December, 1983] © 1983 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 56, 3845—3846 (1983)

Absolute Configurations Assigned to Some Octahedral *cis*-Bis(diamine)cobalt(III) Complexes on the Basis of Their Stereoselective Interactions in Solution

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(Received June 21, 1983)

Synopsis. Absolute configurations are assigned to some cationic *cis*-$[Co(diamine)_2(X)(Y)]^{n+}$-type complexes by detecting the direction of the chiral equilibrium shift induced for $[Cr(ox)_3]^{3-}$ in the presence of these chiral complexes in water–dioxane mixtures. The assignments are found all consistent with those made earlier by CD spectra.

In our previous work,1) it was established that the Δ isomer of $[Cr(ox)_3]^{3-}$ is gradually enriched when the racemate is mixed with Λ-*cis*-$[M(diamine)_2(X)(Y)]^{n+}$-type complexes ($M=Co^{3+}$ or Cr^{3+}, diamine=ethylenediamine (en) or trimethylenediamine (tn), and X and/or Y=anionic ligand) in water–dioxane mixtures. This implies that a heterochiral2) combination (Δ-Λ or Λ-Δ) is favored over a homochiral one (Δ-Δ or Λ-Λ) in the stereoselective interaction between $[Cr(ox)_3]^{3-}$ and *cis*-$[M(diamine)_2(X)(Y)]^{n+}$ in solution, and that the above phenomenon called the Pfeiffer effect3) provides a new technique for assigning the absolute configuration to these optically stable, cationic complexes. In the present study, an attempt is made to extend the applicability of the above technique to other *cis*-$[M(diamine)_2(X)(Y)]^{n+}$-type complexes.

Experimental

Preparation of Complexes. The following complexes were prepared and resolved as described by earlier workers; *cis*-$[Co(CN)(X)(en)_2]^{n+}$ ($X=NO_2^-$, Cl^-, Br^-, and OH_2),4) *cis*-$[Cr(CN)_2(en)_2]^+$,5,6) *cis*-$[Co(Cl)(RNH_2)(en)_2]^{2+}$ ($R=CH_3$ and C_2H_5),7) *cis*-$[Co(Cl)(RNH_2)(tn)_2]^{2+}$ (R=H and CH_3),8) *cis*-$[Co(NCS)_2(tn)_2]^+$,9) $[Co(gly)(tn)_2]^{2+}$,10) *cis*-$[Co(Cl)(OH_2)(en)_2]^{2+}$,11,12) *cis*-$[Co(NO_2)(OH_2)(en)_2]^{2+}$,11) *cis*-$[Co(Cl)(NCS)(en)_2]^{2+}$,13) and *cis*-$[Co(NCS)(OH_2)(en)_2]^{2+}$.11) The purity of these complexes was checked by both ion-exchange chromatography and absorption and/or CD spectra. The λ_{max} of the first d-d band for *cis*-$[Co(CN)(NO_2)(en)_2]^+$ was reported to be 437 nm in Ref. 4, but our sample had an absorption maximum at 423—424 nm. As judged from the λ_{max} values for the *cis*-dinitro (439 nm) and *cis*-dicyano (400 nm) complexes, the value reported in Ref. 4 is probably in error.

Detection of Pfeiffer Effect. The Pfeiffer effect of $[Cr(ox)_3]^{3-}$ was detected in the same manner as before.1) That is, the sample solution was prepared by adding aqueous racemic $K_3[Cr(ox)_3]\cdot 3H_2O$ (8×10^{-5} mol) to the above optically active complex (2×10^{-4} mol) in a volumetric flask (10 ml) to which 3 ml of dioxane was added. After it was kept standing overnight in the dark, it was passed through a cation-exchange column (Dowex 50 W X1, Na^+-form) to remove the optically active, cationic complex added as an environment substance.3) The absorption and CD spectra of the effluent were recorded as quickly as possible on a Shimadzu UV-200 and a JASCO J-40CS spectrometers, respectively. The direction and degree of the equilibrium shift in initially racemic $[Cr(ox)_3]^{3-}$ were determined by comparing the sign and intenity of the CD spectrum thus recorded with those of optically pure $[Cr(ox)_3]^{3-}$.14)

Results and Discussion

In Table 1 is listed the enantiomer of $[Cr(ox)_3]^{3-}$ enriched when *cis*-$[M(diamine)_2(X)(Y)]^{n+}$-type complexes given in the first column are employed as a chiral environment substance in water–dioxane mixtures. Except for the last two tn complexes, a Λ configuration

TABLE 1. ABSOLUTE CONFIGURATION OF ENRICHED ISOMER OF $[Cr(ox)_3]^{3-}$

Environment substance (Λ-configuration)	Assigned by (Ref.)	Enriched isomer
$(+)_{589}$-*cis*-$[Co(en)_2(CN)_2]^+$	X-ray a)	Δ
$(+)_{546}$-*cis*-$[Co(en)_2(CN)(NO_2)]^+$	CD(4)	Δ
$(-)_{546}$-*cis*-$[Co(en)_2(CN)(Cl)]^+$	CD(4)	Δ
$(-)_{546}$-*cis*-$[Co(en)_2(CN)(Br)]^+$	CD(4)	Δ
$(+)_{546}$-*cis*-$[Co(en)_2(CN)(OH_2)]^{2+}$	CD(4)	Δ
$(+)_{546}$-*cis*-$[Cr(en)_2(CN)_2]^+$	CD(5)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(Cl)(NH_3)]^{2+}$	X-ray b)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(Cl)(CH_3NH_2)]^{2+}$	CD(7)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(Cl)(C_2H_5NH_2)]^{2+}$	CD(7)	Δ
$(+)_{546}$-*cis*-$[Co(en)_2(Cl)(NCS)]^+$	CD(13), CT c)(11)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(NCS)(OH_2)]^{2+}$	CT c)(11)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(Cl)(OH_2)]^{2+}$	CT c)(11)	Δ
$(+)_{589}$-*cis*-$[Co(en)_2(NO_2)(OH_2)]^{2+}$	CT c)(11)	Δ
$(+)_{589}$-$[Co(tn)_2(gly)]^{2+}$	CD(10)	Δ
$(-)_{589}$-*cis*-$[Co(tn)_2(NCS)_2]^+$	X-ray(17)	Δ
$(-)^{CD}_{500}$-*cis*-$[Co(tn)_2(Cl)(NH_3)]^{2+}$	d)	Δ
$(-)^{CD}_{490}$-*cis*-$[Co(tn)_2(Cl)(CH_3NH_2)]^{2+}$	d)	Δ

a) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **44**, 2721 (1971). b) M. Kuramoto, Y. Kushi, and H. Yoneda, *ibid.*, **51**, 3196 (1978). c) CT refers to chemical transformation. d) Assigned by the present work.

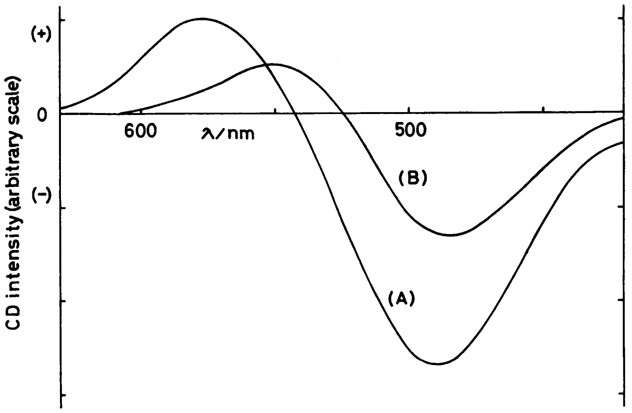

Fig. 1. CD patterns of $(-)^{\mathrm{CD}}_{490}$-*cis*-$[\mathrm{Co(Cl)(CH_3NH_2)(tn)_2}]^{2+}$ (A) and of $(-)^{\mathrm{CD}}_{485}$-*cis*-$[\mathrm{Co(CH_3NH_2)_2(tn)_2}]^{3+}$ derived therefrom (B).

has been assigned to these bis(diamine) complexes mainly on the basis of their CD spectra in the first d-d band. It is evident in Table 1 that the chiral equilibrium of $[\mathrm{Cr(ox)_3}]^{3-}$ is always displaced toward its Δ enantiomer in the presence of Λ-*cis*-$[\mathrm{M(diamine)_2(X)(Y)}]^{n+}$-type complexes. The enantiomer excess actually attained at equilibrium is around 1.0 and 1.5% under the present experimental conditions for uni- and bi-valent environment substances, respectively, in keeping with our previous results.[1] If the heterochiral combination (Δ-Λ or Λ-Δ) is favored as before, it is concluded that the absolute configurations assigned earlier to these complexes are all consistent with our present experimental results.

The last two bis(tn) complexes have already been resolved,[8] but the absolute configuration is not yet assigned to them. In Fig. 1 is shown the CD pattern of partially resolved $(-)^{\mathrm{CD}}_{490}$-*cis*-$[\mathrm{Co(Cl)(CH_3NH_2)(tn)_2}]^{2+}$ forming a less-soluble diastereomer with bis[μ-(+)-tartrato(4−)]bis[arsenate(III)]$^{2-}$ ion. The corresponding ammine complex exhibits a similar CD pattern as expected. These tn complexes have a negative major CD component at the higher energy side, suggesting a Δ configuration.[15] Our experimental results, however, lead us to assign a Λ configuration to these complexes, since they enrich the Δ enantiomer of $[\mathrm{Cr(ox)_3}]^{3-}$. Then, $(-)^{\mathrm{CD}}_{490}$-*cis*-$[\mathrm{Co(Cl)(CH_3NH_2)(tn)_2}]^{2+}$ was converted to the corresponding bis(methylamine) complex by refluxing it in liquid methylamine, followed by purification with use of ion-exchange chromatography. Figure 1 clearly shows that the CD pattern of the bis(methylamine) complex thus derived is quite similar to that of Λ-*cis*-$[\mathrm{Co(NH_3)_2(tn)_2}]^{3+}$ reported by Sano *et al.*[16] This observation is consistent with our present assignment made by the Pfeiffer effect, if so-called Walden inversion does not take place in the above substitution reaction as in the reaction of $(+)_{\mathrm{D}}$-*cis*-$[\mathrm{Co(Cl)(NH_3)(en)_2}]^{2+}$ with $\mathrm{NH_3}$ to give $(+)_{\mathrm{D}}$-*cis*-$[\mathrm{Co(NH_3)_2(en)_2}]$,$^{3+}$.[11] Thus, the criteria proposed by McCaffery *et al.*[13–15] for predicting the absolute configuration on the basis of the CD spectra, seem not to hold for these complexes with six-membered tn chelates, though they are fairly valid for the *cis*-$[\mathrm{M(X)_2(tn)_2}]^{+}$-type complexes[17] as well as for $[\mathrm{M(acac)(tn)_2}]^{2+}$,[18] $[\mathrm{Co(gly)(tn)_2}]^{2+}$,[10] and $[\mathrm{M(ox)(tn)_2}]^{+}$.[19]

In this way, our newly proposed technique serves well as a useful means to predict the absolute configuration of *cis*-$[\mathrm{M(diamine)_2(X)(Y)}]^{n+}$-type complexes in which X and/or Y are anionic ligands and M may be other than $\mathrm{Co^{3+}}$ or $\mathrm{Cr^{3+}}$. As a result, the Pfeiffer effect is applicable to deduce the absolute configuration of not only optically labile complexes[3,20,21] whose chiral equilibria are to be displaced, but also optically stable complexes when they are employed as an environment substance.

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