has already been demonstrated from the structure of several nitrosyl and carbonyl derivatives of cobalt[21] and nickel[22] with np_3, in which an apical nitrogen atom is not coordinated to the metal. Further corroboration comes from the fact that for the alkyl derivatives of the ligand pp_3, which differs from np_3 by the presence of a phosphorus in the place of the apical nitrogen, and for whose derivatives no evidence has been found for compounds with the apical donor atom noncoordinated, no carbon monoxide insertion takes place.

Cobalt Complexes. The cobalt(I) five-coordinate complexes having formula $[CoBr(L)]$ ($L = np_3$, pp_3) react with the stoichiometric amount of the appropriate lithium salt to give crystalline compounds with formula $[CoR(L)]$ ($L = np_3$, pp_3; $R = CH_3$, C_6H_5). Analytical data of these complexes are reported in Table I. These cobalt organo complexes are slightly soluble in tetrahydrofuran, benzene, and nitroethane. The solutions of these complexes are stable under nitrogen but decompose quickly in air; in the solid state the compounds are reasonably air-stable. Reflectance spectra are identical with those in solution and show an intense band at ca. 2.25 μm^{-1} (Table XI). All the complexes are diamagnetic, being low-spin d^8 compounds. A trigonal-bipyramidal geometry is assigned to the cobalt.

The five-coordinate cobalt(II) complexes having the general formula $[CoBr(np_3)]BPh_4$ react with Grignard reagents (CH_3MgI and $C_6H_5CH_2MgBr$) to give compounds with formula $[CoR(np_3)]BPh_4$ ($R = CH_3$, $CH_2C_6H_5$). In Table I analytical data of the complexes are reported; they behave as 1:1 electrolytes in nitroethane solution. The complexes have a μ_{eff} of ca. 2.1 μ_B corresponding to d^7 low spin (Table I). Electronic spectra both in the solid state and in solution show two bands at 7.6 and 2.00 μm^{-1} and two shoulders at ca. 1.00 and 2.63 μm^{-1}, respectively. The features of the spectra are similar to those of cobalt(II) five-coordinate complexes.[23]

The methyl derivative reacts with carbon monoxide to give the corresponding acetyl derivative $[Co(COCH_3)(np_3)]BPh_4$. The C═O stretching vibration is at 1604 cm^{-1}. The compound has a μ_{eff} of 2.18 μ_B (Table I).

The benzyl derivative reacts with carbon monoxide to give the carbonyl derivative $[Co(CO)(np_3)]BPh_4$, previously described. The complex probably reacts in the same way as $(CH_2C_6H_5)_2TiCp_2$.[19]

Acknowledgment. Thanks are expressed to Mr. P. Innocenti for technical assistance and Mr. F. Nuzzi for microanalyses.

Registry No. I, 60790-37-6; II, 65045-69-4; $[Ni(COCH_3)(nas_3)]BPh_4$, 65027-75-0; $[Ni(COC_2H_5)(nas_3)]BPh_4$, 65027-77-2; $[Ni(COCH_2C_6H_5)(nas_3)]BPh_4$, 65027-79-4; $[Ni(COC_2H_5)(np_3)]BPh_4$, 65027-81-8; $[Ni(COCH_2C_6H_5)(np_3)]BPh_4$, 65027-83-0; $[0.5\{Ni(COC_2H_5)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4$, 65027-85-2; $[0.5\{Ni(COCH_2C_6H_5)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4$, 65027-86-3; $Co(CH_3)(np_3)$, 65027-87-4; $Co(CH_3)(pp_3)$, 65027-72-7; $Co(C_6H_5)(np_3)$, 65027-73-8; $Co(C_6H_5)(pp_3)$, 65036-10-4; $[Co(CH_3)(np_3)]BPh_4$, 65036-12-6; $[Co(CH_2C_6H_5)(np_3)]BPh_4$, 65036-14-8; $[Co(COCH_3)(np_3)]BPh_4$, 65036-16-0; $[Ni(CH_3)(nas_3)]BPh_4$, 62520-88-1; $[Ni(C_2H_5)(nas_3)]BPh_4$, 62520-90-5; $[Ni(CH_2C_6H_5)(nas_3)]BPh_4$, 62520-92-7; $[Ni(CH_3)(np_3)]BPh_4$, 60790-34-3; $[Ni(C_2H_5)(np_3)]BPh_4$, 62520-84-7; $[Ni(CH_2C_6H_5)(np_3)]BPh_4$, 62520-86-9; $[CoBr(np_3)]BPh_4$, 65036-18-2; CO, 630-08-0.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. Calderazzo, *Angew. Chem.*, **89**, 305 (1977).
(2) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).
(3) (a) H. F. Klein, *Angew. Chem.*, **85**, 403 (1973); (b) H. F. Klein and H. H. Karsch, *Chem. Ber.*, **109**, 2524 (1976); (c) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Am. Chem. Soc.*, **95**, 3180 (1973).
(4) L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti, and C. Benelli, *Inorg. Chem.*, **16**, 1669 (1977).
(5) H. F. Klein and H. H. Karsch, *Chem. Ber.*, **109**, 1453 (1976).
(6) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **7**, 1417 (1968).
(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **16**, 197 (1967).
(8) Hamilton's GONO9 program, with local modifications.
(9) D. T. Cromer and G. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(11) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(12) J. M. Stewart, F. A. Kundall, and J. C. Baldwin, Ed., "X-Ray 72", Technical Report TR 192, University of Maryland, 1972.
(13) A. Domenicano and A. Vaciago, *Acta Crystallogr., Sect. B*, **31**, 2553 (1975).
(14) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, 540 (1967).
(15) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **7**, 1417 (1968); L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **89**, 2235 (1967).
(16) G. Huttner, O. Orama, and V. Bejenke, *Chem. Ber.*, **109**, 2533 (1967).
(17) L. Sacconi, C. A. Ghilardi, C. Mealli, and F. Zanobini, *Inorg. Chem.*, **14**, 1380 (1975).
(18) G. Booth and J. Chatt, *J. Chem. Soc.*, 634 (1966).
(19) G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 654 (1972).
(20) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962); R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964); K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10**, 101 (1967); K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968).
(21) M. Di Vaira, C. A. Ghilardi, and L. Sacconi, *Inorg. Chem.*, **15**, 1555 (1976).
(22) C. A. Ghilardi, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, **15**, 2763 (1976).
(23) R. Morassi, I. Bertini, and L. Sacconi, *Coord. Chem. Rev.*, **11**, 343 (1973).

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Stereochemistry of Bis(1,10-phenanthroline) Complexes of Cobalt(III) with *meso*-Tartrate or D-(−)-Malate Ion

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The *meso*-tartratobis(1,10-phenanthroline)cobalt(III) complex has been prepared, and four possible isomers, Δ-LD (Δ isomer containing an L-asymmetric carbon in the chelate ring), Λ-LD, Δ-DL (Δ isomer containing a D-asymmetric carbon in the chelate ring), and Λ-DL, have been separated by column chromatography on SP-Sephadex and CM-Sephadex. These complexes have been characterized by absorption, circular dichroism, infrared, and ^1H NMR spectra. The chromatographic behavior and the formation ratios of these isomers are discussed in comparison with the case of L-(+)- or D-(−)-tartrato complexes. The isolation and spectroscopic data of the two diastereoisomers of the analogous bis(phenanthroline) complexes containing D-(−)-malic acid are also reported.

Introduction

Recently, we have reported the study on the configurationally optically active isomers of $[Co(tart)(phen\ or\ bpy)_2]^+$, where tart is the dinegative L-(+)- or D-(−)-tartrate anion and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively.[1] Furthermore, an extension to chromium(III)

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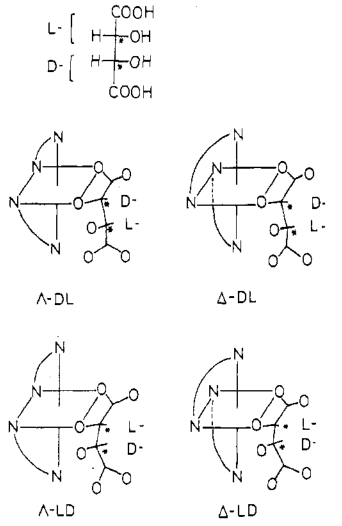

Figure 1. Spatial arrangement of *meso*-tartaric acid and schematic structure of four possible isomers of $[Co(ms\text{-}tart)(phen)_2]^+$.

complexes has been also carried out.[2] The L-(+)- or D-(−)-tartrate ion in these complexes was found to coordinate through a carboxylic group and a deprotonated α-hydroxyl group to form a five-membered chelate ring. When a *meso*-tartrate ion coordinates to a cobalt(III) ion, it can be expected that two linkage isomers are formed in terms of the signs of the asymmetric carbon contained in the chelate ring, with each of the linkage isomers made of two optical isomers due to the configurational dissymmetry, Δ and Λ, around the cobalt(III) ion, that is, the isomers containing L-asymmetric carbon in the chelate ring with Δ or Λ configuration (abbreviated as Δ-LD or Λ-LD) and the isomers containing D-asymmetric carbon in the chelate ring (abbreviated as Δ-DL or Λ-DL) (Figure 1). In the present paper the isolation of all four possible isomers of the $[Co(ms\text{-}tart)(phen)_2]^+$ complex ion and their characterization will be presented. For comparison, the isolation and the CD spectra of two diastereoisomers of analogous $[Co(D\text{-}malato)(phen)_2]^+$ will be also presented.

Experimental Section

Preparation and Chromatographic Separation of the Isomers. (1) *meso*-Tartrato Complexes. ms-$H_2tart{\cdot}H_2O$ (1.0 g, obtained from Tokyo Chemical Industry Co., Ltd.) was dissolved in 20 mL of water, and the solution was adjusted to about pH 7 by adding NaOH solution (total volume about 30 mL). To this solution $[CoCl_2(phen)_2]Cl{\cdot}3H_2O$ (3.2 g) was added, and the mixture was stirred at 60 °C for 0.5 h and then passed through a short column containing SP-Sephadex C-25 to remove reaction by-products such as $[Co(H_2O)_2(phen)_2]^{3+}$ or $[Co(phen)_3]^{3+}$. The deep red solution thus obtained was evaporated almost to dryness below 35 °C in a rotary evaporator under reduced pressure. The solid product was obtained by adding ethanol and then diethyl ether to the viscous liquid. A solution of about 0.7 g of this product dissolved in 10 mL of an eluent was poured into an SP-Sephadex column (3.0 × 130 cm) and was eluted by a 0.15 M $Na_2[Sb_2(L\text{-}tart)_2]$ aqueous solution at a rate of 0.4–0.6 mL/min. The band of the red complex separated into two bands, A and B. The eluate of each band was collected separately. After concentration under reduced pressure at room temperature and removal of the precipitate of the eluting agent by adding ethanol, the solutions were again concentrated using a vacuum evaporator to evaporate ethanol. The concentrate thus obtained was subjected to column (3.0 × 50 cm) chromatography on CM-Sephadex, previously treated with dilute hydrochloric acid, with 0.2 M $Na_2[Sb_2(L\text{-}tart)_2]$ aqueous solution as the eluent. Two separated bands arising from the fractions of band A, A-1 and A-2 in the order of elution, appeared. Similarly two bands, B-1 and B-2, separated from the fractions of band B. The eluate of each band was concentrated, and the eluting agent was removed as described above. To the concentrate, sodium perchlorate solution was added, and the mixture was allowed to stand overnight in a refrigerator. The complex obtained was recrystallized from water containing a small amount of perchloric acid. Thus, four isomers, A-1, A-2, B-1, and B-2, were isolated as the perchlorates. Anal. Calcd for $[Co(ms\text{-}tart)(phen)_2]ClO_4{\cdot}3H_2O$ ($CoC_{28}H_{26}N_4O_{13}Cl$): C, 46.65; H, 3.64; N, 7.77. Found for A-1: C, 46.44; H, 3.12; N, 7.62. Found for B-1: C, 46.74; H, 3.24; N, 7.75. Calcd for $[Co(ms\text{-}tart)(phen)_2]ClO_4{\cdot}2H_2O$ ($CoC_{28}H_{24}N_4O_{12}Cl$): C, 47.84; H, 3.44; N, 7.97. Found for A-2: C, 47.06; H, 3.05; N, 7.90. Found for B-2: C, 47.40; H, 3.05; N, 7.78.

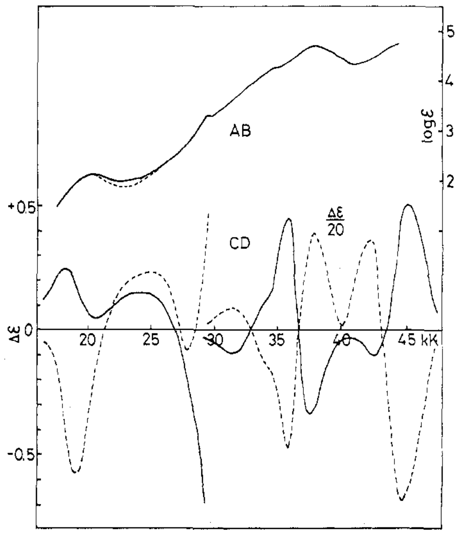

Figure 2. AB and CD spectra of isomers A-1 (Λ-DL) (—) and A-2 (Δ-DL) (---) of $[Co(ms\text{-}tart)(phen)_2]^+$.

(2) D-(−)-Malato Complexes. The preparation of the complex corresponding to $[Co(D\text{-}malato)(phen)_2]^+$ was carried out in a similar manner to that for the *ms*-tart complex, except for the use of D-(−)-malic acid (obtained from Wako Pure Chemicals) in place of *meso*-tartaric acid. The separation of the diastereoisomers of the D-malato complex could be achieved by column (3.0 × 25 cm) chromatography using CM-Sephadex of H form (as used for separating the linkage isomers of the *ms*-tart complex into optical isomers) and 0.125 M $Na_2[Sb_2(L\text{-}tart)_2]$ solution as the eluent. The adsorbed bands gradually separated into two bands. The crystals were then obtained as the perchlorate salts in a procedure analogous to that for the *ms*-tart complex. Anal. Calcd for $[Co(D\text{-}malato)(phen)_2]ClO_4{\cdot}2H_2O$ ($CoC_{28}H_{24}N_4O_{11}Cl$): C, 48.96; H, 3.52; N, 8.16. Found for band 1: C, 48.70; H, 3.21; N, 8.12. Calcd for $[Co(D\text{-}malato)(phen)_2]ClO_4{\cdot}1.5H_2O$ ($CoC_{28}H_{23}N_4O_{10.5}Cl$): C, 49.61; H, 3.42; N, 8.26. Found for band 2: C, 49.67; H, 3.41; N, 8.19.

Measurements. Absorption (AB) and CD spectra were recorded on a Shimadzu MPS-50L recording spectrophotometer and a JASCO J-20 spectrophotometer for aqueous solutions at room temperature. 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 in a Nihondenshi JNM-PFT 60 spectrometer using $Me_2SO\text{-}d_6$ as a solvent and Me_4Si as an internal standard. Elemental analyses were carried out by Wako Pure Chemical Industries, Ltd., Osaka.

Results and Discussion

Absorption (AB) and Circular Dichroism (CD) Spectra. The AB and CD spectra of the isomers are shown in Figures 2 and 3 and their numerical data are summarized in Table I. The AB spectra of all of the complexes in this study show only one band in the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition region (O_h parentage) and the intense ultraviolet absorption bands characteristic of the phenanthroline ligands. The absorption band in the $^1T_{2g}$ region is obscured completely by the intense charge-transfer bands. These features of the AB spectra are closely similar to those of the spectrum of the L- or D-tartratobis(phenanthroline) complex reported previously.[1]

The CD spectra of isomers A-1 and A-2 (Figure 2) resemble those of two diastereoisomers (Λ-D and Δ-D) of the corresponding D-(−)-tart complexes[1] in shape and are enantiomeric to those of B-1 and B-2 (see footnote *a*, Table I), respectively,

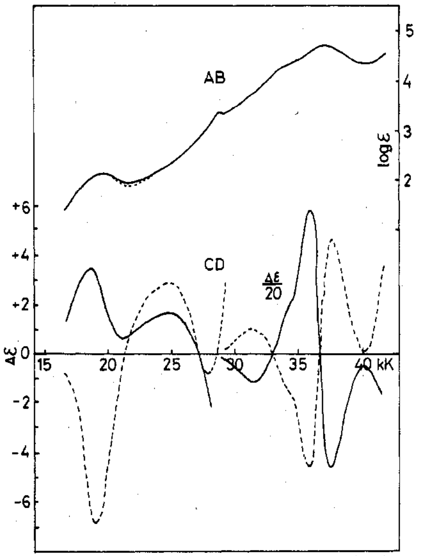

Figure 3. AB and CD spectra of Λ-[Co(D-malato)(phen)$_2$]$^+$ (—) and Δ-[Co(D-malato)(phen)$_2$]$^+$ (- - -).

Table I. AB and CD Spectra of the Isomers ($\times 10^3$ cm^{-1})

Isomer^a	AB^b	CD^c
A-1 (Λ-DL)	19.19 (2.10)	18.18 (+0.24)
	28.41 (3.36)	24.39 (+0.14)
	33.90^d (4.27)	31.25 (−1.87)
	36.70 (4.69)	35.71 (+8.91)
		37.45 (−6.73)
		42.37 (−2.21)
		45.05 (+10.07)
A-2 (Δ-DL)	19.12 (2.08)	18.87 (−0.58)
	28.41 (3.37)	25.00 (+0.23)
	33.90^d (4.30)	27.86 (−0.08)
	36.70 (4.70)	31.25 (+1.71)
		35.84 (−9.39)
		37.74 (+7.69)
		42.19 (+7.14)
		44.64 (−13.69)
Λ-(+)$_D$-[Co(D-malato)(phen)$_2$]$^+$	19.34 (2.12)	18.52 (+3.40)
	28.57 (3.36)	25.00 (+1.58)
	33.90^d (4.29)	31.25 (−23.24)
	36.76 (4.72)	35.71 (+115.4)
		37.45 (−92.95)
		42.19 (−47.30)
		44.84 (+138.6)
Δ-(−)$_D$-[Co(D-malato)(phen)$_2$]$^+$	19.31 (2.10)	18.87 (−6.88)
	28.57 (3.34)	25.00 (+2.80)
	33.90^d (4.29)	27.78 (−0.82)
	36.76 (4.72)	31.25 (+18.14)
		35.71 (−91.51)
		37.45 (+89.36)
		42.02 (+75.84)
		44.64 (−156.3)

[a] The symbols for the isomers of the *ms*-tart complex are given in the text. Since B-1 (Δ-LD) (or B-2 (Λ-LD)) gives essentially the same AB spectrum as that of A-1 (or A-2) and exhibits virtually an enantiomeric CD curve, only A-1 and A-2 are listed. [b] log ϵ_{max} in parentheses. [c] $\Delta\epsilon_{ext}$ in parentheses. [d] Shoulder.

which show the CD spectra similar to those of diastereoisomers (Δ-L and Λ-L) of the corresponding L-(+)-tart complexes.[1] The optical rotations shown by A-1, A-2, B-1, and B-2 are +, −, −, and + for 589 nm. It is known that the contributions from the chirality of chelate rings (configurational effect) and the optically active center in a ligand (vicinal effect) are additive in the CD curves of the cobalt(III) complexes containing an optically active ligand.[3-5] The configurational and vicinal effect curves evaluated from the CD spectra of A-1 and A-2 by a conventional method are shown in Figure 4. Again, the vicinal effect curves of A-1 and A-2 are very similar to those due to the corresponding D-(−)-tart complexes in shape and show mirror-image curves to those of B-1 and B-2. This fact indicates that A-1 and A-2 contain D-asymmetric carbon in the chelate ring and that B-1 and B-2 contain L-asymmetric carbon. The vicinal-effect intensity of the *ms*-tart complexes is diminished to much lower rotational strength than that of the D- or L-tart complex, and this may be attributed to the contribution from another asymmetric carbon with opposite sign adjacent to an asymmetric carbon in the chelate ring. The presence of another optically active center with opposite sign outside the chelate ring decreases greatly the overall optical activity as well as the vicinal contribution although the reason is not clear. The CD intensity of the D-malato complexes without a second optically active center, as for the *ms*-tart complexes, is comparable to that of the corresponding D-tart complexes.

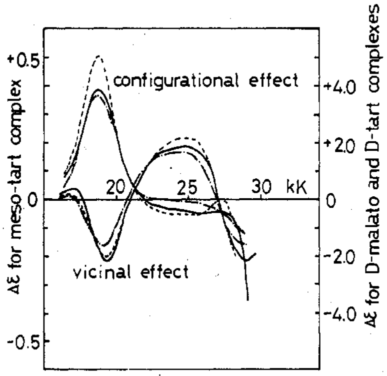

Figure 4. Configurational and vicinal effect curves for the Λ-DL isomer of [Co(*ms*-tart)(phen)$_2$]$^+$ (—), Λ-[Co(D-malato)(phen)$_2$]$^+$ (- - -), and Λ-[Co(D-tart)(phen)$_2$]$^+$ (–·–).

The absolute configuration of the cobalt(III) complexes can be assigned on the basis of the signs of the dominant CD peak in the first absorption band region.[6] Isomer A-1 has a positive dominant CD peak and shows the vicinal contribution due to D-asymmetric carbon, indicating that A-1 can be assigned to Λ-DL. Since isomer A-2 has a negative dominant CD peak and shows the same vicinal effect as that of A-1, A-2 can be assigned to Δ-DL. Similarly B-1 and B-2 are assigned to Δ-LD and Λ-LD, respectively.

Independently of the method based on the signs of the dominant CD peak in the $^1T_{1g}$ region, assignments of absolute configuration can be made from CD spectra in the ligand $\pi-\pi^*$ transition region.[7-9] Each isomer obtained here shows two intense CD peaks of opposite sign in this region (about 3.7 μm^{-1}) characteristic of (phen)$_2$ complexes; that is, the (+)$_D$ isomers of both *ms*-tart complexes (A-1 and B-2) and the D-malato complex have a positive and a negative CD peak from the lower frequency side characteristic of Λ configuration and the reverse is found for the (−)$_D$ isomers of both *ms*-tart complexes (A-2 and B-1) and the D-malato complex. Thus it can be concluded that each (+)$_D$ isomer has the Λ configuration and each (−)$_D$ isomer has the Δ configuration for [Co(*ms*-tart or D-malato)(phen)$_2$]$^+$, being consistent with the above-mentioned assignment.

Properties of the Complexes. The ^{1}H NMR spectra of the free ligand (*meso*-tartaric acid and D-(−)-malic acid) and the complexes have been measured in Me$_2$SO-d_6 relative to Me$_4$Si (Figure 5). The CH protons of *meso*-tartaric acid exhibited a single sharp resonance line at 4.24 ppm and the CH and CH$_2$ protons of malic acid showed a typical ABX pattern (with chemical shifts at about 2.47 and 2.60 (δ_A and δ_B) and about 4.28 ppm (δ_X). However, the ^{1}H NMR spectra of *meso*-tartrate and malate ligand in the complexes were too broad to determine the chemical shifts and coupling constants in this

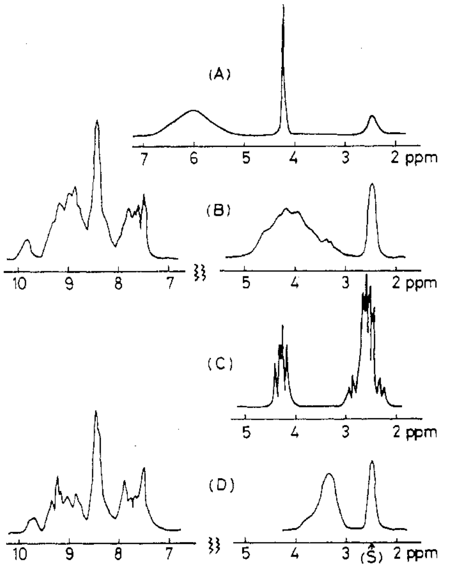

Figure 5. ^{1}H NMR spectra of *meso*-tartaric acid (A), the Δ-DL isomer of $[Co(ms\text{-}tart)(phen)_2]^+$ (B), D-(−)-malic acid (C), and Δ-$[Co(D\text{-}malato)(phen)_2]^+$ (D) in Me_2SO-d_6 (S).

region. Therefore, although differences in the chemical shifts between the Δ and Λ isomers may be expected by the effect of ring current of the neighboring phenanthroline ligand, they could not be observed. The ^{1}H NMR spectra of the phenanthroline protons for all of the complexes showed the NMR pattern characteristic of $(phen)_2$ complexes.[10-13]

The IR spectra were taken to clarify the characterization of coordinated *ms*-tart and malate ligand in the complex. The IR spectra obtained display COO stretching bands at 1710 and 1660 cm^{-1} for *ms*-tart complexes and at 1720 and around 1640 cm^{-1} for malato complexes, indicating the presence of two kinds of COO in a complex. It is well-known that the COO stretching band of COOH occurs at 1750–1700 cm^{-1}, whereas the COO stretching band of COOM (M denotes metal ion) is at 1650–1590 cm^{-1}.[14] Therefore, there is an uncoordinated free COOH group in the complexes where the proton may come from deprotonation due to coordination of a OH group to cobalt(III) ion. This indicates that the *meso*-tartrate or D-(−)-malate ion coordinates through a carboxylate group and a deprotonated α-hydroxyl group and has the uncoordinated tail of a free carboxylic acid group as could be seen in other tart complexes.[1,15,16]

Chromatographic Behavior and Formation Ratio. When an SP-Sephadex column was used for the *ms*-tart complex, the isomers were eluted in the order band A followed by B, in which were the linkage isomers containing D-asymmetric carbon and L-asymmetric carbon, respectively, in the chelate ring. Subsequently, when a CM-Sephadex column in H form was used for these linkage isomers, they were separated into the configurationally optically active isomers. The use of CM-Sephadex of H form was also effective in separation of two diastereoisomers of the D-malato complex though it was impossible to separate them by the use of SP-Sephadex. The elution order, A-1 (Λ-DL), A-2 (Δ-DL) for band A of the *ms*-tart complex, B-1 (Δ-LD), B-2 (Λ-LD) for band B, and Λ-D, Δ-D for the D-malato complex, was the same as that of the corresponding D- or L-tart complex,[1] indicating that the elution order in this system depends on the signs of asymmetric carbon contained in the chelate ring. This suggests that a kind of stereoselective interaction between the optically active dextrane matrix of SP- or CM-Sephadex and the asymmetric carbon in the chelate ring of tartrate or malate ion plays an important role in separation of these diastereoisomers. Then, it is interesting to note that for L- or D-tart complexes the configurationally optically active isomers in terms of the cobalt center are separated whereas for *ms*-tart complexes the linkage isomers in terms of the carbon asymmetric center are separated by the same chromatographic method using SP-Sephadex.

The formation ratios of the isomer were as follows: for the *ms*-tart complex, A-1 (Λ-DL):A-2 (Δ-DL):B-1 (Δ-LD):B-2 (Λ-LD) = 26:24:27:23 and for the D-malato complex, Λ-D:Δ-D = 52:48, indicating that little stereoselective formation exists.

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Registry No. A-1, 65390-82-1; A-2, 65378-02-1; B-1, 65378-04-3; B-2, 65338-55-8; Λ-$(+)_D$-$[Co(D\text{-}malato)(phen)_2]ClO_4$, 65338-53-6; Δ-$(-)_D$-$[Co(D\text{-}malato)(phen)_2]ClO_4$, 65391-27-7; *meso*-tartaric acid, 147-73-9; D-(−)-malic acid, 636-61-3; $[CoCl_2(phen)_2]Cl$, 14267-71-1.

References and Notes

(1) A. Tatehata, *Inorg. Chem.*, **15**, 2086 (1976).
(2) A. Tatehata, *Inorg. Chem.*, **16**, 1247 (1977).
(3) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).
(4) S. K. Hall and B. E. Douglas, *Inorg. Chem.*, **8**, 372 (1969).
(5) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley, New York, N.Y., 1971, p 176.
(6) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
(7) S. F. Mason, *Inorg. Chim. Acta, Rev.*, **2**, 89 (1968).
(8) B. Bosnich, *Inorg. Chem.*, **7**, 178, 2379 (1968).
(9) J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).
(10) J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 519 (1969).
(11) J. A. Broomhead and W. Grumley, *Inorg. Chem.*, **10**, 2002 (1971).
(12) H. Ito, J. Fujita, and T. Ito, *Bull. Chem. Soc. Jpn.*, **44**, 723 (1971).
(13) M. P. Hancock, J. Josephsen, and C. E. Schäffer, *Acta Chem. Scand., Ser. A*, **30**, 79 (1976).
(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y., 1970, p 238.
(15) R. A. Haines, E. B. Kipp, and M. Reimer, *Inorg. Chem.*, **13**, 2413 (1974).
(16) R. A. Haines and D. W. Bailey, *Inorg. Chem.*, **14**, 1310 (1975).