$(dmgH)_2$–py-4-NH_2, 59492-96-5; *n*-C_3H_7–$Co(dmgH)_2$–NC–Co$(dmgH)_2$–py-4-NH_2, 59492-97-6; *i*-C_3H_7–$Co(dmgH)_2$–NC–Co$(dmgH)_2$–py-4-NH_2, 59492-98-7; C_6H_{11}–$Co(dmgH)_2$–NC–Co$(dmgH)_2$–py-4-NH_2, 59492-99-8; CF_3–$Co(dmgH)_2$–NC–Co$(dmgH)_2$–pip, 59531-96-3; CF_3–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 59493-00-4; C_2H_5–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 53667-49-5; *n*-C_3H_7–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 53533-65-6; *i*-C_3H_7–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 59493-01-5; C_6H_{11}–Co$(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 59493-02-6; C_2H_5–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–pip, 59573-29-4; *n*-C_3H_7–$Co(dmgH)_2$–NC–Co$(dmgH)_2$–pip, 59573-30-7; *i*-C_3H_7–$Co(dmgH)_2$–NC–$Co(dmgH)_2$–pip, 59493-03-7; $Co(dmgH)_2(CF_3)(H_2O)$, 59493-04-8; $Co(dmgH)_2$$(C_2H_5)(H_2O)$, 26025-30-9; $Co(dmgH)_2$(*n*-C_3H_7)(H_2O), 28182-23-2; $Co(dmgH)_2$(*i*-C_3H_7)(H_2O), 30974-89-1; $Co(dmgH)_2(C_6H_{11})(H_2O)$, 52970-74-8; py, 110-86-1; $[AsPh_4][Co(dmgH)_2(C_2H_5)(CN)]$, 59493-05-9; $[AsPh_4]$[$Co(dmgH)_2$(*i*-C_3H_7)(CN)], 59493-07-1; $Co(dmgH)_2(CN)$(py-4-NH_2), 57808-59-0; $Co(dmgH)_2(CN)(NH_3)$, 19570-05-9; $Co(dmgH)_2(CH_3)$(py-4-NH_2), 38685-14-2; CH_3–Co$(dmgH)_2$–NC–$Co(dmgH)_2$–NH_3, 53533-64-5.

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(18) The ^1H NMR spectrum of the compound $(CH_3)Co(dmgH)_2$–NC–$Co(dmgH)_2(NH_3)$ warrants additional comment. This compound was found to be only sparingly soluble in $CHCl_3$ to give a hazy solution. A ^1H NMR spectrum of such a solution was obtained in spite of this haziness, and these are the data listed in Table V. In addition to the resonances listed for this compound, another dmgH resonance was observed and assigned to the dimethylglyoxime protons of pentacoordinate Co$(dmgH)_2(CH_3)$. This material was present in solution as a result of a dissociation of the cyano-bridged dicobaloxime to give $Co(dmgH)_2(CH_3)$ and $Co(dmgH)_2(CN)(NH_3)$. The latter compound is insoluble in $CHCl_3$ and was responsible for the haziness of the above solution. This was shown by isolating the precipitated material from a solution of $(CH_3)Co(dmgH)_2$–NC–$Co(dmgH)_2(NH_3)$ and then obtaining its infrared spectrum.

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Isolation and Absolute Configuration of the Optically Active Isomers of Bis(1,10-phenanthroline)- and Bis(2,2′-bipyridine)cobalt(III) Complexes Containing L-(+)- or D-(−)-Tartrate Ion

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The configurationally optically active isomers of the tartratobis(1,10-phenanthroline)cobalt(III) and tartratobis(2,2′-bipyridine)cobalt(III) complexes are isolated by column chromatography using SP-Sephadex. The electronic absorption and circular dichroism spectra are measured over the range of visible–ultraviolet regions and the absolute configurations of the complexes are assigned by empirical and nonempirical methods. The properties of the tartrate in the complexes are discussed on the basis of ir spectra and the pH titration. The chromatographic behavior of these isomers is also described. Appreciable stereoselectivity in the formation of the configurationally optically active isomers is observed.

Introduction

In the previous paper we have reported on the preparation and absolute configuration of both diastereoisomers of L-(+)-tartratobis(1,10-phenanthroline)cobalt(III) complexes.[1] We have further investigated the isolation and CD spectra of compounds of the type [Co(tart)(phen or bpy)$_2$]$^+$, where tart is the dianion of L-(+)- or D-(−)-tartaric acid, and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively. During the course of our investigations, we found surprising the claim for the presence of only one diastereoisomer.[2] In the present paper it is shown that the species isolated in ref 2 is a mixture of two diastereoisomers and the reported preference for only one diastereoisomer could not be observed by our experiments. The absolute configurations of our complexes are assigned by the nonempirical methods due to CD spectra in the region of the ligand π–π^* transitions in addition to the empirical methods based on the Cotton effects in the T_{1g} region of the d–d transitions. The quantitative curves for the configurational and the vicinal contribution to the optical activity are evaluated and compared with those of the related complexes. The chromatographic behavior and stereoselective formation of the complexes and the acidic properties of the coordinated tartrate ions are also discussed.

Experimental Section

The dichloro complexes obtained by the literature methods, *cis*-$[CoCl_2(phen)_2]Cl\cdot3H_2O$[3] and *cis*-$[CoCl_2(bpy)_2]Cl\cdot3H_2O$[4], were used as the starting complexes for the preparation.

(1) Isolation of Two Diastereoisomers of L-(+)-Tartratobis(1,10-phenanthroline)cobalt(III) Perchlorate. To a solution of 0.84 g of sodium L-(+)-tartrate dihydrate in 30 ml of water, 1.6 g of *cis*-$[CoCl_2(phen)_2]Cl\cdot3H_2O$ was added. The mixture was allowed to stand at 60 °C with mechanical stirring for 0.5 h. The color of the solution turned from violet to wine red. When the reaction was over, the solution was evaporated almost to dryness below 50 °C in a rotary evaporator under reduced pressure. The crude wine red product was obtained by adding 30 ml of ethanol–ether (1:1) mixture to the viscous liquid. About 0.5 g of this product was dissolved in 5 ml of an eluent and the solution was poured into a column (2.7 × 40 cm) containing SP-Sephadex C-25 ion exchanger (particle size 40–120 μ, capacity 2.3 ± 0.3 mequiv/g, sodium form). By eluting with 0.15 M $Na_2[Sb_2(\text{L-tart})_2]$ aqueous solution at a rate of 0.4–0.6 ml/min, the adsorbed bands were gradually separated into five bands. The eluates of the first band and the second one (in the order of elution) were collected separately and were concentrated in a rotary evaporator under reduced pressure at room temperature. To the concentrated solution, sodium perchlorate solution was added and the mixture was allowed to stand overnight in a refrigerator. The complexes thus obtained were recrystallized from water containing a small amount of sodium perchlorate. The crystals were filtered off and washed with a little amount of water, ethanol, and ether. Anal. Calcd for $CoC_{28}H_{26}N_4O_{13}Cl$: C, 46.65; H, 3.64; N, 7.77. Found for band 1: C, 46.44; H, 3.12; N, 7.62. Calcd for $CoC_{28}H_{24}N_4O_{12}Cl$: C, 47.84; H, 3.44; N, 7.97. Found for band 2: C, 47.47; H, 3.69; N, 7.53.

On the basis of the absorption and the CD spectra, as has been reported previously,[1] bands 3–5 have been identified as follows. Band 3 was found to be an optically active $(phen)_2$ complex containing tartrate as a unidentate ligand. Bands 4 and 5 were shown to be optically inactive by-products, that is, $[CoCl(H_2O)(phen)_2]^{2+}$ and/or $[Co(H_2O)_2(phen)_2]^{3+}$ for band 4 and $[Co(phen)_3]^{3+}$ for band 5.

(2) Diastereoisomers of D-(−)-Tartratobis(1,10-phenanthroline)cobalt(III) Perchlorate. These complexes were prepared and separated in the same manner as L-tart complexes except that the D-(−)-tartrate solution prepared by neutralizing the free acid with sodium hydroxide was used. Anal. Calcd for $CoC_{28}H_{26}N_4O_{13}Cl$: C, 46.64; H, 3.64; N, 7.77. Found for band 1: C, 46.54; H, 3.54; N, 7.33. Anal. Calcd for $CoC_{28}H_{24}N_4O_{12}Cl$: C, 47.84; H, 3.44; N, 7.97. Found for band 2: C, 47.70; H, 3.09; N, 7.97.

(3) Diastereoisomers of L-(+)- and D-(−)-Tartratobis(2,2′-bipyridine)cobalt(III) Perchlorates. The preparation and separation were carried out by using the same method as for the corresponding phen complexes. Anal. Calcd for $CoC_{24}H_{26}N_4O_{13}Cl$: C, 42.84; H, 3.90; N, 8.33. Found for band 1 of L-tart complexes: C, 42.52; H, 3.71; N, 8.12. Found for band 1 of D-tart complexes: C, 41.57; H, 3.65; N, 8.37. Calcd for $CoC_{24}H_{24}N_4O_{12}Cl$: C, 44.02; H, 3.69; N, 8.56. Found for band 2 of L-tart complexes: C, 44.31; H, 3.48; N, 8.54. Found for band 2 of D-tart complexes: C, 44.49; H, 3.57; N, 8.50.

For comparison of ir spectra, $[Co(\text{L-tart})(NH_3)_4]ClO_4\cdot2H_2O$ was prepared according to the method of Gillard and Price.[5] To elucidate the characterization of coordinated OH group in analogous hydroxy acid complexes, the compound $[Co(\text{L-lac})(phen)_2](ClO_4)_2\cdot H_2O$ was prepared by the reaction between $[CoCl_2(phen)_2]Cl\cdot3H_2O$ and lithium L-lactate, where L-lac is the anion of L-lactic acid ($H_3CCH(OH)COO^-$). Anal. Calcd for $CoC_{27}H_{23}N_4O_{12}Cl$: C, 44.70; H, 3.20; N, 7.73. Found: C, 44.13; H, 3.04; N, 7.62. The eluting agent, $Na_2[Sb_2(\text{L-tart})_2]$, was prepared by reaction between Sb_2O_3 and L-tartaric acid, followed by neutralizing with sodium hydroxide. The yield was over 95%.

Table I. AB and CD Spectra of the Complexes[a]

Complexes	AB[b] $\tilde{\nu}_{max}$ (log ϵ)	CD[b] $\tilde{\nu}_{ext}$ ($\Delta\epsilon_{ext}$)	Transition
Δ-(−)$_D$-[Co(L-tart)-(phen)$_2$]ClO$_4\cdot$3H$_2$O	19.23 (2.12)	18.87 (−2.19)	1st d–d band
	36.70 (4.67)	35.97 (−47.8)	A state
		37.59 (+38.2)	B state
Λ-(+)$_D$-[Co(L-tart)-phen)$_2$]ClO$_4\cdot$2H$_2$O	19.08 (2.10)	19.05 (+5.05)	1st d–d band
	36.70 (4.74)	35.97 (+45.8)	A state
		37.74 (−43.2)	B state
Δ-(−)$_D$-[Co(L-tart)-(bpy)$_2$]ClO$_4\cdot$3H$_2$O	19.46 (2.13)	18.52 (−2.04)	1st d–d band
	32.05 (4.32)	31.95 (−6.1)	A state
	33.00 (4.35)	33.67 (+4.6)	B state
Λ-(+)$_D$-[Co(L-tart)-(bpy)$_2$]ClO$_4\cdot$2H$_2$O	19.34 (2.11)	19.23 (+5.60)	1st d–d band
	32.05 (4.32)	31.55 (+5.5)	A state
	33.00 (4.38)	33.56 (−3.9)	B state

[a] As Δ-L and Λ-D (or Λ-L and Δ-D) give the same AB spectra and exhibit virtually mirror-image CD curves, only L-tart complexes are listed. [b] The data for the first absorption band and the long-axis polarized π–π^* ligand band region are given in the units of 10^3 cm^{-1}.

Measurements. The electronic absorption and the CD spectra were recorded for the aqueous solutions at room temperature on a Shimadzu MPS-50L recording spectrophotometer and on a JASCO Model ORD/UV-5 optical rotatory dispersion recorder with a CD attachment, respectively. Ir spectra were measured over the range of 400–4000 cm^{-1} with a Hitachi EPI-G 3 grating spectrophotometer by the Nujol mull method. ^1H NMR spectra were obtained for DMSO-d_6 solutions on a Nihondenshi JNM-PFT 60 spectrometer using TMS as an internal standard. pH measurements were carried out with a Hitachi Horiba F-5 pH meter using a glass electrode and a calomel reference electrode. The elemental analyses were carried out by Wako Pure Chemical Industries, Ltd., Osaka.

Results and Discussion

Absorption (AB) and Circular Dichroism (CD) Spectra. The AB spectrum of each complex shows only one band in the d–d transition region and the intense ultraviolet absorption bands characteristic of the heteroaromatic ligands. The second absorption band is completely obscured by the intense charge-transfer band. It is well-known that the position of the spectra of metal complexes is principally determined by the donor group microsymmetry. Thus, the complexes $[Co(tart)(\text{phen or bpy})_2]^+$ can be treated as belonging to the C_{2v} group. Under the C_{2v} molecular field, the octahedral $^1T_{1g}$ breaks down into the $^1B_1$ and ($^1A_2$ + $^1B_2$) states. The spectra of $[Co(\text{L-tart})_3]^{3-}$, $[Co(phen)_3]^{3+}$, and $[Co(bpy)_3]^{3+}$ have been reported with the first absorption band at 15.63,[6] 21.28,[7] and 22.22 kK,[8] respectively. From the theoretical study on shifting and splitting of the d–d band due to substitution of ligands,[9] the predicted position of the first absorption bands leads to 18.44 kK ($^1A_1 \rightarrow {}^1B_1$) and 19.85 kK ($^1A_1 \rightarrow {}^1A_2 + {}^1B_2$) for $[Co(\text{L-tart})(phen)_2]^+$ and 18.93 kK ($^1A_1 \rightarrow {}^1B_1$) and 20.57 kK ($^1A_1 \rightarrow {}^1A_2 + {}^1B_2$) for $[Co(\text{L-tart})(bpy)_2]^+$. The positions of the observed bands are satisfactorily consistent with the prediction by assuming the rule of an average ligand field environment (Table I).

The CD spectra of the complexes exhibit one dominant peak in the first-band region (Figures 1 and 2). It was proposed that the dominant CD band includes the A_2 component (derived from E_a in the D_3 symmetry) and provides a most reliable basis for assignment of the absolute configuration in the series of C_{2v} complexes.[10,14] The major CD peak in the first absorption region is positive for each (+)$_D$ isomer of the L-tart and D-tart complexes and negative for each (−)$_D$ isomer. On this basis, (+)$_D$ isomers are assigned to Λ configuration and (−)$_D$ isomers to Δ configuration for both the phen and the bpy complexes. The CD spectra of (+)$_D$ isomers of the D-tart

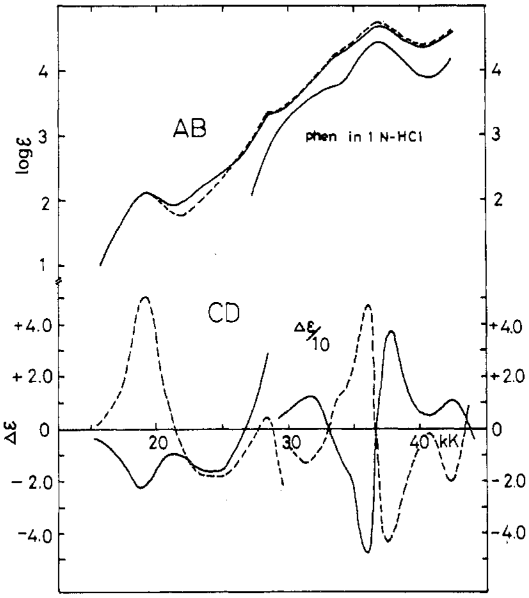

Figure 1. AB and CD spectra of Δ-[Co(L-tart)(phen)$_2$]$^+$ (——) and Λ-[Co(L-tart)(phen)$_2$]$^+$ (- - - -).

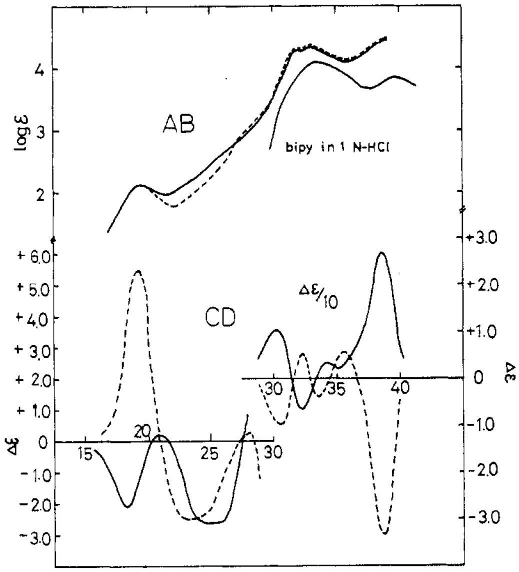

Figure 2. AB and CD spectra of Δ-[Co(L-tart)(bpy)$_2$]$^+$ (——) and Λ-[Co(L-tart)(bpy)$_2$]$^+$ (- - - -).

complexes (Λ-D) gave virtually mirror-image CD spectra of (−)$_D$ isomers of the L-tart complexes (Δ-L). The same was true for the opposite pair of isomers (Δ-D and Λ-L).

On the other hand, assignment of the absolute configuration can also be made from CD spectra in the ligand π–π* transition region.[8,11-14] According to the exciton theory of the optical activity, it can be predicted that (phen)$_2$ or (bpy)$_2$ complexes show two intense CD peaks of opposite sign in this region, that is, for Λ configuration strongly positive at lower energies and strongly negative at higher energies and the reverse for Δ configuration. Two nearly equally intense CD peaks of opposite sign are observed here for the phen complexes (about 37 kK) and two relatively weak CD peaks of opposite sign are observed for the bpy complexes (about 33 kK, Figures 1 and 2). It may be assumed that the weak CD peaks for bpy complexes result from the partial cancellation of the overlapping Cotton effects from the neighboring charge-transfer bands. The charge-transfer bands are close to π–π* transitions for the bpy complexes, whereas they are apart from π–π* transitions for the phen complexes. Thus, from the prediction of the exciton theory it can be concluded that each (+)$_D$ isomer is assigned to Λ configuration and each (−)$_D$ isomer to Δ configuration for [Co(L- or D-tart)(phen or bpy)$_2$]$^+$, this being consistent with the assignment based on the d–d transition region.

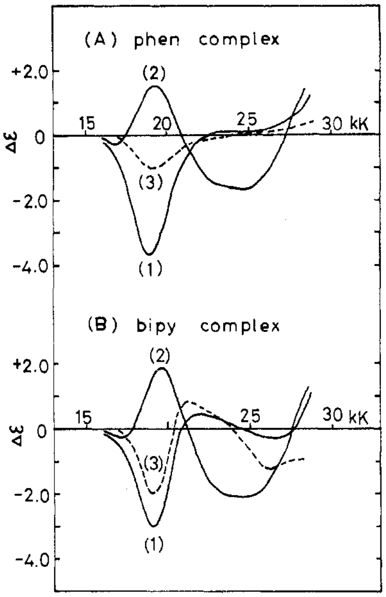

Figure 3. Configurational-effect curves for the Δ configuration (1), vicinal-effect curves (2) of the [Co(L-tart)(phen)$_2$]$^+$ complex (A) and of the [Co(L-tart)(bpy)$_2$]$^+$ complex (B), and CD curves (3) reported[8] for the Δ isomers of the corresponding [Co(ox)(phen or bpy)$_2$]$^+$ complexes (for comparison).

Configurational and Vicinal Effects. It has been known that configurational and vicinal contributions to the optical activity are essentially separable and additive.[15-17] The CD curves of these contributions calculated from the diastereomeric pair Δ-L and Λ-L by a conventional method are shown for the phen and bpy complexes (Figure 3). Each configurational effect curve exhibits a dominant peak in the first-band region and the shape is very similar to that of the corresponding [Co(ox)(phen)$_2$]$^+$ or [Co(ox)(bpy)$_2$]$^+$.[8] The vicinal-effect curves show a (−, +, −) sign pattern in the d–d band region. Though the presence of chelate rings of phen or bpy gives rise to the great enhancement of the vicinal contribution, the vicinal-effect curves are similar to the CD spectrum of [Co(L-tart)(NH$_3$)$_4$]$^+$.[5] Again, the two peaks at lower energies may be attributed to the B$_1$ and (A$_2$ + B$_2$) components and the other broad band at higher energies (octahedral T$_{2g}$ region) may rise from overlapping of the neighboring charge-transfer band. The vicinal effects of the complexes reported here are comparable in intensity to the configurational effects and make a very significant contribution to the observed CD spectra of the diastereoisomers. Similar results have been reported for other complexes in which the vicinal contribution from the coordinated hydroxy acid was greater than that obtained for the corresponding amino acid complexes. This fact was accounted for in terms of the large energy separation of the component d–d transitions in the hydroxy acid complexes.[18,19] Furthermore, it may be due in part to a significant difference in the role of transmission of the electronic asymmetry effect from the asymmetric carbon atom to the central metal between the oxygen atom and the nitrogen atom.

Properties of Complexes. When the pH of the reaction mixture between [CoCl$_2$(phen)$_2$]Cl·3H$_2$O and Na$_2$(L-tart) was measured, the solutions became acidic, indicating that the coordinated OH group of the tartrate is deprotonated on chelation. To elucidate the properties of the coordinated OH group, the pH titrations were carried out for the tartrate complexes and [Co(L-lac)(phen)$_2$]$^{2+}$ (for comparison). A pK_a

Table II. 60-MHz ^1H NMR Spectra of the Complexes in DMSO-d_6[a]

Complexes	CH[b]	Aromatic ligand
Δ-[Co(L-tart)(phen)$_2$]ClO$_4$·3H$_2$O	3.93, 4.03	7.66–9.22
Λ-[Co(L-tart)(phen)$_2$]ClO$_4$·2H$_2$O	3.92, 4.05	7.51–9.14
Δ-[Co(L-tart)(bpy)$_2$]ClO$_4$·3H$_2$O	3.79, 4.00	7.46–8.81
Λ-[Co(L-tart)(bpy)$_2$]ClO$_4$·2H$_2$O	3.66, 4.04	7.27–8.76

[a] Values in ppm downfield from internal TMS. [b] Chemical shift for the CH protons of tartrate in the complexes.

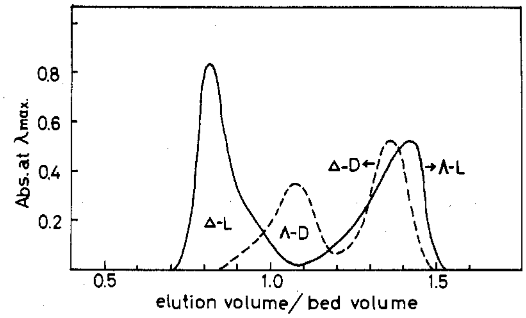

Figure 4. Elution curves of the diastereoisomers of [Co(L-tart)(phen)$_2$]$^+$ (——) and [Co(D-tart)(phen)$_2$]$^+$ (- - - -).

value of 3.51 was obtained for [Co(L-lac)(phen)$_2$]$^{2+}$. Since the L-lactate ion has an electron-releasing –CH$_3$ group instead of an electron-attracting CH(OH)COO$^-$ group of the tartrate ion as the side chain, the pK_a due to deprotonation of the coordinated OH group in the tartrate complexes can be expected to be lower than that of [Co(L-lac)(phen)$_2$]$^{2+}$. In fact, the pK_a values of ca. 2.3 and 2.45 have been reported for [Co(L-tart)(NH$_3$)$_4$]$^+$ and [(en)$_2$Co(L-tart)Co(en)$_2$]$^{2+}$.[5] We obtained the pK_a values of 4.08 and 3.81 for Δ- and Λ-[Co(L-tart)(phen)$_2$]$^+$ and 3.85 and 3.72 for Δ- and Λ-[Co(L-tart)(bpy)$_2$]$^+$, respectively. These are higher than the pK_a values (2.3–3.5) expected from the deprotonation of the coordinated OH group in the tartrate complexes and rather close to the value of 4.23 for the pK_2 of free tartaric acid. These results may indicate that in the phen and the bpy complexes obtained here the coordinated OH group is already deprotonated and an equimolar quantity of protons is dissociated from the uncoordinated free carboxylate group. Support for this comes also from the fact that the infrared spectra in the carboxylate region show the broad band at 1630–1650 cm^{-1} and a band at 1730 cm^{-1} (both COO$^-$ and COOM show bands at 1600–1650 cm^{-1}, whereas COOH has a band at about 1750 cm^{-1}).

In DMSO-d_6, the ^1H NMR spectrum of the CH protons of tartaric acid exhibits a single sharp resonance line at 4.35 ppm. The CH protons of tartrate in the complexes show two peaks, indicating that the CH groups are not equivalent (Table II). The ^1H NMR spectra in the aromatic ligand region were similar to those of (phen)$_2$ complexes reported elsewhere.[20,21] Although the chemical shifts of one diastereoisomer are slightly different from those of the other diastereoisomer, attempts to relate the ^1H NMR spectra to absolute configurations of isomers were unfruitful.

Chromatographic Behavior and Formation Ratios. The elution curves for the phen complexes of L-tart and D-tart reveal that the bands of two diastereoisomers for D-tart complexes were somewhat difficult to separate sufficiently (Figure 4). Similar elution curves were obtained for the corresponding bpy complexes. The good separation for the D-tart complexes was achieved by making use of a longer column than that used for the L-tart complexes. The order of elution is particularly interesting: for the L-tart complexes the first eluted band was the (−)D-Δ isomer and the second band was the (+)D-Λ isomer, whereas the reverse was found for D-tart complexes. This suggests that a kind of stereoselective interaction between the optically active dextrane matrix of SP-Sephadex and the tartrate side in the complexes rather than the α-diimine side is distinguished in the elution process. The coordinated tartrate in the Δ isomer can be expected to differ from that in the Λ isomer under the influence of the π-electron cloud of the α-diimine or of the α hydrogen of α-diimine. This may be also reflected in the formation ratio. The formation ratios of Δ-L:Λ-L = 43:57 and Λ-D:Δ-D = 39:61 were obtained for the phen complexes and those for the bpy complexes were Δ-L:Λ-L = 45:55 and Λ-D:Δ-D = 44:56. This different formation ratio is considered to be evidence that the stereoselective reaction has occurred in this system, but the degree of stereoselectivity is slight. At any rate there is no evidence for the reported preference of only one diastereoisomer.[2] We have followed the reaction of [CoCO$_3$(phen)$_2$]Cl·5H$_2$O and L-H$_2$tart exactly according to the reported procedure and have separated the reaction product into two diastereoisomers by the method reported in this paper (Figure 5). The formation ratios were found to be Δ-L:Λ-L = 27.6:72.4. From these values and our CD spectra data for Δ-L and Λ-L, the value of 0.276(Δ-L) + 0.724(Λ-L) was calculated in the range of 600–350 nm. This calculated CD curve is in good agreement with the curve reported in ref 2 (Figure 6). This indicates that the species should be a mixture of two diastereoisomers. It is of interest that the stereoselectivity is better in the method reported in ref 2 than in our method, as seen in the formation ratios. This may be because of the differences in starting materials and reaction temperatures.

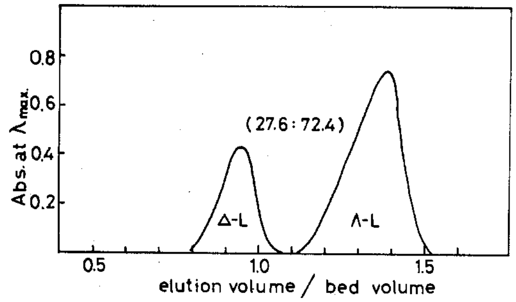

Figure 5. Elution curve of the reaction mixture obtained according to the reported procedure[2] (1.0 g of [CoCO$_3$(phen)$_2$]Cl·5H$_2$O and 0.28 g of L-(+)-tartaric acid in 20 ml of water were reacted at room temperature in the dark for 7 days).

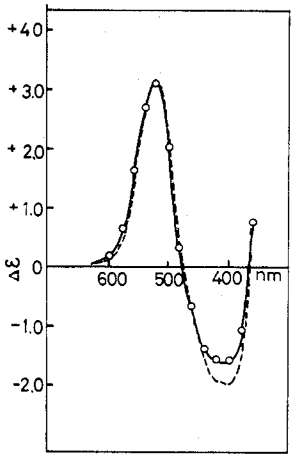

Figure 6. Calculated CD curve (0.276(Δ-L) + 0.724(Λ-L) (—o—) and CD curve reported in ref 2 (- - - -).

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Registry No. Δ-(−)$_D$-[Co(L-tart)(phen)$_2$]ClO_4, 59532-75-1; Λ-(+)$_D$-[Co(L-tart)(phen)$_2$]ClO_4, 59573-75-0; Δ-(−)$_D$-[Co(L-tart)(bpy)$_2$]ClO_4, 59532-77-3; Λ-(+)$_D$-[Co(L-tart)(bpy)$_2$]ClO_4, 59573-76-1; *cis*-[$CoCl_2$(bpy)$_2$]Cl, 14522-39-5; *cis*-[$CoCl_2$(phen)$_2$]Cl, 14267-71-1.

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The Effect of Coordination Geometry on Electrochemical Oxidation and Reduction of *N*-Methylporphyrin Complexes of Cobalt(II) and Manganese(II)

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The metal atoms in complexes of the *N*-methylporphyrins must lie significantly out of the plane of the four nitrogen atoms of the chelating ligand. In the square-pyramidal geometry of these complexes, overlap of the metal-type orbitals with the porphyrin π system appears to be significantly less than in the corresponding complexes of planar porphyrin ligands. The half-wave potentials for the reversible metal oxidations of complexes in acetonitrile occur at 0.77 V (vs. Ag|AgCl) for Co(II)–Co(III) in chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraporphinatocobalt(II), 0.72 V for Co(II)–Co(III) in chloro(*N*-methyldeuteroporphyrin IX dimethyl ester)cobalt(II), and 0.77 V for Mn(II)–Mn(III) in chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatomanganese(II). The ligand oxidations for the *N*-methyltetraphenylporphyrin complexes are 1.2–1.3 and 1.4–1.6 V. The lack of a peak between 0.0 to 0.9 V in the cyclic voltammogram of chloro-*N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatozinc(II) and appearance of peaks at 1.1 and 1.5 V supports the oxidation potential assignments. Very similar oxidation potentials are exhibited by the cobalt(II) and manganese(II) complexes. The potential for manganese(II) oxidation is much different from the value found for the planar tetraphenylporphyrin complexes, demonstrating less stabilization of high oxidation states in the nonoctahedral geometry of the *N*-methylporphyrin complexes. Reduction of the complexes leads to two very similar half-wave potentials (at −0.77 and −0.78 V and at −1.26 and −1.23 V for Co(II) and Mn(II), respectively) which are assigned to ligand reduction. There is no evidence for reduction to Co(I) in this distorted coordination geometry which will not allow a planar environment for the d^8 species.

Introduction

Porphyrin ligands often stabilize high oxidation states of transition metal ions. Such species as Ag(II) and Mn(III) are found as common stable oxidation states in porphyrin complexes exposed to air.[1] Complexes of Cr(IV),[2] Fe(IV),[3] Ag(III),[4] Pb(IV),[5] and other high oxidation state metalloporphyrins have been generated by electrochemical means. The stability of high oxidation states of metal atoms in porphyrins has been related to the restricted size and concomitant strong σ interaction of the coordination site[6] and the ability of the porphyrin ligand to delocalize positive charge via the conjugated π system and "soften" the metal atom.[7]

In view of the pattern of stabilization of higher oxidation states, it is interesting to note that the porphyrins (and related corroles) also stabilize the 1+ oxidation state of cobalt. Early extended Hückel calculations[8] indicated that the lowest available orbital of CoTPP would be an orbital of predominantly metal character while for other first row transition metal complexes with an oxidation state of two the lowest lying orbital would be of predominantly ligand character. The reduction of $Co^{II}TPP$ to $Co^{I}TPP^-$ has been well documented[9,10] and occurs in DMSO solution at −0.82 V. The Co(I) center is implicated in the function of vitamin B_{12},[11] so that reduction of Co(II) in tetrapyrrole macrocycles takes on biological significance. Since the Co(I) complexes of tetraphenylporphyrin and the corrole ligand in vitamin B_{12} are both diamagnetic, strong tetragonal distortion of the ligand field is indicated. The d^8 configuration of Co(I) would be most stabilized in a ligand field that is highly tetragonal and which could allow for some π back-bonding from the metal to the ligand. Co(I) is stabilized by such π back-bonding in carbonyl, isonitrile, and phosphine complexes.[12]

We are interested in the changes in the coordination chemistry of the porphyrins caused by N-methylation. The methylation of a pyrrolic nitrogen requires that the ligand be deformed. The bound metal atom must lie out of the plane of the four nitrogen atoms of the coordination site. The size of the region about the metal atom opposite to the porphyrin appears from molecular models to be large enough to accommodate bidentate as well as unidentate ligands although present evidence[13,14] is based only on unidentate ligands and shows single axial ligation in *N*-methylporphyrin complexes. Two recent crystal structure determinations of chlorocobalt(II) N-alkylated porphyrins[15,16] show five-coordinate geometry bonding to all four porphyrin nitrogen atoms and the chloride ligand. We propose a similar geometry for the chloromanganese(II) complex.

In this report the electrochemical properties of the cobalt(II), manganese(II), and zinc(II) complexes of *N*-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin are compared to those of the corresponding nonmethylated porphyrin complexes. The change in coordination geometry of the metal center dramatically alters the ease of oxidation of the metal atoms.

Experimental Section

Preparation of *N*-Methylporphyrins. *N*-Methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphine ($NCH_3TPP$) was prepared from CH_3SO_3F (Aldrich)