

is necessary to disrupt the liquid crystalline order than to destroy crystalline order in the solid state. The corresponding value of 1-TD could not be obtained by DSC analysis due to thermal decomposition before reaching isotropization temperature.

Conclusion

Following conclusions can be drawn from the results of the present study:

- 1) The presence of mesogenic unit in a molecule does not guarantee for the compound to become liquid crystalline.
- 2) When a compound is dimesogenic, *i.e.*, contains two mesogenic units, linear molecular shape is prerequisite to be mesomorphic.
- 3) A trimesogenic and star-shaped compound is not able to form a mesophase when the mesogenic units are connected directly to the central core.

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Dichloro and Ethylenediamine Rhodium(III) Complexes of Ethylenediamine-N,N'-di- α -butyric Acid

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Dichloro and ethylenediamine rhodium(III) complexes of a flexible N_2O_2 -type tetradentate ligand, ethylenediamine-N,N'-di- α -butyric acid(eddb), have been prepared. Both *s-cis*- and *uns-cis* geometrical isomers have been yielded in the $[Rh(eddb)Cl_2]^-$ and $[Rh(eddb)(en)]^+$ complexes. Ir, pmr, and electronic absorption spectra are used to characterize the complexes obtained in this work.

Introduction

A linear flexible N_2O_2 -type tetradentate ligand such as edda (ethylenediamine-N,N'-diacetic acid, $HOOCCH_2NHCH_2CH_2NHCH_2COOH$) can occupy four coordination sites in an octahedral complex with three geometrical isomers possible *s-cis* (symmetric *cis*), *uns-cis* (unsymmetric *cis*), and *trans* (Figure 1). A good number of N_2O_2 -type ligands and the cobalt(III) complexes of these ligands have been prepared.¹⁻³ While no *trans* isomers have so far been observed, *s-cis* and/or *uns-cis* isomers have been yielded in the cobalt(III) complexes of the N_2O_2 -type ligands, $[Co(N_2O_2 \text{ ligand})L]^n+$ depending upon the nature of the N_2O_2 -type ligand and the ligand L which occupy the remaining two sites in an octahedral complex. Only a few such works have been reported

on the complexes of metal ions other than the cobalt(III) ion. Liu *et al.*⁴ reported the synthesis of the *s-cis* and *uns-cis* isomers of the rhodium(III) complexes of the ethylenediamine-N,N'-di-S- α -propionic acid (SS-eddp). Recently we have prepared the rhodium(III) complexes of N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda), in which both the *s-cis* and *uns-cis* isomers have been yielded.⁵

Recently we reported the synthesis of a flexible N_2O_2 -type ligand, ethylenediamine-N,N'-di- α -butyric acid, $HOOCCH(C_2H_5)NHCH_2CH_2NHCH(C_2H_5)COOH$ (eddb).⁶ The cobalt(III) complexes of $[Co(eddb)L]^n+$ (L = Cl_2 , $(H_2O)_2ClH_2O$, CO_3) have yielded the *s-cis* isomer only. The present work involves the rhodium(III) complexes of the eddb ligand. It is of interest to observe what isomers are obtained upon coordination of the eddb ligand to the rhodium(III) ion. It will be

shown that both the *s-cis* and *uns-cis* isomers are formed in the dichloro and ethylenediamine rhodium (III) complexes of eddb.

Experimental

Ethylenediamine-*N,N'*-di- α -butyric Acid (eddb).

This was prepared by the method reported.⁶

Hydrogen dichloro (ethylenediamine-*N,N'*-di- α -butyrate)-rhodate (III), $H[Rh(eddb)Cl_2]$. H_2O to a solution of 0.10g of $LiOH \cdot H_2O$ dissolved in 20 ml of water was added 0.31g of ethylenediamine-*N,N'*-di- α -butyric acid and 0.26g of rhodium (III) chloride trihydrate. The pH of the solution was adjusted to 2 with dilute HCl and the solution was refluxed for two hrs. The solution was cooled and its pH was adjusted to 5 with dilute HCl. The solution was refluxed again for 5 hrs. The pH of the solution was adjusted to 5 with LiOH and was cooled to room temperature. The solution was concentrated to a small volume. It was passed into a cation exchange resin (Dowex 50W-8X, 50-100 mesh, H^+ form) column to remove Li^+ using triply distilled water as eluent. The solution was concentrated to a small volume and poured into an anion exchange resin column (Dowex 1-8X, 100-200 mesh, Cl^- form) using 0.1N HCl as eluent. The solution separated into two bands, with the *s-cis* isomer eluting before the *uns-cis* isomer. The separated solution containing each isomer was evaporated to a small volume. Upon addition of acetone bright yellow crystals of *s-cis* isomer (0.10g) and dark yellow crystals of *uns-cis* isomer (0.03g) were obtained. Anal. Calcd for *s-cis*- $RhC_{10}H_{19}N_2O_4Cl_2 \cdot H_2O$: C, 28.4 H, 5.0 N, 6.6. Found: C, 28.2 H, 5.1 N, 6.8. Calcd for *uns-cis*- $RhC_{10}H_{19}N_2O_4Cl_2 \cdot H_2O$: C, 28.4 H, 5.0 N, 6.6. Found: C, 28.1 H, 5.0 N, 6.7.

s-cis-Ethylenediamine (ethylenediamine-*N,N'*-di- α -butyrate) rhodium(III) chloride, *s-cis*- $[Rh(eddb)(en)]Cl$. 0.03g of *s-cis*- $H[Rh(eddb)Cl_2] \cdot H_2O$ was dissolved in 20 ml of freshly distilled dimethylformamide (DMF) and two drops of pure ethylenediamine were added to this solution. The solution was refluxed for 5 hrs. The solution was cooled in an ice bath. The white product was filtered and washed with ethanol and ether. Yield 0.01g. Anal. Calcd for $RhC_{12}H_{26}N_4O_4Cl$: C, 36.0 H, 6.5 N, 7.0. Found: C 35.8 H, 6.6 N, 7.2.

uns-cis-Ethylenediamine(ethylenediamine-*N,N'*-di- α -butyrate)rhodium (III) chloride, *uns-cis*- $[Rh(eddb)(en)]Cl$. This was prepared by the same method as described above using *uns-cis*- $H[Rh(eddb)Cl_2] \cdot H_2O$ in place of *s-cis*- $H[Rh(eddb)Cl_2] \cdot H_2O$. Anal. Calcd for $RhC_{12}H_{26}N_4O_4Cl$: C, 36.0 H, 6.5 N, 7.0. Found: C, 36.1 H, 6.4 N, 6.9.

Physical Measurements. Electronic 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.

Results and Discussion

Two geometrical isomers, *s-cis* and *uns-cis*, have been yielded in the dichloro rhodium (III) complexes of eddb in contrast with the dichloro cobalt (III) complex of eddb in

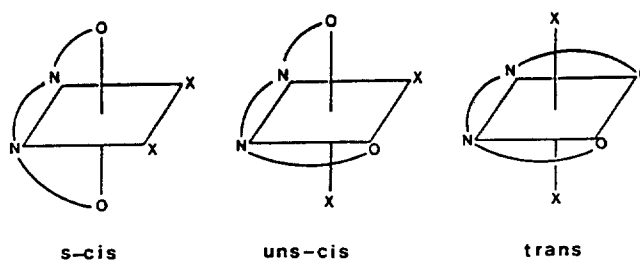


Figure 1. The possible geometric isomers of the $[Rh(eddb)X_2]^{n+}$ complexes.

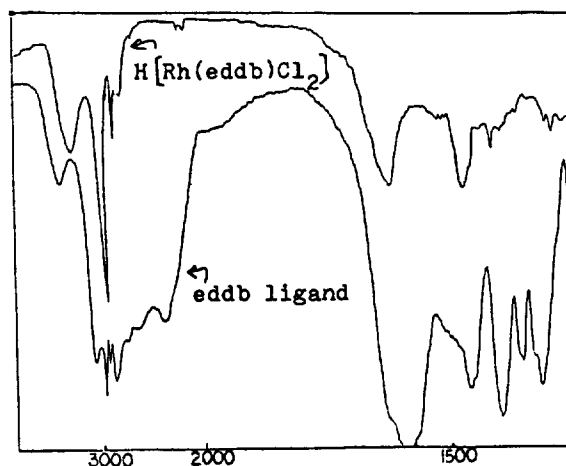


Figure 2. Infrared spectra of eddb ligand and $H[Rh(eddb)Cl_2]$.

which only the *s-cis* isomer has been obtained. The *s-cis* isomer eluted prior to the *uns-cis* isomer. The same elution pattern has been observed for the isomers of $[Co(eddp)(en)]^+$ (eddp is ethylenediamine-*N,N'*-dipropionic acid)⁷ and of $[Co(edda)L]^-$ (L is oxalato or malonato ligand).⁸ It is expected that the *s-cis* isomer with a small dipole moment would be eluted before the *uns-cis* isomer.

The infrared spectrum of the $[Rh(eddb)Cl_2]^-$ complex shows the coordinated coo^- stretching vibration at 1620 cm^{-1} (Figure 2). Although both the *s-cis* and *uns-cis* isomers are essentially the *cis*- $RhN_2O_2Cl_2$ system, the electronic absorption spectra (Figure 3) are helpful in distinguishing the geometrical isomers. Two observations can be made from the absorption spectra of the *s-cis* and *uns-cis* isomers. Firstly, the peaks in the *uns-cis* isomer are at slightly higher energy than the corresponding peaks in the *s-cis* isomer. These band shifts are consistent with those observed for the $[Rh(SS-eddp)Cl_2]^-$ isomers⁴ and the $[Rh(dmedda)Cl_2]^-$ isomers.⁵ Secondly, as was the case for the isomers of $[Co(edda)L]^{n+}$ series,⁸ $[Rh(ss-eddp)Cl_2]^-$, and $[Rh(dmedda)Cl_2]^-$, the absorption band of the higher symmetry *s-cis* isomer has the smaller extinction coefficient in the shorter wavelength band than in the corresponding band of the *uns-cis* isomer. The absorption band in the long wavelength side is due to this $^1A_{1g} \rightarrow ^1T_{1g}$ electronic transition and that in the shorter wavelength side is due to the $^1A_{1g} \rightarrow ^1T_{2g}$ electronic transition, which are in accordance with the *d-d* transitions observed for the d^6 electronic system.⁹

The *s-cis* and *uns-cis* isomers are clearly distinguished by their pmr spectra shown in Figure 4. In Figure 4, the *s-cis* isomer shows a distinct methyl triplet at 1.7 ppm, while the

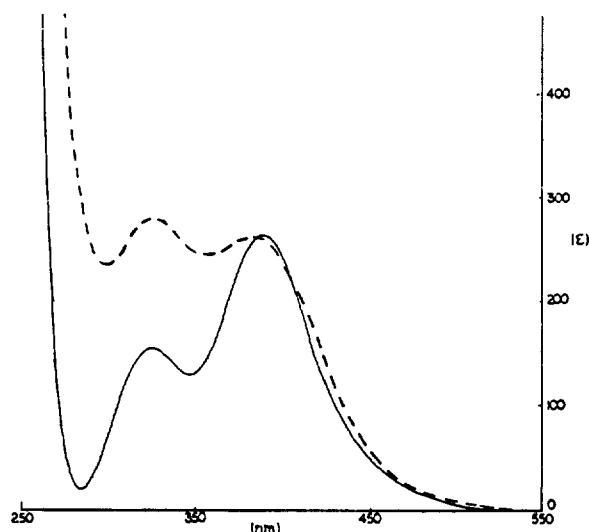


Figure 3. Electronic absorption spectra of *s-cis*-[Rh(eddb)Cl₂]⁻ (—) and *uns-cis*-[Rh(eddb)Cl₂]⁻ (----).

and *uns-cis*-[Rh(eddb)Cl₂]⁻ complexes. The electronic absorption spectra of the *s-cis*-[Rh(eddb)(en)]⁺ and *uns-cis*-[Rh(eddb)(en)]⁺ complexes show the same pattern observed for the *s-cis*-[Rh(eddp)(en)]⁺ and *uns-cis*-[Rh(eddb)(en)]⁺ complexes, respectively.¹¹ As observed in the isomers of [Rh(edda)L]³⁺, [Rh(eddb)Cl₂]⁻, and [Rh(eddp)(en)]⁺, the absorption band of the higher symmetry *s-cis*-[Rh(eddb)(en)]⁺ has the smaller extinction coefficient in the shorter wavelength band than in the corresponding band of the *uns-cis*-[Rh(eddb)(en)]⁺.

It is interesting to observe that the dichloro rhodium (III) complexes of eddb have yielded both the *s-cis* and *uns-cis* geometrical isomers, while only the *s-cis* isomer has been obtained in the case of the dichloro cobalt (III) complex of the same eddb ligand. Such observation may be understood on the basis of the relative sizes of the cobalt (III) and rhodium (III) ions. The rhodium (III) ion is larger in size than the cobalt (III) ion. In the *uns-cis* isomer two chelate rings are coplanar, which cause some ring strain. The butyrato chelate rings are less puckered than the central chelate ring due to the presence of the carboxylate groups. Because of such ring strain the *uns-cis* isomer would not be favored when the cobalt (III) complexes of eddb are formed. However, such ring strain will be lessened in the rhodium (III) complexes of eddb, thereby paving the way for the formation of the *uns-cis* isomer.

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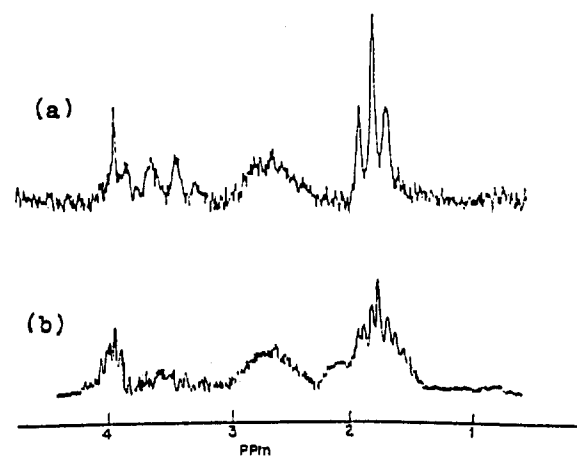


Figure 4. PMR spectra of (a) *s-cis*-[Rh(eddb)Cl₂]⁻ and (b) *uns-cis*-[Rh(eddb)Cl₂]⁻ in D₂O.

uns-cis isomer in Figure 4 shows two overlapping methyl triplets at near 1.7 ppm. The *s-cis* isomer shows a methyne triplet at 3.9 ppm whereas the *uns-cis* isomer shows the overlapping peaks at the same region. The *s-cis* isomer has a C₂ symmetry and the two butyrato arms are equivalent. Only one methyl triplet and only one methyne triplet are expected in this *s-cis* isomer. The *uns-cis* isomer, however, has only C₁ symmetry, and the two butyrato arms are no longer equivalent. Thus, two methyl triplets and two methyne triplets are expected as shown in Figure 4. Such chemical shifts in these complexes has been demonstrated in terms of the magnetic anisotropy of the C-N bond.^{7,10}

The *s-cis*-[Rh(eddb)(en)]⁺ and *uns-cis*-[Rh(eddb)(en)]⁺ isomers have been obtained in this work from the reactions of ethylenediamine with, respectively, *s-cis*-[Rh(eddb)Cl₂]⁻

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