

Contribution from the Department of Chemistry,
Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Application of the Pfeiffer Effect to the Assignment of Absolute Configurations to Octahedral Metal Complexes of the Type $cis-[M(\text{diamine})_2(X)(Y)]^{n+}$ and Related Complexes¹

KATSUHIKO MIYOSHI, YUUKO MATSUMOTO, and HAYAMI YONEDA*

Received July 8, 1980

The Pfeiffer effect of $[\text{Cr}(\text{ox})_3]^{3-}$ (ox = oxalate dianion) was examined by using as a chiral environment substance optically stable metal complexes of the type $cis-[M(\text{diamine})_2(X)(Y)]^{n+}$ ($M = \text{Co}^{3+}$ or Cr^{3+} , diamine = ethylenediamine (en) or trimethylenediamine (tn), and X and/or Y = anionic monodentate ligand) and their related complexes in dioxane-water mixtures. It was found that the chiral equilibrium of $[\text{Cr}(\text{ox})_3]^{3-}$ is always displaced in favor of its Δ enantiomer in the presence of Λ enantiomers of these complexes added as an environment substance. This was interpreted to mean that Λ - $cis-[M(\text{diamine})_2(X)(Y)]^{n+}$ complexes associate more preferably with Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ than with its antipode, the inversion rate of Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ being thereby retarded relative to that of the antipode. On the basis of this finding, it was proposed that the absolute configuration of $cis-[M(\text{en or tn})_2(X)(Y)]^{n+}$ and of the related complexes is inferred from the direction of the equilibrium shift in racemic $[\text{Cr}(\text{ox})_3]^{3-}$ induced by these chiral complexes. An association model was also proposed for the stereoselective interaction between $cis-[M(\text{diamine})_2(X)(Y)]^{n+}$ and $[\text{Cr}(\text{ox})_3]^{3-}$.

Introduction

Several methods have been devised so far to assign the absolute (or relative) configuration to octahedral transition-metal complexes.²⁻⁴ Among them, the method based on the CD spectra⁴ has been most widely applied to various types of metal complexes with d^3 and d^6 electronic configurations.⁵⁻⁷ In particular, so-called exciton CD^{8,9} affords a fairly reliable assignment to those complexes which have phen, bpy, acac⁻, cat²⁻, etc. as coordinated ligands (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine, acac⁻ = acetylacetonate anion, and cat²⁻ = catecholate anion).^{10,11}

Another method which should be noted and which is expected to be promising in the future is the one which is based on the phenomena associated with chiral discrimination.^{3b,12} For example, Yamasaki and Yoshikawa¹³ attempted to resolve several cobalt(III) complexes on ion-exchange cellulose and discussed their results in relation to the absolute configuration of the enantiomers eluted faster. Furthermore, the same authors¹⁴ and Yoneda et al.¹⁵ found in the study on the chromatographic resolution of some cationic cobalt(III)-amine

complexes that their Λ enantiomers are eluted faster through an SP-Sephadex ion-exchange column with aqueous sodium (*R,R*)-tartrate solutions as an eluant. However, the elution orders thus obtained do not serve as a reliable means to assign the absolute configuration until the nature of the discriminating interaction of these complexes with cellulose or (*R,R*)-tartrate ion is clearly elucidated.

The Pfeiffer effect,^{16,17} one of the fascinating subjects closely related to chiral discrimination in the field of coordination chemistry, refers to a shift in a chiral equilibrium between the two enantiomers of a labile metal complex in solution upon the addition of an optically active compound called an environment substance hereafter. Mayer and Brasted¹⁸ found that the chiral equilibrium of labile $[M(\text{phen})_3]^{2+}$ and $[M(\text{bpy})_3]^{2+}$ ($M = \text{Ni}^{2+}$ and Cd^{2+}) is displaced toward their Δ enantiomers in the presence of potassium (*R,R*)-tartratoantimonate(III) in water. Kirschner and co-workers reported, on the other hand, that Λ - and Δ - $[M(\text{phen})_3]^{2+}$ are enriched upon the addition of α -hydroxycarboxylic acids with *R* and *S* configurations,¹⁹ respectively, while Λ - $[M(\text{ox})_3]^{3-}$ or Δ - $[M(\text{phen})_3]^{2+}$ and their respective antipodes are enriched in the presence of *d*-(8*R*,9*S*)-cinchoninium and *l*-(8*S*,9*R*)-cinchonidinium ions,²¹ respectively, irrespective of the central metal ions *M*. These findings imply that the chiral equilibrium of a particular family of labile metal complexes, e.g., $[M(\text{phen})_3]^{2+}$ or $[M(\text{ox})_3]^{3-}$, is displaced toward the same direction (Λ or Δ) by a particular environment substance, e.g., *d*-cinchoninium ion. Therefore, the Pfeiffer effect is potentially applied to deduce the absolute configurations of labile metal complexes, but it has an inevitable disadvantage in that it applies at present only to limited families of labile metal complexes. However, if the Pfeiffer effect can be applied to assign the absolute configuration of the environment substances added to induce a shift in the chiral equilibrium of a given metal complex, its applicability is remarkably extended. Actually, Kirschner et al.^{19,22} attempted to predict the absolute configurations of several α -hydroxycarboxylic acids by de-

- (1) Part of this work was communicated in preliminary form: Y. Wada, K. Miyoshi, and H. Yoneda, *Chem. Lett.*, 763 (1978).
- (2) R. D. Gillard, *Prog. Inorg. Chem.*, **7**, 215 (1966).
- (3) (a) K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 6084 (1965); *J. Chem. Soc. A*, 201, 204 (1966); *Coord. Chem. Rev.*, **1**, 179 (1966); (b) *J. Chem. Soc. A*, 802 (1966), and references cited therein.
- (4) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley, New York, 1971.
- (5) (a) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965); (b) A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 5094 (1965).
- (6) B. J. Norman, *Inorg. Chim. Acta*, **1**, 177 (1967).
- (7) (a) K. Ohkawa, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 2830 (1967); (b) K. Yamasaki, J. Hidaka, and Y. Shimura, *ibid.*, **49**, 3060 (1976).
- (8) B. Bosnich, *Inorg. Chem.*, **7**, 178, 2379 (1968); *Acc. Chem. Res.*, **2**, 266 (1969); "Fundamental Aspects and Recent Developments in Rotatory Dispersion and Circular Dichroism", F. Ciardelli and P. Salvadori, Eds., Heyden and Sons, New York, 1973.
- (9) S. F. Mason, *Inorg. Chim. Acta Rev.*, **2**, 89 (1968); A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1428 (1969); S. F. Mason, B. J. Peart, and R. E. Wadell, *J. Chem. Soc., Dalton Trans.*, 944 (1973); S. F. Mason and B. J. Peart, *ibid.*, 949 (1973).
- (10) N. A. P. Kane-Maguire and D. E. Richardson, *J. Am. Chem. Soc.*, **97**, 7194 (1975).
- (11) Y. Ohashi, K. Yanagi, Y. Mitsuhashi, K. Nagata, Y. Kaizu, Y. Sasada, and H. Kobayashi, *J. Am. Chem. Soc.*, **101**, 4739 (1979).
- (12) D. P. Craig and D. P. Mellor, *Top. Current Chem.*, **63**, 1 (1976); S. F. Mason, *Annu. Rep. Prog. Chem., Sect. A: Phys. Inorg. Chem.*, **73**, 53 (1976).
- (13) K. Yamasaki and Y. Yoshikawa, *Rev. Roum. Chim.*, **22**, 801 (1977).
- (14) Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, **28**, 205 (1979).
- (15) K. Miyoshi, C. E. Oh, H. Nakazawa, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **51**, 2946 (1978); H. Nakazawa, C. E. Oh, K. Miyoshi, and H. Yoneda, *ibid.*, **53**, 273 (1980).

- (16) S. Kirschner and N. Ahmad, "Coordination Chemistry", S. Kirschner, Ed., Plenum Press, New York, 1969, p 42; R. C. Brasted, V. Landis, E. J. Kuhajek, P. E. R. Nordquist, and L. Mayer, *ibid.*, p 64.
- (17) S. Kirschner, N. Ahmad, and K. R. Magnell, *Coord. Chem. Rev.*, **3**, 201 (1968); S. Kirschner, *Rec. Chem. Prog.*, **32**, 29 (1971).
- (18) L. A. Mayer and R. C. Brasted, *J. Coord. Chem.*, **3**, 85 (1973).
- (19) S. Kirschner, N. Ahmad, C. Munir, and R. J. Pollock, *Pure Appl. Chem.*, **51**, 913 (1979).
- (20) N. Ahmad and S. Kirschner, *Inorg. Chim. Acta*, **14**, 215 (1975).
- (21) K. Miyoshi, Y. Kuroda, J. Takeda, H. Yoneda, and I. Takagi, *Inorg. Chem.*, **18**, 1425 (1979).
- (22) S. Kirschner, *J. Indian Chem. Soc.*, **51**, 28 (1974); P. J. Pollock, Ph.D. Dissertation, Wayne State University, 1972.

tecting the direction of the equilibrium shift in racemic $[\text{Co}(\text{phen})_3]^{2+}$ induced by the Pfeiffer effect.

In this paper, we propose that the Pfeiffer effect can be used to infer the absolute configurations of optically stable metal complexes of the type $\text{cis-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ ($\text{M} = \text{Co}^{3+}$ or Cr^{3+} , diamine = en or tn, and X and/or Y = anionic monodentate ligand) and of the related complexes if they are employed as a chiral environment substance to racemic $[\text{Cr}(\text{ox})_3]^{3-}$ in dioxane-water mixtures.

Experimental Section

Preparation of Metal Complexes. The metal complexes used in the study of the Pfeiffer effect were prepared as appropriate salts and were resolved according to the methods described in the literature: $[\text{Cr}(\text{ox})_3]^{3-}$,²³ $[\text{Cr}(\text{mal})_3]^{3-}$,²⁴ $[\text{Co}(\text{en})_2(\text{gly})]^{2+}$,²⁵ $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$,²⁶ $[\text{Co}(\text{en})_2(\text{ox})]^{2+}$,²⁷ $[\text{Co}(\text{en})_2(\text{sal})]^{2+}$,²⁸ $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^{2+}$,²⁹ $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{N}_3)]^{2+}$,^{7b} $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$,^{7b} $\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{Cl})]^{2+}$,^{3b} $\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{N}_3)]^{2+}$,^{7b} $\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{NCS})]^{2+}$,^{7b} $\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$,³⁰ $\text{cis-}[\text{Co}(\text{en})_2(\text{CN})]^{2+}$,³¹ $\text{cis-}[\text{Co}(\text{en})_2(\text{NCS})_2]^{2+}$,^{7b,32} $\text{cis-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^{2+}$,^{7b,33} $[\text{Co}(\text{tn})_2(\text{acac})]^{2+}$,³⁴ $\text{cis-}[\text{Co}(\text{tn})_2(\text{NO}_2)_2]^{2+}$,³⁵ $\text{cis-}\alpha$ - and $\text{cis-}\beta$ - $[\text{Co}(\text{trien})(\text{NO}_2)_2]^{2+}$,³⁶ $\text{cis-}\alpha$ - $[\text{Co}(\text{trien})(\text{N}_3)_2]^{2+}$,³⁷ $[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$,³⁸ $\text{cis-}[\text{Cr}(\text{en})_2(\text{NCS})_2]^{2+}$,³² and $\text{cis-}[\text{Cr}(\text{en})_2(\text{N}_3)_2]^{2+}$,³³ where ox, mal, gly, sal, acac, en, tn, and trien stand for oxalate, malonate, glycinate, salicylate, acetylacetonate, ethylenediamine, trimethylenediamine, and triethylenetetramine, respectively.

The complexes added in the racemization study of $[\text{Cr}(\text{ox})_3]^{3-}$ were $\text{rac-}[\text{Co}(\text{phen})_3]\text{Cl}_3$, Δ -, Δ -, and $\text{rac-cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Br}$, Δ - and $\text{rac-}[\text{Co}(\text{en})_2(\text{acac})]\text{I}_2$, Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]\text{Cl}_2$, Δ - and $\text{rac-}[\text{Co}(\text{en})_2(\text{ox})]\text{Cl}$, $\text{rac-}[\text{Co}(\text{en})_2(\text{acac})]\text{I}$,³⁹ $\text{rac-}[\text{Co}(\text{en})_2(\text{gly})]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, $\text{trans-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$, and $\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$, all of which were prepared by well-established methods and which were identified by their absorption and/or CD spectra. Other chemicals used were of reagent grade.

Detection of the Pfeiffer Effect. The same procedures and instruments as described earlier⁴⁰ were adopted with use of $\text{K}_3[\text{Cr}(\text{ox})_3]$ (or $\text{K}_3[\text{Cr}(\text{mal})_3]$) as a racemic complex. After an appropriate amount of dioxane was added to an aqueous mixture of racemic $[\text{Cr}(\text{ox})_3]^{3-}$ with resolved $\text{cis-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$, the mixture was kept standing overnight in the dark, and then it was passed through a cation-exchange column packed with SP-sephadex C-25 to remove the cationic, optically active $\text{cis-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$. The absorption and CD spectra of the effluent from the column were recorded

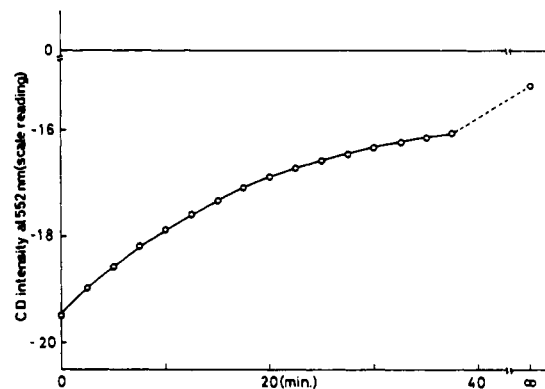


Figure 1. Plot of the CD intensity at 552 nm as a function of time (min) elapsed after racemic $\text{K}_3[\text{Cr}(\text{ox})_3]$ (13 mM) is mixed with Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$ (25 mM) in water at 25 °C.

as quickly as possible. The column was cooled with ice water to depress the thermal racemization of an enriched enantiomer of $[\text{Cr}(\text{ox})_3]^{3-}$. The direction of the equilibrium shift and the percentage resolution attained by the Pfeiffer effect were easily determined by comparing the sign and the intensity of the CD spectrum thus obtained with those of optically pure $[\text{Cr}(\text{ox})_3]^{3-}$ ($\Delta\epsilon = +2.83$ at 552 nm for Δ - $(+)_D$ enantiomer^{3a,24b}).

Kinetic Measurements. The rate of appearance of the Pfeiffer effect (antiracemization) of $[\text{Cr}(\text{ox})_3]^{3-}$ was followed by measuring the CD intensity at 552 nm as a function of time (min) elapsed after racemic $\text{K}_3[\text{Cr}(\text{ox})_3]$ (13 mM) was mixed with Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$ or Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$ (25 mM) in water at 25 °C. The racemization of Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ (9 mM) was followed in aqueous solutions containing various metal complexes at 25 °C over 2 half-lives by tracing the decay of the CD intensity at 630 nm but not at 552 nm so as to avoid the interference due to appreciable absorption and/or CD intensities of the complexes added.

Results and Discussion

A number of Pfeiffer-active systems have been reported so far,^{16,17} and it has been established that the origin of the Pfeiffer effect lies in a displacement of the chiral equilibrium between the two enantiomers of a labile metal complex in the presence of a chiral environment substance.^{10,16,41} However, only organic compounds have been used so far as an environment substance, e.g., *d*-tartaric acid, *d*-cinchoninium, *l*-strychninium, or *d*-3-bromocamphor-9-sulfonate ions, most of which have long been used as resolving agents for metal complexes. In recent years, on the other hand, resolved metal complexes have often been used successfully to resolve other metal complexes.^{27a} Thus, resolved metal complexes are expected to serve also as environment substances in the Pfeiffer effect. With this expectation in mind, the Pfeiffer effect of $[\text{Cr}(\text{ox})_3]^{3-}$ was examined with use of chiral metal complexes of the type $\text{cis-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ ($\text{M} = \text{Co}^{3+}$ or Cr^{3+} , diamine = en or tn, and X and/or Y = anionic monodentate ligand) and the related complexes as environment substances in dioxane-water mixtures.

Rate of Appearance of the Pfeiffer Effect. Figure 1 shows the change in the CD intensity at 552 nm with time (min) elapsed after Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$ (25 mM) was mixed with racemic $\text{K}_3[\text{Cr}(\text{ox})_3]$ (13 mM) in water at 25 °C. The open circle at $t = 0$ corresponds to the CD intensity solely due to Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$ which does not racemize at all under usual conditions. It is evident in Figure 1 that the CD intensity at 552 nm changes exponentially with time, suggesting a gradual displacement of the chiral equilibrium of $[\text{Cr}(\text{ox})_3]^{3-}$. Figure 1 also shows that Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ is being enriched in the presence of Δ - $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$, since Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ has a positive main CD component at 552

- (23) (a) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Synth.*, **1**, 35 (1939); J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, **8**, 1201 (1969); (b) K. B. Butler and M. R. Snow, *Chem. Commun.*, **1971**, 550.
 (24) (a) J. C. Chang, *Inorg. Synth.*, **16**, 80, (1976); (b) K. B. Butler and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 251 (1976).
 (25) (a) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); (b) S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).
 (26) L. J. Boucher, *Inorg. Chim. Acta*, **6**, 29 (1972).
 (27) (a) W. T. Jodan, B. J. Brennan, L. R. Froebe, and B. E. Douglas, *Inorg. Chem.*, **12**, 1827 (1973); (b) T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **46**, 159 (1973).
 (28) (a) K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 979 (1968); (b) A. G. Beaumont and R. D. Gillard, *Chem. Commun.*, 438 (1969).
 (29) M. Kuramoto, Y. Kushi, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **51**, 3196 (1978).
 (30) (a) J. Springörg and C. E. Schäffer, *Inorg. Synth.*, **14**, 72 (1973); (b) F. P. Dwyer and F. L. Garvan, *ibid.*, **6**, 195 (1960); (c) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **45**, 1755 (1972).
 (31) (a) S. C. Chang and M. L. Tobe, *J. Chem. Soc.*, 966 (1963); (b) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **44**, 2721 (1971).
 (32) (a) D. A. House, *J. Inorg. Nucl. Chem.*, **35**, 3103 (1973); (b) R. D. Gillard and R. Maskill, *Chem. Commun.*, 723 (1970); *J. Chem. Soc. A*, 2813 (1971).
 (33) I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem.*, **37**, 1359 (1975).
 (34) H. Kawaguchi, K. Matsumoto, H. Kuroya, S. Kawaguchi, *Chem. Lett.*, 125 (1972).
 (35) M. B. Celap, M. J. Malinar, and P. N. Padivojsa, *Inorg. Chem.*, **14**, 2965 (1975).
 (36) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965); **6**, 787 (1967).
 (37) S. Yamazaki and H. Yoneda, *J. Chromatogr.*, **177**, 227 (1979).
 (38) S. Kaizaki, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **12**, 135 (1973).
 (39) R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965); L. J. Boucher, *ibid.*, **9**, 1202 (1970).
 (40) K. Miyoshi, Y. Wada, and H. Yoneda, *Inorg. Chem.*, **17**, 751 (1978).

- (41) S. Kirschner and N. Ahmad, *J. Am. Chem. Soc.*, **90**, 1910 (1968).

nm.^{5a,23b,24b} Then, the mixture, which was kept standing for 3 h, was passed through a cation-exchange column as quickly as possible. The CD pattern obtained for the effluent from the column agreed completely with that of Λ -[Cr(ox)₃]³⁻, confirming an equilibrium shift toward the Λ enantiomer.

From a standard analysis²¹ of the plot shown in Figure 1, the rate constant of antiracemization, k_{anti} (rate of appearance of the Pfeiffer effect), was estimated to be $7.62 \times 10^{-4}/\text{s}$, which is somewhat greater than the racemization rate constant k_{rac}° of [Cr(ox)₃]³⁻ in pure water at 25 °C ($6.26 \times 10^{-4}/\text{s}$).^{21,42} Also, the same trend in the rate constants and the equilibrium shift toward the same direction were observed when Δ -*cis*-[Co(en)₂(NO₂)₂]⁺ was used as an environment substance. These facts mean that the inversion rate constant of Λ -[Cr(ox)₃]³⁻ (k_{Λ}) is smaller than that of the antipode (k_{Δ}) in the presence of Δ -*cis*-[Co(en)₂(NH₃)(NO₂)₂]²⁺ or of Δ -*cis*-[Co(en)₂(NO₂)₂]⁺, Λ -[Cr(ox)₃]³⁻ being thereby in excess at equilibrium. The reversed situation should be encountered when Λ enantiomers of these complexes are employed as environment substances. However, since k_{anti} of [Cr(ox)₃]³⁻ obtained in the Pfeiffer effect is the sum of k_{Λ} and k_{Δ} in the presence of an environment substance,²¹ both k_{Λ} and k_{Δ} or at least either k_{Λ} or k_{Δ} must be greater than the inversion rate constant k_i° in pure water, in order for the k_{anti} obtained in the present systems to be greater than k_{rac}° which is equal to 2 times k_i° .

By contrast, k_{anti} obtained in the [Cr(ox)₃]³⁻-*d*-cinchoninium system in water is definitely smaller than k_{rac}° ; k_{Λ} is preferentially lowered in the presence of *d*-cinchoninium ion, while k_{Δ} is almost identical with k_i° .²¹ This contrasting situation probably comes from the mechanistic aspects characteristic of the present Pfeiffer systems. Then, the racemization of Δ -[Cr(ox)₃]³⁻ (9 mM) was measured at 25 °C in aqueous solutions containing various metal complexes. The rate constants derived from a usual analysis are listed in Table I. For comparison, the effect of added tetraalkylammonium salts R₄NX (R = H, Me, Et, *n*-Pr, and *n*-Bu, and X = Cl, Br, or I) was also examined.

It is noted in Table I that highly charged cationic complexes have in general a greater effect on the racemization rate and added anions have little or no effect.⁴² This is to be expected from the electrostatic point of view and is attributed to outer-sphere association of [Cr(ox)₃]³⁻ with added cation complexes. However, a close inspection of Table I reveals that the k_{rac} values obtained are greater or smaller than k_{rac}° , depending on the nature of added complexes. Roughly speaking, hydrophilic complexes accelerate the racemization of [Cr(ox)₃]³⁻, while hydrophobic ones having phen or acac⁻ as coordinated ligands retard it. A similar tendency is observed when a series of tetraalkylammonium salts R₄NX are added; k_{rac} is greater than k_{rac}° for R = H, while it tends to be progressively smaller than k_{rac}° as R becomes bulky, i.e., as the added R₄N⁺ ion bears more hydrophobic character.⁴³

The retarded racemization of [Cr(ox)₃]³⁻ has been well interpreted by Odell and Shooter⁴² in terms of "local dehydration" in the second coordination sphere of the complex brought about by the association with hydrophobic cations. That is, the water molecules surrounding [Cr(ox)₃]³⁻ are partially removed when the complex forms an ion pair with a hydrophobic cation, so that the effective dielectric constant experienced by [Cr(ox)₃]³⁻ is lowered, the one-ended dissociation of ox²⁻ ligand being thereby hindered.⁴⁴ In this respect, added hydrophobic cations have essentially the same effect

Table I. Racemization Rate Constants k_{rac} ($\times 10^4/\text{s}$) of K₃(Δ -[Cr(ox)₃]) (9 mM) in Aqueous Solutions at 25 °C

added complex	concn, mM	k_{rac}
<i>rac</i> -[Co(en) ₂ (gly)]Cl ₂	10.0	9.00
Δ - <i>cis</i> -[Co(en) ₂ (NH ₃)(NO ₂)]Cl ₂	14.3	8.70
[Co(NH ₃) ₅ (NO ₂)]Cl ₂	10.0	8.35
Λ -[Co(en) ₂ (ox)]Cl	42.3	7.49
<i>rac</i> -[Co(en) ₂ (ox)]Cl	42.3	7.50
<i>rac</i> -[Co(en) ₂ (ox)]Cl	30.0	7.27
Λ - <i>cis</i> -[Co(en) ₂ (NO ₂) ₂]Br	30.0	6.87
Λ - <i>cis</i> -[Co(en) ₂ (NO ₂) ₂]Br	30.0	7.03
<i>rac-cis</i> -[Co(en) ₂ (NO ₂) ₂]Br	30.0	6.96
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]NO ₃	30.0	7.23
<i>cis</i> -[Co(NH ₃) ₄ (NO ₂) ₂]NO ₃	30.0	7.58
Λ -[Co(en) ₂ (acac)]I ₂	10.0	6.10
<i>rac</i> -[Co(en) ₂ (acac)]I ₂	10.0	6.18
<i>rac</i> -[Co(en)(acac)]I	10.0	5.98
<i>rac</i> -[Co(phen) ₃]Cl ₃	10.0	3.73
<i>rac</i> -[Co(phen) ₃]Cl ₃	5.0	4.75
NH ₄ Cl	30.0	6.74
NH ₄ I	30.0	6.75
Me ₄ NBr	30.0	5.78
Et ₄ NBr	30.0	5.27
<i>n</i> -Pr ₄ NBr	30.0	4.80
<i>n</i> -Bu ₄ NBr	30.0	4.72
		6.26 ^a

^a In pure water.

as nonpolar organic solvents added.^{21,42,44}

On the other hand, it is not easy at present to provide a reasonable interpretation for the accelerated racemization of [Cr(ox)₃]³⁻ in the presence of hydrophilic complexes. However, it is certain that divalent complexes (e.g., [Co(NH₃)₅(NO₂)]²⁺ or [Co(en)₂(gly)]²⁺) lead to a greater change in k_{rac} than monovalent ones (e.g., *cis*-[Co(NH₃)₄(NO₂)₂]⁺ or *cis*- and *trans*-[Co(en)₂(NO₂)₂]⁺), where the total ionic strength is kept constant. As a result, the accelerated racemization of [Cr(ox)₃]³⁻ is also attributed to outer-sphere association with added hydrophilic complexes.

Added transition-metal aqua ions are known to have an accelerating effect on the racemization of [Cr(ox)₃]³⁻, which has been ascribed to the formation of a "binuclear complex" with [Cr(ox)₃]³⁻.⁴⁵ However, the same interpretation does not apply here, since the metal complexes added have no ability to form such a binuclear complex (but they have N-H protons available for hydrogen bonding with ox²⁻). One of the plausible interpretations is to assume that added hydrophilic cationic complexes neutralize the negative charge generated when the one-ended dissociation of ox²⁻ from [Cr(ox)₃]³⁻ takes place, the transition state being thus stabilized electrostatically and then the racemization promoted. Hydrogen bonding may work to accelerate the racemization of [Cr(ox)₃]³⁻ when added hydrophilic complexes have N-H protons.

A similar charge neutralization effect will naturally be operative when hydrophobic complexes are added, but the "dehydration effect" mentioned above probably offsets the "charge neutralization effect", and the accelerated racemization by hydrogen bonding will not be expected.

Another important fact to be noted in Table I is that addition of Λ and Δ enantiomers or of a racemate of a particular complex results in slightly but definitely different k_{rac} values. For example, Λ -, Δ -, and *rac-cis*-[Co(en)₂(NO₂)₂]⁺ accelerate the racemization of Δ -[Cr(ox)₃]³⁻, but it racemizes more rapidly in the presence of Δ -*cis*-[Co(en)₂(NO₂)₂]⁺ than in the presence of its antipode. Therefore, if racemic [Cr(ox)₃]³⁻ is mixed with Δ -*cis*-[Co(en)₂(NO₂)₂]⁺, Λ -[Cr(ox)₃]³⁻ should be enriched with a rate constant greater than k_{rac}° , as is really

(42) A. L. Odell and D. Shooter, *J. Chem. Soc., Dalton Trans.*, 135 (1972).

(43) W. Y. Wen "Water and Aqueous Solutions", R. A. Horne, Ed., Wiley, New York, 1972, p 613; T. S. Sarma and J. C. Ahluwalia, *Chem. Soc. Rev.*, 2, 203 (1973).

(44) G. A. Lawrence and D. R. Stranks, *Inorg. Chem.*, 16, 929 (1977), and references cited therein.

(45) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967, Chapter 4.

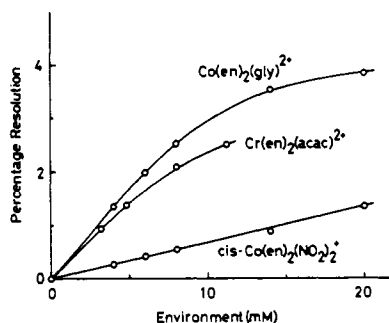


Figure 2. Plots of the percentage resolution of $[\text{Cr}(\text{ox})_3]^{3-}$ attained by the Pfeiffer effect as a function of the concentration of the environment substance. $[[\text{Cr}(\text{ox})_3]^{3-}] = 8 \text{ mM}$ and $[\text{dioxane}] = 10 \text{ mL}/25 \text{ mL}$ (total volume).

the case. The same holds for the *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$ system (vide supra). Conversely, Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ should be enriched when its racemate is mixed with Λ enantiomers of these complexes. When Λ - $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$ is used, Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ should be enriched with a rate constant smaller than k_{rac}^0 , as judged from the k_{rac} values in Table I. Unfortunately, the k_{anti} value of this system could not be obtained owing to an appreciable CD intensity due to $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$ at 552 nm. In any case, the results shown in Table I are completely consistent with the kinetic data obtained in the antiracemization study.

Influence of the Amounts of Added Environment Substances and Dioxane. In Figure 2 there is plotted the percentage resolution attained by the Pfeiffer effect against the amount of the added environment substance for the $[\text{Cr}(\text{ox})_3]^{3-}$ - Λ - $[\text{Co}(\text{en})_2(\text{gly})]^{2+}$, Λ - $[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$, and Λ -*cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$ systems, in all of which Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ is enriched. It is seen that the percentage resolution increases with increasing concentration of the environment substance for all the systems and that it is greater when divalent Λ - $[\text{Co}(\text{en})_2(\text{gly})]^{2+}$ and Λ - $[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$ are employed.

Figure 3 shows the influence of added dioxane on the percentage resolution attained in the $[\text{Cr}(\text{ox})_3]^{3-}$ - Λ - $[\text{Co}(\text{en})_2(\text{gly})]^{2+}$ and Λ -*cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$ systems. It is evident that added dioxane considerably enhances the percentage resolution for both systems. The addition of tetrahydrofuran (THF) leads to a similar enhancement of the Pfeiffer effect. Since both dioxane and THF are almost nonpolar, the addition of these solvents lowers the dielectric constant of the medium. As a result, it is concluded that electrostatic interaction plays a dominant role in the chiral discrimination effected in the present Pfeiffer systems. This conclusion is supported by the fact that divalent $[\text{Co}(\text{en})_2(\text{gly})]^{2+}$ and $[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$ are more effective in inducing an equilibrium shift in $[\text{Cr}(\text{ox})_3]^{3-}$ than monovalent *cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$, as shown in Figure 2. The nature of the discriminating interaction in the present Pfeiffer systems will be discussed later.

When chiral metal complexes are employed as environment substances, it is in general impossible to record the CD spectrum of an enriched enantiomer of an initially racemic complex over the whole d-d transition region because of its much lower CD intensity compared to the CD intensity of the environment substance present. Therefore, the labile complex whose chiral equilibrium has been displaced must be separated from the environment substance to detect the Pfeiffer effect quantitatively. In other words, the optical activity of the enriched enantiomer must survive fully until it is passed through a cation-exchange column and is subjected to absorption and CD measurements. In this respect, $[\text{Cr}(\text{ox})_3]^{3-}$ is most suitable; its half-life of racemization is not too long and not too short (18.4 min in H_2O at 25 °C), and it becomes

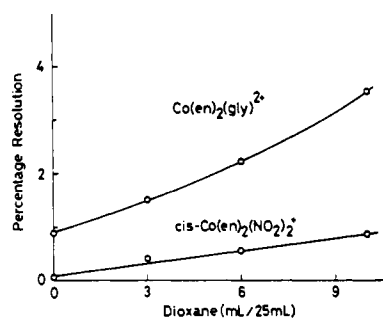


Figure 3. Influence of the amount of added dioxane on the percentage resolution of $[\text{Cr}(\text{ox})_3]^{3-}$ attained by the Pfeiffer effect. $[[\text{Cr}(\text{ox})_3]^{3-}] = 8 \text{ mM}$ and $[\text{environment substance}] = 14 \text{ mM}$. Total volume = 25 mL.

longer upon the addition of dioxane.^{21,42,44} Furthermore, the CD intensity of optically pure $[\text{Cr}(\text{ox})_3]^{3-}$ is so high that the percentage resolution attained can be estimated down to 0.1%.

The Pfeiffer effect is observed only for optically labile complexes. Since these complexes are also in general substitution labile, they often suffer ligand substitution by the environment substance. For example, when racemic $[\text{Cr}(\text{ox})_3]^{3-}$ is mixed with *d*-tartaric acid or sodium *d*-tartrate, ox^{2-} in the complex is gradually replaced by *d*-tartrate ion, giving an optically active mixed-ligand complex. The same phenomenon is observed when racemic $[\text{Co}(\text{phen})_3]^{2+}$ is mixed with *d*-tartrate ion,⁴⁶ and it is not the true Pfeiffer effect. However, the environment substances employed here are stable complexes which have no ability to participate in such a substitution reaction. This is a noteworthy and preferable characteristic of the present Pfeiffer systems in which the chiral environment is provided by "inert" metal complexes.

Prediction of the Absolute Configuration of *cis*- $[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ Complexes. In Table II there are listed the absolute configurations of $[\text{Cr}(\text{ox})_3]^{3-}$ (or $[\text{Cr}(\text{mal})_3]^{3-}$ ^{24b}) enriched when chiral metal complexes of the type *cis*- $[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ (and related complexes which are assigned to have a Λ configuration) are employed as environment substances. In the second column of Table II are listed the methods by which the absolute configurations of the environment substances (listed in the first column) are determined or assigned. Trivalent complexes such as $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{tn})_3]^{3+}$, *cis*- $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$, $[\text{Co}(\text{en})_2(\text{phen})]^{3+}$, and $[\text{Co}(\text{bpy})_3]^{3+}$ cannot be employed because of the formation of a precipitate with $[\text{Cr}(\text{ox})_3]^{3-}$.

It is evident in Table II that, with few exceptions, Δ - $[\text{Cr}(\text{ox})_3]^{3-}$ is enriched in the presence of Λ enantiomers of the environment substances employed here. The same is true when $[\text{Cr}(\text{mal})_3]^{3-}$ is used as a racemic complex, though only two chiral complexes, Λ -*cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^{2+}$ and Λ - $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$ are examined here. If the chiral equilibrium of $[\text{Cr}(\text{ox})_3]^{3-}$ is always displaced in favor of its Δ enantiomer when Λ -*cis*- $[\text{M}(\text{en or tn})_2(\text{X})(\text{Y})]^{n+}$ complexes are employed as environment substances, the absolute configurations of these chiral complexes are inferred from the direction of the equilibrium shift of racemic $[\text{Cr}(\text{ox})_3]^{3-}$.

Two unexpected findings are noted in Table II. The first is that the Λ enantiomers of the two diazido-cobalt(III) complexes, *cis*- $[\text{Co}(\text{en})_2(\text{N}_3)_2]^{2+}$ and *cis*- α - $[\text{Co}(\text{trien})(\text{N}_3)_2]^{2+}$, whose absolute configurations are assigned on the basis of their CD spectra,⁴⁷ enrich Λ - $[\text{Cr}(\text{ox})_3]^{3-}$, unlike other complexes with Λ configurations, while *cis*- $[\text{Cr}(\text{en})_2(\text{N}_3)_2]^{2+}$ behaves normally. This fact leads us to suppose that the absolute

(46) Y. Kuroda, K. Miyoshi, and H. Yoneda, *Inorg. Chim. Acta*, **28**, 211 (1978).

(47) The absolute configuration of *cis*- α - $[\text{Co}(\text{trien})(\text{N}_3)_2]^{2+}$ is assigned by the comparison of its CD spectrum with that of *cis*- $[\text{Co}(\text{en})_2(\text{N}_3)_2]^{2+}$.

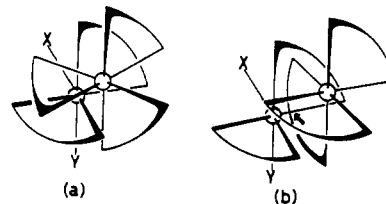
Table II. Absolute Configuration of $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{mal})_3]^{3-}$ Enriched by the Pfeiffer Effect

environment substance	assignt	ref	enriched enantiomer ^a
$\Lambda\text{-}(+)\text{}_{589}\text{-}[\text{Co}(\text{en})_2(\text{gly})]^{2+}$	CD	25b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}[\text{Co}(\text{en})_2(\text{acac})]^{2+}$	CD	5b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}[\text{Co}(\text{en})_2(\text{ox})]^{2+}$	X-ray	27b	e
$\Lambda\text{-}(+)\text{}_{589}\text{-}[\text{Co}(\text{en})_2(\text{sal})]^+$	CT ^b	28b	e
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^{2+}$	X-ray	29	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{N}_3)]^{2+}$	CD	7b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NO}_2)]^{2+}$	CD ^c	7b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{Cl})]^+$	CD ^c	7b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{N}_3)]^+$	CD	7b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)(\text{NCS})]^+$	CD ^c	7b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$	X-ray	30c	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{CN})_2]^+$	X-ray	31b	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NCS})_2]^+$	CD ^c	32a	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$	CD	5b	Λ^f
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{tn})_2(\text{acac})]^{2+}$	X-ray	34	Δ
$\Lambda\text{-}(+)\text{}_{546}\text{-}cis\text{-}[\text{Co}(\text{tn})_2(\text{NO}_2)_2]^+$	CD	35	Δ
$\Lambda\text{-}(+)\text{}_{546}\text{-}cis\text{-}\alpha\text{-}[\text{Co}(\text{trien})(\text{NO}_2)_2]^+$	CD	36	Δ
$\Lambda\text{-}(+)\text{}_{546}\text{-}cis\text{-}\beta\text{-}[\text{Co}(\text{trien})(\text{NO}_2)_2]^+$	CD	36	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}\alpha\text{-}[\text{Co}(\text{trien})(\text{N}_3)_2]^+$	CD ^d	47	Λ^f
$\Lambda\text{-}(+)\text{}_{546}\text{-}[\text{Cr}(\text{en})_2(\text{acac})]^{2+}$	CD	38	Δ
$\Lambda\text{-}(+)\text{}_{436}\text{-}cis\text{-}[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$	CD	32a	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Cr}(\text{en})_2(\text{N}_3)_2]^+$	CD	33	Δ
$\Lambda\text{-}(+)\text{}_{589}\text{-}[\text{Co}(\text{en})_2(\text{acac})]^{2+}$	CD	5b	Δ^g
$\Lambda\text{-}(+)\text{}_{589}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$	X-ray	30c	Δ^g

^a Absolute configuration of an enriched enantiomer of $[\text{Cr}(\text{ox})_3]^{3-}$ unless otherwise stated. ^b Assigned by chemical transformation (CT). ^c Also assigned by CT.^{3a,32b} ^d Assigned by comparison with the CD spectrum of $cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$. ^e No Pfeiffer effect detected. ^f See the text. ^g Absolute configuration of an enriched enantiomer of $[\text{Cr}(\text{mal})_3]^{3-}$.

configuration is incorrectly assigned to the two diazido-cobalt(III) complexes. In fact, Kindred and House³³ have already expressed doubt about the absolute configuration of $cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$ assigned by McCaffery et al.,^{5b} and they concluded from their elaborate experimental results that the assignment made to this complex on the basis of its CD spectrum is erroneous. The same conclusion is drawn from the studies of the chemical transformation made by Buckingham et al.⁴⁸ and of the chromatographic resolution attempted by Yamazaki and Yoneda.³⁷ Therefore, the two diazido-cobalt(III) complexes listed in Table II actually have a Δ configuration,⁴⁹ $\Lambda\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ being thus enriched. In other words, the two diazido complexes also behave normally. Recently, Akamatsu and Shimura⁵⁰ assigned a Λ configuration to $(+)\text{}_{D}\text{-}cis\text{-}[\text{Co}(\text{N},\text{N}\text{-}\text{Me}_2(\text{en}))_2(\text{N}_3)_2]^+$ from a comparison of its CD spectrum with that of $cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$. We suppose that their assignment is also erroneous.

Another finding to be noted is that neither $[\text{Co}(\text{en})_2(\text{ox})]^+$ nor $[\text{Co}(\text{en})_2(\text{sal})]^+$ serves as an environment substance to $[\text{Cr}(\text{ox})_3]^{3-}$ even if a considerable amount of dioxane is added to enhance their electrostatic attraction. This is an unexpected finding but is consistent with the kinetic data obtained in the racemization study (Table I); the k_{rac} value of $\Delta\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ is not affected by whether the added $[\text{Co}(\text{en})_2(\text{ox})]^+$ is racemic or optically active. Though $[\text{Co}(\text{en})_2(\text{ox})]^+$ certainly interacts to some extent with $[\text{Cr}(\text{ox})_3]^{3-}$, even in water, as judged from the k_{rac} values listed in Table I, why $[\text{Cr}(\text{ox})_3]^{3-}$ does not

**Figure 4.** Proposed models for stereoselective association (a) between $\Delta\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ and $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ and (b) between $\Lambda\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ and $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$.

recognize the chirality of $[\text{Co}(\text{en})_2(\text{ox})]^+$ or $[\text{Co}(\text{en})_2(\text{sal})]^+$ remains as an unsolved problem. The two complexes have seemingly a common characteristic in that two (cis to each other) of the six coordination sites of the central cobalt ion are occupied by anionic oxygen atoms, which will help to challenge this pending problem, but further work is needed.

Proposed Model for Stereoselective Association. Many interaction modes are conceivable between $[\text{Cr}(\text{ox})_3]^{3-}$ and the chiral environment substances $cis\text{-}[\text{M}(\text{en or tn})_2(\text{X})(\text{Y})]^{n+}$. In particular, all of the environment substances employed here have N-H protons available for hydrogen bonding with carbonyl oxygen atoms of ox^{2-} in $[\text{Cr}(\text{ox})_3]^{3-}$. However, we have presented evidence suggesting that electrostatic interaction plays a dominant role in the chiral discrimination effected in the present Pfeiffer systems. A common characteristic of the environment substances employed here is that one or two (cis to each other) of the six coordination sites of the central metal ion are occupied by anionic ligands. Therefore, it is most plausible that anionic $[\text{Cr}(\text{ox})_3]^{3-}$ approaches the cationic $cis\text{-}[\text{M}(\text{en or tn})_2(\text{X})(\text{Y})]^{n+}$ complexes along their C_2 or pseudo- C_2 axis from the side opposite to the anionic ligands X and/or Y, so as not to suffer electrostatic repulsion from these anionic ligands.⁵¹ In other words, $[\text{Cr}(\text{ox})_3]^{3-}$ will experience the $P(C_2)$ chirality (proposed by Mason et al.⁵) built up by the two diamine chelate rings of $\Lambda\text{-}cis\text{-}[\text{M}(\text{en or tn})_2(\text{X})(\text{Y})]^{n+}$. Then the stereoselective association model in Figure 4 is proposed.

In this model, $[\text{Cr}(\text{ox})_3]^{3-}$ faces the $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ with its C_3 axis in front so that it may associate with the environment substance as closely as possible. It is evident on the basis of this model that the association takes place smoothly between $\Delta\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ and $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$, while the steric hindrance anticipated between the chelating ligands (indicated by an arrow) renders the association between $\Lambda\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ and $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ unfavorable. In short, the $P(C_3)\text{-}P(C_2)$ combination is favorable, while its diastereomeric combination, $M(C_3)\text{-}P(C_2)$ is unfavorable. If this interaction mode retards the inversion rate of $\Delta\text{-}[\text{Cr}(\text{ox})_3]^{3-}$ relative to that of its antipode, the chiral equilibrium of $[\text{Cr}(\text{ox})_3]^{3-}$ should be always displaced in favor of its Δ enantiomer in the presence of $\Lambda\text{-}cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ type complexes and their related complexes, as is found experimentally (Table II).

Other interaction modes such as hydrogen bonding are of course not ruled out, though they are probably not stereoselective. For example, should $[\text{Cr}(\text{ox})_3]^{3-}$ interact with $cis\text{-}[\text{M}(\text{diamine})_2(\text{X})(\text{Y})]^{n+}$ only through the association model proposed above, its racemization rate constant would not be directly subjected to the influence of the anionic ligands X and/or Y. In reality, the k_{rac} value of $[\text{Cr}(\text{ox})_3]^{3-}$ is dependent on the nature of the anionic ligands; $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$ slightly retards the racemization of $[\text{Cr}(\text{ox})_3]^{3-}$ unlike hydrophilic complexes, suggesting some chance for even anionic acac^- in $[\text{Co}(\text{en})_2(\text{acac})]^{2+}$ to interact with anionic $[\text{Cr}(\text{ox})_3]^{3-}$.

(48) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1807 (1967).

(49) Recent X-ray analysis of the less-soluble diastereomer of $cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$ with ((*R,R*)-tartarato)antimonate(III) revealed that $(+)\text{}_{D}\text{-}cis\text{-}[\text{Co}(\text{en})_2(\text{N}_3)_2]^+$ has a Λ configuration in disagreement with the assignment made from the CD spectrum: A. Miyayama, Y. Kushi, and H. Yoneda, manuscript in preparation.

(50) K. Akamatsu and Y. Shimura, *Bull. Chem. Soc., Jpn.*, **51**, 2586 (1978).

(51) U. Sakaguchi, H. Nakazawa, and H. Yoneda, *J. Chem. Soc., Chem. Commun.*, 356 (1979).

Anyway, if the chiral discrimination is effected in the association model shown in Figure 4, we are obliged to assume that the stereoselective association proposed above retards the inversion rate of Δ -[Cr(ox)₃]³⁻ preferentially, while other interaction modes, which are supposed not to be stereoselective, accelerate or retard the inversion rate of both Λ - and Δ -[Cr(ox)₃]³⁻ to the same extent, depending on whether the environment substances are hydrophilic or hydrophobic, respectively. It must be noted, however, that the association model proposed above is no more than a tentative one. For example, our model does not afford any interpretation of the fact that [Co(en)₂(ox)]⁺ and [Co(en)₂(sal)]⁺ do not induce an equilibrium shift in racemic [Cr(ox)₃]³⁻ at all. Nevertheless, our model at present explains best our experimental finding that the chiral equilibrium of [Cr(ox)₃]³⁻ (or [Cr(mal)₃]³⁻) is always displaced toward its Δ enantiomer in the presence of Λ -*cis*-[M(diamine)₂(X)(Y)]^{nt+} type complexes and related complexes in which one or two (*cis* to each other) of the six coordination sites are occupied by anionic ligand atoms. As a result, we propose here that the absolute configurations of *cis*-[M(en or tn)₂(X)(Y)]^{nt+} type complexes and related complexes can be inferred from the direction of the equilibrium shift in initially racemic [Cr(ox)₃]³⁻ when they are employed as chiral environment substances. In addition, the central metal ion M may be other than Co³⁺ and Cr³⁺, provided that the environment substances *cis*-[M(diamine)₂(X)(Y)]^{nt+} are positively charged and optically stable.

Several methods based on chiral discrimination such as diastereomer solubility, active racemate, elution order in chromatography, etc. have been proposed so far to assign

absolute configurations to metal complexes. However, most of these methods are empirical and/or not without risk, and they are at most applicable to limited cases.^{2,3b,4} On the contrary, the new method proposed in the present study is based on a relatively sound experimental foundation, and its applicability is clarified to a considerable extent.

Registry No. K₃(Δ -[Cr(ox)₃]), 25978-34-1; *rac*-K₃[Cr(ox)₃], 14217-01-7; *rac*-K₃[Cr(mal)₃], 23555-18-2; *rac*-[Co(en)₂(gly)]Cl₂, 14408-57-2; Δ -*cis*-[Co(en)₂(NH₃)(NO₂)Cl]₂, 76377-40-7; [Co(NH₃)₅(NO₂)Cl]₂, 13782-02-0; Λ -[Co(en)₂(ox)]Cl, 31716-15-1; *rac*-[Co(en)₂(ox)]Cl, 17439-00-8; Λ -*cis*-[Co(en)₂(NO₂)₂Br], 15352-27-9; Δ -*cis*-[Co(en)₂(NO₂)₂Br], 21350-93-6; *rac-cis*-[Co(en)₂(NO₂)₂Br], 20298-24-2; *trans*-[Co(en)₂(NO₂)₂NO₃], 14240-12-1; *cis*-[Co(NH₃)₄(NO₂)₂]NO₃, 13782-03-1; Λ -[Co(en)₂(acac)]I₂, 36186-04-6; *rac*-[Co(en)₂(acac)]I₂, 15627-56-2; *rac*-[Co(en)(acac)₂]I, 76377-41-8; *rac*-[Co(phen)₃]Cl₃, 15406-83-4; NH₄Cl, 12125-02-9; NH₄I, 12027-06-4; Me₄NBr, 64-20-0; Et₄NBr, 71-91-0; *n*-Pr₄NBr, 1941-30-6; *n*-Bu₄NBr, 1643-19-2; Λ -(+)₅₈₉-[Co(en)₂(gly)]²⁺, 19657-80-8; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NH₃)(Cl)]²⁺, 45837-30-7; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NH₃)(N₃)]²⁺, 46139-34-8; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NH₃)(NO₂)]²⁺, 48131-50-6; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NO₂)(Cl)]²⁺, 20150-51-0; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NO₂)(N₃)]²⁺, 61586-09-2; Λ -(+)₅₈₉-*cis*-[Co(en)₂(NO₂)(NCS)]⁺, 46360-18-3; Λ -(+)₅₈₉-*cis*-[Co(en)₂(CN)₂]⁺, 18660-79-2; Λ -(-)₅₈₉-*cis*-[Co(en)₂(NCS)₂]⁺, 50762-67-9; Δ -(-)₅₈₉-*cis*-[Co(en)₂(N₃)₂]⁺, 39502-33-5; Λ -(+)₅₈₉-*cis*-[Co(tn)₂(acac)]²⁺, 76420-15-0; Λ -(+)₅₄₆-*cis*-[Co(tn)₂(NO₂)₂]⁺, 56498-54-5; Λ -(+)₅₄₆-*cis*- α -[Co(trien)(NO₂)₂]⁺, 46750-39-4; Λ -(+)₅₄₆-*cis*- β -[Co(trien)(NO₂)₂]⁺, 46750-44-1; Δ -(-)₅₈₉-*cis*- α -[Co(trien)(N₃)₂]⁺, 76465-70-8; Λ -(+)₅₄₆-[Cr(en)₂(acac)]²⁺, 60633-74-1; Λ -(-)₄₃₆-*cis*-[Cr(en)₂(NCS)]²⁺, 49552-96-7; Λ (+)₅₈₉-*cis*-[Cr(en)₂(N₃)₂]⁺, 56846-49-2; Δ -(+)_D-*cis*-[Co(*N,N*-Me₂(en))₂(N₃)₂]⁺, 68509-65-9; dioxane, 123-91-1.

Contribution from the Institute for Inorganic Chemistry, University of Munich, D-8000 Munich 2, West Germany

Metal Tetrahydridoborates and (Tetrahydroborato)metalates. 10.¹ NMR Study of the Systems AlH₃/BH₃/THF and LiAlH₄/BH₃/THF

HEINRICH NÖTH* and ROBERT RURLÄNDER

Received August 1, 1980

The systems AlH₃/BH₃/THF and LiAlH₄/BH₃/THF have been investigated by means of ¹¹B and ²⁷Al NMR spectroscopy. The NMR spectra indicate equilibria of the types AlH₃ + *n*BH₃ \rightleftharpoons AlH_{3-n}(BH₄)_n and 2AlH_{3-n}(BH₄)_n \rightleftharpoons AlH_{3-(n+1)}(BH₄)_{n+1} + AlH_{3-(n-1)}(BH₄)_{n-1} with all Al species and BH₃ coordinated with THF. An even more complex situation holds for the LiAlH₄/BH₃/THF system. The species formed are LiBH₄ and AlH_{3-n}(BH₄)_n in equilibrium with LiAlH_{3-n}(BH₄)_{n+1}. The equilibria are shifted toward the (tetrahydroborato)aluminates more strongly with increasing *n* and decreasing temperatures. At higher temperatures a rapid BH₄⁻ exchange prevails. Moreover, at high *n* values it is not only THF that competes with Al-H for BH₃ but also BH₄⁻ which gives rise to B₂H₇⁻.

Introduction

The interaction of diborane with lithium tetrahydridoaluminate (LiAlH₄) in the presence of ethers has been studied in several laboratories, and the results obtained were in part contradictory. According to Wiberg and Schrauzer the following compounds can be isolated at low temperatures from a tetrahydrofuran (THF) solution: LiAlH₄·4BH₃·*n*THF = LiAl(BH₄)₄·*n*THF, decomposing with BH₃·THF elimination above -25 °C and forming LiAlH(BH₄)₃·(n-1)THF, stable up to room temperature. This product loses another mole of BH₃·THF, and LiAlH₄·2BH₃·*m*THF was obtained. In addition LiAlH₄·BH₃·*x*THF was prepared in THF from the

components. It was also observed that the electrical conductivity of a LiAlH₄ solution in THF increases drastically by adding more than 2 molar equiv of BH₃.²

Ashby and Foster³ questioned the existence of these triple metal hydrides, in particular the high thermal stability of LiAlH₄·2BH₃·*n*THF and LiAlH₄·BH₃·*n*THF. They showed by means of IR spectra that LiBH₄ and AlH_{3-n}(BH₄)_n are present in ether or THF solutions. They isolated under their experimental conditions the product LiAlH₄·2BH₃·*n*THF which on benzene extraction yielded LiBH₄ and H₂AlBH₄·THF. Workup of a 1:4 reaction of LiAlH₄ with BH₃ after 10 days led to LiBH₄ and C₄H₉OAl(BH₄)₂.

(1) K. Frauz, H. Fusstetter, and H. Nöth, *Z. Anorg. Allg. Chem.*, **427**, 97 (1976).

(2) G. N. Schrauzer, Ph.D. Thesis, University of Munich, Munich, 1965; E. Wiberg and G. N. Schrauzer, German Patent DP 1066553 (1960).
(3) E. C. Ashby and W. E. Foster, *J. Am. Chem. Soc.*, **88**, 3248 (1966).