parently ready formation of ion–molecule products in organometallic systems at low pressure by direct association and stabilization without neutral product formation,[11] in contrast to the well known low probability of such processes in hydrocarbon and related ion–molecule systems. The mechanism of stabilization of the association complex is presumably collisional rather than radiative, since the rate of ion–neutral collision at the pressures used is of the order of 100 s^{-1}, while the radiative deexcitation rate is probably[12] of the order of 1 s^{-1} or less. The long lifetime of such complex association ions is an interesting phenomenon worthy of further exploration, but beyond noting that the amount of stabilized product ion increased with increasing pressure, no quantitative characterization of this system was attempted.

Experiments performed with C_6H_5Cl gave rise to a product with *m/e* 198 corresponding to $Fe(C_5H_5)(C_6H_5)^{+\cdot}$. Double resonance experiments indicated the reaction:

$$FeC_5H_5^+ + C_6H_5Cl \rightarrow Fe(C_5H_5)(C_6H_5)^{+\cdot} + Cl\cdot \qquad (2)$$

A reaction analogous to (2) was found in solution under Friedel-Crafts conditions using C_6H_5Br, whereas the reaction of ferrocene with C_6H_5Cl under identical solution conditions produced $Fe(C_5H_5)(C_6H_5Cl)^+$ and $Fe(C_5H_5)(C_6H_5C_6H_5)^+$.[5a] The solution results were presumed to occur through dehalogenation after ligand exchange in the π complex.

ICR data do not yield structural information. However, a sandwich structure obeying the 18-electron rule can be drawn for each complex assuming, in the naphthalene case, that six of the ten π electrons are delocalized into the metal; these complexes are formally isoelectronic with ferrocene. In view of the method of formation of these species, and the close formal analogy with ferrocene, it seems entirely reasonable to assume a $(\eta^5\text{-}C_5H_5)(\eta^6\text{-Ar})Fe^+$ sandwich structure.

The pyridinecyclopentadienyliron cation need not necessarily have the π-bonded sandwich structure since the high basicity of the lone pair electrons of the nitrogen atom may result in σ bonding to the iron atom. Experiments performed with a mixture of ferrocene and CH_3NH_2 showed a product with *m/e* 152 corresponding to $Fe(C_5H_5)NH_2CH_3^+$ at pressures approaching 1×10^{-4} Torr. The very low intensity of this ion inhibited meaningful double resonance experiments. It may be inferred from the greater ease of formation of the pyridine complex compared to the methyl amine complex that the pyridinecyclopentadienyl complex is likely to exist as a π-bonded system.

Most of the species described here, while novel as gas-phase ions, are known species in solution. However, there has been a conspicuous failure to prepare arenecyclopentadienyliron complexes in which strongly electron withdrawing substituents such as NO_2 are attached to the arene. In view of the fact that the $Fe(C_5H_5)(C_6H_5NO_2)^+$ ion has been found in this investigation there appears to be no inherent reason why a suitably designed solution attack should not succeed.

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Registry No. $FeC_5H_5C_6H_6^+$, 51364-24-0; $FeC_5H_5C_6H_5CH_3^+$, 32760-28-4; $FeC_5H_5C_6H_5NO_2^+$, 61827-25-6; $FeC_5H_5C_{10}H_8^+$, 46466-61-9; $FeC_5H_5C_6H_5OCH_3^+$, 32758-64-8; $FeC_5H_5C_5H_5N^+$, 61827-26-7; $FeC_5H_5^+$, 61827-27-8.

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Diastereoisomers of Bis(1,10-phenanthroline) and Bis(2,2′-bipyridine)chromium(III) Complexes Containing L-(+)-Tartrate Ion

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Circular dichroism (CD) spectra of cobalt(III) complexes containing optically active chelate ligands have been studied extensively. However, there have been few studies on the analogous chromium(III) complexes containing optically active chelate ligands. Information regarding the spectroscopic properties of chromium(III) complexes in the chiral environment can be useful for comparison of the two systems. We have previously reported on separation and characterization of the configurationally optically active isomers of $[Co(tart)(phen\ or\ bpy)_2]^+$, where tart is the dianion of L-(+)- or D-(−)-tartaric acid, and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively.[1,2] It has been shown that use of an SP-Sephadex column is effective for the separation of the diastereoisomers of this type and that the interactions between SP-Sephadex and the tartrate side in the complexes distinguishes one diastereoisomer from the other in the elution process. An extension of this investigation to chromium(III) complexes has been carried out. We present here the absorption (AB) and the CD spectra and the optical rotatory dispersion (ORD) curves of L-tartratobis(phen or bpy)chromium(III) complexes having the coordination chromphore CrO_2N_4, which is identical to that for oxalatobis(phen or bpy)chromium(III) complexes.[3,4] The AB and CD spectra of these tartrato complexes are discussed in comparison with those of the corresponding oxalato complexes.

Experimental Section

Preparation and Separation. (1) Δ- and Λ-[Cr(L-tart)(phen)$_2$]ClO$_4$. To 1.0 g (1.8 mmol) of $[CrCl_2(phen)_2]Cl\cdot 2H_2O$[5] dissolved in 30 ml of water, 0.46 g (2.0 mmol) of sodium L-tartrate dihydrate (Na_2(L-tart)$\cdot 2H_2O$) was added. The mixture was heated on a boiling water bath for 2 h. The reaction mixture was evaporated almost to dryness in a rotary evaporator under reduced pressure. Thirty milliliters of ethanol–ether (1:1) mixture was added, and then the reaction product was filtered off. About 0.5 g of the reaction product dissolved in 5 ml of 0.2 M $Na_2[Sb_2$(L-tart)$_2]$ aqueous solution as the eluent was filtered in order to remove the unreacted $[CrCl_2(phen)_2]Cl\cdot 2H_2O$, and the filtrate was subjected to column (2.7 × 50 cm) chromatography on SP-Sephadex C-25, with 0.2 M $Na_2[Sb_2$(L-tart)$_2]$. The first band and the second one (in the order of elution) were separately collected, and their effluent was concentrated in a rotary evaporator under reduced pressure at room temperature. After filtering off the precipitate of the eluting agent by adding ethanol, the filtrate was

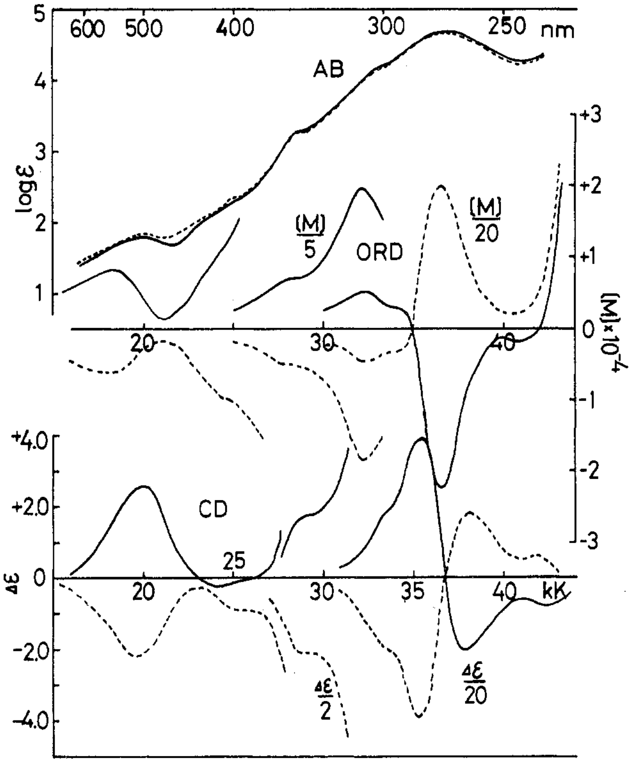

Figure 1. AB and CD spectra and ORD curves of Δ-[Cr(L-tart)-$(phen)_2]^+$ (- - -) and Λ-$[Cr(L\text{-}tart)(phen)_2]^+$ (—).

again evaporated to a small volume under reduced pressure at room temperature. To the resulting solution, sodium perchlorate solution was added and the mixture was allowed to stand overnight in a refrigerator. The product was recrystallized from water containing a small amount of sodium perchlorate. The crystals obtained were filtered off and washed with a little ice water, ethanol, and then ether. Anal. Calcd for $CrC_{28}H_{30}N_4O_{15}Cl$ = $[Cr(L\text{-}tart)(phen)_2]ClO_4{\cdot}5H_2O$: C, 44.84; H, 4.03; N, 7.47. Found for band 1: C, 44.91; H, 3.43; N, 7.25. Anal. Calcd for $CrC_{28}H_{26}N_4O_{13}Cl$ = $[Cr(L\text{-}tart)(phen)_2]ClO_4{\cdot}3H_2O$: C, 47.10; H, 3.67; N, 7.85. Found for band 2: C, 47.19; H, 3.44; N, 7.80.

(2) Δ- and Λ-[Cr(L-tart)(bpy)$_2$]ClO$_4$. These complexes were prepared by the same method as that used for the Cr(III) complexes, using an equimolar quantity (0.91 g) of $[CrCl_2(bpy)_2]Cl{\cdot}2H_2O$[6] instead of 1.0 g of $[CrCl_2(phen)_2]Cl{\cdot}2H_2O$. Anal. Calcd for $CrC_{24}H_{30}N_4O_{15}Cl$ = $[Cr(L\text{-}tart)(bpy)_2]ClO_4{\cdot}5H_2O$: C, 41.07; H, 4.31; N, 7.98. Found for band 1: C, 40.54; H, 3.22; N, 8.19. Anal. Calcd for $CrC_{24}H_{26}N_4O_{13}Cl$ = $[Cr(L\text{-}tart)(bpy)_2]ClO_4{\cdot}3H_2O$: C, 43.29; H, 3.94; N, 8.41. Found for band 2: C, 42.84; H, 3.69; N, 8.35.

Measurements. The electronic absorption spectra were recorded on a Shimadzu MPS-50L recording spectrophotometer. The CD spectra and the ORD curves were recorded on a JASCO Model ORD/UV-5 optical rotatory dispersion recorder with a CD attachment. All the measurements were carried out in aqueous solutions at room temperature. The elemental analyses were performed by Wako Pure Chemical Industries, Ltd., Osaka.

Results and Discussion

The electronic absorption (AB) and CD spectra and ORD curves of the complexes are shown in Figures 1 and 2, and their data are tabulated in Table I. The AB spectra for L-tartrato complexes, in particular of $(bpy)_2Cr^{III}$, show four obvious bands (or shoulders) in the first and the second spin-allowed d–d absorption band region. The features of the AB spectra of L-tartrato complexes are similar to those of oxalato complexes,[3] which were characterized by Perumareddi.[7] That is, the complexes being treated as approximately belonging to pseudo-D_{4h} symmetry, the four bands were assigned to $^4B_1 \rightarrow {}^4B_2$ and ^4E transitions in the first absorption band region and to $^4B_1 \rightarrow {}^4E$ and $^4A_2$ transitions in the second absorption band region. However, some ambiguities remain for the adequacy of the absorption band assignment because of the overlapping of the neighboring charge-transfer band owing to the heteroaromatic ligands present. In fact, the observed spectra of both the oxalato and the L-tartratobis(phen or bpy)chromium(III) complexes, unlike the cobalt(III) complex analogues, reveal the invalidity of the average ligand field environment rule by comparison with 10*Dq* values expected from the literature for $Cr(ox)_3^{3-}$,[8] $Cr(L\text{-}tart)_3^{3-}$,[8] $Cr(phen)_3^{3+}$,[3,4] and $Cr(bpy)_3^{3+}$.[6]

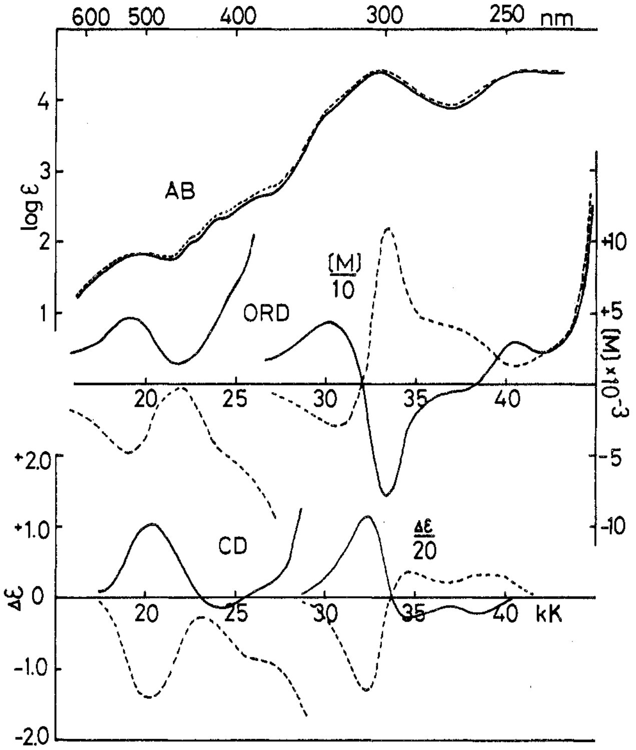

Figure 2. AB and CD spectra and ORD curves of Δ-[Cr(L-tart)-$(bpy)_2]^+$ (- - -) and Λ-$[Cr(L\text{-}tart)(bpy)_2]^+$ (—).

Table I. Absorption and Circular Dichroism Spectra[a]

Complexes	AB $\tilde{\nu}_{max}$ (log ε)	CD $\tilde{\nu}_{ext}$ ($\Delta\epsilon_{ext}$)
$(-)_D$-Δ-$[Cr(L\text{-}tart)(phen)_2]^+$	19.80 (1.86)	20.0 (−2.16)
	ca. 23.8* (2.25)	23.3 (−0.26)
	28.49 (3.28)	25.0 (−0.84)
	ca. 29.9* (3.42)	28.6 (−4.1)
	ca. 33.3* (4.20)	ca. 33.3* (−36.6)
	36.50 (4.63)	35.3 (−78.0)
		38.0 (+36.9)
$(+)_D$-Λ-$[Cr(L\text{-}tart)(phen)_2]^+$	19.76 (1.79)	20.0 (+2.56)
	ca. 23.8* (2.15)	24.4 (−0.17)
	28.49 (3.28)	28.6 (+3.5)
	ca. 29.9* (3.42)	ca. 33.3* (+34.1)
	ca. 33.3* (4.20)	35.3 (+78.1)
	36.50 (4.62)	38.0 (−39.6)
$(-)_D$-Δ-$[Cr(L\text{-}tart)(bpy)_2]^+$	20.16 (1.79)	20.2 (−1.46)
	ca. 22.5* (2.10)	23.3 (−0.30)
	ca. 24.2* (2.45)	ca. 26.3* (−0.90)
	ca. 25.6* (2.61)	
	32.68 (4.38)	32.3 (−26.7)
	ca. 33.9* (4.32)	34.5 (+6.7)
$(+)_D$-Λ-$[Cr(L\text{-}tart)(bpy)_2]^+$	19.84 (1.80)	20.4 (+1.00)
	22.52 (1.94)	24.1 (−0.16)
	ca. 24.2* (2.31)	
	ca. 25.6* (2.51)	
	32.68 (4.35)	32.3 (+22.3)
	ca. 33.9* (4.28)	34.5 (−6.0)

[a] The wavenumbers are given in 10^3 cm^{-1}. The asterisk denotes a shoulder.

The ORD curves of the diastereoisomers are almost mirror images over the range of the d–d band region–ligand π–π* transition region but, in the energy region higher than about 4.1 μm^{-1}, exhibit strongly positive optical activity because of asymmetric carbons of L-(+)-tartrate ion contained in the complexes.

The CD spectra of the L-tartrato and oxalato complexes[4] are also similar to each other. Both complexes show one dominant CD band in the first absorption band region (at about 2.0 μm^{-1}) and the weak CD band in the second absorption band region (at about 2.5 μm^{-1}). On the basis of the sign of the dominant CD peak in the first absorption band region, absolute configuration of L-tartrato complexes can be assigned. Each $(-)_D$ isomer with a negative major CD peak is assigned to Δ configuration and each $(+)_D$ isomer with a positive major CD peak to Λ configuration (Figures 1 and 2).

On the other hand, according to the exciton theory it can be predicted that bis(phen) or bis(bpy) complexes show a positive and a negative CD band from the lower frequency side in the ligand π–π^* transition region for Λ configuration and the reverse holds for Δ configuration.[9-11] The exciton CD bands are observed here at about 3.7 μm^{-1} for the phen complexes and at about 3.3 μm^{-1} for the bpy complexes. Thus, from the prediction of the exciton theory it can be concluded that $(+)_D$ isomers should be assigned to Λ configuration and $(-)_D$ isomers to Δ configuration for $[Cr(L\text{-tart})(phen\ or\ bpy)_2]^+$, being consistent with the assignment based on the major CD component in the first absorption band region.

On the other hand, although $(-)_D$-$[Cr(ox)(bpy)_2]^+$ shows a minor positive CD peak ($\Delta\epsilon$ +0.055 at 1.792 μm^{-1}) and a major negative CD peak ($\Delta\epsilon$ –1.274 at 2.055 μm^{-1}) in the first absorption band and shows two intense CD peaks of opposite sign ($\Delta\epsilon$ –17.63 at 3.226 μm^{-1} and $\Delta\epsilon$ +7.12 at 3.435 μm^{-1}) in the ligand π–π^* transition region, ref 4 attributes the CD spectrum obtained for $(-)_D$-$[Cr(ox)(bpy)_2]^+$ to Λ configuration.[4] However, on the basis of the similar CD spectra between $(-)_D$-$[Cr(ox)(bpy)_2]^+$ and $(-)_D$-$[Cr(L\text{-tart})(bpy)_2]^+$ and of the elution order for the diastereoisomers of the L-tartratobis(phen or bpy)chromium(III) and -cobalt(III) complexes in our study, $(-)_D$-$[Cr(ox)(bpy)_2]^+$ has the same absolute configuration as $(-)_D$-$[Cr(L\text{-tart})(phen\ or\ bpy)_2]^+$ and should be assigned to the Δ configuration.

The elution curves of the chromium(III) complexes were similar to those of the corresponding cobalt(III) complexes[2] for both the phen and the bpy systems and the elution order of the diastereoisomers was also the same as that observed for the cobalt(III) complexes; that is, the first eluted band was the $(-)_D$-Δ isomer and the second band was the $(+)_D$-Λ isomer. From the area of the band in the elution curves and the molar extinction coefficient, the formation ratios of the isomers were evaluated.

The value Δ-L:Λ-L = 1.2:1.0 was obtained for the phen complexes and the value Δ-L:Λ-L = 1.3:1.0 for the bpy complexes. These formation ratios (Δ-L:Λ-L) of the chromium(III) complexes are quite different from those of the corresponding cobalt(III) complexes: Δ-L > Λ-L for Cr(III) complexes, whereas Δ-L < Λ-L for Co(III) complexes. This fact may suggest that the mechanism of ligand substitution reaction differs for the two systems, even though it should be related in part to the difference of the reaction conditions (temperature and reaction time).

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Registry No. $(-)_D$-Δ-$[Cr(L\text{-tart})(phen)_2]ClO_4$, 61812-71-3; $(+)_D$-Λ-$[Cr(L\text{-tart})(phen)_2]ClO_4$, 61849-37-4; $(-)_D$-Δ-$[Cr(L\text{-tart})(bpy)_2]ClO_4$, 61812-73-5; $(+)_D$-Λ-$[Cr(L\text{-tart})(bpy)_2]ClO_4$, 61849-39-6; $[CrCl_2(phen)_2]Cl$, 31282-15-2; $[CrCl_2(bpy)_2]Cl$, 26154-79-0.

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Influence of Coordinated Thioethers in the Iron(II) Reduction of *cis*-Dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) Perchlorate

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The initial observations concerning the role of sulfur on rate enhancement,[1-3] kinetic trans effects,[4-6] and electronic ground state modifications[7] are the results of model system investigations using transition metal complexes containing coordinated sulfur.

A comparison of rate constants for reduction of cobalt(III) complexes containing halide or pseudohalide ions positioned cis and trans to nitrogen donors with rate constants for cobalt(III) complexes having thioether donors cis and/or trans to possible bridging groups demonstrates the unique influence of sulfur.[2,3] A similar comparison using reduction potentials for Cu(II)/Cu(I) chelates of cyclic and open chain polythiaethers and aminothiaethers further suggests that the enhanced reducibility of the complexes is not dependent on increased chelation or coordinative distortion.[8]

This report deals with the rate and mechanism for the iron(II) reduction of *s-cis*-dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate, *s-cis*-$[Co(eee)Br_2]ClO_4$, in aqueous perchloric acid.

Experimental Section

Preparation of *s-cis*-$[Co(eee)Br_2]ClO_4$. This complex was prepared as the bromide salt following literature procedures[9,10] and precipitated as the perchlorate salt from aqueous $LiClO_4$–$HClO_4$ media, λ_{max} (ϵ) 625.5 nm (ϵ 377). Prior to conversion to the perchlorate salt a portion of it was converted to *s-cis*-$Co(eee)Cl_2^+$ and *s-cis*-$Co(eee)(NO_2)_2^+$. The visible, ultraviolet, and infrared absorption spectra were found to be identical with those of authentic cis isomers previously prepared. This was to ensure that the complex reported in this study was indeed the cis isomer and not a trans species.

Materials. Stock solutions of $Fe(ClO_4)_2$, $LiClO_4$, and $HClO_4$ were prepared and standardized as reported earlier.[3]

Kinetic Measurements. The complex was dissolved in 0.098 M $HClO_4$; then precalculated volumes of complex, $HClO_4$, $LiClO_4$, and H_2O were delivered via syringe techniques into a 5.0-cm spectrophotometer cell. After temperature equilibrium was established, the iron(II) solution was added and the cell was shaken and placed in the Cary 14 temperature controlled cell holder. The reaction was followed by a decrease in absorbance at 625.5 nm as a function of time for over 10 half-lives. In all experiments the iron(II) concentration was in excess with respect to cobalt(III) and pseudo-first-order rate constants were obtained from computer calculated least-squares slopes of log $(D_t - D_\infty)$ vs. time plots. The plots were linear over 95% of reaction and did not exhibit signs of competitive reactions, as would be expected if the complex was not a pure single entity. All runs were performed in duplicate or triplicate if the average deviation of the