June, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***60,*** *2283—2285 (1987)* 2283

Enantioselective Ion-Association Mode between the Tris(ethylenediamine)cobalt(III) Cation and the Bis(μ-($-$)$_{589}$-2,3-dimethyltartrato)diantimonate(III) Anion in Solution

Hayami YONEDA,* Ushio SAKAGUCHI, and Hiroshi NAKAZAWA
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

(Received January 20, 1987)

Synopsis. By analyzing the intensity changes in the circular dichroism spectra, the association constants of the Λ- and Δ-[Co(en)$_3$]$^{3+}$ ions with the bis(μ-($-$)$_{589}$-2,3-dimethyltartrato)diantimonate(III) ion were determined to be 58.4±1.9 and 38.6±0.4 respectively in H_2O (mol^{-1} dm^3 at 25 °C and μ=0.1 (NaClO$_4$)). Based on these data together with the chromatographic data, the enantioselective association mode was discussed.

It is well-known that the bis(μ-*d*-tartrato)diantimonate(III) ion, [Sb$_2$(*d*-tart)$_2$]$^{2-}$, is an effective chiral selector for chromatographic optical resolution of many types of octahedral metal chelate complexes.[1] Concerning the mechanism of chiral discrimination by this anion, we proposed previously the L-J model where attention was paid to an opening formed between chelate rings of a complex to be resolved.[2] An opening between chelate rings in the Λ configuration has a shape of L and is called an L-shaped channel. In contrast, an opening between chelate rings in the Δ configuration has a shape reverse to an L-shaped channel and is called a J-shaped channel. A counter ion which makes a good fit to an L-shaped channel does not make a good fit to a J-shaped channel. Such a counter ion associates more favorably with a complex having an L-shaped channel than with a complex having a J-shaped channel, and can be utilized as a chiral selector. The [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion is considered to have a skeleton which makes a good fit to the L-shaped channel in a complex cation. Based on this idea the efficiency of chiral discrimination by this anion was successfully explained for a series of [Co(N)$_6$]$^{3+}$ complex cations having different numbers of L-shaped channels.[2]

The L-J model was originally born as a conceptual idea having no specified mode of association. However, using molecular models, we found that either one of the two tartrate backbones bridging the two Sb atoms makes a good fit to an L-shaped channel, and proposed a concrete mode of ion association for chiral discrimination in which the anion accepts a complex cation coming along the y direction in Fig. 1. This mode of association does not exclude any other possibilities for the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion to discriminate the chirality of the complex cation. In fact, it was shown by Sakaguchi et al. that the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion can discriminate the chirality of the [Co(en)$_3$]$^{3+}$ and its related complex cations coming along the x direction in Fig. 1.[3] In addition, the third concrete mode of association was put forward by Miyoshi et al., in which the two oxygen atoms of the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion participate in the double hydrogen bonding to two of the three axial N-H bonds directed along the C_3 axis of the complex, and the remaining part of the anion is disposed opposite to the third N-H bond which is not involved in hydrogen bonding.[4] In this third association mode, the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion accepts the complex cation coming along the x direction in Fig. 1.

All these modes of association basically explain the situation of chiral discrimination of [Co(N)$_6$]$^{3+}$ complex cations, but differ in the mode of orientation of the complex cation around the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion. To specify the direction of access of the complex cation toward the [Sb$_2$(*d*-tart)$_2$]$^{2-}$ anion, we have prepared the methyl-substituted derivative of this anion, bis(μ-($-$)$_{589}$-2,3-dimethyltartrato)diantimonate(III) anion (abbreviated as [Sb$_2$(($-$)-dmt)$_2$]$^{2-}$) in which each tartrate backbone has two methyl substituents. According to the original L-J model, a good fit to an L-shaped channel is expected to be lost by such methyl substitution. Therefore, the efficiency of chiral discrimination should be markedly decreased with methyl substitution. In contrast, according to the other models, the methyl groups do not seem to effect any significant steric repulsion in ion-association, so that the efficiency of chiral discrimination should not be influenced greatly by methyl substitution. The results of the experiments in the present study imply that when the chiral anion discriminates the chirality of complex cations, it directs the x axis towards the complex cations.

Experimental

Material. The complexes used were the perchlorate salts of Λ- and Δ-[Co(en)$_3$]$^{3+}$. Na$_2$[Sb$_2$(($-$)-dmt)$_2$]·4H_2O was prepared according to the literature,[5] and purified by recrystallization from water.

Measurements of Ion-Association Constants and Chromatographic Resolution. The ion-association constants were

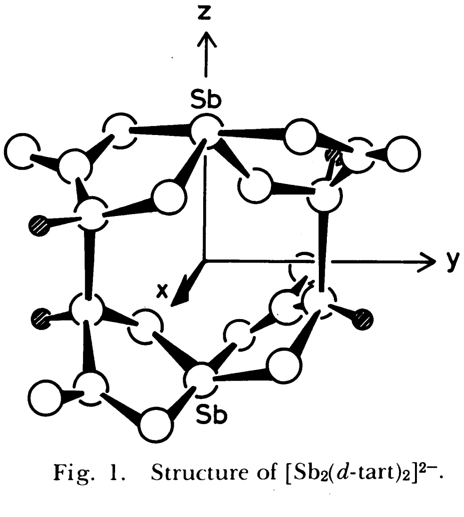

Fig. 1. Structure of [Sb$_2$(*d*-tart)$_2$]$^{2-}$.

obtained by using CD intensity changes upon addition of chiral anions. The CD spectra were measured on a JASCO J-40CS recording spectropolarimeter. The sample cell was kept at 25±0.2 °C with a Haake circulator Model FK. For the Δ-[Co(en)$_3$]$^{3+}$ cation, the concentration of the cation, C_M, was fixed at 3.0×10^{-3} mol dm^{-3}, and that of the [Sb$_2$((−)-dmt)$_2$]$^{2-}$ anion, C_A, was varied from 0 to 2.7×10^{-2} mol dm^{-3}. A sample cell of 1-cm length was used. In the case of the Λ-[Co(en)$_3$]$^{3+}$ cation, C_M was set to 6.0×10^{-4} mol dm^{-3} (C_A=0 to 1.5×10^{-2} mol dm^{-3}), because of the low solubility of the [Sb$_2$((−)-dmt)$_2$]$^{2-}$ salt of this enantiomer, and the sample cell of 10-cm length was used for the CD measurement. The ionic strength was adjusted to μ=0.1 with sodium perchlorate. The CD intensity change of the chiral complex upon addition of [Sb$_2$((−)-dmt)$_2$]$^{2-}$ salt was measured at 440 nm.

Chromatographic data were obtained as follows. The aqueous solution containing the racemic [Co(en)$_3$]$^{3+}$ complex was loaded on the IEX-510 cation-exchange resin (7.5×0.75 cm I. D.). The adsorbed complex was eluted with a 0.1 mol dm^{-3} aqueous solution of Na$_2$[Sb$_2$((−)-dmt)$_2$]. Blue Dextran 2000 was used as a marker for the void volume measurememt of the column. The eluate was guided to a flow cell to detect the complex at 460 nm with a Shimadzu UV-140 spectrophotometer. The adjusted retention volumes were estimated from the elution curve thus recorded.

Results and Discussion

According to our recent X-ray analysis of Λ-[Co(en)$_3$][Sb$_2$((−)-dmt)$_2$]ClO$_4\cdot$7H$_2$O, the absolute configuration of the 2 and 3 carbons of the 2,3-dimethyltartrate moiety in the [Sb$_2$((−)-dmt)$_2$]$^{2-}$ was established to be R, R which corresponds to those of the 2 and 3 carbons of the *d*-tartrate moiety in [Sb$_2$(*d*-tart)$_2$]$^{2-}$.[6)]

The CD spectra of Λ-[Co(en)$_3$]$^{3+}$ with and without [Sb$_2$((−)-dmt)$_2$]$^{2-}$ are shown in Fig. 2 together with their difference (DCD spectrum). The DCD spectrum is quite similar in shape to that obtained with the unmethylated anion used as an additive, and the both DCD spectra have the same sign.[3)]

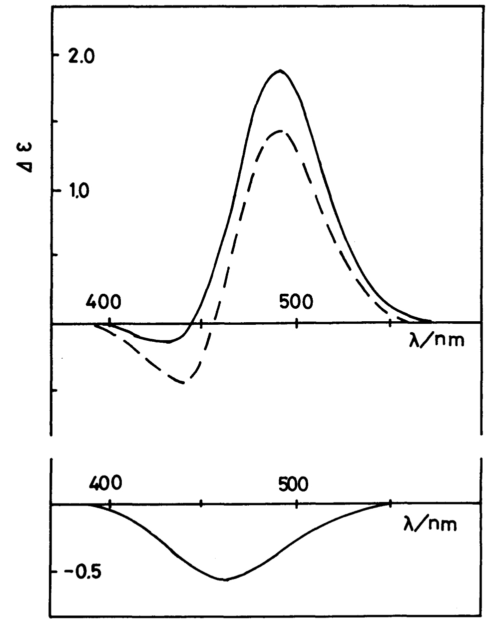

Fig. 2. Upper curves: CD spectra of Λ-[Co(en)$_3$]$^{3+}$ (——) and of the ion-pair with [Sb$_2$((−)-dmt)$_2$]$^{2-}$ (----). Lower curve: the DCD spectrum.

Table 1. Association Constants at 25 °C and μ=0.1 (NaClO$_4$)

System	K	D
Λ-[Co(en)$_3$]$^{3+}$.....[Sb$_2$(*d*-tart)$_2$]$^{2-}$	47.3±0.6	29
Δ-[Co(en)$_3$]$^{3+}$.....[Sb$_2$(*d*-tart)$_2$]$^{2-}$	26.0±0.3	
Λ-[Co(en)$_3$]$^{3+}$.....[Sb$_2$((−)-dmt)$_2$]$^{2-}$	58.4±1.9	20
Δ-[Co(en)$_3$]$^{3+}$.....[Sb$_2$((−)-dmt)$_2$]$^{2-}$	38.6±0.4	

$$D=\frac{K_\Lambda-K_\Delta}{K_\Lambda+K_\Delta}\times100$$

Table 2. Retention Volume(V) and Separation Factor(α) of [Co(en)$_3$]$^{3+}$

Eluent	V_1 (ml)	V_2 (ml)	α
Na$_2$[Sb$_2$(*d*-tart)$_2$]	40.9 (Λ)	59.9 (Δ)	1.46
Na$_2$[Sb$_2$((−)-dmt)$_2$]	27.9 (Λ)	38.6 (Δ)	1.38

The ion-association constants obtained by using the CD intensity changes upon addition of the chiral anion are listed in Table 1 with those for the [Co(en)$_3$]$^{3+}$ ··· [Sb$_2$(*d*-tart)$_2$]$^{2-}$ system. Comparison of the corresponding values revealed the following two points. The first point noted is that the value of K_Λ is greater than that of K_Δ in both the methylated and unmethylated chiral anions. This suggests that the methyl substitution does not cause inversion of chiral discrimination. The second point noted is that the values of K for both Λ and Δ-[Co(en)$_3$]$^{3+}$ complexes are greater in [Sb$_2$((−)-dmt)$_2$]$^{2-}$ than in [Sb$_2$(*d*-tart)$_2$]$^{2-}$ (58.4 vs. 47.3 and 38.6 vs. 26.0). However, the value of D which is defined as $(K_\Lambda-K_\Delta)/(K_\Lambda+K_\Delta)\times100$ and is considered as a measure of the efficiency of chiral discrimination, shows only a slight decrease from the original chiral anion to the methyl-substituted chiral anion.

These features are reflected in the chromatographic data as shown in Table 2.[7)] The values of V_1 and V_2 for [Sb$_2$((−)-dmt)$_2$]$^{2-}$ are both smaller than the corresponding values for [Sb$_2$(*d*-tart)$_2$]$^{2-}$. The value of the separation factor α for [Sb$_2$((−)-dmt)$_2$]$^{2-}$ is smaller than that for [Sb$_2$(*d*-tart)$_2$]$^{2-}$. However, the decrease in the values of α is not so great.

It can be concluded that the methyl substitution does not cause a significant influence upon the chiral discrimination on a chiral selector. Thus, we feel tempted to look with favor upon the models in which the chiral anion directs its x axis to the complex cation to recognize the chirality.

The preparation of the bis(μ-(−)$_{589}$-2,3-dimethyltartrato)diantimonate(III) salt was performed by U.S. in the laboratory of Prof. Yoshiharu Izumi, Director of Institute for Protein Research, Osaka University, under his instruction. His kind and helpful guidance is highly appreciated. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 60470047 from the Ministry of Education, Science and Culture.

References

1) H. Yoneda, *J. Chromatogr.*, **313**, 59 (1985); H. Yoneda, *J. Liquid Chromatogr.*, **2**, 1157 (1979); Y. Yoshikawa and K.

Yamasaki, *Coord. Chem. Rev.*, **28**, 205 (1975).

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

3) U. Sakaguchi, A. Tsuge, and H. Yoneda, *Inorg. Chem.*, **22**, 3735 (1983).

4) K. Miyoshi, S. Izumoto, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **59**, 3475 (1986); K. Miyoshi, S. Izumoto, K. Nakai, and H. Yoneda, submitted for publication.

5) S. Tatsumi, Y. Izumi, M. Imaida, Y. Fukuda, and S. Akabori, *Bull. Chem. Soc. Jpn.*, **39**, 602 (1966).

6) S. Izumoto, Y. Kushi, and H. Yoneda, under preparation for publication. Crystals of Λ-tris(ethylenediamine)cobalt(III) bis(μ-$(-)_{589}$-2,3-dimethyltartrato)diantimonate(III) perchlorate heptahydrate, Λ-$[Co(en)_3][Sb_2((-)\text{-dmt})_2]\cdot ClO_4\cdot 7H_2O$, are bright orange, trigonal, space group $P3_121$, a=10.496(3), c=29.570(6) Å, Z=3, D_c=1.87 g cm^{-3}. The structure was solved from 1723 Mo K_α reflections ($F_o>3\,\sigma F_o$). The final discrepancy factors were R=0.067 and R_w=0.072. In the $(-)_{589}$-2,3-dimethyltartrato groups, the absolute configuration of the two asymmetric carbon atoms are both having an R configuration from the comparison with that of the Λ-$[Co(en)_3]^{3+}$ cation.

7) The order of the ion-association constants in Table 1 and that of the retention volumes in Table 2 are not exactly the same, presumably because the entity of ion-associated species recognized by CD spectra and that by ion-exchange chromatography are not always the same.