

**TABLE 3: Parameters for PS(1)-acetone(2) System Having Molecular weights 19,800 of PS**

$r_1/r_2$	$2\chi r_2$
146.1	$\frac{1329.4}{T} - 6.6527 + 0.01153 T$

**TABLE 4: Parameters for PVA(1)-water(2) System having Various Molecular Weights 140,000 of PVA**

$r_1/r_2$	$2\chi r_2$
3035.3	$\frac{-392.83}{T} + 3.1598 - 2.8256 \times 10^{-3} T$

## Conclusion

The partial miscibilities in polymer-polymer or polymer-solvent systems have been explained in terms of the extended form of the Flory-Huggins lattice theory. Mathematical conditions for the four partial miscibilities were derived, and the results were in good agreement with the experimental results of PS-PVME, PS-cyclohexane, PS-acetone, and PVA-water systems.

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## Synthesis and Stereochemistry of the Complexes of Cobalt(III) with New Tetradentate Ligands. Cobalt(III) Complex of Ethylenediamine-N,N'-di- $\alpha$ -butyric Acid

Moo-Jin Jun†, Chang-Yoon Han, Yoon-Bong Park and Sung Rack Choi

Department of Chemistry, Yonsei University, Seoul 120, Korea (Received December 19, 1984)

A new flexible N<sub>2</sub>O<sub>2</sub>-type tetradentate ligand, ethylene-diamine-N,N'-di- $\alpha$ -butyric acid (eddb), has been synthesized, and a series of cobalt (III) complexes of eddb, [Co(eddb)L]<sup>3+</sup> (L = Cl<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub>, Cl H<sub>2</sub>O, and Co<sup>3+</sup>), have been prepared. Only *s-cis* isomers have been yielded during the preparation of complexes. Ring strain is cited as the primary cause for the preference for the *s-cis* geometric configuration.

A linear flexible edda-type ligand (edda = ethylenediamine-diacetic acid, HOOCCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>COOH) can occupy four coordination sites with three geometric isomers possible: *trans*, *s-cis* (symmetric *cis*), and *uns-cis* (unsymmetric *cis*)

Mori *et al*<sup>1</sup> were the first to report the synthesis of cobalt (III) complexes of edda. They prepared the carbonato, diaqua and dinitro complexes, and postulated the *s-cis* configuration from a comparative analysis of absorption spectra. Legg and Cooke<sup>2</sup> prepared [Co(edda) (am)]<sup>3+</sup>, (am = en, 2NH<sub>3</sub>) and Co (III) complexes of N-alkyl substituted analogue of edda. They isolated the *s-cis* and *uns-cis* isomers for the edda complex although the latter isomers were obtained in trace quantities only. Kuroda<sup>3-5</sup> prepared a group of edda cobalt (III) complexes with ammonia, en, pyridine, 2,2'-bipyridyl, and observed that the coordination mode of edda depended upon the temperature. Later, Legg<sup>6-7</sup> and others<sup>8-11</sup> prepared and characterized *uns-cis*

isomers of [Co(edda) (L)]<sup>3+</sup> (L = en, S-alanine, R-propylenediamine).

The first C-alkyl-substituted analogue of edda was ethylenediamine-N,N'-dis- $\alpha$ -propionate, HOOCCH(CH<sub>3</sub>)NHCH<sub>2</sub>CH<sub>2</sub>NHCH(CH<sub>3</sub>)COOH, (SS-eddp) prepared by Liu and co-workers.<sup>12</sup> Both *s-cis* and *uns-cis* isomers of [Co(SS-eddp) (L)]<sup>3+</sup> (L = en, R-Pn) were isolated. Recently, two other C-alkyl-substituted edda ligands have been reported. One is S-stilbenediamine-N,N'-diacetate (S-sdda)<sup>13</sup> whose cobalt (III) complexes, [Co(S-sdda) (L)]<sup>3+</sup>, (L = en, S-stilbenediamine) has yielded only *s-cis* isomer, and the other ethylenediamine-N,N'-di-S- $\alpha$ -isovalerate(ven)<sup>14,15</sup>. The [Co(ven) (H<sub>2</sub>O)NO<sub>3</sub>] complex existed only as the *s-cis* isomer, while in the case of [Co(ven) (H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> and [Co(ven) (en)]<sup>3+</sup> complexes both *s-cis* and *uns-cis* were found to exist. Woon and O'Connor,<sup>16</sup> and strasak and Bachraty<sup>17</sup> have independently prepared 2s, 2's-1, 1'-(ethane-1, 2-diyl)

bis(pyrrolidine-2-carboxylate) (pren), in which the nitrogen atom and the  $\alpha$ -carbon atom are connected by a pyrrolidine ring by virtue of proline. The  $[\text{Co}(\text{pren})\text{L}_2]^{n+}$  complexes of pren has yielded only *s-cis* isomers when  $\text{L} = \text{Cl}$  or  $\text{H}_2\text{O}$ , while both *s-cis* and *uns-cis* isomers have been isolated when  $\text{L}_2 = \text{en}$ .

This paper will describe the synthesis of a new C-alkyl-substituted analogue of edda, ethylenediamine-N,N'-di- $\alpha$ -butyric acid,  $\text{HOOCCH}(\text{C}_2\text{H}_5)\text{-NHCH}_2\text{CH}_2\text{NHCH}(\text{C}_2\text{H}_5)\text{COOH}$ , (eddb) and the preparation of several cobalt (III) complexes of this ligand,  $[\text{Co}(\text{eddb})(\text{L})]^{n+}$ , ( $\text{L} = \text{Cl}_2$ ,  $(\text{H}_2\text{O})_2$ ,  $(\text{H}_2\text{O})(\text{Cl})$ ). While the cobalt (III) complexes of edda and eddp ligands yielded both *s-cis* and *uns-cis* geometrical isomers, the cobalt (III) complex of sdda gave *s-cis* isomer only. Therefore, it will be of interest to see what isomers will be obtained from the preparation of cobalt (III) complexes of eddb. It will be shown that only *s-cis* isomer is formed in the dichloro cobalt (III) complex of eddb.

## Experimental

1,2-Dibromoethane was purchased from Tokyo Kasei Kogyo Co. Tokyo, Japan and DL- $\alpha$ -amino-*n*-butyric acid was obtained from Wako Pure Chemical Ind. Ltd., Tokyo, Japan.

**Preparation of Ethylenediamine-N,N'-di- $\alpha$ -butyric acid (eddb).** To a solution of 10.3g of DL- $\alpha$ -amino-*n*-butyric acid in 20 ml of water with stirring and cooling in an ice-bath. After maintaining at 40°C for 30 min., 5.3g  $\text{Na}_2\text{CO}_3$  and 8.7g of 1,2-dibromoethane were added in portions to this solution. The reaction mixture was then heated at 60°C for 33 hrs. The reaction mixture was cooled and then acidified to pH 2 with 17% HCl. The product was collected on a filter, washed several times with water, and dried in vacuo at 44°C for several days. The product was recrystallized from water. Yield : 3.49(29%) mp 307-309°C. *Anal.* Calcd for  $\text{C}_{10}\text{H}_{20}\text{N}_2\text{H}_2\text{O}_4$ : C, 51.71; H, 8.68; N, 12.06. Found : C, 50.20; H, 8.49; N, 12.31.

**Preparation of *s-cis* Hydrogen Dichloro (ethylenediamine-N,N'-di- $\alpha$ -butyrato) cobaltate (III), *s-cis*- $\alpha$ -H  $[\text{Co}(\text{eddb})\text{Cl}_2]$ .** In 40 ml of water, 2.3 g of ethylenediamine-N,N'-di- $\alpha$ -butyric acid, 0.80 g of sodium hydroxide, and 2.3 g of cobalt (II) chloride hexahydrate were added in this order. Air was bubbled through the reaction mixture. 10 ml of hydrogen peroxide (30%) was added dropwise, and then air bubbling was continued for 5 hours during which time the color of the solution changed from dark brown to dark red-violet and finally deep red violet. 80 ml of concentrated hydrochloric acid was added and the mixture was concentrated on a water bath with continuous stirring to about 40 ml. A dark blue precipitate appeared. After cooling the precipitates were collected on a filter, and washed with hydrochloric acid, methanol and ether. Yield 0.8 g. Attempts to obtain any other isomers from the filtrate after the blue precipitate was filtered out did not give any positive results. *Anal.* Calcd for  $\text{H}[\text{Co}(\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4)\text{Cl}_2] \cdot 1.5\text{H}_2\text{O}$ : C, 30.95; H, 5.71; N, 7.22. Found : C, 30.80; H, 5.80; N, 6.96.

**Preparation of *s-cis*- $[\text{Co}(\text{eddb})\text{Cl} \cdot \text{H}_2\text{O}]$  in Situ.**  $1.6 \times 10^{-2}$  g of  $\text{H}[\text{Co}(\text{eddb})\text{Cl}_2] \cdot 1.5\text{H}_2\text{O}$  was dissolved in 20 ml of cold 0.01 N perchloric acid and stirred at 20°C for 30 min. At this point the electronic absorption spectrum was recorded.

**Preparation of *s-cis*- $[\text{Co}(\text{eddb})\text{CO}_3]^-$  in Situ.** When an ex-

cess amount of  $\text{NaHCO}_3$  (ca. 0.05 g) was added to the redishpink solution obtained above, the color of solution changed immediately to violet pink. After 30 min. of standing, the absorption spectrum of the *s-cis*- $[\text{Co}(\text{eddb})\text{CO}_3]^-$  was taken.

**Preparation of *s-cis*- $[\text{Co}(\text{eddb})(\text{H}_2\text{O})_2]^+$  in Situ.** 11.6 N  $\text{HClO}_4$  was added dropwise to the solution of  $[\text{Co}(\text{eddb})\text{CO}_3]^-$  until pH of the solution was ca. 2. The color of solution became purple, and after standing at room temperature for 15 min, the absorption spectrum was taken.

**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.

## Results and Discussion

The eddb ligand, ethylenediamine-N,N'-di- $\alpha$ -butyric acid, has been prepared in this work mainly from the reaction between 1,2-dibromoethane and DL-2-amino-*n*-butyric acid as depicted below :

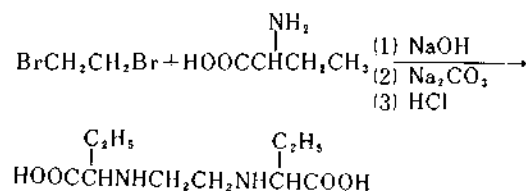


Figure 2 shows the pmr spectrum of the eddb ligand. The methyl protons (marked a) are shown at 1.1 ppm as a triplet,

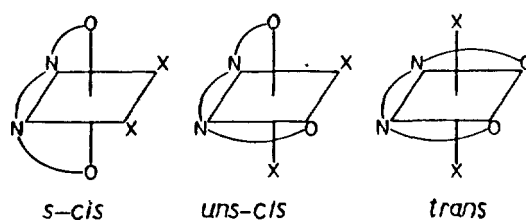


Figure 1. Possible geometrical isomers of  $[\text{Co}(\text{eddb})\text{X}_2]^{3+}$  complex in octahedral structure

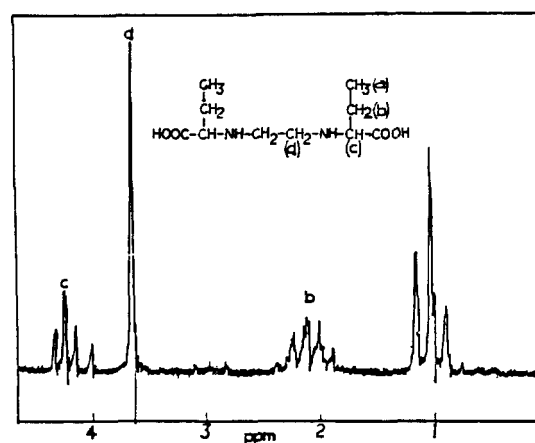


Figure 2. Pmr spectrum of ethylenediamine-N,N'-di- $\alpha$ -butyric acid (in  $\text{D}_2\text{O}$ )

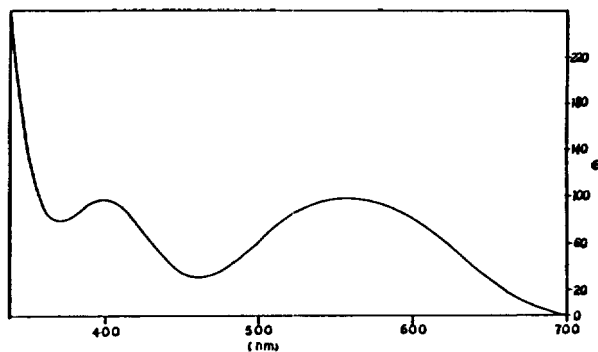


Figure 3. Electronic absorption spectrum of  $s$ - $cis$ -[Co(eddb)Cl<sub>2</sub>]<sup>-</sup>

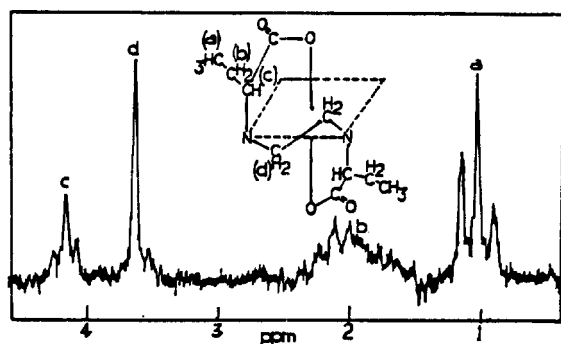


Figure 4. Pmr spectrum of  $s$ - $cis$ -[Co(eddb)Cl<sub>2</sub>]<sup>-</sup> in D<sub>2</sub>O.

the methylene protons (marked b) in the ethyl group at 2.1 ppm as a quintet, and the CH proton (marked c) is shown at 4.2 ppm as a triplet. The methylene protons between nitrogen atoms resonate at about 3.6 ppm.

The dichloro cobalt (III) complex of eddb has yielded only one isomer during the course of our preparation. The electronic absorption spectrum of this complex is shown in Figure 3. The band I and band II, which are due to the d-d transitions in the octahedral CoN<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> system, appear between 380–600 nm. The shape of the first band is nearly symmetrical, although a small deformation (expansion) in the high-energy region (~540 nm) of the band is observable. If the complex has the *trans* configuration (*trans* in Figure 1), a large split in the first band would be observed as the *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, because of the *trans*-coordination of the two chlorine atoms.<sup>16-18</sup> Therefore, the possibility of the *trans* geometric configuration is eliminated. If the complex is the *uns-cis* isomer (Figure 1), two atoms of the same kinds (Cl-Cl, N-N, O-O) are at the *cis*-positions, and a very intense absorption would be expected, since the ligand field around the central atom is highly unsymmetrical. The *s-cis* configuration, though the evidence from the electronic absorption spectrum alone is not conclusive, is the most reasonable assignment for the dichloro complex, and the small deformation mentioned above may be attributed to the *trans*(O)-component of the coordination mode.

The fact that the dichloro cobalt (III) complex of eddb prepared in this work has the *s-cis* configuration is clearly shown in the pmr spectrum shown in Figure 4. A single methyl (a) triplet is nicely shown at 1.1 ppm and a single CH(e) triplet is also clearly seen at 4.2 ppm. If the complex has a *uns-cis* configuration, the same methyl (a) should show two triplets and the CH (c) proton should also show two triplets. The *uns-cis* isomer has only C<sub>1</sub> symmetry and the two butyrate arms are

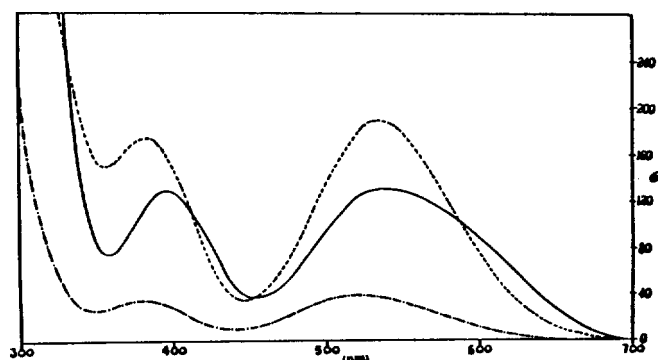
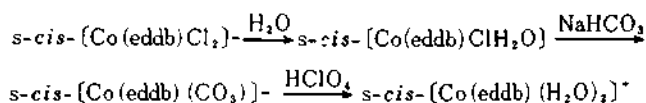


Figure 5. Electronic absorption spectra of  $s$ - $cis$ -[Co(eddb)Cl(H<sub>2</sub>O)]<sup>-</sup> (—),  $s$ - $cis$ -[Co(eddb)(CO<sub>3</sub>)]<sup>-</sup> (---), and  $s$ - $cis$ -[Co(eddb)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> (- · - ·).

no longer equivalent in the *uns-cis* geometry. The methyl (a) protons as well as the CH (c) proton in the planar carboxylate arm in the *uns-cis* geometry no longer lie in the same shielding area of the C-N bond: such loss of shielding would cause it to resonate at lower fields with two triplets rather than a single triplet. An *s-cis* configuration can, therefore, be assigned to the isomer obtained in this work. The methylene (b) multiplet and other methylene (d) protons are shown, respectively, at 2.1 ppm and 3.6 ppm in Figure 4.

Figure shows the electronic absorption spectra for the complexes obtained from the following series of reactions:



The absorption maxima and their intensities of the above series of complexes are on the ordinary line of the spectrochemical and hyperchromic series.

Although in the systems so far reported<sup>1,13-17,21,22</sup> the *s-cis* isomer appears to have been formed exclusively, it is quite interesting to observe that the cobalt (III) complexes of our new ligand eddb has yield only *s-cis* isomer. Severe ring strain totally prevents the formation of the *trans* isomer. Because of the tetrahedral nature of the nitrogen the puckered chelate rings in the *uns-cis* isomer are somewhat strained and slightly distorted from the plane containing the nitrogen atoms so that the *uns-cis* isomer is expected to be less stable than the *s-cis* isomer.<sup>19,20</sup> In the cobalt (III) complexes of edda it has been postulated that non-bonding interactions between the sterically restricted amine protons and edda prevented the formation of substantial amounts of the *uns-cis* isomers.<sup>19</sup> The eddb ligand, like edda, certainly favors an *s-cis* configuration due to such increased steric interaction between the ligands in the *uns-cis* isomer. The eddb ligand has an ethyl substituent at each of two  $\alpha$ -carbon atom and, because of such ethyl group, the strain would be greater for the "in plane" chelate rings if an *uns-cis* isomer were to be formed.

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## Catalysis by the Fe(III) Complex of *N*-Dodecyl-3,4-dihydroxybenzamide in the Hydroxylation of Anisole with Hydrogen Peroxide\*

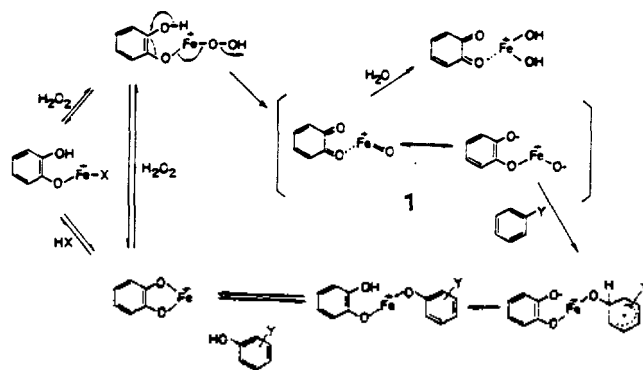
Junghun Suh<sup>†</sup> and Keehyung Nahm

Department of Chemistry, Seoul National University, Seoul 151, Korea (Received January 19, 1985)

Hydroxylation of anisole with  $H_2O_2$  was investigated by employing Fe(III) ion and *N*-dodecyl-3,4-dihydroxybenzamide (DDHB) as a catalyst. The study was aimed at obtaining an insoluble catalyst with a long catalytic life, in view of the inactivation of the catechol portion of the catalyst during the reaction. The rate of decomposition of  $H_2O_2$  under various conditions indicated that the reaction proceeds through the catalytic participation of Fe(III)·DDHB. Yield of the hydroxylation products under various conditions revealed that Fe(III)·DDHB is not inactivated during the reaction.

Hydroxylation of aromatic compounds with Fenton reagent (Fe(II) +  $H_2O_2$ ) has been subjected to extensive mechanistic and synthetic studies.<sup>1</sup> Addition of enediols such as ascorbic acid, hydroquinone, or catechol enhances the rate and yield of Fe(III) or Fe(II) ion-catalyzed hydroxylation of aromatic compounds with  $H_2O_2$ .<sup>2,3</sup> The proposed mechanism<sup>3,4</sup> of the Fe(III)-catechol-catalyzed aromatic hydroxylation is summarized in Scheme 1. Inactivation of the catalyst by the water attack at catalytic intermediate I has been proposed to occur as the reaction proceeds.<sup>3,4</sup> Thus, the reaction stops when all of the catalyst is destroyed and the relative rates of the attack at I by water and by the aromatic substrate affect the yield.

In an attempt to immobilize the Fe(III)-catechol catalyst and in an attempt to provide hydrophobic environment to the catalytic center so that the water attack at I is suppressed, a polystyrene-supported catechol (2) was prepared previously.<sup>5</sup> Catechol 2, however, was inactivated during the hydroxylation



Scheme 1

reaction.<sup>6</sup> In the present study, *N*-dodecyl-3,4-dihydroxybenzamide (DDHB) was employed as the insoluble hydrophobic catechol. The Fe(III)·DDHB-catalyzed hydroxylation of anisole with  $H_2O_2$  proceeded without appreciable destruction of the catechol moiety, as will be reported in this paper.

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