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Synthesis and Stereochemistry of Dichlororhodium(III) Complexes of Ethylenediamine-*N*,*N*′-di-(*S*)-α-propionic Acid

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Tetradentate chelating agents that have one or more optically active centers coordinate stereospecifically to metal ions and assume a variety of orientations in octahedral complexes that are dependent on the steric requirements of the ligands. A good number of investigations have been made on the stereochemistry of the cobalt(III) complexes of such chelate systems, and the absolute configurations of those complexes have been rationalized in terms of the positions of the substituents in the main tetradentate skeleton.[2,3] Only a few such works have been reported on the complexes of metal ions other than cobalt(III). Recently, Muir et al.[4] reported the synthesis of the cis-α, cis-β, and trans isomers of rhodium(III) complexes of (*S*,*S*)-2,9-dimethyltriethylenetetramine in which the Λ and Δ absolute configurations have been assigned, respectively, to the cis-α and cis-β isomers.

In the present work the stereochemistry of the complexes of rhodium(III) with an optically active diamine dicarboxylate ligand, ethylenediamine-*N*,*N*′-di-(*S*)-propionic acid (*S*,*S*-EDDP), has been investigated. The ligand was expected to possess the ability to coordinate stereospecifically as shown by its coordination to the cobalt(III) ion that yielded the Δ-cis-α, Λ-cis-α, and Λ-cis-β isomers.[5] It is of interest to see how the stereospecificity of this ligand is exhibited upon coordination to rhodium(III).

Experimental Section

Ethylenediamine-*N*,*N*′-di-(*S*)-α-propionic Acid (*S*,*S*-EDDP). This was prepared by the method reported.[5] Anal. Calcd for $C_8H_{16}N_2O_4$: C, 46.90; H, 7.89; N, 13.70. Found: C, 46.85; H, 7.92; N, 13.68.

Isomers of Hydrogen Dichloro(ethylenediamine-*N*,*N*′-di-(*S*)-α-propionato)rhodate(III). To a solution of 0.32 g of $LiOH·H_2O$ in 20 mL of water was added 1.55 g of *S*,*S*-EDDP. A 2.0 g sample of $RhCl_3·3H_2O$ was added, and the reaction mixture was refluxed for 1 h. The pH was adjusted to 5.0 with a dilute LiOH solution. The refluxing was continued for an additional 5 h. Further LiOH was added to the boiling solution until the pH had settled at 5.0. The solution was cooled and filtered to remove traces of any solids.

Separation of the isomers of $[Rh(S,S\text{-EDDP})Cl_2]^-$ was accomplished by two methods. During one of the syntheses the above filtrate was chromatographed on a column of Dowex 1-X8 anion-exchange resin, 100–200 mesh. Dilute HCl (0.01 M) was used as an eluent. The solution separated cleanly into two bands, with the cis-α isomer eluting before the cis-β isomer.

The isomers were also separated directly from the reaction mixture by evaporating the filtrate on a steam bath under an air stream to about half-volume. Then, 5–10 mL of concentrated HCl was added, and the evaporation was continued until crystals covered the surface of the solution. The mixture was cooled in ice, and the yellow-orange cis-α isomer was filtered off and washed with methanol and ether. A second crop of this isomer was obtained by further evaporation and cooling with scratching. The remaining solution was heated with slow addition of acetone until the solution turned murky and then the flask was scratched vigorously and refrigerated overnight. This resulted in the growth of very fine, bright yellow needles of the cis-β isomer. The yields were 0.98 g of the cis-α isomer and 1.25 g of the cis-β isomer. Anal. Calcd for *cis*-α-$RhC_8H_{15}N_2O_4Cl_2·H_2O$: C, 24.30; H, 4.30; N, 7.09. Found: C, 24.27; H, 4.33; N, 7.05. Calcd for *cis*-β-$RhC_8H_{15}N_2O_4Cl_2·3H_2O$: C, 22.27; H, 4.87; N, 6.49. Found: C, 22.22; H, 4.83; N, 6.52.

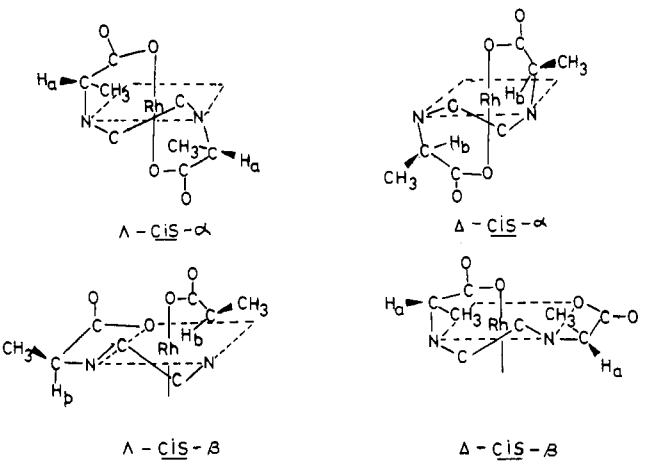

Figure 1. The four possible isomers of $[Rh(S,S\text{-EDDP})Cl_2]^-$.

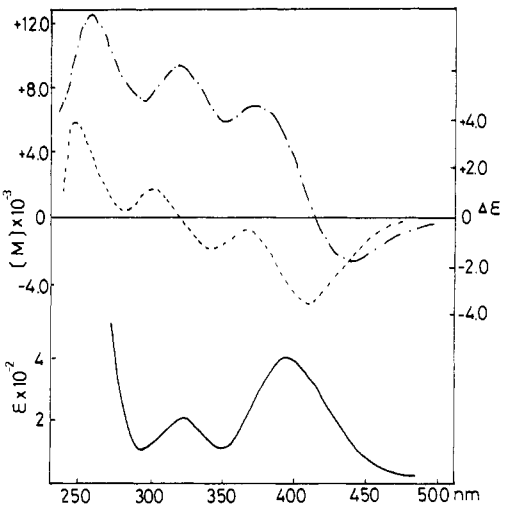

Figure 2. Electronic absorption (—), ORD (-·-), and CD (---) spectra of Δ-*cis*-α-$[Rh(S,S\text{-EDDP})Cl_2]^-$.

Δ-*cis*-α-[Rh(*S*,*S*-EDDP)(H_2O)(H_2O)Cl]. A 10-mL aqueous solution of 0.197 g of Δ-*cis*-α-$H[Rh(S,S\text{-EDDP})Cl_2]·H_2O$ was heated on a steam bath and then 0.085 g of $AgNO_3$ in 5 mL of water was added. The mixture was heated an additional 20 min on the steam bath. The AgCl precipitate was filtered off with the use of Celite. Slow evaporation under moving air led to the crystallization of the neutral, yellow complex Δ-*cis*-α-[Rh(*S*,*S*-EDDP)(H_2O)Cl] in approximately quantitative yield. The product was filtered and washed with ethanol and ether. Anal. Calcd for $RhC_8H_{16}N_2O_5Cl$: C, 26.78; H, 4.47; N, 7.81. Found: C, 26.62; H, 4.60; N, 7.84.

Results and Discussion

The complexes were prepared by the reaction of *S*,*S*-EDDP with an aqueous solution of $RhCl_3·3H_2O$, maintaining the pH below 5.0 to prevent the precipitation of insoluble rhodium hydroxide. While the *S*,*S*-EDDP ligand yielded three isomers (Δ- and Λ-cis-α and Λ-cis-β isomers) in the case of dichlorocobalt(III) complexes,[5] only two isomers (Δ-cis-α and

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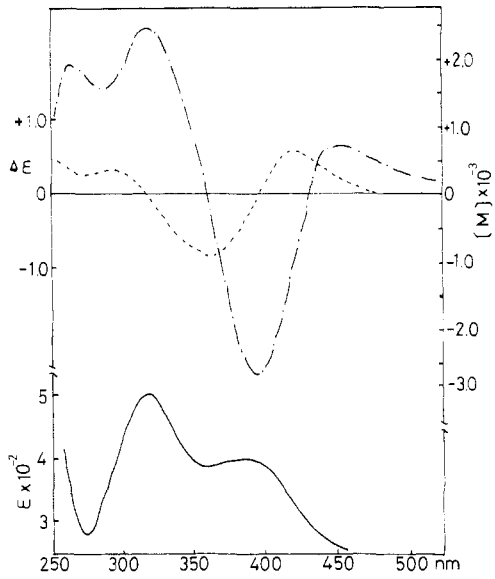

Figure 3. Electronic absorption (—), ORD (-·-), and CD (---) spectra of Λ-*cis*-β-[Rh(*S*,*S*-EDDP)Cl_2]$^-$.

Λ-cis-β) of the possible four isomers depicted in Figure 1 were formed.

The electronic absorption spectra of the cis-α and cis-β isomers are shown in Figures 2 and 3, respectively. Since both isomers are essentially *cis*-$RhN_2O_2Cl_2$, the absorption spectra are not particularly helpful in distinguishing the geometric isomers. It is noted, however, that the peaks in the cis-β isomer are at slightly higher energy than the corresponding peaks in the cis-α isomer particularly in the long-wavelength region. Such band shifts are consistent with those observed for the [Co(*S*,*S*-EDDP)(en)]$^+$ isomers. As was also the case for the isomers of the [Co(*S*,*S*-EDDP)(en)]$^+$ and [Co(*S*,*S*-EDDA)L]$^-$ series,[5-7] the absorption bands of the higher symmetry (C_2) cis-α isomer have smaller extinction coefficients than the corresponding bands of the cis-β isomer.

The cis-α and cis-β isomers have been clearly distinguished by their ^{1}H NMR spectra: while the cis-α isomer has shown a distinct methyl doublet (δ 1.68) and the H_b proton quartet (δ 3.61), two methyl doublets (δ 1.41 and 1.41) and two overlapping proton quartets have been shown in the cis-β isomer.

Figure 4 shows portions of the ^{1}H NMR spectra of *cis*-α-[Co(EDDA)(en)]$^+$, Λ-*cis*-α- and Δ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$, and *cis*-α-[Rh(*S*,*S*-EDDP)Cl_2]$^-$. The chemical shifts can be explained in terms of the magnetic anisotropy of the C–N bond,[5,8] since the ligand is rigidly oriented in the complex. In particular, the chemical shifts of the α protons of EDDA (labeled H_a and H_b) can be distinguished because of the magnetic anisotropic shielding of the C–N bond. The H_b protons are situated almost directly over the C–N bond of the ethylenediamine backbone ring and are shielded by it, while the B_a protons are not affected by this bond.[7] Thus, the H_a protons resonate at lower fields than the H_b protons.

Only an H_a proton signal is exhibited in Λ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$ and only an H_b proton signal in Δ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$. Such assignments of the absolute configurations for the isomers of the cobalt(III) complexes could be made from the known absolute configuration of the tetradentate ligand.[5,9] By analogy, the *cis*-α-[Rh(*S*,*S*-EDDP)Cl_2]$^-$ showed only the H_b proton quartet at δ 3.61, and a Δ absolute configuration is assigned to this complex. By

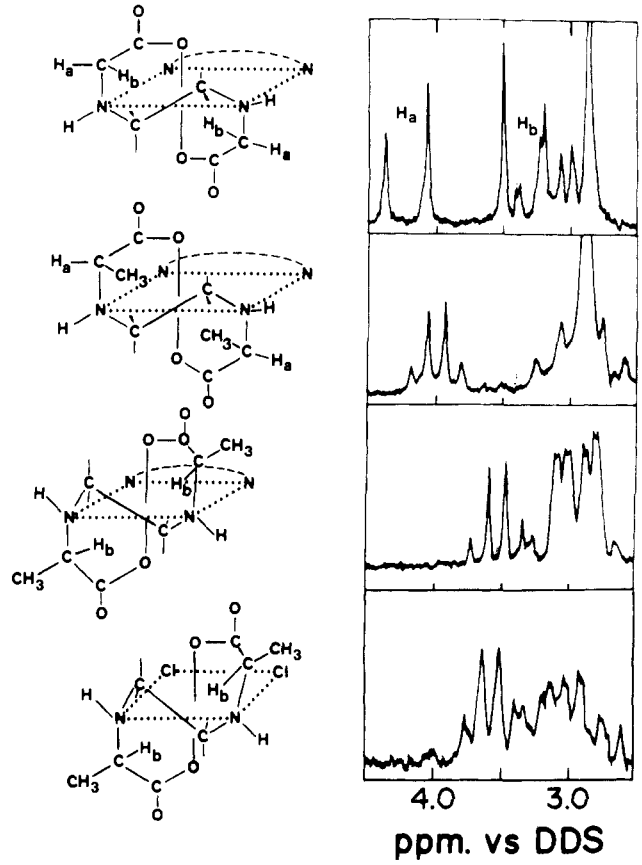

Figure 4. 60-MHz ^{1}H NMR spectra of (from top to bottom) *cis*-α-[Co(EDDA)(en)]$^+$, Λ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$, Δ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$, and Δ-*cis*-α-[Rh(*S*,*S*-EDDP)Cl_2]$^-$. Stereochemical representations are shown at the left.

comparison, the H_b proton quartet for the Δ-*cis*-α Co(III) complex was at 3.53 ppm and the H_a proton quartet of the Λ-*cis*-α Co(III) complex at 3.99 ppm.[5] The resonances of the rhodium(III) complexes are shifted downfield from the Co(III) isomers, which is probably due to the different electronic environment of the rhodium(III) complex ion.

The cis-β isomer has only C_1 symmetry, and the propionate arms are no longer equivalent. Thus, two methyl doublets and two overlapping proton quartets are expected. The facial arm of the Λ-cis-β isomer is almost identical with one arm of the Δ-cis-α isomer (Figure 1). The α protons of these similar arms should resonate at nearly the same value. The H_b proton in the planar carboxylate arm no longer lies in the shielding area of the C–N bond; such loss of shielding causes it to resonate at lower fields. These two proton quartets are clearly seen, though not well resolved, at 3.60–4.05 ppm, and an Λ absolute configuration may be assigned to the cis-β isomer isolated in this work.

The Cotton effect signs for both Δ-cis-α and Λ-cis-β isomers shown in Figures 2 and 3, respectively, are in agreement with the absolute configuration assignments made from ^{1}H NMR spectra. In the Δ-*cis*-α Cl_2 isomer, a negative CE is seen, which is in agreement with the Δ-*cis*-α-[Co(*S*,*S*-EDDP)(en)]$^+$ spectrum. Both Δ-[Rh(en)$_3$]$^{3+}$ and Δ-[Rh(en)$_2$(*S*-Met)]$^{2+}$ show a negative CE.[10-12] The Rh(III) cis-α complex of *S*,*S*-EDDP retains effective C_2 symmetry,[13] and a negative CE is expected for the Δ-cis-α isomer by analogy to the en complex. On the other hand, the cis-β isomer shows a positive CE

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whose Λ configuration was expected via its ^{1}H NMR spectrum.

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Registry No. H[Rh(*S*,*S*-EDDP)Cl$_2$], 89460-80-0; Δ-*cis*-α-H[Rh(*S*,*S*-EDDP)Cl$_2$], 85504-79-6; Γ-*cis*-β-H[Rh(*S*,*S*-EDDP)Cl$_2$], 85107-97-7; Δ-*cis*-α-[Rh(*S*,*S*-EDDP)(H$_2$O)Cl], 89397-59-1.

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N,*N*′,*N*″,*N*‴-Tetrakis(2-hydroxyethyl)cyclam, an N-Donor Macrocycle with Rapid Metalation Reactions

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The nitrogen-donor macrocycles with their cavities of fairly fixed size[1] should display much greater selectivity for metal ions on the basis of the size of the metal ions than is found for open-chain polyamines. An immediate application might be the attachment of macrocycles such as cyclam (1,4,8,11-tetraazacyclotetradecane) to polystyrene beads so as to produce ion-exchange resins capable of selectively extracting metal ions, either in waste treatment or in hydrometallurgical applications. This has been done,[2] but it was found that the rate of metal ion extraction, even for the normally labile Cu(II) ion, was so slow that reasonable rates of extraction could only be obtained at 80 °C, at which temperature the lifetime of most polystyrene based ion-exchangers is very short. What is obviously required for the successful utilization of the greater size selectivity expected for macrocycles is an approach to speeding up their reaction rates, which are very slow[3,4] in comparison with those of noncyclic ligands.

It has been shown that the slowness of the metalation reactions of N-donor macrocycles relates to slow rates of reaction of the metal ion with protonated forms of the ligand.[3,4] This results from the fact that the incoming metal ion is formed in close proximity to any remaining protons on the macrocycle, and the reaction intermediate is thus destabilized by electrostatic repulsion. One approach to overcoming this problem is to attach a donor atom outside of the macrocyclic ring, which then forms a point of initial attachment for the metal ion where electrostatic repulsion with protons in the cavity of the macrocycle will not be as severe. This approach has been successful[5] in that attachment of acetate "arms" to porphyrins has lead to rapid metalation reactions.

At this stage several cyclam derivatives with groups substituted onto the nitrogens are known,[6-9] among which is a

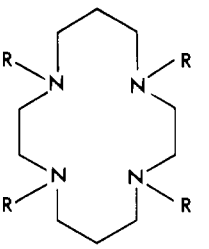

Figure 1. Structure of tetraaza macrocycles discussed in this paper. R = H is cyclam; R = CH_3 is TMC, tetramethylcyclam; R = CH_2COO^- is CTA, cyclamtetraacetate; R = CH_2CH_2OH is THEC, tetrakis(2-hydroxyethyl)cyclam; R = CH_2CH_2CN is TCEC, tetrakis(2-cyanoethyl)cyclam.

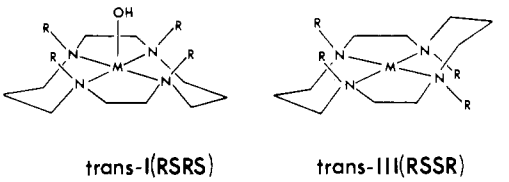

Figure 2. Structure of the *trans*-(*RSRS*)-I and *trans*-(*RSSR*)-III conformers of tetraaza macrocyclic complexes, showing the *trans*-(*RSRS*)-I form with a unidentate ligand coordinated in the axial position to give a square-pyramidal five-coordinate complex.

tetraacetate.[7] One might have expected this to produce the desired rapid metalation, but a detailed study[10] of the complexation reactions indicates that metal ions such as Co(II), Ni(II), and Cu(II) do not actually enter the cavity of the macrocycle but instead form complexes in which the metal ion is held outside of the ring, bonding to two acetates and only two of the nitrogens of the macrocyclic ring. This mode of bonding produces, instead of enhanced selectivity, an unusually closely bunched set of formation constants for the set of metal ions studied.[7] An interpretation of the unusual bonding found for cyclamtetraacetate might be that the complex formed held outside of the ring is actually more stable than that held in the ring and that the reluctance to move into the ring is not a simple kinetic effect, as will be discussed below.

An interesting example of enhanced lability among nitrogen-donor macrocycles has been reported by Barefield et al.,[6] with the ligand TMC, tetramethylcyclam (Figure 1). Although the methyl groups on TMC are not potential donor groups, the ligand is fairly labile. This may relate in part to the lower pK_a values found for TMC,[11,12] which means that at any given pH the concentration of free TMC, and TMC species with few protons attached, is much higher than for cyclam, resulting in more rapid complex formation. Another important aspect here relates to the mode of entry of the metal ion into the cavity of a nitrogen-donor macrocycle. This involves initial reaction with the folded form of the macrocycle to produce the *trans*-(*RSRS*)-I type of structure, shown in Figure 2, followed by base-catalyzed conversion through inversion at the nitrogens to give the *trans*-(*RSSR*)-III type structure. As pointed out by Barefield et al.,[6] TMC complexes have tertiary nitrogens and so cannot be deprotonated to allow inversion at the nitrogens to give the final *trans*-(*RSSR*)-III structure. The unusual five-coordinate structure found[6] in the TMC complexes might lead to unusual selectivities in both TMC complexes and the complexes of other ligands where this

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