

## L-Cysteinesulfenato and L-Cysteinesulfinato Cobalt(III) Complexes of N,N'-Dimethylethylenediamine-N,N'-diacetic Acid

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Several workers<sup>1-6</sup> have shown that in the cysteinato cobalt(III) complexes of ethylenediamine,  $[\text{Co}(\text{en})_2(\text{cys})]^{2+}$  (cys: L-cysteine), the controlled oxidation of the coordinated sulfur leads to coordinated S-bonded sulfenatos and sulfinatos. All such known works have been accomplished in the bis(en)cobalt(III) complex systems.

In this work the oxidation of the coordinated sulfur to the sulfenato and sulfinato stages in an  $\text{N}_2\text{O}_2$ -type tetradentate cobalt(III) complexes of L-cysteine is accomplished. N,N'-Dimethylethylenediamine-N,N'-diacetic acid (dmedda) is chosen as an  $\text{N}_2\text{O}_2$ -type ligand. It is also shown that L-cysteinine is stereospecifically coordinated to the racemic *s-cis*- $[\text{Co}(\text{dmedda})\text{CO}_3]^-$  to give  $\Delta$ -*s-cis*- $[\text{Co}(\text{dmexda})(\text{L-cys})]$ .

### Experimental Section

Dowex 50W-X4 cation exchange resin (200-400 mesh,  $\text{H}^+$  form) was used after repeated purifications. Electronic absorption and infrared spectra were recorded on a Shimadzu UV-240 double Beam Spectrometer and a Shimadzu IR 435 Spectrometer, respectively. <sup>1</sup>H NMR spectra were measured with a 270 MHz JEOL GSX-270 Spectrometer. Circular Dichroism spectra were obtained from a JASCO J-550 Spectrometer. Elemental analyses were performed by Micro-Tech Analytical Lab., Skokie, Illinois, USA.

**Preparation of  $\Delta$ -*s-cis*-Sodium L-cysteinato-N,N'-dimethylethylenediamine-N,N'-diacetatocobaltate(III),  $\Delta$ -*s-cis*- $[\text{Co}(\text{dmedda})(\text{L-cys})]$  (1).** 1.38 g (4 mmol) of *s-cis*- $\text{Na}[\text{Co}(\text{dmedda})\text{Cl}_2]$ <sup>7,8</sup> dissolved in 60 mL of water was heated at 60 mL for 30 min with stirring and then cooled to 0 °C. 0.63 g (4.0 mmol) of L-cysteine·HCl·H<sub>2</sub>O was added and pH of the solution was adjusted to 10 with 1.0 N NaOH. The solution was vigorously stirred at 0 °C for 5 hrs. The solution was concentrated to 30 mL, and 30 mL of absolute ethanol was added. The solution was filtered and washed with absolute ethanol. The combined filtrate and washing was concentrated to 10 mL, which was admitted to a column packed with Dowex 50W-X4 cation exchange resin (200-400 mesh,  $\text{Na}^+$  form). Two bands were detected by elution with water. The violet first band fraction was the unreacted reactant. The red violet second band fraction was collected and evaporated to 10 mL, which was stored in a refrigerator overnight. The precipitated red violet product was collected

by filtration, washed with absolute ethanol and ether, and vacuum dried. Yield: 0.52 g (33%). Calcd for  $\text{C}_{11}\text{H}_{19}\text{CoN}_3\text{NaO}_6\text{S}$ : C, 32.76; H, 4.75; N, 10.42; S, 7.95. Found: C, 32.74; H, 4.68; N, 10.51; S, 7.86.

**Preparation of  $\Delta$ -*s-cis*-sodium L-cysteininesulfenato-N,N'-dimethylethylenediamine-N,N'-diacetatocobaltate(III),  $\Delta$ -*s-cis*- $\text{Na}[\text{Co}(\text{dmedda})(\text{L-cys-O})]$  (2).** 0.40 g (1.0 mmol) of  $\Delta$ -*s-cis*- $\text{Na}[\text{Co}(\text{dmedda})(\text{L-cys})]$  was dissolved in 15 mL of water and stirred at room temperature for 30 min. 1.3 mL (1.0 mmol) of a solution prepared by adding 1 mL of 30%  $\text{H}_2\text{O}_2$  to 10 mL of water was added to this solution dropwise for 50 min. Stirring was continued at room temperature for 1 hr. The solution was concentrated to 10 mL and filtered. 100 mL of acetone was added to the filtrate and the solution was stored in a refrigerator for 1 day. The solution was filtered and the filtrate was concentrated until precipitates were formed. The red violet product was collected by filtration, washed with acetone and ether, and vacuum dried. Yield: 0.31 g (74%). Anal. Calcd for  $\text{C}_{11}\text{H}_{19}\text{CoN}_3\text{NaO}_7\text{S}$ : C, 31.51; H, 4.57; N, 10.02; S, 7.63. Found: C, 31.38; H, 4.55; N, 10.06; S, 7.65.

**Preparation of  $\Delta$ -*s-cis*-sodium (L-cysteinesulfinato)(N,N'-dimethylethylenediamine-N,N'-diacetato)cobaltate(III),  $\Delta$ -*s-cis*- $\text{Na}[\text{Co}(\text{dmedda})(\text{L-Cys-O})]$  (3).** 0.40 g (1.0 mmol) of  $\Delta$ -*s-cis*- $\text{Na}[\text{Co}(\text{dmedda})(\text{L-cys})]$  was dissolved in 15 mL of water and stirred at room temperature for 30 min. 3.9 mL (3.0 mmol) of a solution prepared adding 1 mL of 30%  $\text{H}_2\text{O}_2$  to 10 mL of water was added to this solution dropwise for 50 min. The solution was allowed to react 12 hrs. 200 mL of acetone was added and the solution was stored in a refrigerator for 1 day. The solution was filtered and the filtrate was concentrated until precipitates were formed. The red violet product was collected, washed with acetone and ether, and vacuum dried. Yield: 0.30 g (70%). Anal. Calcd for  $\text{C}_{11}\text{H}_{19}\text{CoN}_3\text{NaO}_8\text{S}$ : C, 30.35; H, 4.40; N, 9.65; S, 7.35. Found: C, 30.22; H, 4.41; N, 9.70; S, 7.32.

### Results and Discussion

Reactions accomplished in this work are depicted in Figure 1. The compound **1** is prepared from the reaction between the racemic *s-cis*- $[\text{Co}(\text{dmedda})\text{CO}_3]^-$  and L-cysteine. The IR spectrum of **1** shows both the coordinated carboxylate group of dmedda at  $1635\text{ cm}^{-1}$  and the uncoordinated

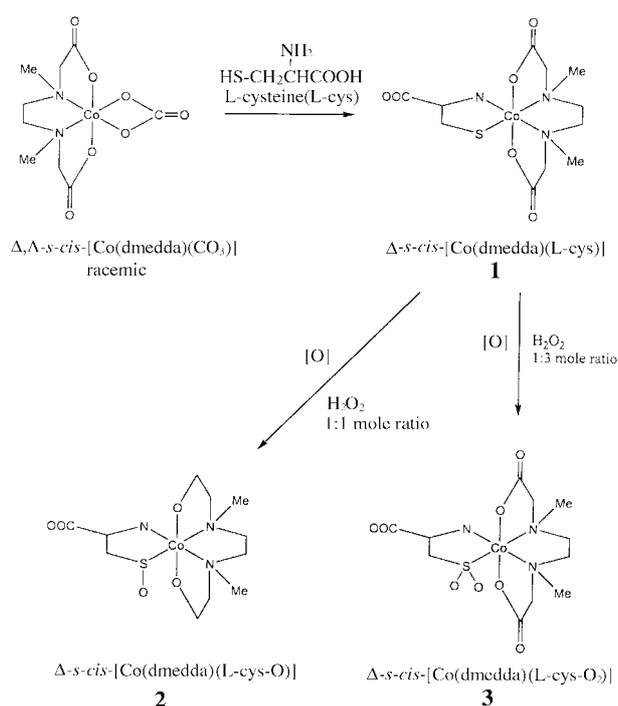


Figure 1

carboxylate group at near  $1630\text{ cm}^{-1}$ . The absorption at  $2500\text{ cm}^{-1}$  for the S-H stretching vibration for the free L-cys ligand is absent in **1**, which indicates that L-cysteine has coordinated to cobalt(III) ion *via* the S donor atom.<sup>9,10</sup> The electronic absorption spectra are particularly helpful in determining whether the sulfur atom is coordinated or uncoordinated.<sup>4,11-13</sup> The absorption spectrum of **1** (Figure 2) shows the  $\lambda_{\text{max}}$  in the  $A_{1g} \rightarrow T_{1g}(\text{Oh})$  region at  $576\text{ nm}$  which is expected for a  $\text{CoN}_3\text{O}_2\text{S}$  system,<sup>14-19</sup> indicating that coordination of L-cysteine has taken place through nitrogen and sulfur donor atoms in **1**. The CD curve of **1** (Figure 2) shows the negative dominant Cotton effect in the  $T_{1g}$  region ( $\lambda_{\text{max}}$  at near  $570\text{ nm}$ ) which indicates that **1** has a  $\Delta$  absolute configuration.<sup>17,20-22</sup> The optically active L-cysteine has shown a significant stereospecificity to give the  $\Delta$  stereoisomer in its coordination to the racemic  $s\text{-cis-}[\text{Co}(\text{dmedda})\text{CO}_3]^-$  complex. In the  $^1\text{H NMR}$  spectrum the M-methyl protons of dmedda are shown at 2.4 and 2.7 ppm as singlets, which are expected because of the  $C_1$  symmetry of **1**.

The sulfenato complex **2** has been obtained *via* oxidation of **1** with stoichiometric amount of  $\text{H}_2\text{O}_2$ . The new S-O stretching vibration, which was not detected in **1**, is shown at  $1020\text{ cm}^{-1}$ . The visible spectrum of **2** (Figure 2) shows the  $\lambda_{\text{max}}$  at  $560\text{ nm}$ , which is shifted toward the shorter wavelength side by about  $16\text{ nm}$  upon oxidation of **1** by  $\text{H}_2\text{O}_2$  to **2**. Such shift is due to of the sulfur atom. The CD curve of **2** (Figure 2) shows the major negative CE in the  $T_{1g}$  region ( $\lambda_{\text{max}}$  at neat  $565\text{ nm}$ ) as expected for the  $\Delta$  absolute configuration.  $\Delta\epsilon$  has been diminished somewhat here due to contribution from the sulfur atom, which becomes a racemic chiral center upon oxidation. The N-methyl protons of dmedda are shown at 2.4 and 2.7 ppm as singlet for **2**.

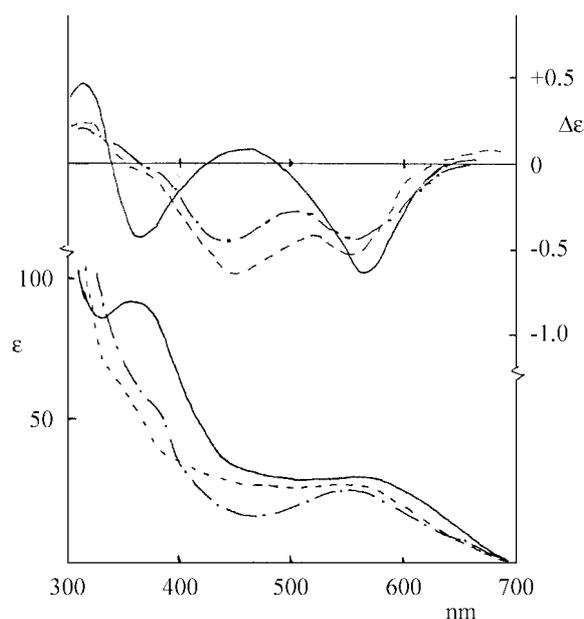


Figure 2

Oxidation of **1** by  $\text{H}_2\text{O}_2$  with 1:3 mole ratio for a prolonged period of time has yielded the sulfonato complex of **3**. The IR spectrum of **3** shows the S-O stretching vibrations at  $1050\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  as expected for sulfonato complexes. The visible spectrum of **3** (Figure 2) shows the  $\lambda_{\text{max}}$  in the  $A_{1g} \rightarrow T_{1g}(\text{Oh})$  region at  $550\text{ nm}$ , which is shifted further toward the shorter wavelength side than **2** as a result of the oxidation to the sulfonato stage. As expected for the  $\Delta$  absolute configuration, the CD curve of **3** (Figure 2) shows the negative CE in the  $T_{1g}$  region with  $\lambda_{\text{max}}$  at near  $560\text{ nm}$ , in which  $\Delta\epsilon$  is diminished more than **2** and the effect of the racemic sulfur atom of  $\Delta\epsilon$  is more pronounced than **2**. Finally it is interesting to note that the L-cysteine gas shown a significant stereospecificity in its coordination to the racemic cobalt(III) complex of **1** to give a  $\Delta$  absolute configuration.

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