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L-Methionine and L-Methioninesulfenate Cobalt (III) Complexes of N,N'-dimethylethylenediamine-N,N'-diacetic Acid

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The cobalt(III) complexes of the N,N'-dimethylethylenediamine-N,N'-diacetic acid (H₂dmedda)¹⁻⁵ and the N,N'-dimethylethylenediamine-N,N'-di- α -butyric acid (H₂dmedba)⁶ have been found to yield the *s-cis* (symmetric) geometrical isomers only. Sloan and Krueger,⁷ and Deutsch, *et al.*^{8,9} have shown that in the cobalt(III) complexes such as [Co(en)₂(SCH₂CH₂NH₂)₂]²⁺, [Co(en)₂(SCH₂-CH(COO)NH₂)₂]⁺, and [Co(en)₂(SCH₂COO)]⁺ the controlled oxidation of thiol which are coordinated to cobalt(III) ion leads to the coordinated, S-bonded sulfenatos.

We have been interested in the oxidation of sulfur to the sulfenate stage in an uncoordinated sulfur atom in a metal complex of an amino acid containing a sulfur atom, it appeared that the methionine cobalt(III) complex of dmedda would be a useful choice for such a study, for such cobalt(III) complexes containing the oxidized methionine will likely be resulted in possessing the uncoordinated sulfur atom as desired in this study.

Experimental

s-Cis-Sodium Carbonato(N,N'-dimethylethylenediamine-N,N'-diacetato) cobaltate(III), s-cis-Na[Co(dmedda)CO₃] (1). 1.70 g (5.0 mmol) of Ba(dmedda)¹ was added to 20 mL of water and stirred. 5.6 mL of a solution prepared by diluting 5 mL of conc H₂SO₄ in 100 mL of water was added slowly to this solution. The solution was heated 50 °C and stirred for 30 min. The solution was filtered while hot to remove BaSO₄. 1.81 g (5.0 mmol) of Na₂[Co(CO₃)₃]·3H₂O

dissolved in 20 mL of water was slowly added to the filtrate with vigorous stirring. The solution was heated to 50 °C and stirred for 1 hr, during which period the solution change to violet color. The solution was filtered and the filtrate was concentrated to one half of its original volume. 25 mL of absolute ethanol was added to this solution, which was filtered. The filtrate was concentrated to 5 mL and 25 mL of absolute ethanol was added. The resultant solution was stored in a refrigerator for 1 day. The precipitates formed was filtered and the violet product was recrystallized from water and ethanol. Yield: 0.72 g (42%). Anal Calcd for NaCoC₉H₁₄O₇N₂: C, 31.41; H, 4.10; N, 8.14 Found: C, 30.19; H, 3.98; N, 8.25.

Δ -s-cis-N,N'-dimethylethylenediamine-N,N'-diacetato (L-methioninato)cobalt(III), Δ -s-cis-[Co(dmedda)(L-met)] (2). 1.72 g (5.0 mmol) of 1 was dissolved in 30 mL of water and heated at 60 °C for 30 min with stirring. 0.74 g (5.0 mmol) of L-methionine was added. 4.2 mL of a solution prepared by diluting 1 mL of conc HCl in 10 mL of water was slowly added to this solution. The pH of the solution was adjusted to 8.5 and 0.1 g of activated carbon was added. The reaction mixture was heated at 60 °C for 5 hrs. The reaction mixture was heated at 60 °C for 5 hrs. The reaction mixture was filtered and the filtrate was concentrated to 5 mL. 50 mL of absolute ethanol was slowly added and filtered. The filtrate was concentrated to 5 mL, which was admitted to a column packed with Dowex 50 W-X4 cation exchange resin (200-400 mesh, H⁺ 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 obtain the red violet product, which was recrystallized from water and ethanol, and vacuum dried. Yield: 0.84 g (41%). Anal Calcd for CoC₁₃H₂₄O₆N₃S: C, 38.15; H, 5.91; N, 10.42; S, 7.95 Found: C, 37.87; H, 5.77; N, 10.52; S, 7.77.

Δ -s-cis-N,N'-dimethylethylenediamine-N,N'-diacetato(L-methioninesulfenatonato) cobalt(III), Δ -s-cis-[Co(dedda)(L-met-O)] (3). *via* oxidation of 2. 0.41 g (1.0 mmol) of 1 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% H₂O₂ 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 5 mL and filtered. The filtrate was admitted to a column packed with Dowex 50W-X4 cation exchange resin (200-400 mesh, H⁺ form). Two bands were detected by elution with water. The red violet second band fraction was collected and concentrated until precipitates were formed. The red violet product was obtained by filtration and vacuum dried. Yield: 0.30 (70%). Anal Calcd for CoC₁₃H₂₄O₇N₃S: C, 36.71; H, 5.69; N, 9.88; S, 7.52. Found: C, 36.66; H, 5.56; N, 10.01; S, 7.46.

L-Methioninesulfenate (5). 4.48 g (30 mmol) of L-methionine was dissolved in 60 mL of acetic and cooled to 12 °C. 3.5 mL of 30% H₂O₂ was slowly added for 4 hrs. The solution was filtered and filtrate was concentrated to 30 mL. 30 mL of acetone was slowly added and the solution was stored in refrigerator for 1 day. The white precipitates were collected by filtration, recrystallized once from water and ethanol, and vacuum dried. Yield: 2.64 g (53%).

Δ -s-cis-N,N'-dimethylethylenediamine-N,N'-diacetato(L-methioninesulfenato) cobalt(III), Δ -s-cis-[Co(dmedda)(L-met-O)] (4). *via* Direct Reaction of 1 with 5. 0.68 g (2.0 mmol) of 1 was dissolved in 20 mL of water. The solution was heated to 60 °C and stirred for 30 min. 0.33 g (2.0 mmol) of 5 and 1.7 mL a solution prepared by diluting 1 mL of conc HCl in 10 mL of water were added. The resultant solution was stirred at 60 °C for 30 min. The pH of the solution was adjusted to 8.5 with 1 N NaOH and stirring was continued for 2 hrs. The solution was filtered and the filtrate was concentrated to 5 mL. The concentrated solution was admitted to a column packed with Dowex 50W-X4 cation exchange resin (200-400 mesh, H⁺ form). Two bands were detected by elution with water. The red violet second band fraction was collected and evaporated to obtain the red violet product, which was recrystallized from water and ethanol, and vacuum dried. Yield: 0.54 g (63%). Anal Calcd for CoC₁₃H₂₄O₇N₃S: C, 36.71; H, 5.69; N, 9.88; S, 7.52. Found: C, 36.70; H, 5.66; N, 9.85; S, 7.54.

Results and Discussion

A series of synthetic reactions accomplished in this work is depicted in Figure 1. The compound 2 is prepared from the reaction of the racemic *s-cis*-[Co(dmedda)CO₃]⁻ complex (1) with L-met ligand. The compound 3 is obtained upon oxidation of sulfur in 2 by the stoichiometric amount of H₂O₂. In a separate experiment, the L-met is oxidized by a stoichiometric amount of H₂O₂ to give the L-methioninesulfenate (5). The direct reaction of this sulfenate (5) with the racemic *s-cis*-[Co(dmedda)CO₃]⁻ complex (1) yields 4, which has been turned out to be the same structure and absolute configuration as 2.

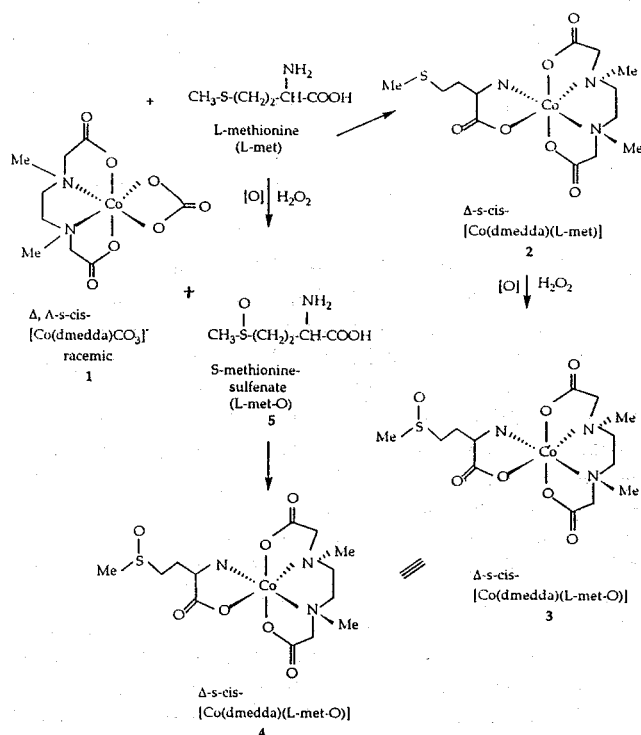


Figure 1. Synthetic reactions to prepare compounds 2, 3, 4, and 5.

ration as 3.

The methionine possesses three different donor atoms (N, O, S) and thus can have three geometrical isomers as shown in Figure 2 in the *s-cis*-[Co(dmedda)(met)] complex. The infrared spectrum of 2 shows the coordinated -COO⁻ stretching vibration at 1640 cm⁻¹, which rules out the structure I (Figure 2). The electronic absorption spectra are particularly helpful in distinguishing whether the sulfur atom is coordinated (Structure II) or uncoordinated (Structure III).¹²⁻¹⁵ The visible spectrum of 2 (Figure 3) shows the d-d transition at 530 nm for the $A_{1g} \rightarrow T_{1g}(O_h)$ transition and at 370 nm for the $A_{1g} \rightarrow T_{2g}(O_h)$ transition. If the S donor atom is coordinated, the visible spectrum of 2 would have shown the d-d transitions at much longer wavelength (~600 nm) than those observed in this work.¹⁶⁻¹⁹ reflecting the relative positions of the groups in the spectrochemical series $S^- < \text{amine} < CO_2^-$. Therefore, the structure II is eliminated, and in the *s-cis*-[Co(dmedda)(met)] complex, the coordination of the L-met ligand takes place through the amine and carboxylate groups (Structure III) to give a meridional N, O chelation.

The CD spectrum of 2 shows the negative dominant Cotton effect in the $A_{1g} \rightarrow T_{1g}(O_h)$ region indicating the fact that 2 has a Δ absolute configuration.¹⁰⁻¹⁸ In the ¹H NMR spectra of 2, the N-methyl protons of dmedda are shown at 2.4 and 2.7 ppm, while the S-methyl protons of met at 2.5 or 2.8 ppm. The α -carbon protons of met are shown at 4.0 ppm, and the β - and γ -carbon protons of met at, respectively, 3.0

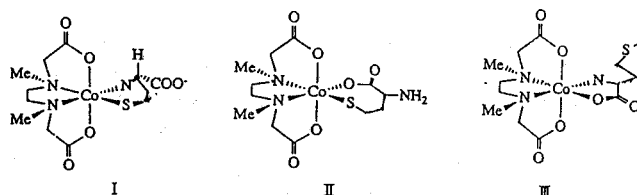


Figure 2. The geometrical isomers of *s-cis* [Co(dmedda)(met)] complex.

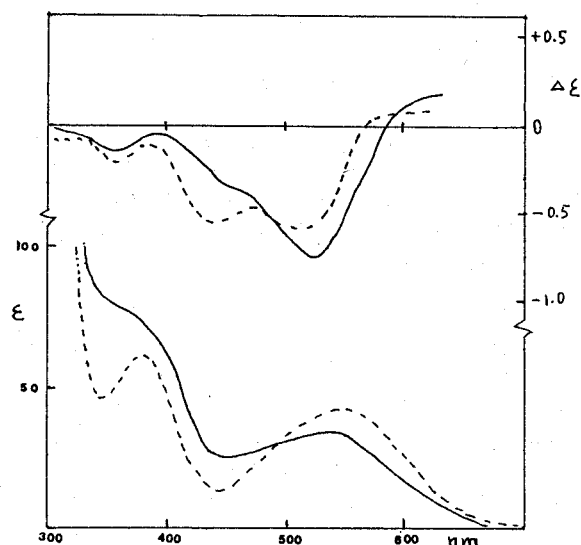


Figure 3. Electronic absorption and CD spectra of Δ -s-cis-[Co(dmedda)(L-met)] (—) and Δ -s-cis-[Co(dmedda)(L-met-O)] (---).

and 4.2 ppm as overlapped peaks with other protons.

Oxidation of 2 with H_2O_2 in a 1:1 mole ratio has yielded a sulfenato complex of 3 as a red violet crystalline solid. The infrared spectrum of 3 shows the S-O stretching vibration at 1020 cm^{-1} . The visible spectrum of 3 (Figure 4) shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}(O_h)$ transition region at 546 nm, which is shifted to ward the longer wavelength side by 16 nm than the unoxidized $[\text{Co}(\text{dmedda})(\text{L-met})]$ complex. Such shift is due to the electron withdrawing effect of SO as a result of the oxidation at sulfur atom. It is interesting to note that the H_2O_2 oxidation of 2 has occurred without disruption of the primary coordination sphere of the cobalt center. The CD curve for 3 (Figure 3) is somewhat different from that of 2 because of the contribution from the sulfur atom which becomes a racemic chiral center upon oxidation, although the configuration around this oxidized sulfur atom is likely a racemic mixture of R and S. The pmr spectrum of 3 shows a downfield shift and more broad peaks than the unoxidized species of 2 owing to the electron withdrawing character of the SO group upon oxidation of sulfur. The S-methyl protons are shifted to 2.65 ppm and 2.25 ppm of 2, while the β and γ methylene protons of L-met-O to, respectively, 2.7-3.0 ppm and 2.7-3.1 ppm from 2.0-2.4 ppm.

In a separate experiment, oxidation of L-methionine with stoichiometric amount of H_2O_2 has yielded the L-methionine-sulfenato compound (5). The direct reaction of 5 with the racemic *s-cis*- $[\text{Co}(\text{dmedda})\text{CO}_3]^-$ complex (1) has given 4. The ^1H NMR, ir and visible absorption spectral data indicate that the compounds 3 and 4 have the same structure and absolute configuration. The visible spectrum of 4 shows the λ_{max} for the $A_{1g} \rightarrow T_{1g}(O_h)$ transition at 546 nm as is the case for 3. As observed for 3, the CD curve shows the dominant negative Cotton effect in the $A_{1g} \rightarrow T_{1g}(O_h)$ transition region, indicating a Δ absolute configuration. As observed in the stereospecific coordination of L-met to the racemic 1, it is noted very interestingly that the L-met-O has shown a remarkable stereospecificity in its coordination to the racemic complex of 1 in this work.

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Stereospecific Coordination of L-Cysteine and Oxidation at the Coordinated Sulfur Atom in the L-Cysteine Cobalt(III) Complex of N,N'-Dimethylethylenediamine-N,N'-di- α -butyric Acid

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N,N'-dimethylethylenediamine-N,N'-di- α -butyric acid (H_2dmedba), an ONNO- type tetradentate ligand, has been found to yield exclusively the *s-cis* (symmetric *cis*) geometrical isomer in a series of cobalt(III) complexes, $[\text{Co}(\text{dmedba})(\text{L})]^{n+}$ ($\text{L} = \text{Cl}_2, (\text{H}_2\text{O})_2, \text{ClH}_2\text{O}, \text{CO}_3^{2-}$). The geometrical isomerism in the cobalt(III) complexes of the ONNO- type tetradentate ligands has been studied extensively.²⁻⁸ L-Cysteine (L-cys) has been found to yield both Δ and Λ isomers in the $[\text{Co}(\text{en})_2(\text{L-cys})]^{2+}$ complex.⁹⁻¹¹ Several workers¹²⁻¹⁵ have shown that in the cysteinato cobalt(III) complexes of ethylenediamine, $[\text{Co}(\text{en})_2(\text{cys})]^{2+}$, the controlled oxidation of the coordinated sulfur atom leads to S-bonded sulfenatos and sulfinateos.

In this paper the stereospecific coordination of L-cysteine in its reaction with racemic *s-cis*- $[\text{Co}(\text{dmedba})\text{Cl}_2]^-$ (1) to yield Λ -*s-cis*- $[\text{Co}(\text{dmedba})(\text{L-cys})]^-$ (2) and the oxidation of the coordinated sulfur atom to the sulfenato and sulfinate stages are described.