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Optically Active Tris(dithiocarbamato)cobalt(III) Chelates. Preparation and Assignment of Absolute Configuration

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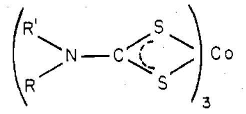
A series of optically active tris(dithiocarbamato)cobalt(III) complexes, $Co(R_2(dtc))_3$ (R = Me; Et; *i*-Pr; *n*-Bu; *i*-Bu; pyrrolidyl; morpholyl; phenyl; benzyl; *t*-Bu, CH_2CH_2OH), has been prepared by a ligand-relacement reaction of the optically active cobalt complexes of ethylenediaminetetraacetic acid, $(+)_{546}$-K[Co(EDTA)]·$2H_2O$, 1, 2-propanediaminetetraacetic acid, $(+)_{546}$-K[Co((−)-PDTA)]·$3H_2O$, and ethylenediaminedisuccinic acid, $(+)_{546}$-Na[Co(EDDS)]·H_2O, with the sodium salt of the appropriate dithiocarbamate in aqueous or aqueous/acetone media. The partially resolved optically active $Co(R_2(dtc))_3$ complexes are precipitated in high yield. The absolute configuration of the compounds is deduced from the sign of the circular dichroism band in the visible spectral region arising from the $^1A_1 \rightarrow {}^1E_a$ transition in D_3 symmetry. Those species which exhibit a negative CD band in chloroform solution are assigned the Δ absolute configuration. The peak profile and position of the CD spectrum is little affected by solvent interactions. When established structural features of the starting materials are considered, certain steric effects are seen to be important in directing the course of replacement of the chiral hexadentate ligand. Such effects are most evident in the reactions involving the $(+)_{546}$-$[Co((-)\text{-PDTA})]^-$ anion where the equatorial methyl group has a strong nonbonded interaction with the incoming $R_2(dtc)^-$ ion for *all* R substituents. The compounds prepared in this reaction show negative CD bands for the $^1A_1 \rightarrow {}^1E_a$ transition and have the Δ absolute configuration. The absolute configuration of the active $Co(R_2(dtc))_3$ compounds prepared from the $(+)_{546}$-$[Co(EDTA)]^-$ and $(+)_{546}$-$[Co(EDDS)]^-$ ions is dependent on the R substituent, particularly where R is a bulky group such as *i*-Pr. In these cases there are appreciable nonbonded interactions with the chiral ligand during its displacement, and both Δ and Λ forms are isolated depending on the R substituent of the dithiocarbamate.

Introduction

The tris-chelated cobalt(III) complexes $Co(R,R'\text{-dtc})_3$[1] of (*N*,*N*-disubstituted)dithiocarbamates (**1**) (the R groups may



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be identical, nonidentical, or part of a cyclic structure) are noncharged species. Although such species are dissymmetric at the metal center, are kinetically inert, and should, in principle, be resolvable into optical enantiomers, no general method has been reported for the preparation of the active species.

Noncharged compounds containing other bidentate ligands have been resolved by a variety of methods, most of which involve tedious procedures which often lead to low levels of optical purity. An often used technique is that of partial adsorption of enantiomers on optically active substrates such as D-lactose in column chromatographic separation. Some compounds which have been resolved into Δ and Λ[2] isomers of varying optical purities include the facial and meridional isomers of tris(5-methylhexane-2,4-dionato)- and tris(4-phenylbutane-2,4-dionato)cobalt(III) complexes.[3,4] Successful resolution of tris(pentane-2,4-dionato)cobalt(III) has also been achieved.[5,6]

Thin-layer chromatography on silica gel adsorbent has been most effectively used to resolve optical isomers of tris[(+)-3-acetylcamphorato]cobalt(III). The separation relies on the differing adsorption of the various diastereoisomers present.[7]

A novel resolution of the neutral facial tris(thiobenzohydroxamato)cobalt(III) complex has recently been reported.[8] The trianion of the compound prepared by deprotonation was resolved via ion-pair diastereoisomer formation with the optically active tris(1,2-diaminoethane)cobalt(III) cation. The resultant diastereoisomers were protonated, and the neutral optically active species were extracted into chloroform.

There has been much interest in the intramolecular metal-centered ($\Delta \rightleftarrows \Lambda$) inversion of dissymmetric tris(chelate)metal(III) species in general and in particular of cobalt(III) compounds of α-substituted tropolones[9] and β-diketones.[3] A variety of tris(dithiocarbamato)metal(III) and -(IV) complexes has also been studied,[10,11] and a trigonal twisting mechanism has been proposed to account for the optical inversion of **1** (R = R′ = benzyl) in solution.[10] Because the mechanism was not definitively proven for this compound, it seemed desirable to prepare a wider range of dithiocarbamates in order to study the process in more detail. Furthermore, previous studies have been restricted to compounds containing diastereotopic groups where coalescence patterns of proton NMR signals have been used to assign the mechanism. Optical resolution of the complexes would afford a more extensive range of compounds and in addition allow direct polarimetric measurement of loss of optical activity without the requirement of a diastereotopic substituent in the compound.[12]

Partial chromatographic resolution of **1** (R = CH_3, R′ = C_6H_4OH) has been reported. The active substrate was starch and this method was also used for the resolution of several related tris(xanthato)cobalt(III) species.[13] Separation of diastereomers of tris(*l*-menthyl xanthato)cobalt(III) on alumina has been described.[14] In initial studies on a range of tris(dithiocarbamato)cobalt(III) compounds, we have been unable to achieve measurable resolution on optically active substrates such as lactose, cellulose, and starch using a variety of organic solvents.

Ligand-exchange reactions of the optically active $[Co(EDTA)]^-$ or $[Co(PDTA)]^-$ complex ions with 1,2-diaminoethane and 1,2-diaminopropane have been reported to yield the corresponding optically active tris(diaminoalkane)cobalt(III) cation.[15-27] A recent study has shown that the reaction also occurs with the cobalt(III) complex of the hexadentate ligand derived from 1,3-diaminopropane.[23]

Preliminary experiments[24] indicated that the sodium salts of a number of dithiocarbamates reacted with optically active $[Co(EDTA)]^-$ or $[Co((-)\text{-PDTA})]^-$ in aqueous or aqueous/acetone media to give optically active precipitates of type **1**. The present paper gives full details of the preparative method, and, in addition, assignment of the absolute configuration of the active tris(dithiocarbamato)cobalt(III) complex is discussed.

Experimental Section

Preparation of Starting Materials. The sodium salts of the *N*,*N*-dialkyldithiocarbamates were prepared by reaction of CS_2 with the appropriate secondary amine in the presence of sodium hydroxide.[25]

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Table I. Specific Rotations,[a] $[\alpha]_{546}$ (deg), of Tris(dithiocarbamato)cobalt(III) Complexes

	substituent									
initial complex	Me	Et	*i*-Pr	*n*-Bu	*i*-Bu	pyrr	morph	Ph	Bz	*t*-Bu, CH_2CH_2OH
$(+)_{546}$-$K[Co(EDTA)]\cdot 2H_2O$	+208	+56	−485	+64	−63	+412	*b*	+1470	+227	*b*
$(+)_{546}$-$K[Co((-)\text{-}PDTA)]\cdot 3H_2O$	+402	+226	+232	*b*	*b*	+195	*b*	+286	+72	*b*
$(+)_{546}$-$Na[Co(EDDS)]\cdot H_2O$	−195	−254	+405	*b*	+262	−4008	+404	*b*	*b*	+1400

[a] $[\alpha]_{546} = [\alpha° \times 100]/[c\ (g/100\ cm^3) \times \text{path length (dm)}]$: $c = 0.03$ g/100 cm³ of $CHCl_3$. [b] Not measured.

All compounds were recrystallized as white solids from ethanol–diethyl ether or acetone–diethyl ether mixtures. The diphenyl derivative was prepared using sodamide.[26]

The following cobalt(III) complexes were prepared by standard literature procedures: *cis*-$[Co(en)_2(NO_2)_2]NO_2$;[27] $(+)_{589}$-$[Co(en)_2(NO_2)_2]Br$;[28] $(+)_{546}$-$K[Co(EDTA)]\cdot 2H_2O$,[14,28] $[\alpha]_{546} = +980°$ (c = 0.016 g/100 cm³ of H_2O), lit.[29] +1000° (it was found necessary to add a 20% excess over the amount of racemic K[Co(EDTA)] recommended to prevent significant deposition of the resolving agent during crystallization of the diastereoisomer); $(+)_{546}$-$Na[Co(EDDS)]\cdot H_2O$,[30] $[\alpha]_{546} = +233°$ (c = 0.021 g/100 cm³ of H_2O).

$(-)_{589}$-1,2-Diaminopropanetetraacetic acid monohydrate,[31] $[\alpha]_D = -46°$ (c = 0.74 g/cm³ of H_2O), lit.[31] − 47°, prepared from resolved 1,2-diaminopropane,[32] was used to prepare $(+)_{546}$-$K[Co((-)\text{-}PDTA)]\cdot 3H_2O$,[19] $[\alpha]_{546} = 950°$ (c = 0.020 g/cm³ of H_2O), lit.[33] +1000°.

Preparation of Co(R,R′-dtc). The racemic $Co(R,R'\text{-}dtc)_3$ compounds were prepared by either of two methods. (a) An aqueous or aqueous/acetone solution of the appropriate sodium salt of the ligand is added to an aqueous solution of cobaltous chloride.[34] Rapid air oxidation ensues and the required dark green cobalt(III) complex is collected, washed thoroughly with water, and dried in vacuo. Compounds prepared in this way are analytically pure but may be recrystallized from chloroform/ethanol, chloroform/heptane, or dichloromethane/heptane mixtures. The compounds recrystallized in this manner contain varying amounts of solvent.[35,36] (b) Ligand-replacement reactions were used to prepare some racemic materials and all of the optically active species. A typical reaction is as follows: $(+)_{546}$-$K[Co(EDTA)]\cdot 2H_2O$, $[\alpha]_{546} = +980°$ (0.54 g, 1.3×10^{-3} mol), in water (10 cm³) was added to $Na(i\text{-}Pr_2(dtc))$ (4.62 g, 2.3×10^{-2} mol) in water (15 cm³). The solution was stirred at room temperature for 1 h and the precipitated green $Co(i\text{-}Pr_2(dtc))_3$ was collected by filtration, washed thoroughly with distilled water, and dried in vacuo over anhydrous $CaCl_2$; yield 0.51 g, 68%; $[\alpha]_{546} = -485°$ (c = 0.045 g/100 cm³ of $CHCl_3$). Anal. Calcd for $C_{21}H_{42}N_3S_6Co$: C, 42.90; H, 7.20; N, 7.15; S, 32.72. Found: C, 43.01; H, 7.11; N, 7.00; S, 32.9. When $Na(Me_2(dtc))$ or $Na(Et_2(dtc))$ were used, the precipitated products $Co(Me_2(dtc))_3$ and $Co(Et_2(dtc))_3$, respectively, were collected after a reaction time of 5 min to prevent the occurrence of significant racemization during the replacement reaction.

The ligand replacement using $(+)_{546}$-$K[Co((-)\text{-}PDTA)]\cdot 3H_2O$ or $(+)_{546}$-$Na[Co(EDDS)]\cdot H_2O$ was carried out in an identical manner. The highest recorded specific rotations of the products from at least three separate preparations are recorded in Table I. All compounds were pure on the basis of ^1H and ^{13}C NMR spectra in a variety of solvents.[37]

Physical Measurements. Optical rotations of solutions in 1-cm cells were recorded on a Perkin-Elmer 141M spectropolarimeter. Circular dichroism spectra were recorded on a CNRS-Roussel Jouan Dichrograph(III) or a Jasco J-40CS recording spectropolarimeter.

Cary Model 14 and Beckman DK2A spectrophotometers were used to measure ultraviolet–visible spectra, and ^1H and ^{13}C NMR spectra were recorded on Varian Associates T-60 and Japan Electronics Jeol-JNM-PS 100 spectrometers, respectively.

Results and Discussion

The reaction of excess $Na(R_2(dtc))$ with $(+)_{546}$-$K[Co(EDTA)]\cdot 2H_2O$ in aqueous media may be written as

$$K[Co(EDTA)] + 3Na(R_2(dtc)) \rightarrow Co(R_2(dtc))_3 + KNa_3(EDTA)$$

Similar equations represent the reaction with $(+)_{546}$-$K[Co((-)\text{-}PDTA)]\cdot 3H_2O$ and $(+)_{546}$-$Na[Co(EDDS)]\cdot H_2O$. The green $Co(R_2(dtc))_3$ complex precipitates from solution and is easily isolated in chemically pure form after washing it with water and drying the product. The rate of the ligand replacement is somewhat ligand dependent with significant precipitation of the methyl, ethyl, isopropyl, and pyrrolidyl species occurring within 0.5 h. The diphenyl complex is precipitated over a 24-h period. The conditions given in the Experimental Section allow products of significant optical activity to be collected in a reasonable working time. The reaction proceeds with stoichiometric amounts of reactants but it is much faster in the presence of the large excess of sodium salt of the appropriate ligand. The specific rotations shown in Table I represent the highest value obtained from a minimum of three preparations.

Efforts to determine the optical purity of the products have at this stage been only partially successful. Examination of X-ray powder photographs of the products in attempts to estimate the amount of racemate in the product leads to a conservative estimate of 20% resolution for $Co(i\text{-}Pr_2(dtc))_3$ in its most active form. This method requires that the material examined be crystalline, but in all cases recrystallization of the initially precipitated products caused considerable racemization.[38]

In the absence of a fully resolved, crystalline enantiomer, no solid-state absolute configuration of a $Co(R_2(dtc))_3$ compound has been determined. In the present study the absolute configuration has been inferred from the results of circular dichroism (CD) measurements in the visible spectral region of chloroform solutions of the partially resolved species.

The single-crystal spectrum of $Co(Et_2(dtc))_3$ in the host crystal $In(Et_2(dtc))_3$ has been reported.[39] Selection rules for point group D_3 symmetry are clearly followed with the following transitions being observed: $^1A_1 \rightarrow {}^1A_2$ (649 nm), $^1A_1 \rightarrow {}^1E_a$ (T_{1g}) (637 nm), $^1A_1 \rightarrow {}^1E_b$ (T_{2g}) (485 nm). The approximate D_3 symmetry of the Co–S_6 coordination sphere has been established for several $Co(R_2(dtc))_3$ compounds by single-crystal X-ray structural determinations.[35,40,41] The CD spectrum of a compound with D_3 symmetry can be expected to show the transitions $^1A_1 \rightarrow {}^1E_a + A_2$ and $^1A_1 \rightarrow {}^1E_b$, where the E_b component is predicted to be very small and in addition $\Delta\epsilon(E_a) \gg \Delta\epsilon(A_2)$.[42,43] The solution absorption and CD spectra of $(-)_{546}$-$Co(pyrr(dtc))_3$ are shown in Figure 1. The corresponding data for a number of active compounds are shown in Table II. In the absorption spectra the $^1A_1 \rightarrow {}^1A_2$ transition is not resolved. If we accept the established assumption that the E_a component dominates the CD spectra and that compounds of D_3 symmetry which exhibits positive E_a components under the low-energy visible absorption band will have the Λ absolute configuration,[44-46] the predictions of configuration given in Table II follow. In particular $(+)_{546}$-$Co(R_2(dtc))_3 \equiv \Delta$ and $(-)_{546}$-$Co(R_2(dtc))_3 \equiv \Lambda$. It has been pointed out that solvent interactions can cause considerable changes in CD spectra which may lead to incorrect conclusions concerning absolute configuration assignment.[46,47] In the present study the CD spectrum of $(-)_{546}$-$Co(i\text{-}Pr_2(dtc))_3$ showed only minor changes in both $\Delta\epsilon$ and the absorption maximum of $^1A_1 \rightarrow {}^1E_a$ in a range of solvents (Table III).

Additional strength is given to the assignment of absolute configuration of $Co(R_2(dtc))_3$ when the CD spectrum of the tris(thiooxalato)cobalt(III) ion is considered. The complex

Table II. Band Maxima, Molar Absorptivity, and Circular Dichroism in the Visible Spectral Region of Optically Active $Co(R_2(dtc))_3$ in Chloroform Solution

compd	spectral band maxima,[a,b] nm	CD band maxima,[a-c] nm $^1A_1 \rightarrow {}^1E_a$, $^1A_1 \rightarrow {}^1E_b$	absolute confign[d]
$(+)_{546}$-$Co(Me_2(dtc))_3$	640 (433) 475 sh (647)	645 (−0.14), 487 (−0.03)	Δ
$(-)_{546}$-$Co(i\text{-}Pr_2(dtc))_3$	629 (609) 476 sh (1009)	625 (1.03), 477 (0.21)	Λ
$(-)_{546}$-$Co(pyrr(dtc))_3$	652 (403) 488 (568)	648 (6.51), 487 (1.24)	Λ
$(+)_{546}$-$Co(Ph_2(dtc))_3$	631 (501)	641 (−3.60), 490 (−0.88)	Δ
$(+)_{546}$-$Co(morph(dtc))_3$	642 (497) 480 sh (788)	647 (−0.70), 492 (−0.12)	Δ

[a] Product with highest rotation (Table I). [b] ε and Δε are given in parentheses immediately following the spectral or CD band maxima. Units are L mol^{-1} cm^{-1}. [c] CD assignment for D_3 symmetry. [d] Based on the sign of $^1A_1 \rightarrow {}^1E_a$ transition–see text.

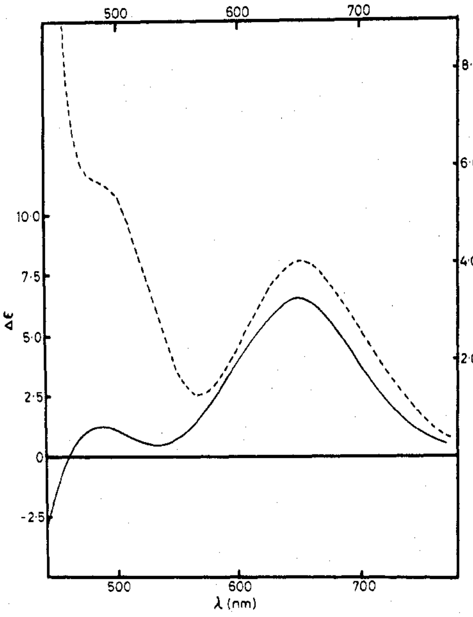

Figure 1. Visible absorption (- - -) and CD (—) spectra of $(-)_{546}$-$Co(pyrr(dtc))_3$ in chloroform.

anion represents the only structurally characterized $Co-S_6$ system of known absolute configuration. The compound $KCa\text{-}(+)_{589}\text{-}[Co(thiox)_3]\cdot 4H_2O$ has the Λ configuration[48,49] and the dominant $^1A_1 \rightarrow {}^1E_a$ transition at 529 nm in the CD spectrum is positive.[43]

The results shown in Tables I and II indicate that firm stereochemical patterns are followed in the ligand-replacement reaction, and postulated mechanisms must involve a predominant pathway which can account for relationships 1–3.

$$(+)_{546}\text{-}[Co((-)\text{-PDTA})]^- \rightarrow \Delta\text{-}Co(R_2(dtc))_3 \quad \text{for } \textit{all} \text{ R substituents} \qquad (1)$$

$$\begin{aligned}&(+)_{546}\text{-}[Co(EDTA)]^-\\ &\quad\rightarrow \Delta\text{-}Co(R_2(dtc))_3 \ (R = Me, Et, n\text{-Bu, pyrr, Ph, Bz})\\ &\quad\rightarrow \Lambda\text{-}Co(R_2(dtc))_3 \ (R = i\text{-Pr}, i\text{-Bu}) \qquad (2)\end{aligned}$$

$$\begin{aligned}&(+)_{546}\text{-}[Co(EDDS)]^-\\ &\quad\rightarrow \Delta\text{-}Co(R_2(dtc))_3 \ (R = i\text{-Pr}; i\text{-Bu; morph}; t\text{-Bu}, CH_2CH_2OH)\\ &\quad\rightarrow \Lambda\text{-}Co(R_2(dtc))_3 \ (R = Me, Et, pyrr) \qquad (3)\end{aligned}$$

Table III. Solvent Dependence of CD Absorption Maximum and Δε for the $^1A_1 \rightarrow {}^1E_a$ Transition in $(-)_{546}$-$Co(i\text{-}Pr_2(dtc))_3$[a]

solvent	λ_{max}, nm	Δε, L mol^{-1} cm^{-1}
dimethyl sulfoxide	620	0.76
carbon tetrachloride	623	0.71
chlorobenzene	624	0.76
acetonitrile	621	0.74
dimethylformamide	619	0.71
toluene	620	0.80
chloroform	620	0.67

[a] $[\alpha]_{546} = -350°$ (c = 0.03 g/cm^3 of $CHCl_3$).

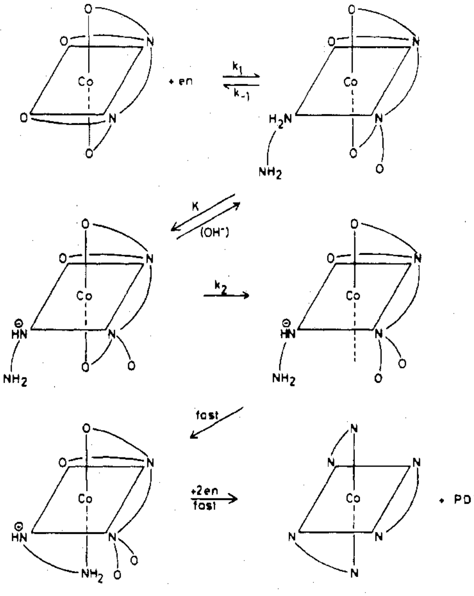

Figure 2. Mechanism of displacement of $PDTA^{4-}$ from $[Co(PDTA)]^-$ by ethylenediamine.[22]

When the visible spectrum of aqueous or aqueous/acetone mixtures of $(-)_{546}$-$K[Co(EDTA)]$ (1.6 × 10^{-3} M) and $Na(i\text{-}Pr_2(dtc))$ (1.0 × 10^{-2} M) was measured over a period of 30 min (i.e., before the green replacement product was visibly precipitated), the peak due to the $[Co(EDTA)]^-$ ion (531 nm) decreased in intensity and an absorption maximum at 625 nm which is due to $Co(i\text{-}Pr_2(dtc))_3$ gradually increased in intensity. The CD spectrum showed a decrease in the positive band at 590 nm and the growth of a negative component at 625 nm. No intermediates were observed. Although the optical purity of the product is not known with certainty (vide supra), the fact that optically active $Co(R_2(dtc))_3$ species are obtained indicates that the chiral nature of the cobalt environment is at least partially retained during the ligand replacement. Previous investigations indicated that the replacement reaction of $PDTA^{4-}$ from $[Co(PDTA)]^-$ by ethylenediamine is pH dependent and in particular at pH 9.5–11.5 involves the ethylenediamine first interacting with the cobalt atom as a monodentate ligand. A conjugate-base mechanism operates and the sequence of reactions shown in Figure 2 ensues.[22] Such a pH dependence was not found in the present case. The only noticeable effect of acidity occurs at pH <3 when ligand decomposition is observed.

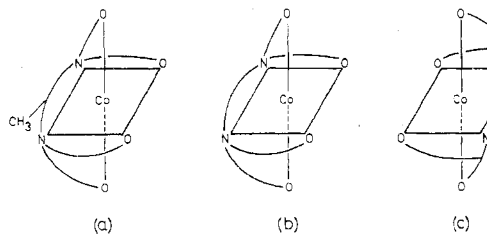

Figure 3. Schematic representation of the absolute configuration of (a) $(+)_{549}$-K[Co((−)-(PDTA))]·$3H_2O$, (b) $(+)_{546}$-K[Co(EDTA)]·$2H_2O$, and (c) $(+)_{546}$-[Co(EDDS)]·H_2O.

These results, taken in conjunction with well-established structural features of the optically active starting materials and the use of stereomodels to assess the effects of strong nonbonded interactions in various intermediates, give some indication of the possible mechanisms of replacement leading to a particular absolute configuration of the product.

The 1,2-propanediaminetetraacetate ion coordinates stereospecifically to the cobalt(III) ion and the structure of $(+)_{546}$-K[Co((−)-PDTA)]·$3H_2O$ has the absolute configuration shown schematically in Figure 3a[50] as does that for $(+)_{546}$-K[Co(EDTA)·$2H_2O$ (Figure 3b) which has an almost indentical optical rotatory dispersion spectrum[51] to that of the former compound. The absolute configuration of $(+)_{546}$-Na[Co(EDDS)]·H_2O is shown in Figure 3c. The structure of the ammonium salt has been determined by a single-crystal X-ray diffraction study.[52] The salt has the same NMR, electronic, infrared, and ORD spectra as the sodium salt. The six-membered chelate rings are equatorially disposed.[53]

The first step in the replacement reaction of the $(+)_{546}$-[Co((−)-(PDTA))] ion may reasonably be assumed to involve the dissociation of the equatorial carboxylato group(s) in the plane containing the cobalt and nitrogen atoms. Structural studies[54] on the $[Co(EDTA)]^-$ ion have established that these two glycinato rings are considerably strained. The four-membered dithiocarbamato ligand then occupies the two equatorial coordination positions to form a chelate ring. Examination of Dreiding stereomodels indicates that the equatorial methyl group on the 1,2-diaminopropane backbone strongly directs the formation of the ultimate $Co(R_2(dtc))_3$ product as the donor atoms of the PDTA chelate are successively replaced. Possible routes are shown in Figure 4. Replacement of the axial oxygen donors by sulfur atoms of two additional dithiocarbamate ligands followed by replacement of the nitrogens of the PDTA molecule and ring closure of the ligands gives (a) Λ configuration or (b) Δ configuration. There are significant nonbonded interactions during the formation of the product via route (a) as the incoming dithiocarbamate interacts with the equatorial methyl group as the PDTA molecule is released from the coordination sphere. Such interactions are clearly less important in route (b) and the Δ absolute configuration is strongly preferred, regardless of the R substituent, and an overall predominance of Δ-$Co(R_2(dtc))_3$ would be expected in the replacement product. Such a result is in accord with predictions made from the solution CD spectra (vide supra).

The stereochemical implications in the reaction of $(+)_{546}$-$[Co(EDTA)]^-$ with $Na(R_2(dtc))$ are not defined so clearly as in the corresponding PDTA case. However, it appears that the bulky *i*-Pr and *i*-Bu groups are controlling the absolute configuration of the final product.

Significant steric effects seem likely to operate in the reaction involving $(+)_{546}$-$[Co(EDDS)]^-$. When R is *i*-Pr; *i*-Bu; *t*-Bu, CH_2CH_2OH; and morph (the first three cases clearly involve substituents which are likely to cause considerable nonbonded interactions as the EDDS molecule is displaced because of their bulkiness; the role of the morpholine is not so obvious), the absolute configuration of the product is enantiomeric to that obtained when other substituents are involved. The prediction of the replacement route is not as straightforward as in the PDTA system. However, certain factors are important which influence the assignment of a reasonable mechanism which explains the absolute configuration found for the product. The choice of dissociation of either equatorial or axial carboxylato groups in the first step is not clear-cut. The structure of the $(+)_{546}$-$[Co(EDDS)]^-$ ion has relatively unstrained six-membered equatorial rings, and it is evident from an examination of molecular models that the choice of the initial dissociative step has a significant influence on the product configuration. Construction of stereo models, bearing in mind that the overall chiral nature of the species in the various steps must be retained to account for the overall observed optical activity in the product, indicates some significant nonbonded interactions.

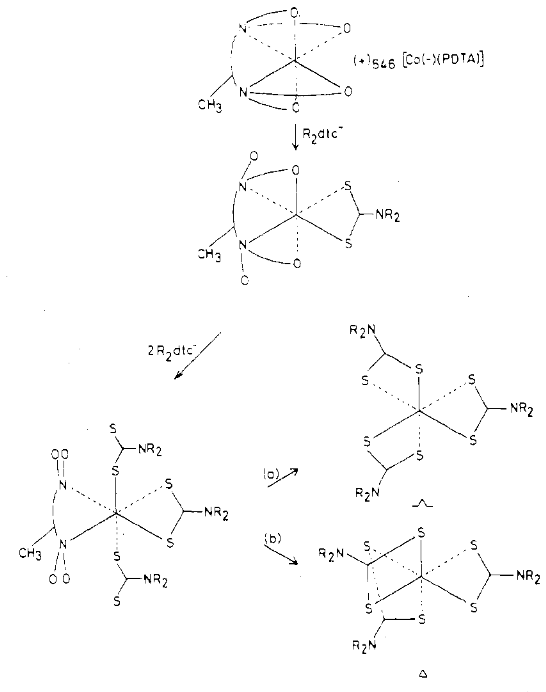

Figure 4. Reaction pathways for the replacement of $PDTA^{4-}$ from $(+)_{546}$-$[Co((-)-(PDTA))]^-$ to give $Co(R_2(dtc))_3$.

The replacement sequences considered as most reasonable could involve (i) initial replacement of *equatorial* carboxylato groups or (ii) initial replacement of an *axial* carboxylato group.

(i) When the equatorial carboxylato groups are dissociated, it is expected that the incoming dithiocarbamato ligand would coordinate strongly at the two vacated positions to form a chelate ring. There is no steric effect operating at this stage. However, if the *axial* oxygen groups are next replaced, followed by ring closure as the EDDS molecule is finally displaced, there is prohibitive nonbonding interaction between the CS_2^- carbon atom and groups on the asymmetric carbon atom of the EDDS as its N atoms are displaced in formation of the Δ configuration of the product even with small R groups.

(ii) If initial replacement of *axial* oxygens occurs followed by replacement of the *equatorial* oxygens and finally the nitrogen atoms of the EDDS molecule are replaced, the Δ form of the final product is especially favored when R is a bulky group such as *i*-Pr. There are no significant nonbonded interactions in this situation. With less bulky R groups such as Me, Et, and pyrr, the formation of the Λ configuration is possible.

Initial replacement of the *axial* oxygen atoms of the EDDS molecule is suggested because of the observation of both Δ- and Λ-$Co(R_2(dtc))_3$ products depending on the R substituent of the dithiocarbamate ligand.

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Registry No. $(+)_{546}$-K[Co(EDTA)], 40029-01-4; $(+)_{546}$-K[Co((−)-PDTA))], 69176-58-5; $(+)_{546}$-Na[Co(EDDS)], 21670-22-4; $(+)_{546}$-Co(Me_2(dtc))$_3$, 69176-59-6; $(-)_{546}$-Co(Me_2(dtc))$_3$, 69176-60-9; $(+)_{546}$-Co(Et_2(dtc))$_3$, 69176-61-0; $(-)_{546}$-Co(Et_2(dtc))$_3$, 69176-62-1; $(-)_{546}$-Co(*i*-Pr_2(dtc))$_3$, 69176-63-2; $(+)_{546}$-Co(*i*-Pr_2(dtc))$_3$, 69176-64-3; $(+)_{546}$-Co(*n*-Bu_2(dtc))$_3$, 69176-65-4; $(-)_{546}$-Co(*i*-Bu_2(dtc))$_3$, 69176-66-5; $(+)_{546}$-Co(*i*-Bu_2(dtc))$_3$, 69176-67-6; $(+)_{546}$-Co(pyrr(dtc))$_3$, 69176-68-7; $(-)_{546}$-Co(pyrr(dtc))$_3$, 69176-69-8; $(+)_{546}$-Co(morph(dtc))$_3$, 69222-29-3; $(+)_{546}$-Co(Ph_2(dtc))$_3$, 52562-97-7; $(+)_{546}$-Co(Bz_2(dtc))$_3$, 69176-70-1; $(+)_{546}$-Co(*t*-Bu,CH_2CH_2OH(dtc))$_3$, 69120-61-2.

References and Notes

(1) Abbreviations used in this paper are as follows. R,R-dtc is N-substituted dithiocarbamate where R = Me (methyl), Et (ethyl), *i*-Pr (isopropyl), *n*-Bu (*n*-butyl), *i*-Bu (isobutyl), Bz (benzyl), or Ph, (phenyl), R,R = pyrr (pyrrolidyl) or morph (morpholyl), and R = *t*-Bu, CH_2CH_2OH (*tert*-butyl, 2-hydroxyethyl). EDTA = ethylenediaminetetraacetate anion; PDTA = 1,2-propanediaminetetraacetate anion; EDDS = ethylenediaminedisuccinate tetraanion; en = ethylenediamine (1,2-diaminoethane).

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Novel Reactions of 1,2-Disubstituted Benzenes Coordinated to Cobalt(III): Neighboring-Group Participation

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The pentaamminecobalt(III) complex of 1,2-dicyanobenzene reacts with a stoichiometric amount of base to give the coordinated carboxamido complex $(NH_3)_5$Co(2-carboxamidobenzonitrile)$^{2+}$. The latter complex cyclizes in base to the pentaamminecobalt(III) complex of 1-oxo-3-iminoisoindolin-2-yl. However, in acid solution the coordinated amide complex undergoes an intramolecular rearrangement to form the coordinated nitrile-free amide compound $(NH_3)_5$Co(2-cyanobenzamide)$^{3+}$. This nitrile complex is rapidly hydrolyzed, the reaction involving intramolecular catalysis by the free amide group. The product of the hydrolysis reaction, $(NH_3)_5$Co(2-carboxamidobenzamide)$^{2+}$, cyclizes in acidic solution to $(NH_3)_5$Co(1-oxo-3-iminoisoindoline)$^{3+}$ where the metal is coordinated to the exocyclic nitrogen (3 position). The characterization of the above complexes is described, and mechanisms for their formation are considered.

Introduction

The activating role of transition metals in promoting hydrolysis reactions is well-known.[1] For example, the hydrolysis of nitriles to carboxamides is accelerated by approximately 10^6–10^8 over that of the uncoordinated ligands.[2] Furthermore, rate enhancements are much larger for reactions where intramolecular paths are possible. Evidence for such paths involving coordinated nucleophiles has arisen mainly from kinetic data and the isolation of new complexes which can only result from the intramolecular reactions.[3]

In organic reactions intramolecular catalysis has been effected by the suitable positioning of functional groups (usually ortho to each other) on a single molecule. This mode of activation is termed neighboring-group participation.[4] One

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