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

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Several workers[1-6] have shown that in the cysteinato cobalt(III) complexes of ethylenediamine, $[Co(en)_2(cys)]^{2+}$ (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 N_2O_2-type tetradentate cobalt(III) complexes of L-cysteine is accomplished. N,N'-Dimethylethylenediamine-N,N-diacetic acid (dmedda) is chosen as an N_2O_2-type ligand. It is also shown that L-cysteine is steroespecifically coordinated to the racemic s-*cis*-$[Co(dmedda)CO_3]^-$ to give Δ-s-*cis*-[Co(dmexda)(L-cys)].

Experimental Section

Dowex 50W-X4 cation exchange resin (200-400 mesh, H^+form) was used after repeated purifications. Electronic absorption and infrared sepctra were recorded on a Shimadzu UV-240 double Beam Spectrometer and a Shimadzu IR 435 Spectrometer, respectively. ^1H 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 Δ-s-*cis*-Sodium L-cysteinato-N,N'-dimethylethylenediamine-N,N'-diacetatocobaltate(III), Δ-s-*cis*-[Co(dmedda)(L-cys)] (1). 1.38 g (4 mmol) of s-*cis*-$Na[Co(dmedda)Cl_2]$[7,8] 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_2O 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, 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 $C_{11}H_{19}CoN_3NaO_6S$: 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 Δ-s-*cis*-sodium L-cysteninesulfenato-N,N'-dimetheylethylenediamine-N,N'-diacetatocobaltate (III), Δ-s-*cis*-Na[Co(dmedda)(L-cys-O)] (2). 0.40 g (1.0 mmol) of Δ-s-*cis*-Na[Co(dmedda)(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% H_2O_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 $C_{11}H_{19}CoN_3NaO_7S$: 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 Δ-s-*cis*-sodium (L-cysteinesulfinato)(N,N'-dimetheylethylenediamine-N,N'-diacetato)cobaltate (III), Δ-s-*cis*-Na[Co(dmedda)(L-Cys-O)] (3). 0.40 g (1.0 mmol) of Δ-s-*cis*-Na[Co(dmedda)(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% H_2O_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 $C_{11}H_{19}CoN_3NaO_8S$: 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*-$[Co(dmeedda)CO_3]^-$ and L-cysteine. The IR spectrum of **1** shows both the coordinated carboxylate group of dmedda at 1635 cm^{-1} and the uncoordinated

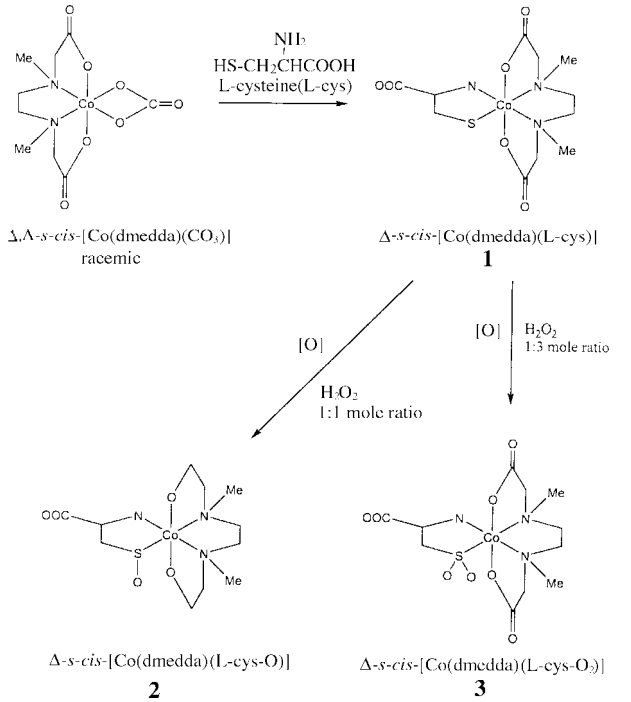

Figure 1

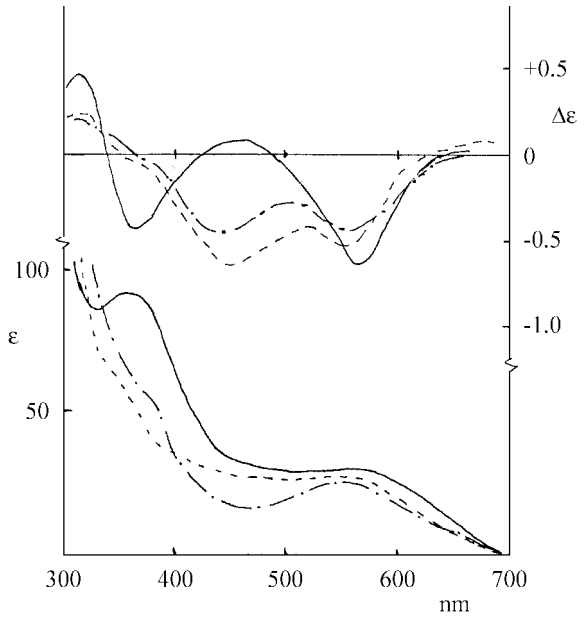

Figure 2

carboxylate group at near 1630 cm^{-1}. The absorption at 2500 cm^{-1} for the S-H stretching vibration for the free L-sys ligand is absent in **1**, which indicates the that L-cysteine has coordinated to cobalt(III) ion *via* the S donor atom.[9,10] The electronic absorption spectra are particularly helpful in determining whether the sulfur atom is coordinated or uncoordinated.[4,11-13] The absorption spectrum of **1** (Figure 2) shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}(O_h)$ region at 576 nm which is expected for a CoN_3O_2S system.[14-19] 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 (λ_{max} at near 570 nm) which indicates that **1** has a Δ absolute configuration.[17,20-22] The optically active L-cysteine has shown a significant stereospecificity to give the Δ stereoisomer in its coordination to the racemic s-*cis*-$[Co(dmedda)CO_3]^-$ complex. In the ^1H 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 H_2O_2. The new S-O stretching vibration, which was not detected in **1**, is shown at 1020 cm^{-1}. The visible spectrum of **2** (Figure 2) shows the λ_{max} at 560 nm, which is shifted toward the shorten wavelength side by about 16 nm upon oxidation of **1** by H_2O_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 (λ_{max} at neat 565 nm) as expected for the Δ absolute configuration. Δε 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**.

Oxidation of **1** by H_2O_2 with 1 : 3 mole ratio for a prolonged period of time has yielded the sulfinato complex of **3**. The IR spectrum of **3** shows the S-O stretching vibrations at 1050 cm^{-1} and 1200 cm^{-1} as expected for sulfinato complexes. The visible spectrum of **3** (Figure 2) shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}(Oh)$ region at 550 nm, which is shifted further toward the shorter wavelength side than **2** as a result of the oxidation to the sulfinato stage. As expected for the Δ absolute configuration, the CD curve of **3** (Figure 2) shows the negative CE in the T_{1g} region with λ_{max} at near 560 nm, in which Δε is diminished more than **2** and the effect of the racemic sulfur atom of Δε 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 Δ absolute configuration.

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