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Stereoselective Formation of Bis(phenanthroline)cobalt(III) Complexes Containing Tartaric and Malic Acids

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The preparation and characterization of certain diastereoisomers of the tartratobis(phenanthroline)cobalt(III) and malatobis(phenanthroline)cobalt(III) ions are reported. It has been found that the Λ complexes are formed stereoselectively when the *R* acid forms part of the complex while the Δ configuration is formed preferentially with the *S* acids. Possible reasons for the stereoselectivity are discussed and the spectral data are compared with those for analogous compounds.

Introduction

Although complexes of cobalt(III) containing two coordinated diamines have been extensively reported in the literature, relatively few bis(phenanthroline)cobalt(III) complexes are known. This is unfortunate since the required planarity of the phenanthroline ligand makes these complexes quite different from their analogous diamine counterparts. One consequence of the planar requirement is the necessity that the complexes have the cis configuration. Rund[1] has shown that for the trans isomers of Rh(III) and Pd(II) mutual repulsions occur for the protons at the 2 and 9 positions of the adjacent ligands. For a smaller ion such as Co(III), this repulsion would be expected to be even greater.

In recent papers[2-4] we have reported some properties of compounds of the type $[Co(diamine)_2ha]^+$, where ha is the anion of an optically active hydroxy acid. It has been found that the vicinal effect of the coordinated hydroxy acid anion is quite pronounced and makes a very significant contribution to the observed optical activity for these complexes. Unfortunately it is difficult to attribute this enhanced optical activity solely to the coordinated acid since the diamines can also make a contribution due to preferred conformations. Hence the use of phenanthroline instead of a diamine would allow a closer examination of the vicinal effect of the hydroxy acid anion itself since the phenanthroline ligands must remain planar. We are now investigating this area of study and in this paper we report the results using tartaric and malic acids.

Experimental Section

Time Studies. A mixture of 1.0 g of $[Co(phen)_2CO_3]Cl\cdot5H_2O$ and an equimolar quantity of optically active tartaric or malic acid was dissolved in 30 ml of water and set aside in the dark. The courses of the reactions were followed by withdrawing aliquots of the mixture at various time intervals and monitoring changes in ORD, CD, and visible absorption spectra. For the tartaric acid reactions the spectral data indicated that maximum optical activity was reached after 7 days while only 3 days was necessary in the case of malic acid. Unfortunately heating of the reaction mixtures readily produced $[Co(phen)_3]^{3+}$ and hence the reactions had to be carried out at room temperature.

Tartratobis(phenanthroline)cobalt(III) Perchlorate Trihydrate, $[Co(phen)_2(C_4H_4O_6)]ClO_4\cdot3H_2O$. The (*R*)-(+)-tartratobis(phenanthroline)cobalt(III) ion was prepared by mixing $[Co(phen)_2CO_3]Cl\cdot5H_2O$ (1.0 g, 1.6×10^{-3} mol) prepared by the method of Ablov[5] and 0.28 g (1.8×10^{-3} mol) of (*R*)-(+)-tartaric acid in ~20 ml of water. The reaction mixture was kept in the dark for 7 days and then passed through a cation-exchange column containing Dowex 50W-X8 resin to remove small amounts of $[Co(phen)_3]^{3+}$. Excess sodium perchlorate was then added to the mixture to precipitate the perchlorate salt which was collected by filtration and washed with copious amounts of water, followed by ethanol and ether. The crystals were stored in a desiccator and kept in the dark; yield 0.46 g.

The corresponding (*S*)-(−)-tartrato complex was prepared in a similar manner using the same quantities of the carbonato complex and (*S*)-(−)-tartaric acid; yield 0.43 g.

Anal. Calcd for $CoC_{28}H_{26}N_4O_{13}Cl$: C, 46.64; H, 3.64; N, 7.77; Cl, 4.92. Found, for (*R*)-(+)-tartaric acid: C, 46.09; H, 3.77; N, 7.90; Cl, 5.13. Found, for (*S*)-(−)-tartaric acid: C, 46.71; H, 3.44; N, 7.92; Cl, 5.10.

Malatobis(phenanthroline)cobalt(III) Perchlorate Dihydrate, $[Co(phen)_2(C_4H_4O_5)]ClO_4\cdot2H_2O$. $[Co(phen)_2CO_3]Cl\cdot5H_2O$ was mixed with 0.22 g of (*R*)-(+)-malic acid in 20 ml of water and set aside in the dark for 3 days. The solid was then isolated as for the corresponding tartaric acid complexes; yield 0.25 g. The (*S*)-(−)-malato complex was prepared in an analogous way using (*S*)-(−)-malic acid; yield 0.29 g.

Anal. Calcd for $CoC_{28}H_{24}N_4O_{11}Cl$: C, 48.95; H, 3.52; N, 7.95; Cl, 5.16. Found, for (*R*)-(+)-malic acid: C, 48.11; H, 3.35; N, 7.97; Cl, 5.28. Found, for (*S*)-(−)-malic acid: C, 48.72; H, 3.50; N, 7.92; Cl, 5.27.

General Data. The starting chemicals were obtained from either Eastman Organic Chemicals or Aldrich Chemical Co. and were used directly without further purification. Absorption spectra were recorded on a Beckman DK-1 spectrophotometer while ORD and CD measurements were made on a Durrum-Jasco Model ORD/UV-5/CD-1 spectropolarimeter. Infrared spectra were determined using KBr disks on a Beckman IR-10 spectrophotometer. NMR spectra were obtained from Varian A-60 and HA-100 Instruments using dimethyl sulfoxide as solvent and *tert*-butyl alcohol as an internal reference. Microanalyses were performed by Alfred Bernhardt, Mülheim, West Germany and A. B. Gygli, Toronto, Ontario, Canada.

Results and Discussion

All of the phenanthroline complexes studied exhibited marked photosensitivity. The reaction mixtures and aqueous solutions of the products on exposure to light gradually turned from a cherry red color to orangish yellow. Crystalline samples were isolated from these solutions which showed spectral characteristics of the orange diaquobis(phenanthroline)cobalt(III) and the yellow tris(phenanthroline)cobalt(III) ions. Photochemical reactions were also evident in the solid state and red crystalline samples became orangish yellow over a period of time when exposed to sunlight. Thermal disproportionation reactions also occurred on heating the reaction mixtures or the compounds themselves.

In order to minimize the above problems, the syntheses of the cationic cobalt(III) complexes were performed at room temperature in the dark. After the optimum reaction period (see Experimental Section), the mixtures were passed through a strong-acid ion-exchange column to remove the more highly charged $[Co(phen)_3]^{3+}$ and $[Co(phen)_2(H_2O)_2]^{3+}$ species. The product was then isolated as the perchlorate salt. Washing with copious amount of water removed any further contaminants.

Despite their photosensitivity, the complexes are sufficiently stable to permit quantitative spectral measurements. The visible absorption spectra of the complexes shown in Figures 1 and 2 are typical of other bis(phenanthroline)cobalt(III) complexes.[6] Only one d–d absorption band corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is observed; the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is completely obscured by the intense charge-transfer absorption bands characteristic of the heteroaromatic phenanthroline ligands. The position of the observed band (λ_{max} 520 nm) is consistent with predictions from crystal field theory

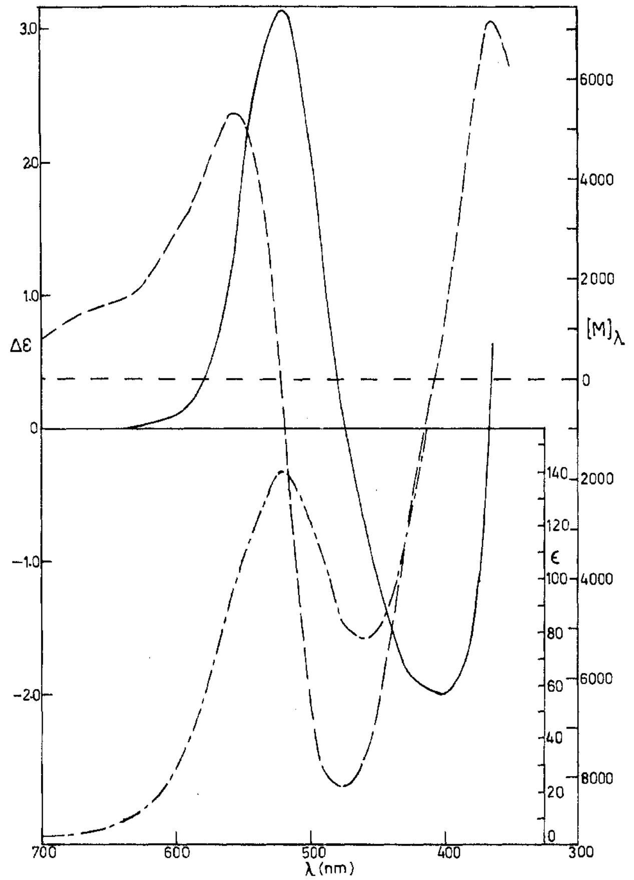

Figure 1. Absorption (- - - -), ORD (— — —), and CD (——) spectra for Λ-[Co(phen)$_2$(*R*(+)-tart)]ClO$_4$·3H$_2$O.

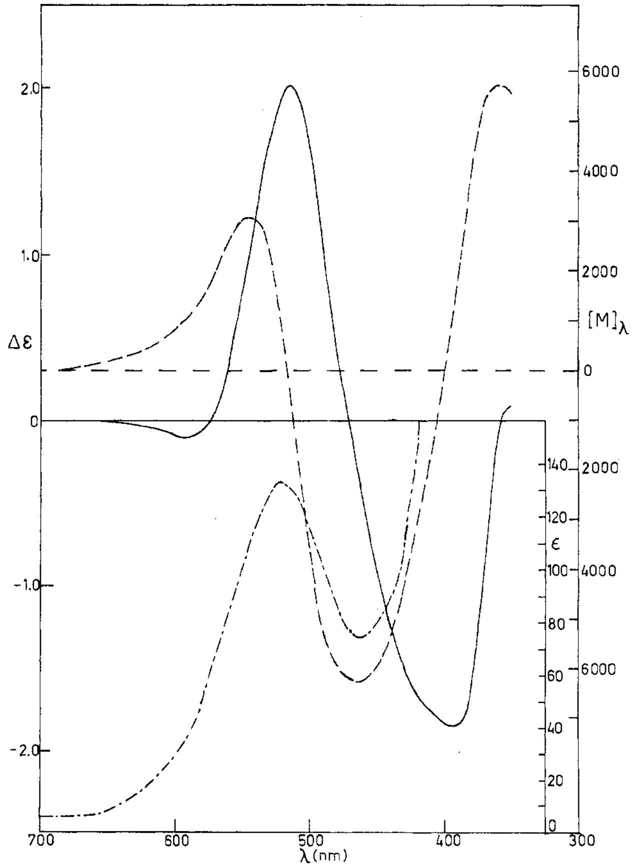

Figure 2. Absorption (- - - -), ORD (— — —), and CD (——) spectra for Λ-[Co(phen)$_2$(*R*(+)-mal)]ClO$_4$·2H$_2$O.

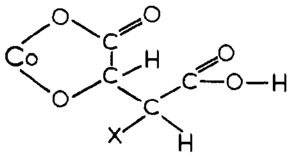

Figure 3. Nature of the chelate ring; X = OH for tartrate; X = H for malate.

since a shift to longer wavelength is predicted upon replacement of one of the strong-field phenanthroline ligands in [Co(phen)$_3$]$^{3+}$ (λ_{max} 470 nm) by a bidentate coordinated tartrate or malate ion.

Because of the several possible coordination sites possessed by tartaric and malic acids, a variety of possible complexes could be formed. The complexes would appear to be similar to those of other hydroxy acid complexes[2-4] and are coordinated through a deprotonated hydroxyl group and a carboxylate group as shown in Figure 3. Infrared spectra support this arrangement and show a band characteristic of a free carboxylic acid group at 1725 cm^{-1} and a band at 1630 cm^{-1} characteristic of a coordinated carboxylate group. Conductivity measurements also support a 1:1 electrolyte in both cases.

NMR spectra are difficult to obtain for these samples due to the relatively limited solubility of the complexes in suitable solvents. Dimethyl sulfoxide (DMSO) and H$_2$O were the only solvents in which the complexes showed any significant solubility. In D$_2$O, problems arose due to the proximity of the HOD solvent peak to the signals of interest. However, in the region of the phenanthroline protons the NMR pattern was similar to that of other bis(phenanthroline) complexes.[7,8] The tartrate complexes each showed an AB pattern on the upfield side of the HOD peak. In DMSO this region was observed more readily and chemical shifts (relative to *t*-BuOH) of δ_A 3.05 and δ_B 2.78 with J_{AB} = 13 Hz were observed. This is consistent with the expected nonequivalence of the tartrate protons.

The situation is somewhat more complicated for the malate complexes. They are not sufficiently soluble in water to allow spectra to be obtained and in DMSO the methylene protons and the DMSO protons resonate at approximately the same position. Even in DMSO-d_6 only a broad signal is observed. However, the methine proton of the malate ligand exhibits resonance as a weak triplet centered at 3.0 ppm downfield from *t*-BuOH with J = 8 Hz.

The observed NMR spectra for all the complexes are consistent with the presence of only one diastereoisomer in each sample and support the arguments that these species are formed stereoselectively (vide infra).

Tartaric Acid Complexes. In theory two diastereoisomers would be predicted to be formed when racemic [Co(phen)$_2$CO$_3$]$^+$ is allowed to react with optically active tartaric acid and these would correspond to either the Λ or Δ overall configurations of the complex [Co(phen)$_2$(C$_4$H$_4$O$_6$)]$^+$. However, it would appear that a stereoselective reaction occurs which favors formation of only one of these. Careful monitoring of the changes in the CD spectra during the course of the reaction showed that a positive CD band at ~520 nm began to appear and intensified throughout the course of the reaction. From this reaction mixture a solid was isolated which showed CD and ORD spectra (Figure 1) which were identical in shape and position with those observed for the reaction mixture. This would suggest that a predominance of this particular species had been formed in the reaction mixture. Moreover, the filtrate from the isolated product still showed strong CD spectra as before. Estimations of concentration made from absorption measurements indicated quantitative CD values which were only approximately 10% lower than those for the isolated solid. Hence it would appear that the

Table I

Complex	CD		Absorption	
	λ, nm	Δε	λ, nm	ε
Λ-$[Co(phen)_2(R(+)\text{-tart})]ClO_4 \cdot 3H_2O$	521	+3.13	521	138
	403	−1.98		
Δ-$[Co(phen)_2(S(-)\text{-tart})]ClO_4 \cdot 3H_2O$	518	−3.13	520	141
	401	+1.93		
Λ-$[Co(phen)_2(R(+)\text{-mal})]ClO_4 \cdot 2H_2O$	589	−0.105	522	133
	514	+2.02		
	394	−1.85		
Δ-$[Co(phen)_2(S(-)\text{-mal})]ClO_4 \cdot 2H_2O$	590	+0.190	520	130
	515	−2.07		
	393	+2.04		

tartrate complex has been formed with a large predominance of one isomer. Assuming that the uncoordinated tartrato residue can be neglected, the complexes may be regarded as having effective C_2 symmetry and the configuration of the complex can thus be related to that of the $[Co(en)_3]^{3+}$ ion through the common C_2 axis. On the basis of the large positive CD band at ~520 nm, the Λ overall configuration is assigned.[9] The high intensity of the CD peak in the T_{2g} region suggests mixing or intensity borrowing from uv transitions. However, it is not anticipated that these effects would dominate intensities for the T_{1g} region. Support for this comes from the fact that Λ-$[Co(phen)_2ox]^+$ shows a similar CD spectrum[10] to that of the tartaric acid complex reported here.

When (*S*)-(−)-tartaric acid is used, the CD spectra obtained are mirror images of those obtained using (*R*)-(+)-tartaric acid. Hence by arguments analogous to those above, preferential formation of the Δ isomer would appear to be favored in this case. Spectral data for both complexes are given in Table I.

Malic Acid Complexes. The reaction of $[Co(phen)_2CO_3]^+$ with optically active malic acid was also monitored by following CD and ORD spectral changes. Spectra similar to those in Figure 2 began to develop shortly after the reaction began and intensified until a steady state was reached. The solid isolated from this solution corresponded to $[Co(phen)_2(mal)]^+$ (mal = malate) and gave the spectral characteristics shown in Figure 2 and Table I. As in the case of the tartrate complexes, the CD spectrum of the mother liquor did not change significantly upon removal of the solid and indicated that a predominance of this species was still present in solution. The CD spectrum is different from that of the corresponding tartaric acid complexes in that two bands are found in the region of the first ligand field absorption hand. For most complexes with this type of symmetry the low-energy component corresponds to the A_2 transition of the corresponding D_3 complex. Hence the assignments, which are normally based on the E component, can be made on the basis of the sign of the band at ~515 nm.[9] Hence Λ-(+)$_{589}$-$[Co(phen)_2(R(+)\text{-mal})]^+$ and Δ-$[Co(phen)_2(S(-)\text{-mal})]^+$ would be the configurations of the preferred species.

Stereoselectivity. Complexes of the type $[Co(en)_2tart]^+$ have also been prepared stereoselectively[4] and the preference for one particular diastereoisomer has been attributed to favorable conformations of the chelate rings and favorable interactions of the carboxylate side chain with the amine hydrogens. For the phenanthroline complexes the rings are planar in the required cis configuration[1] and this is supported by the structure determined for the *cis*-$[Co(phen)_2Cl_2]^+$ ion.[11] Thus any conformational preferences would have to be due exclusively to the coordinated acid chelate ring. However, these rings are not particularly puckered due to the nature of the carboxylate group. Nevertheless the side chain should prefer an equatorial position and hence the *R* acids would be expected to adopt the λ conformation and the *S* acids should have the δ conformation. The energy differences are small but from molecular models it can be seen that when the coordinated acids have the above conformations, the free carboxylate tail can interact favorably with the acidic C_2 proton of one of the phenanthroline ligands. Thus a situation exists which is similar to that for the ethylenediamine counterparts where there is evidence of a favorable interaction with an acidic NH proton.[4] Both the coordinated malate and tartrate ions are capable of having this type of interaction. It is also apparent from other studies in our laboratories that this tail is important to the overall stability of the complex. Attempts to make analogous complexes using the α-hydroxy acid species lactic or mandelic acid have been unsuccessful. These ligands have no polar side chain. The reaction mixtures in these cases turn beige and the only species which can be isolated is $[Co(phen)_3]^{3+}$.

Since only one diastereoisomer could be isolated using tartaric or malic acid, further assessment of the vicinal effect of the coordinated acid has not been possible. This will require the preparation of complexes where both diastereomers can be isolated. To date attempts using other hydroxy acids have been unsuccessful.

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Registry No. Λ-$[Co(phen)_2(R(+)\text{-tart})]ClO_4$, 54657-41-9; Δ-$[Co(phen)_2(S(-)\text{-tart})]ClO_4$, 54676-76-5; Λ-$[Co(phen)_2(R(+)\text{-mal})]ClO_4$, 54657-43-1; Δ-$[Co(phen)_2(S(-)\text{-mal})]ClO_4$, 54676-78-7.

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