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Stereochemical Changes of *N*-(α-Phenylethyl)dithiocarbamate Complexes of Cobalt(III)

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By use of one particular enantiomer of the ligand *N*-(α-phenylethyl)dithiocarbamate (pedtc) the cobalt complexes [Co(pedtc)$_3$] have been prepared in optically active forms. The system shows marked stereoselectivity during synthesis and it has been found that with the (−) ligand, Λ-[Co-(−)-(pedtc)$_3$] can be isolated in pure form while the (+) ligand yields Δ-[Co-(+)-(pedtc)$_3$]. In nonpolar or weakly polar solvents the configuration of the complex has been found to undergo inversion to the opposite chirality, thus yielding a diastereoisomer which can be isolated in pure form. Reasons for the stereochemical preferences and changes are discussed and related to other systems.

Introduction

In recent years a good deal of interest has been given to the preparation and stereochemistry of transition-metal complexes of dithiocarbamates.[1-6] Much of this attention has been due to the stereochemical nonrigidity which has been observed for certain of the tris(dithiocarbamato) complexes. The primary modes of investigation have usually involved NMR studies and have centered on stereochemical changes within a mixture of isomers. In most of the cases studied to date, the dithiocarbamate ligands did not themselves possess optical activity and complexes were not isolated in an optically active form.

We have been interested in the use of optically active ligands and have found that stereoselectivity often occurs during the synthesis of certain complexes.[7,8] We wished to examine sulfur-containing ligands as part of our study, and in this paper, we report the preparation, characterization, and stereochemical changes of optically active cobalt(III) complexes containing specific enantiomers of the ligand *N*-(α-phenylethyl)dithiocarbamate.

Experimental Section

Optically pure (α-phenylethyl)amine was obtained from K & K Laboratories and was used without further purification to prepare the dithiocarbamate as the sodium salt. Sodium hydroxide (5.36 g) was dissolved in 30 mL of water, and 8.1 mL of CS_2 was added. While the solution was stirred vigorously at 0 °C, 15.5 mL of amine was slowly added from a dropping funnel. After stirring of the mixture for 0.5 h, chloroform was used to extract unreacted organic compounds. The aqueous layer was then slowly evaporated to give a solid which was removed by filtration and washed with ether; yield 18.7 g.

The cobalt(III) complexes were prepared by dissolving 0.64 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 15 mL of water. The optically active dithiocarbamate (1.0 g) in 10 mL of water was added slowly with stirring. A dark green precipitate gradually formed over a period of 0.5 h. It was removed by filtration and dissolved in methylene chloride, and the solution was extracted twice with water. A solid dark green complex was obtained after evaporation of the organic solvent; yield 0.58 g. Anal. Calcd for $C_{27}H_{30}N_3S_6Co$: C, 50.06; H, 4.67; N, 6.49; S, 29.69. Found (complex from (−) ligand): C, 49.97; H, 4.73; N, 6.53; S, 29.78. Found (complex from (+) ligand): C, 49.95; H, 4.79; N, 6.51; S, 29.73.

CD spectra were obtained from a Durrum-Jasco ORD-UV-5 spectropolarimeter with CD attachment. Visible absorption spectra were measured on a Cary Model 118 spectrophotometer while NMR spectra were measured on either a Varian T-60 or HA-100 spectrometer. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

Results and Discussion

In the preparation of the cobalt complexes [Co(pedtc)$_3$] oxidation of the metal ion occurred upon addition of the metal salt as evidenced by the diamagnetism of the final product. (Such oxidation also has been noted in earlier cobalt preparations.) The use of an optically active dithiocarbamate ligand in synthesis was briefly reported previously.[9] ORD measurements were made on the product but were not related to the stereochemistry of the species.

For tris complexes involving symmetric ligands, two enantiomers (Λ and Δ) are possible and synthesis of these species gives a racemic mixture. When an optically active ligand is used, two diastereoisomers of opposite chirality are possible, e.g., Λ-(−)(−)(−) and Δ-(−)(−)(−) for the complex from the (−) ligand. These would not be expected to be formed in equal amounts since they possess different properties. Because the species are of opposite overall chiralities, the CD observed in the visible portion of the spectrum should be of opposite sign. Thus, if only a slight predominance of one isomer is formed, a large amount of the CD due to the two species would be canceled, giving rise to a weak resultant CD curve for the mixture. Such an observation was not found, however. With the (−) ligand, the isolated solid gave a very pronounced positive CD band centered at 653 nm. The CD peak is associated with the $A_{1g} \rightarrow T_{1g}$ absorption band and the magnitude of the peak suggested that a high degree of optical purity was present. In an attempt to determine the relative proportions of each diastereoisomer, thin-layer chromatograms of the solid were developed with a variety of solvents. In all cases, only one band could be observed, suggesting the presence of only one species in the solid. This was confirmed by NMR measurements.

As shown in Table I, it can be seen that the NMR spectrum is also consistent with a single complex and one in which all three ligands are equivalent. No significant broadening was observed for the CH_3 peaks either at low temperature or under high resolution. These results are consistent with the presence of only one diastereoisomer and one in which all of the ligands

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Table I. Spectral Characteristics

	Λ-[Co-(−)-(pedtc)$_3$]	Δ-[Co-(−)-(pedtc)$_3$]
visible absorption	λ_{max} 653 nm ϵ 460	λ_{max} 660 nm ϵ 465
circular dichroism	λ_{max} 658 nm $\Delta\epsilon$ +2.04 λ_{max} 500 nm $\Delta\epsilon$ + 0.51	λ_{max} 660 nm $\Delta\epsilon$ −1.07
NMR (CH$_3$)	1.49 ppm, d J = 7 Hz rel intens = 3	1.44 ppm, d J = 7 Hz rel intens = 3
(CH)	5.2 ppm; multiplet for both species; with decoupling produces quartet; J = 7 Hz; rel intens = 1	
N-H	6.9 ppm; broad doublet; rel intens = 1	

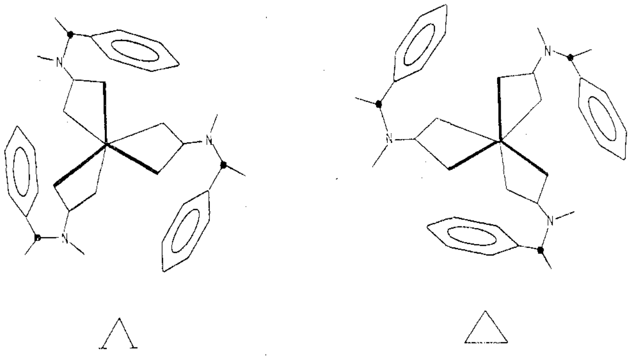

Figure 1. Λ and Δ isomers of [Co-(−)-(pedtc)$_3$] showing stereochemistry of the ligand "tails".

are in similar environments. Thus the species would have a high degree of symmetry and should have a C_3 axis. This necessitates that the tail of the ligand be wrapped around the molecule in one direction only as shown in Figure 1. Molecular models indicate that when the (−) isomer of the ligand is used, minimum steric interaction occurs if the phenyl rings are oriented in a clockwise arrangement about the C_3 axis.

Thus, it would appear that only one diastereoisomer has been isolated from the reaction mixture. From empirical rules, the Λ configuration as shown in Figure 1 is assigned to the complex containing the (−) ligand on the basis of the large positive CD value in the region of the $A_{1g} \rightarrow T_{1g}$ absorption band. When the (+) ligand is used during synthesis, the product, which analyzes correctly for [Co(pedtc)$_3$], gives a CD spectrum which is enantiomeric to that discussed above. A large negative CD peak at 653 nm was found while NMR and TLC results were identical with those for the species obtained by using the (−) ligand. Accordingly the complex containing (+)-pedtc is assigned the Δ configuration. Examination of the original reaction mixture in each case indicated only a small amount of CD was present in the region of 650 nm. However, further solid could be obtained from this mixture on slow evaporation and the solid possessed all of the characteristics of the previously isolated species. Thus it would appear that stereoselective precipitation of one particular diastereoisomer occurs during synthesis and that, in the original solution, equilibrium can shift to continue formation of this species.

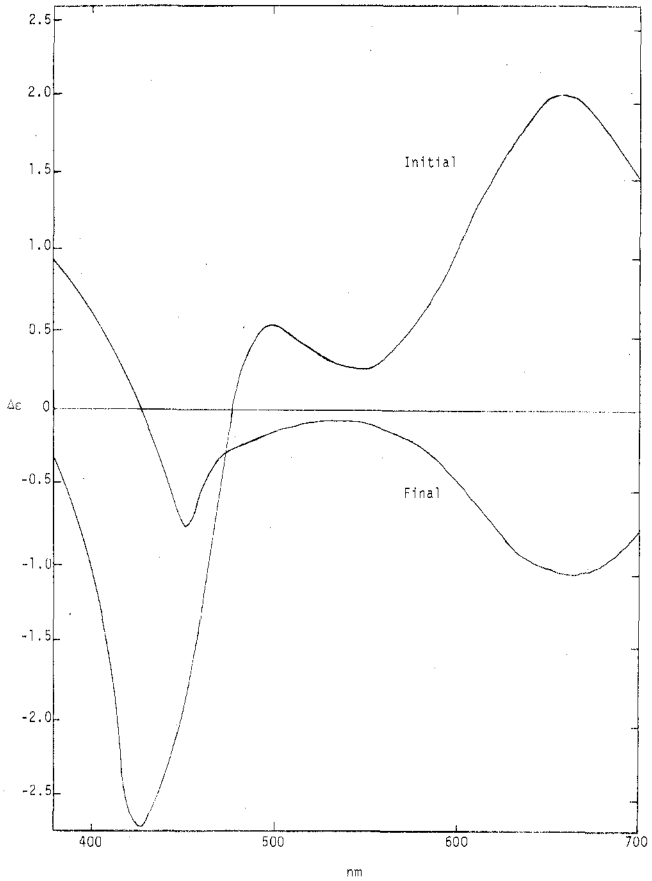

Figure 2. Circular dichroism spectra of [Co-(−)-(pedtc)$_3$] in CH_2Cl_2; final spectrum was achieved after 24 h.

Stereochemical Changes

When a solution containing the optically active [Co-(−)-(pedtc)$_3$] complex is allowed to stand in nonpolar solvents such as methylene chloride or carbon disulfide, certain spectroscopic changes were found to occur. The large positive CD peak at 653 nm gradually decreased in intensity and was replaced by a new negative band centered at 660 nm and these changes are shown in Figure 2. The NMR spectrum also changed during this time. The original CH_3 doublet gradually diminished in intensity and eventually disappeared. During this period it was replaced by a new doublet 0.05 ppm upfield at 1.44 ppm. Both the CD and NMR spectra became constant after 24 h in either methylene chloride or carbon disulfide. In solvents such as methanol, ethanol, and acetone, the changes were much slower, and after 24 h, the original CD intensity had only been diminished by about one-third. Benzene yielded a solution which changed at a rate intermediate between the two above groups of solvents. Reactions using [Co-(+)-(pedtc)$_3$] showed enantiomeric CD changes from those of [Co-(−)-(pedtc)$_3$]. In all cases, the solid isolated from these solutions analyzed correctly for [Co(pedtc)$_3$].

These changes may be interpreted as being due to an inversion process which takes place in solution. Since the sign of the CD inverts during the process, it would appear that there has been a change in overall configuration from Λ to Δ for [Co-(−)-(pedtc)$_3$] and from Δ to Λ for [Co-(+)-(pedtc)$_3$]. In each case, the configuration of the coordinated ligand would remain unchanged. Consequently, the initial and final solutions would contain diastereomeric species and hence would not be expected to have CD curves which were mirror images. Moreover, since a diastereomeric relationship would exist, the diastereomeric signals should occur at different positions. Thus it would appear that the diastereoisomer which showed the lowest solubility in water is not the most favored in these organic solvents and an inversion reaction takes place to give the complex of opposite chirality. Unfortunately the complexes could not be redissolved in water and thus studies in that medium were not possible.

The CD of the initial and final species is not enantiomeric because the two species involved are diastereoisomers. If one considers the contributions to optical activity, there will be a contribution due to the dissymmetric arrangement of the

Table II. Rate Constants and Activation Parameters for Inversion Reaction of Λ-[Co-(−)-(pedtc)$_3$]

	CH_2Cl_2	CS_2
$k_{10\,°C}$, s^{-1}	3.8×10^{-5}	1.5×10^{-5}
$k_{25\,°C}$, s^{-1}	2.1×10^{-4}	8.5×10^{-5}
$k_{40\,°C}$, s^{-1}	1.1×10^{-3}	4.4×10^{-4}
$\Delta G^{\ddagger}$, kcal/mol	22.0	22.2
$\Delta H^{\ddagger}$, kcal/mol	19.2	19.0
$\Delta S^{\ddagger}$, eu	−9.4	−10.6

ligands around the metal and this will be of opposite sense for the two species. There will also be a contribution due to the optical activity of the ligands themselves and this contribution would be expected to be of the same sense in both diastereoisomers. Thus, for one diastereoisomer, the two effects will be additive and lead to a large CD while for the other, the effects will partially cancel, leading to diminished CD. This can be seen in Figure 2. For Λ-[Co-(−)-(pedtc)$_3$], positive CD contributions from both effects appear to exist while the Δ isomer shows a diminished effect due to a negative contribution from the overall configuration but a positive contribution from the ligands.

Molecular models reveal an interesting feature for these complexes. Because of the long flexible tail, a minimum of steric interaction exists only when the tails of all three ligands are wrapped around the molecule in the same sense. As shown in Figure 1, where the (−)-pedtc is depicted, this necessarily gives rise to a C_3 axis in the molecule. It can be seen that the tails are arranged with right-handed chirality in both the Λ and Δ configurations. Thus regardless of the principal chirality associated with the arrangement of the chelate rings about the metal, there is a secondary sphere of atoms with one particular chirality. Thus the stereochemical bias found during synthesis and on standing in solution might be attributed to this feature.

Kinetic data and activation parameters were obtained for the inversion reactions in both methylene chloride and carbon disulfide and are shown in Table II. The activation parameters are similar to values previously reported[1] for the tris(*N*,*N*-dibenzyldithiocarbamato)cobalt(III) complex which was studied by NMR. In all cases, high $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ were found, thus leading to a slow rate of inversion. Inversion in these complexes is usually thought to occur by the trigonal twist or Bailar twist mechanism. Because of the planarity of the chelate rings, the overall complex is slightly twisted and this twist permits easier access to the symmetrical trigonal prismatic transition state. The cobalt(III) complex would be expected to show a twist similar to that found in the tris(*N*,*N*-diethyldithiocarbamato)cobalt(III) complex.[10,11] Here X-ray data showed distortions which would favor formation of the trigonal-prismatic intermediate. The higher activation energy for the cobalt(III) complexes relative to other transition metals has been attributed to ligand field effects. Calculations relating ligand field stabilization energies for octahedral and trigonal-prismatic environments[12,13] have shown that the greatest barrier to an octahedral–trigonal-prismatic conversion should occur for d^6 low-spin complexes such as cobalt(III).

The cobalt(III) complexes described here differ from those previously studied in that the dithiocarbamate is only monosubstituted. Earlier studies have dealt with a variety of disubstituted dithiocarbamates where the ligands were not optically active and could give rise to enantiomeric forms only. Hence only dynamic interconversion of the two forms was observed. With the optically active center on the ligand, diastereoisomerism was possible and led to inversion to one specific isomer. The extent and speed of this inversion was very strongly dependent on the solvent chosen. With oxygenated solvents such as alcohols or ketones, very slow changes occurred. This could possibly be attributed to interaction between the oxygen of the solvent and the N–H bonds of the ligands. No such solvent dependency was noted for complexes containing disubstituted ligands. Thus, these solvent interactions could hinder the approach to the transition state. Nonpolar or weakly polar solvents would not show this type of interaction and inversion could occur more readily as was observed in our studies.

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Registry No. Λ-[Co-(−)-(pedtc)$_3$], 69854-26-8; Δ-[Co-(−)-(pedtc)$_3$], 69854-27-9; Δ-[Co-(+)-(pedtc)$_3$], 69854-28-0.

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Synthesis of Transition-Metal Carboxylato Complexes[1,2]

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The preparations in high yields of (carboxylato)pentaamminecobalt(III) complexes from hydroxopentaamminecobalt(III) by reaction with carboxylic acid anhydrides and *p*-nitrophenyl and 2,4-dinitrophenyl esters are described. The stereospecific synthesis of *cis*- and *trans*-bis(acetato) complexes from *cis*- and *trans*-diaquabis(ethylenediamine)cobalt(III), respectively, has been accomplished. The acylation reactions have been extended to the preparation of the (acetato)pentaammine complexes of Cr(III), Rh(III), and Ru(III). The solvolysis in DMF of aquapentaamminecobalt(III) induced by acetyl trifluoromethanesulfonate has been shown to proceed by a mechanism which involves retention of the oxygen atom of the aqua ligand.

Introduction

Carboxylato complexes of transition metals, especially pentaammine(carboxylato)cobalt(III) salts, have been widely investigated in recent years. In particular, Taube, Gould, and their co-workers have examined the electron-transfer reactions of such systems.[4,5] Other workers have studied the photolysis of carboxylato complexes as sources of organic free radicals.[6] It has also been shown that other groups, such as α carbonyl

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