^{2+}$	$(+)_D$-Λ	positive	(Δ)
	$[Co(acac)(en)_2]^{2+}$	$(+)_D$-Λ	positive	(Δ)
	$[Co(ox)(en)_2]^{+}$	$(-)_D$-Δ	positive	(Δ)
	$[Co(mal)(en)_2]^{+}$	$(-)_D$-Δ	positive	(Δ)
	cis-$[Co(CN)_2(en)_2]^{+}$	$(-)_D$-Δ	g)	
	cis-$[Co(NO_2)_2(en)_2]^{+}$	$(-)_D$-Δ	positive	
	cis-$[Co(NCS)_2(en)_2]^{+}$	$(+)_D$-Δ	positive	
	cis-$[Co(N_3)_2(en)_2]^{+}$	$(+)_D$-Λ[c)]	g)	

a) Absolute configuration of the enantiomer eluted faster. b) No resolution. c) Absolute configuration assigned not by its CD spectrum. See Ref. 8. d) Absolute configuration of the enantiomer expected to have a greater affinity for the eluent. e) Very weak. f) No induced CD detected. g) See Fig. 1.

CD exceptionally fails to predict a correct elution order for $[Co(\beta\text{-ala})(en)_2]^{2+}$ and $[Co(acac)(en)_2]^{2+}$ only. A similar apparent discrepancy was observed for *cis*-$[Co(NH_3)_2(en)_2]^{3+}$ with Sb_2*d*-$tart_2^{2-}$ as an eluent.[1)] It seems that Sb_2*d*-$tart_2^{2-}$ associates more easily with the Λ-enantiomers of the two complexes, their CD spectra not being so affected in comparison with those of the Δ-enantiomers, *i.e.*, the stronger interaction with Sb_2*d*-$tart_2^{2-}$ does not lead to a greater CD change for the two complexes.[1)] This suggests that the discriminating interaction with these cobalt(III) complexes essentially differs for *d*-$tart^{2-}$ and Sb_2*d*-$tart_2^{2-}$.[9,10)]

In the case of $[Co(tn)_3]^{3+}$ (Table 1) its Λ-enantiomer has a *negative* main CD component in the first d-d transition region unlike other tris-chelate complexes. However, its magnitude is enhanced upon addition of *d*-$tart^{2-}$ or Sb_2*d*-$tart_2^{2-}$, so that negative and positive induced CD suggest stronger interaction of *d*-$tart^{2-}$ or Sb_2*d*-$tart_2^{2-}$ with the Λ- and Δ-enantiomers, respectively. Thus the induced CD also correctly predicts the elution order[11)] for $[Co(tn)_3]^{3+}$.

The induced CD spectra of bis-chelate complexes of the type *cis*-$[Co(X)_2(en)_2]^{+}$ are complicated (Fig. 1 and Table 1). Their natural CD spectra are enhanced in magnitude for some complexes and are diminished for others upon the addition of *d*-$tart^{2-}$, Sb_2*d*-$tart_2^{2-}$, or oxoanions.[6,12)] It is impossible to predict the elution order from the induced CD spectra for *cis*-$[Co(X)_2(en)_2]^{+}$ complexes.

On the other hand, there seems to be a general trend in the elution order (Table 1) in the present chromatographic resolution. When *d*-$tart^{2-}$ is used, the Λ-enantiomers are eluted faster for all the bis(ethylenediamine) complexes including the tervalent complexes[1)] and $[Co(tn)_3]^{3+}$. When Sb_2*d*-$tart_2^{2-}$ is used, the Λ- and Δ-enantiomers are eluted faster for the bivalent and univalent bis(ethylenediamine) complexes, respectively, except for the diazido complex. The exceptional chromatographic behavior of the diazido complex has been discussed separately.[8)] However, it is not possible at present to interpret the elution order obtained for *cis*-$[Co(X)_2(en)_2]^{+}$ complexes.

References

1) K. Miyoshi, C. E. Oh, H. Nakazawa, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **51**, 2946 (1978).

2) J. C. Bailar, Jr., and J. B. Work, *J. Am. Chem. Soc.*, **68**, 232 (1946).

3) M. Kojima, H. Takayanagi, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 1891 (1977), and references cited therein.

4) L. J. Boucher, *Inorg. Chim. Acta*, **6**, 29 (1972).

5) W. T. Jordan, B. J. Brennan, L. R. Froebe, and B. E. Douglas, *Inorg. Chem.*, **12**, 1827 (1973), and references cited therein.

6) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094, and references cited therein.

7) K. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **49**, 3060 (1976), and references cited therein.

8) S. Yamazaki and H. Yoneda, *J. Chromatogr.*, **177**, 227 (1979).

9) H. Nakazawa and H. Yoneda, *J. Chromatogr.*, **160**, 89 (1978).

10) H. Yoneda, *J. Liquid Chromatogr.*, **2**, 1157 (1979).

11) M. Kojima, H. Yamada, H. Ogino, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 2325 (1977).

12) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).