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Dichlororhodium(III) Complexes of N,N'-Dimethylethylenediamine-N,N'-diacetic Acid

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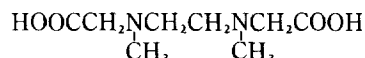
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Dichlororhodium(III) complexes of a flexible quadridentate ligand, N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda), have been prepared. Both *cis-α* and *cis-β* isomers have been yielded in the $K[Rh(dmedda)Cl_2]$ complexes, which were characterized with elemental analyses, electronic absorption and proton nuclear magnetic resonance spectroscopic data.

Introduction

Legg and Cooke¹ prepared N,N'-dimethylethylenediamine-N,N'-diacetic acid(dmedda).



They isolated the *cis-α* isomer for the ethylenediaminecobalt(III) complex of dmedda out of the three possible geometric isomers shown in Figure 1. Diammine and trimethylenediamine cobalt(III) complexes of dmedda were prepared, in which only the *cis-α* isomer could be obtained.² Later Maricondi and Douglas reported the synthesis of the oxalato and ethylenediamine cobalt(III) complexes of dmedda,³ while Jordan and Douglas prepared the dinitro, diammine, and trimethylenediamine cobalt(III) complexes of dmedda,⁴ all of which yielded the *cis-α* isomer only. Recently, the dichloro cobalt(III) complex of dmedda was prepared, in which the only isomer obtained had the *cis-α* configuration.⁵

Although such variety of cobalt(III) complexes of dmedda have been obtained, no metal complexes of dmedda have been reported other than cobalt.^{6,7} We have therefore been interested in seeing what isomers would be obtained from the preparation of rhodium(III) complexes of the dmedda ligand, and this paper is the first report on the preparation of any rhodium(III) complexes of this dmedda ligand. The stereochemistry of the complexes prepared in this study was investigated through ion-exchange chromatography, electronic absorption spectroscopy, and proton nuclear magnetic resonance spectroscopy. It is shown here that both *cis-α* and *cis-β* geometric isomers have been obtained during the course of

our preparation of the dichloro rhodium(III) complexes of dmedda.

Experimental

Physical Measurements. Electron absorption spectra were obtained with a Shimadzu UV-240 Spectrophotometer. Pmr spectra were recorded on a Varian EM 360 L Spectrometer. Infrared spectra were taken with a Shimadzu IR-435 Spectrophotometer. Elemental analyses were performed by Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A.

Preparation of Barium N,N'-Dimethylethylenediamine-N,N'-diacetate (Badmedda). This was prepared essentially by the method of Legg and Cooke¹ with some modification as described previously.⁵

Preparation of Potassium Dichloro-N,N'-dimethylethylenediamine-N,N'-diacetatorhodate(III). 0.34g of Badmedda were dissolved in 10 ml of water, to which 1.0 ml of 1.0 M

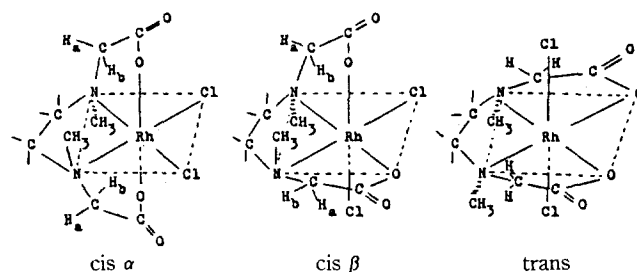


Figure 1. Three possible geometric isomers for the $[Rh(dmedda)Cl_2]$ complexes.

H_2SO_4 was added and stirred for 15 min. The BaSO_4 formed was removed by filtration. To the filtrate 0.04g of $\text{LiOH} \cdot \text{H}_2\text{O}$ dissolved in 10 ml of water was added, followed by the addition of 0.26g of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. The resultant solution was refluxed for one hour, and a dilute solution made up of 0.12g of $\text{LiOH} \cdot \text{H}_2\text{O}$ and 20 ml of water was added dropwise until the pH of the solution reached 5.0. The solution was refluxed for an additional five hours and the pH of the solution was then adjusted to 5.0 with a dilute LiOH solution. The solution was cooled and filtered to remove any unreacted solids. Separation of the isomers of $[\text{Rh}(\text{dmedda})\text{Cl}_2]^-$ was facilitated by a column of Dowex 1-X8 anion-exchange resin (50-200 mesh). 0.1M KCl was used as an eluent with 1.0 cm^3/min flow rate. The solution separated into three bands. The first band showed somewhat complicated absorption peaks and was not further identified. The *cis*- α and *cis*- β isomers were obtained from the next two bands, with the *cis*- α isomer eluting before the *cis*- β isomer. The products were then obtained by evaporating the solution to dryness on a water bath. Yield: 0.02g for the *cis*- α isomer and 0.01g for the *cis*- β isomer. Anal. Calcd for *cis*- α - $\text{K}[\text{RhC}_8\text{H}_{14}\text{N}_2\text{O}_4\text{Cl}_2] \cdot \text{H}_2\text{O}$: C, 22.18; H, 3.72; N, 6.47. Found: C, 22.35; H, 3.85; N, 6.34. Calcd for *cis*- β - $\text{K}[\text{RhC}_8\text{H}_{14}\text{N}_2\text{O}_4\text{Cl}_2] \cdot 1.5\text{H}_2\text{O}$: C, 21.73; H, 3.88; N, 6.34. Found: C, 20.81; H, 3.76; N, 6.18.

Results and Discussion

The complexes were prepared by the reaction of the tetradentate ligand with an aqueous solution of rhodium trichloride trihydrate maintaining the pH below 5.0 to prevent the precipitation of insoluble rhodium hydroxide. This procedure is similar to the one used for the preparation of other rhodium amine complexes.^{8,9} Two isomers, *cis*- α and *cis*- β , were formed with rhodium(III) in contrast with the $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$ where only the *cis*- α isomer was formed. The *cis*- α isomer eluted prior to the *cis*- β isomer. The same elution pattern has been observed for the isomers of $[\text{Co}(\text{eddp})(\text{en})]^+$ (eddp is ethylenediamine-*N,N'*-dipropionic acid)¹⁰ and

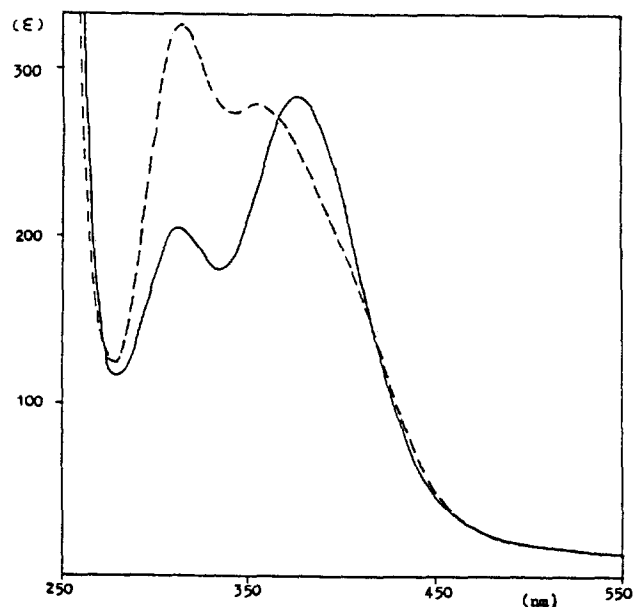


Figure 2. Absorption spectra for *cis*- α - $[\text{Rh}(\text{dmedda})\text{Cl}_2]^-$ (—) *cis*- β - $[\text{Rh}(\text{dmedda})\text{Cl}_2]^-$ (-----).

$[\text{Co}(\text{edda})(\text{L})]^-$ (edda is ethylenediamine-*N,N'*-diacetic acid)¹¹, where L is oxalate or malonate. It is expected that the *cis*- α isomer with a small dipole moment would be eluted before the *cis*- β form.

Since both isomers are essentially *cis*- $\text{RhN}_2\text{O}_2\text{Cl}_2$, the ultraviolet absorption spectra are not particularly helpful in distinguishing the geometric isomers. The absorption spectra of the *cis*- α and *cis*- β isomers are shown in Figure 2, in which two observations can be made. First, the peaks in the *cis*- β isomer are at slightly higher energy particularly in the long wavelength band than the corresponding peaks in the *cis*- α isomer. These band shifts are consistent with those observed for the $[\text{Co}(\text{eddp})(\text{en})]^+$ isomers¹⁰ and the $[\text{Co}(\text{eddp})\text{Cl}_2]^-$ isomers.⁹ Second, as was also the case for the isomers of $[\text{Co}(\text{eddp})(\text{en})]^+$ and $[\text{Co}(\text{edda})\text{L}]^-$ series¹¹ as well as for the isomers of $[\text{Co}(\text{eddp})\text{Cl}_2]^-$, 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 are clearly distinguished by their proton nuclear magnetic resonance spectra shown in Figures 3 and 4. In Fig.3 the *cis*- α isomer shows a distinct N-methyl singlet (δ 2.78), while in Fig.4 the *cis*- β isomer shows

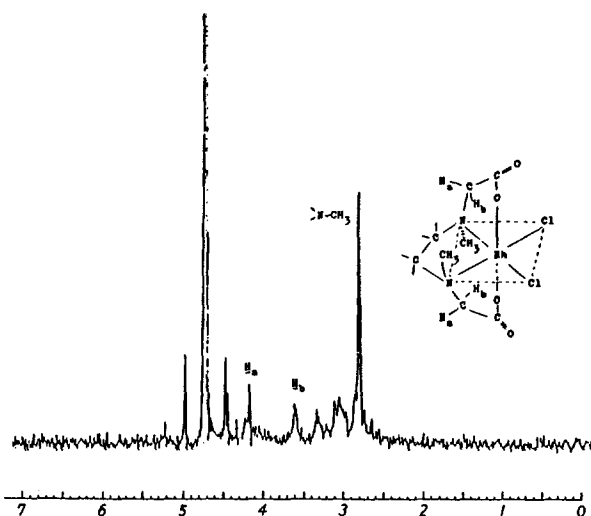


Figure 3. Pmr spectrum of *cis*- α - $[\text{Rh}(\text{dmedda})\text{Cl}_2]^-$ in D_2O .

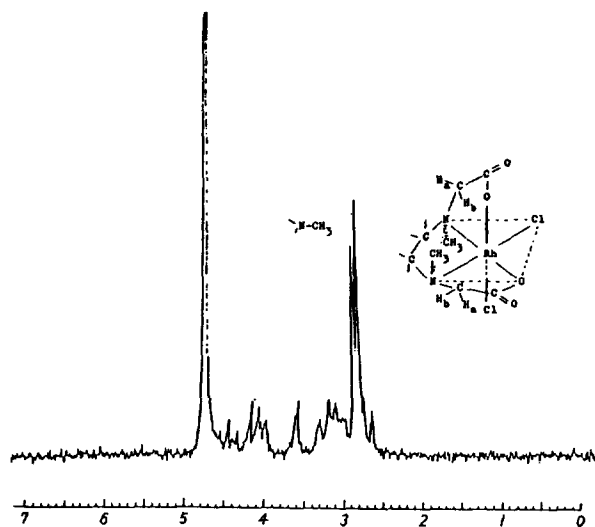


Figure 4. Pmr spectrum of *cis*- β - $[\text{Rh}(\text{dmedda})\text{Cl}_2]^-$ in D_2O .

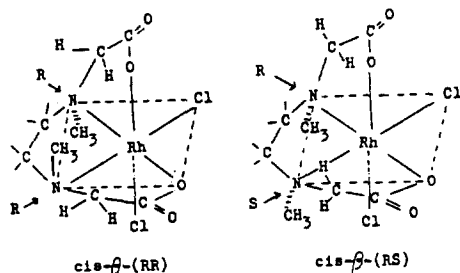


Figure 5. Two possible stereoisomers for the *cis*- β -[Rh(dmedda)Cl₂]-complex.

two overlapping N-methyl singlets (δ 2.80). The *cis*- α isomer has a C₂ symmetry and the two acetate arms are equivalent. Only one N-methyl singlet is expected in this *cis*- α isomer. The *cis*- β isomer has, however, only C₁ symmetry, and the acetate arms are no longer equivalent. Thus, two N-methyl singlets are expected as shown in Figure 2.

The chemical shifts in these complexes can be explained in terms of the magnetic anisotropy of the C-N bond,^{10,12} because the ligand is rigidly oriented in the complex. In particular, the chemical shifts of the protons of dmedda (labeled Ha and Hb) can be distinguished because of the magnetic anisotropic shielding of the C-N bond. The Hb protons are situated almost directly over the C-N bond of the ethylenediamine backbone ring and are shielded by it, while the Ha protons are not affected by this bond.¹³ Thus, the Ha protons resonate at lower fields than the Hb protons. Only an Ha proton signal and only an Hb proton signal should be observed in the *cis*- α isomer as such distinct Ha and Hb signals are shown at δ 3.50-4.20 in Figure 3. On the other hand, somewhat complicated Ha and Hb proton signals are observed at δ 3.50-4.20 in the *cis*- β isomer in Figure 4, because the Hb protons in the planar carboxylate arm no longer lies in the shielding area of the C-N bond in the *cis*- β isomer.

It is noted that, as shown in Fig.5, two stereoisomers, *cis*- β -(RR) and *cis*- β -(RS), are possible in the case of the optically active *cis*- β geometric isomer depending on the absolute configuration of the asymmetric nitrogen atom. In the case of the *cis*- β -(RR) stereoisomer each of the absolute configurations of two asymmetric nitrogen atoms is R. In the case of the *cis*- β -(RS) stereoisomer, on the other hand, the absolute configuration of one asymmetric nitrogen atom is still R, while that of the other asymmetric nitrogen atom is S. A free energy

difference between the two forms is approximately 1.8 kcal/mole, which would result in a predominance of 95% of one form. The *cis*- β -(RR) isomer is favored over the *cis*- β -(RS) isomer, because the RS isomer would require inversion at the nitrogen center in the acetate ring coplanar with the central ethylenediamine backbone.¹¹

It is very interesting to observe that the dichloro rhodium (III) complexes of dmedda have yielded both *cis*- α and *cis*- β geometric isomers, while only the *cis*- α isomer has been obtained in the case of the dichloro cobalt(III) complex of the same dmedda ligand. Such observation may be explained on the basis of the relative sizes of cobalt(III) and rhodium(III) ions. The rhodium(III) ion is certainly larger in size than the cobalt(III) ion. In the *cis*- β isomer two chelate rings should be coplanar, which causes some ring strain. Because of such ring strain the *cis*- β isomer would not be favored when the cobalt(III) complexes of dmedda are formed. However, such ring strain will be lessened in the rhodium(III) complexes of dmedda, thereby paving the way for the formation of the *cis*- β isomer. The *trans* isomer has been ruled out because it is well known that the *trans* isomer is not possible.^{6,7}

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