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Stereochemical Inversion in the Substitution Reactions of Dichloroethylenediamine-N,N′-di-S-α-propionatorhodate(III) Ion

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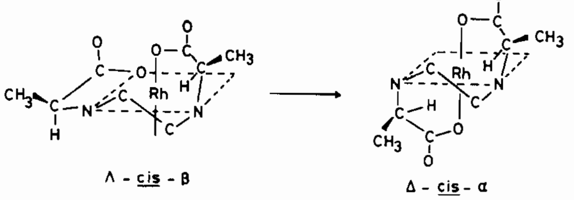
The optically active tetradentate ligand, ethylenediamine-N,N′-di-S-α-propionate (SS-EDDP), has been coordinated to cobalt(III) ion to yield the optically active Δ-*cis*-α, Λ-*cis*-α, and Δ-*cis*-β *isomers of [Co(SS-*EDDP)(en)]$^+$ complex (en = ethylenediamine) [1]. Recently, we have found that the SS-EDDP ligand coordinated stereospecifically to rhodium(III) ion to yield only Δ-*cis*-α and Λ-*cis*-β isomers of [Rh(SS-EDDP)Cl_2]$^-$ complex [2].

While the base hydrolysis of Λ-*cis*-α-[Co(trien)-ClPH]$^+$ (trien = triethylenetetraamine) has been found to occur with optical inversion [3], all of the substitution reactions of the octahedral bis(bidentate) or tetradentate complexes of rhodium(III) that have been reported so far proceed without steric change [4–6]. During our attempted synthesis of Δ-*cis*-α and Λ-*cis*-β isomers of the amino acid complexes of the type [Rh(SS-EDDP)(aa)] (aa = amino acid) via the substitution reactions of [Rh(SS-EDDP)-Cl_2]$^-$ with amino acids, however, we have observed that stereochemical inversion occurred during the substitution reactions.

The substitution reactions of the Δ-*cis*-α-H[Rh-(SS-EDDP)Cl_2]·H_2O isomer with amino acids proceeded with retention of configuration. The substitution reactions of the Λ-*cis*-β-H[Rh(SS-EDDP)Cl_2]·3H_2O complex with amino acids, on the other hand, resulted in stereochemical inversion to give the Δ-*cis*-α products. When a mixture containing Λ-*cis*-β-H[Rh(SS-EDDP)Cl_2]·3H_2O and S-alanine in DMF was refluxed for 5 to 14 hours and then refrigerated for several hours, the CD spectrum of the resultant white product indicated complete isomerization to give the Δ-*cis*-α-[Rh(SS-EDDP)(S-ala)] complex (Fig. 1).



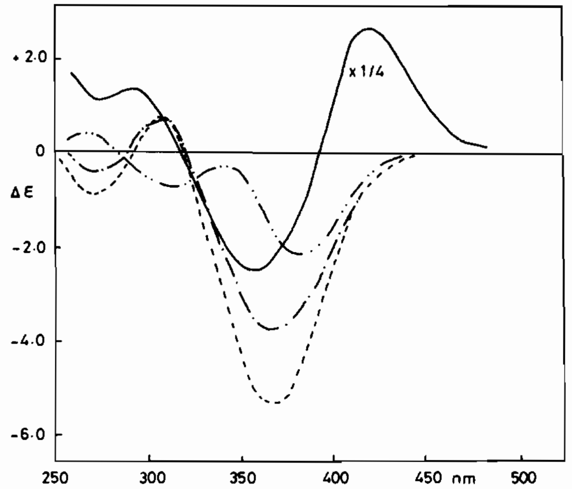


Fig. 1. Circular dichroism spectra of: Λ-*cis*-β-[Rh(SS-EDDP)-Cl_2]$^-$ (———, scale is 4 times actual scale), Δ-*cis*-α-[Rh(SS-EDDP)(H_2O)Cl] (–···–), Δ-*cis*-α-[Rh(SS-EDDP)(S-ala)] (-------), and Δ-*cis*-α-[Rh(SS-EDDP(R-ala)] (–·–·–).

Isomerization of Λ-*cis*-β-[Rh(SS-EDDP)Cl_2]$^-$ complex with R-alanine was also observed, when a solution of the Λ-*cis*-β-Cl_2 complex and R-alanine in DMF was refluxed for over 15 hours. The CD spectrum indicated the formation of a Δ-*cis*-α-[Rh(SS-EDDP)-(R-ala)] product (Fig. 1). The specific rotation was about 1000° higher than the specific rotation of Δ-*cis*-α-R-ala standard complex which was prepared from the reaction of the Δ-*cis*-α-[Rh(SS-EDDP)Cl_2]$^-$ and R-alanine in DMF. The product has i.r. and ^1H pmr spectra indistinguishable from the Δ-*cis*-α-R-ala standard complex. The compound contained one water molecule while the standard was anhydrous. Such anomalous rotation may indicate some stereoselectivity in the reaction of R-alanine with the Δ-*cis*-β-Cl_2 complex.

When a solution of Λ-*cis*-β-[Rh(SS-EDDP)Cl_2]$^-$ complex and a two-fold excess of racemic alanine in DMF was refluxed, the CD of the product showed complete isomerization to the Δ-*cis*-α-[Rh(SS-EDDP)-(R,S-ala)].

Hydrolysis of the Λ-*cis*-β-[Rh(SS-EDDP)Cl_2]$^-$ isomer also led to isomerization to the Δ-*cis*-α complex. When the Λ-*cis*-β-Cl_2 complex was heated in

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the steam bath in basic solution (pH > 8), the only product was the Δ-*cis*-α-[Rh(SS-EDDP)(H_2O)Cl], whose CD spectrum (Fig. 1) was exactly the same as the CD spectrum of the standard Δ-*cis*-α-[Rh(SS-EDDP)Cl_2]$^-$ isomer. The Δ-*cis*-α-Cl_2 complex could be isolated by acidification of the solution containing the hydrolysis product followed by evaporation to crystallization. The Ag^+ catalyzed hydrolysis of the Λ-*cis*-β-Cl_2 isomer also resulted in isomerization to the Δ-*cis*-α product.

The isomerization of the *cis*-β-[Co(EDDA)X_2]$^-$ complex (EDDA = ethylenediamine-N,N′-diacetic acid, X_2 = $(H_2O)_2$, oxalate or malonate) to the more stable *cis*-α form has been reported [7–10]. Molecular models indicate that cumulative ring strain is more appreciable in the *cis*-β isomer than in the *cis*-α isomer. Thus, the stereochemical inversion of the Λ-*cis*-β isomer to the Δ-*cis*-α isomer observed in this work is not unreasonable.

Detailed results of the investigation on the mechanism of the isomerization reactions observed in this study will be reported in another publication.

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