

## Alanine and S-Methylcysteine Cobalt(III) Complexes of Ethylenediamine-N,N'-di- $\alpha$ -butyric Acid

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L-Alanine(L-ala) and S-methyl-L-cysteine(L-mcy) cobalt(III) complexes of a flexible  $N_2O_2$ -type tetradentate ligand ethylenediamine-N,N'-di- $\alpha$ -butyric acid(eddb), *s-cis*-[Co(eddb)(L-ala)] and *s-cis*-[Co(eddb)(L-mcy)], have been prepared via the substitution reactions of the *s-cis*-[Co(eddb)Cl<sub>2</sub>]<sup>-</sup> complex with, respectively, L-alanine and S-methyl-L-cysteine. Both L-alanine and S-methyl-L-cysteine are found to coordinate to the cobalt(III) ion via the nitrogen and oxygen donor atoms to give the meridional *s-cis* isomer. Electronic absorption, ir and pmr spectra are used to characterize the complexes obtained in this work along with elemental analysis data.

### Introduction

Ethylenediamine-N,N'-di- $\alpha$ -butyric acid(eddb) whose configuration is shown below was first prepared in this laboratory.<sup>1</sup> Eddb anion is a tetradentate ligand having two nitrogen and two oxygen donor atoms and has been found to yield exclusively the *s-cis* (symmetric *cis*) geometrical isomer out of the three possible geometrical isomers (Figure 1) in a series of cobalt (III) complexes of eddb, [Co(eddb)L]<sup>n+</sup> [(L-Cl<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub>, CH<sub>2</sub>O, and CO<sub>3</sub><sup>2-</sup>].

The geometrical isomerism in the cobalt (III) complexes of the  $N_2O_2$ -type tetradentate ligands has been studied extensively.<sup>2</sup> When L is a symmetrical bidentate ligand such as ethylenediamine in the [Co( $N_2O_2$ -type ligand)L]<sup>n+</sup> complexes, there are two possible geometrical isomers as shown in Figure 1. When L is an unsymmetrical bidentate ligand such as an amino acid, however, the additional isomerism is possible as depicted in Figure 2. *s-cis-mer* (symmetric-*cis*-meridional), *uns-cis-fac* (unsymmetrical-*cis*-facial), and *cis-mer*.

As part of our continuing study of the cobalt (III) complexes of eddb, we have been interested in the amino acid complexes of the type [Co(eddb)aa]<sup>n+</sup> (aa = amino acid). The earlier studies have been concerned with amino acids having nitrogen and oxygen containing functional groups.<sup>2,3</sup> While alanine is a bidentate ligand having oxygen and nitrogen donor atoms, S-methylcysteine is of particular interest because of the presence of three functional groups including the sulfur donor atom, only two of which can bind to the cobalt (III) ion. Therefore, it is of interest to see what isomers would be obtained from the reaction between the [Co(eddb)Cl<sub>2</sub>]<sup>-</sup> complex and alanine or S-methyl-L-cysteine. It will be shown here that both alanine and S-methylcysteine are found to coordinate to the cobalt (III) ion via the nitrogen and oxygen donor atoms to give the symmetric-*cis*-meridional isomer.

### Experimental

**Physical Measurements and Chemical Reagents Used.** Electronic absorption spectra were measured with a Shimadzu UV-240 Spectrophotometer. Infrared spectra were obtained with a Shimadzu IR-435 Spectrophotometer. Proton magnetic spectra were taken with a Varian EM-360L Spectrometer. Elemental analyses were performed by Mi-

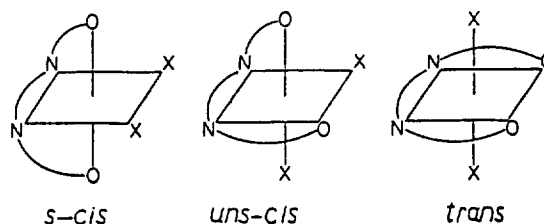


Figure 1. The possible geometric isomers of the [Co(edda)X<sub>2</sub>]<sup>n+</sup> complexes.

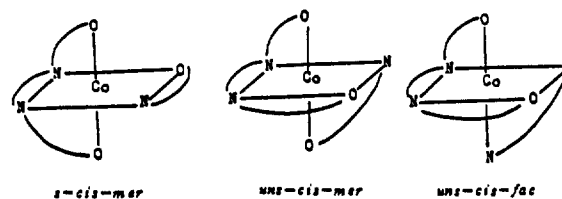


Figure 2. Three possible geometric isomers of [Co(ONNO)(aa)]<sup>n+</sup> (aa = amino acid).

cro-Tech Analytical Lab., Skokie, Illinois, U.S.A. L-Alanine and S-methyl-L-cysteine were purchased from, respectively, Aldrich Chemical Co. and Nutritional Biochemicals Co., and were used without further purification.

**Preparation of *s-cis*-Hydrogen Dichloro(ethylenediamine-N,N'-di- $\alpha$ -butyrate) Cobaltate (III), *s-cis*-H[Co(eddb)Cl<sub>2</sub>].** This was prepared according to the method reported earlier.<sup>1</sup>

**Preparation of *s-cis*-Alaninato-(ethylenediamine-N,N'-di- $\alpha$ -butyrate) cobalt (III), *s-cis*-[Co(eddb)(L-ala)].** 1.93g of *s-cis*-H[Co(eddb)Cl<sub>2</sub>] was dissolved in 30 ml of water and was heated at 60 °C. 0.48g of L-alanine was added to the solution. The pH of the solution was adjusted to 5.0 with 1N NaOH and then heated for 5 hrs. The solution was concentrated to a volume of 5 ml on a rotatory evaporator. The resulting solution was poured into a column containing cation-exchange resin (Dowex 50×4-400, 200-400 mesh, H<sup>+</sup> form) with an elution rate of 2 ml/min using water as the eluent. The solution was separated into two bands. The upper band was turned out to be [Co(eddb)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> and was retarded without elution. The solution of the lower band was evaporated to near dryness and the red purple *s-cis*-[Co(eddb)(L-ala)] was obtained. Yield: 0.50g. Anal. Calcd for CoC<sub>13</sub>H<sub>24</sub>O<sub>6</sub>N<sub>3</sub>: C, 42.52; H, 6.60; N, 11.45. Found: C,

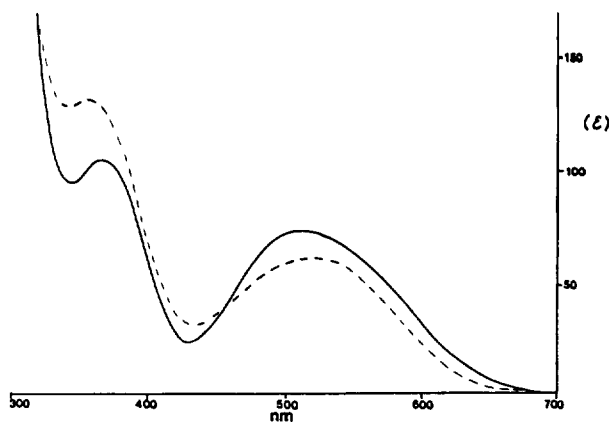


Figure 3. Electronic absorption spectra of *s-cis-mer*-[Co(eddb)(L-ala)] (—) and *s-cis-mer*-[Co(eddb)(L-mcy)] (---).

42.28; H, 6.66; N, 11.50.

**Preparation of *s-cis*-S-Methyl-L-cystinato(ethylenediamine-N,N'-di- $\alpha$ -butyrato) Cobalt (III), *s-cis*-[Co(eddb)(L-mcy)].** A solution of 1.93g of *s-cis*-H[Co(eddb)Cl<sub>2</sub>] dissolved in 30 ml of water was heated at 60°C and 0.67g of S-methyl-L-cysteine was added. The pH of the solution was adjusted to 11 with 1N NaOH and the heat was continued for 5 hrs. The solution was concentrated to a volume of 5 ml on a rotatory evaporator. The resulting solution was poured into a cation-exchange resin column (Dowex 50×4-400, 200-400 mesh, H<sup>+</sup> form) and eluted with water. Two bands appeared in the column. The solution collected from the lower band was evaporated to near dryness and the red purple product *s-cis*-[Co(eddb)(L-mcy)] was obtained. Yield: 0.62g. Anal. Calcd for CoC<sub>14</sub>H<sub>26</sub>O<sub>6</sub>N<sub>3</sub>S: C, 39.71; H, 6.20; N, 9.33. Found: C, 39.59; H, 6.26; N, 9.98.

## Results and Discussion

The substitution reaction of *s-cis*-[Co(eddb)Cl<sub>2</sub>]<sup>-</sup> complex with L-alanine or S-methyl-L-cysteine in aqueous media has resulted in the isolation of the *s-cis*-[Co(eddb)(L-ala)] or *s-cis*-[Co(eddb)(L-mcy)] complex.

The infrared spectrum of the [Co(eddb)(L-ala)] complex (Figure 3) shows the coordinated -COO<sup>-</sup> stretching vibration at 1620 cm<sup>-1</sup>. The electronic absorption is useful in differentiating between the facial and meridional isomers (Figure 2). The loss of symmetry from facial (cubic holohedrized symmetry) to meridional (rhombic holohedrized symmetry) is expected to cause a splitting or at least a broadening of the first absorption band.<sup>4,5</sup> In the electronic absorption spectrum of the [Co(eddb)(L-ala)] complex (Figure 3) the band I and band II appear between 330 and 600 nm. The splitting pattern of the first band having a shoulder at near 560 nm indicates that the [Co(eddb)(L-ala)] complex has a meridional geometry of either *s-cis* or *uns-cis*.

The pmr spectrum shown in Figure 4 clearly indicates that the [Co(eddb)(L-ala)] complex has an *s-cis* geometry. While the methyl protons of the L-alanine resonate at 1.5 ppm as a doublet, the methyl protons of the eddb ligand are shown at 1.0 ppm as a triplet. If the complex has an *uns-cis* geometry, the same methyl protons of the eddb ligand would have shown two triplets, for the two carboxylate arms are

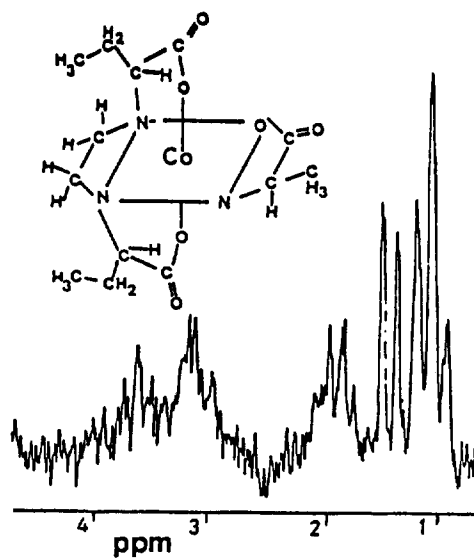


Figure 4. Pmr spectrum of *s-cis-mer*-Co(eddb)(L-ala) in D<sub>2</sub>O.

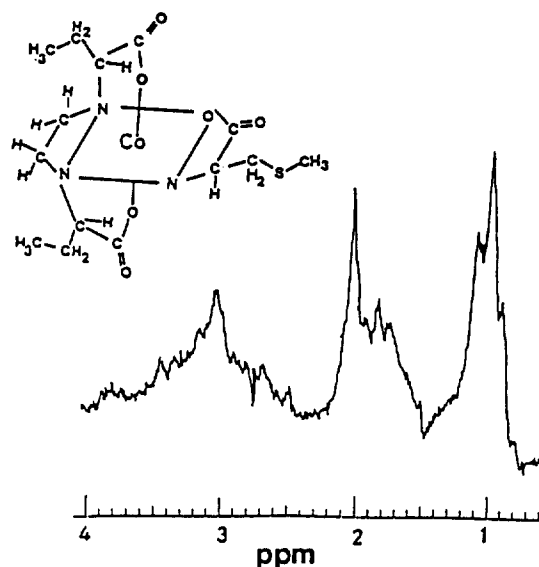


Figure 5. Pmr spectrum of *s-cis-mer*-Co(eddb)(L-mcy) in D<sub>2</sub>O.

not equivalent in the *uns-cis* geometry.<sup>6-8</sup> Therefore, the [Co(eddb)(L-ala)] complex obtained in this work is the *s-cis*-meridional isomer. The  $\lambda_{max}$  for the band I, absorption band of the *s-cis*-[Co(eddb)Cl<sub>2</sub>]<sup>-</sup> is 560 nm, where as the  $\lambda_{max}$  for the same absorption band of the *s-cis*-[Co(eddb)(L-ala)] complex is shown to be 510 nm. Thus, the  $\lambda_{max}$  has been shifted toward the shorter wavelength side as the chloro ligands are substituted by the alanine having the nitrogen and oxygen donor atoms, which is in accordance with the spectrochemical series.

The reaction between the *s-cis*-[Co(eddb)Cl<sub>2</sub>]<sup>-</sup> and the S-methyl-L-cysteine has yielded a red purple complex. Since the S-methyl-L-cysteine has three donor atoms of nitrogen, oxygen and sulfur, the possible coordination system of the L-mcy complex is CoN<sub>3</sub>O<sub>2</sub>, CoN<sub>3</sub>O<sub>2</sub>S or CoN<sub>2</sub>O<sub>3</sub>S. The general features of the CoN<sub>3</sub>O<sub>2</sub>S and CoN<sub>2</sub>O<sub>3</sub>S type complexes are that (1) the color of those complexes is brown, (2) the extinction coefficient of the band II  $\lambda_{max}$  is five times greater than that of the band I  $\lambda_{max}$ , (3) there is no furrow be-

tween the band I and band II absorptions, and (4) the band III appears as a result of the S-Co(III) charge transfer.<sup>9,10</sup> The reddish color and the electronic absorption spectrum shown in Figure 3 suggest that the complex obtained in this work is a  $\text{CoN}_3\text{O}_3$  type complex.

The infrared spectrum of the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex (Figure 3) shows the coordination of L-mcy through the nitrogen and oxygen donor atoms. The band I and band II appear between 330 and 600 nm in the electronic absorption spectrum of the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex (Figure 3). The splitting pattern of the first band having a shoulder at near 480 nm indicates that the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex has a meridional geometry of either *s-cis* or *uns-cis*. The pmr spectrum of the complex shown in Figure 5 suggests that the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex has an *s-cis* configuration. The methyl protons of the eddb ligand resonate at 1.0 ppm as a triplet, whereas the S-methyl protons of the mcy ligand are shown at 2.1 ppm as a singlet. As was the case for the *s-cis*- $[\text{Co}(\text{eddb})(\text{L-ala})]$  complex, the pmr spectrum would have been much more complicated, if the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex has an *uns-cis* geometry. Thus, from the experimental data observed in this work, it is concluded that the  $[\text{Co}(\text{eddb})(\text{L-mcy})]$  complex has the *s-cis*-meridional configuration.

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