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 sulfenate 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 [Co(dmedda)(L-met)] complex. Such shift is due to the electron withdrawing effect of SO as a result of the oxidation at sufur atom. It is interesting to note that the H_2O_2 oxidation of 2 has occured 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 chirai 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 charater of the SO group upon oxidation of sulfur. The S-methlyl protons are shifted to 2.65 ppm 2.25 ppm of 2, while the β and γ methylene protons of L-met-O to, resperctively, 2.7-3.0 ppm and 2.7-3.1 ppm form 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-sulfenate compound (5). The direct reacton of 5 with the racemic s-cis-[Co(dmedda)CO$_3$]$^-$ complex (1) has given 4. The ^{1}H 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 showns 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_2 dmedba), 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, [Co(dmedba)(L)]$^{x+}$ (L=Cl$_2$, (H$_2$O)$_2$, ClH$_2$O, 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 [Co(en)$_2$(L-cys)]$^{2+}$ complex.[9~11] Several workers[12~15] have shown that in the cysteinato cobalt(III) complexes of ethylenediamine, [Co(en)$_2$(cys)]$^{2+}$, the controlled oxidation of the coordinated sulfur atom leads to S-bonded sulfenatos and sulfinatos.

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

Experimental

Preparation of Λ-s-cis-Na[Co(dmedba)(L-cys)] (2).
S-*cis*- H [Co(dmedba)Cl₂] (1.17 g, 3 mmol) were dissolved
in 40 mL of water at 60 ℃ and stirred for 20 min. L-cysteine-
hydrochloridte monohydrate (0.48 g, 3 mmol) was added to
this solution. The pH of the solution was adjusted to 5.0
using 1 N NaOH and stirring was continued for 3 hrs. The
solution was cooled to 15 ℃ and filtered to remove any solid
materials. The purple filtrate was evaporated by a rotary
evaporator to obtain purple solids, which were dissolved in
50 mL of ethanol. The solution was filtered and the filtrate
was evaporated to remove all the solvent. The solid materials
were dissolved in 5 mL of water, which was then admitted
to a column packed with Dowex 50W-X4 cation exchange
resin (200-400 mesh, Na⁺ form). One band was detected by
elution with water. The purple band fraction was collected
and evaporated to yield the purple product, which was wa-
shed with ethanol and ether. Yield: 0.74 g (52%). Anal. Calcd.
for NaCoC₁₅H₂₇O₆N₃S·2H₂O; C, 36.57; H, 6.31; N, 8.48.
Found: C, 36.59; H, 6.32; N, 8.60.

**Preparation of Λ-s-cis-Na[Co(dmedba)(L-cys-O)]
(3).** Λ-s-cis-Na[Co(dmedba)(L-cys)] (0.46 g, 1 mol) was dis-
solved in 10 mL of water. An H₂O₂ solution prepared by
diluting 0.11 mL (1 mmol) of 30% H₂O₂ in 5 mL of water
was slowly added to this solution for a period of 50 min
and stirring was continued for 2 hrs. Acetone (150 mL) was
added and the resultant solution was stored in a refrigerator
for 1 day. The solution was filtered to remove solid materials
and the filtrate was evaporated to obtain reddish purple pre-
cipitates. The reddish purple product was washed with ether.
Yield: 0.26 g (55%). Anal Calcd for NaCoC₁₅H₂₇O₇N₃S: C,
37.92; H, 5.73; N, 8.84. Found: C, 38.10; H, 5.73; N, 8.90.

**Preparation of Λ-s-cis-Na[Co(dmedba)(L-cys-O₂)]
(4).** Λ-s-cis-Na[Co(dmedba)(L-cys)] (0.46 g, 1 mmol) was
dissolved in 10 mL of water. An H₂O₂ solution made by dilu-
ting 0.34 mL (3 mmol) of 30% H₂O₂ in 5 mL of water was
slowly added to this solution for a period of 50 min and
stirring was continued for 12 hrs at room temperature. Ace-
tone (200 mL) was added and the resultand solution was
stored in a refrigerator for 1 day. The solution was filtered
to remove solid materials and the filtrate was evaporated
to obtain violet precipitates. The violet product was washed
with ether. Yield: 0.3 g (61%). Anal Calcd for NaCoC₁₅H₂₇O₈
N₃S: C, 36.67; H, 5.54; N, 8.55. Found: C, 36.55; H, 5.49;
N, 8.60.

Results and Discussion

A series of synthetic reactions accomplished in this work
is depicted in Figure 1. The complex 2 has been prepared
from the reaction of L-cysteine with racemic s-cis-[Co(dme-
dba)Cl₂]⁻ complex (1). The compound 3 is obtained upon
oxidation of sulfur of 2 by the stoichiometric amount of H₂O₂,
while the compound 4 is obtained upon oxidation of sulfur
of 2 by H₂O₂ in a 1:3 mole ratio.

The L-cysteine possesses three different donor atoms (N,
O, S). The infrared spectrum of 2 shows both the coordinated
-COO⁻ group at 1630 cm⁻¹ and the uncoordinated -COO⁻
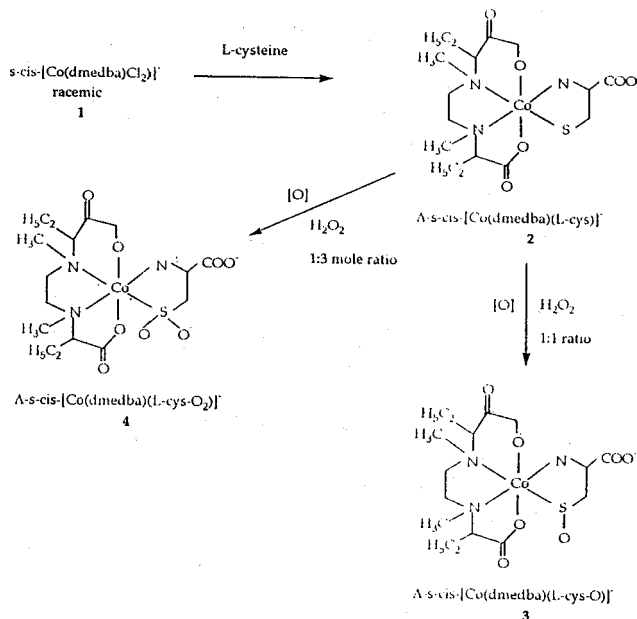group at near 1600 cm⁻¹, while it does not show the S-H

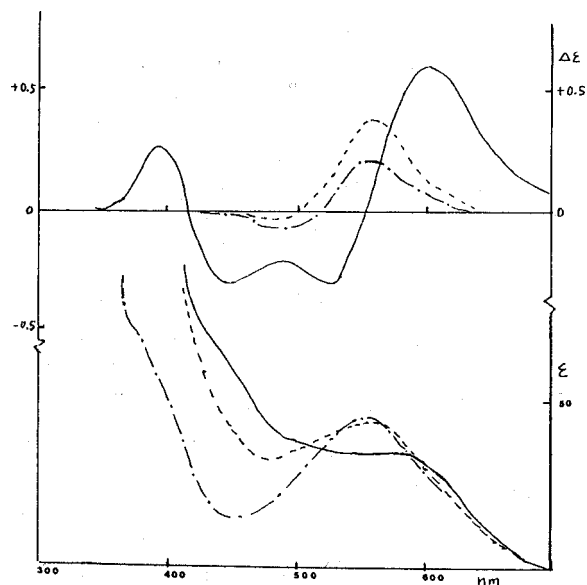**Figure 1.** Synthetic Reactions to prepare compounds 2, 3, and
4.

Figure 2. Electronic absorption and CD spectra of Λ-s-cis-Na[Co
(dmedba)(cys)] (—), Λ-s-cis-Na[Co(dmedba)(cys-O)] (---) and Λ-
s-cis-Na[Co(dmedba)(Cys-O₂)] (-----).

stretching vibration, Which in the case of uncoordinated L-
cysteine is shown at near 2500 cm⁻¹. Thus, the coordination
via S atom of L-cysteine is shown by the infrared spectrum.

The electronic absorption spectra are particularly helpful
in determining whether the sulfur atom is coordinated or
uncoordinated.[9,16-18] The visible spectrum of 2 (Figure 2)
shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}$ (O_h) region at 578 nm expected
for a CoN₃O₂S system,[19-21] indicating the fact that the coordi-
nation of L-cysteine takes place through nitrogen and sulfur
donor atoms in 2.

The CD curve of 2 (Figure 2) shows the positive dominant

Cotton effect in the $A_{1g} \rightarrow T_{1g}$ (O_h) region with λ_{max} at 584 nm indicating that 2 has a Λ absolute configuration.[22~24] In this work the optically active L-cysteine has shown a remarkable stereospecificity in its coordination to the racemic compound 2 to yield a Λ optical isomer.

Upon coordination of L-cysteine to 1 *via* the N, S chelation, the symmetry of the compound is reduced from C_2 (1) to C_1 (2), which is shown in the pmr spectrum of 2. The methyl protons on the ethyl group are shown as double triplets at 1.5 ppm for 2 vs a triplet at 1.3 ppm for 1, while the N-methyl protons are resonated as two singlets between 2.7 and 3.1 ppm for 2 *vs* a singlet at 3.1 ppm for 1.

Oxidation of 2 with stoichiometric amount of H_2O_2 has yielded a sulfenato complex of 3 as a reddish purple solid, while oxidation of 2 with H_2O_2 in a 1 : 3 (H_2O_2) mole ratio has given a sulfinato complex of 4 as a violet solid. The S-O stretching vibration is shown at 1047 cm^{-1}. The visible spectrum of 3 (Figure 2) shows the λ_{max} at 560 nm, which is shifted toward the shorter wavelength side by about 18 nm upon oxidation of 2 by H_2O_2 to 3. Such shift is due to the electron withdrawing effect of SO as a result of the oxidation of the sulfur atom. It is interesting to note that the H_2O_2 oxidation of 2 has occured without disruption of the primary coordination sphere of the cobalt center. The CD curve of 3 (Figure 2) shows the dominant positive Cotton effect in the T_{1g} transition region (λ_{max} near 550 nm) as expected for the Λ absolute configuration, in which the $\Delta\epsilon$ has been diminished considerably because of the contribution from the sulfur atom which becomes a racemic(R, S) chiral center upon oxidation. In the pmr spectrum of 3, the methyl protons of the ethyl group are shown as two triplets at near 1.1 ppm more clearly than those in 2, while the N-methly protons are exhibited as two singlets between 2.5 and 2.9 ppm.

Oxidation of 2 by H_2O_2 with 1 : 3 mole ratio for a prolonged period of time (12 hrs) has yielded the sulfinato complex of 4. The ir spectrum of 3 shows the S-O stretching vibrations at 1100 and 1250 cm^{-1}. The visible spectrum of 4 (Figure 2) shows the λ_{max} in the $A_{1g} \rightarrow T_{1g}$ (O_h) transition region at 552 nm, which shifted further toward the shorter wavelength side than 3. As expected for the Λ absolute configuration, the CD curve of 4 (Figure 2) shows the positive Cotton effect in the T_{1g} transition region with λ_{max} at near 540 nm in which $\Delta\epsilon$ are diminished much more considerably than 3 and the effect of the racemic sulfur atom on $\Delta\epsilon$ is more pronounced here than 3. It is interesing to observe in this work that the L-cysteine has shown the significant stereospecificity in its coordination to the racemic complex of 1.

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Adsorption of Stearic Acid on Hydrophobic Surface : FT-IR Spectroscopic Study

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In the last decade, much attention has been paid to the ultrathin organic films due to their potential application to molecular electronics, optoelectronics, and artificial membranes, etc.[1] In line with this, herein we hope to present the infrared spectroscopic observation made on the consecutive adsorption of octadecyl mercaptan and stearic acid on gold and silver surfaces. The objective of this work is to see how much the orientation of second layer is susceptible to the structure of the first layer and to get information on the adsorption behavior of organic molecules on non-metallic hydrophobic surface.

Initially, the vacuum evaporated silver or gold substrate[2,3] was dipped into 10^{-3} M octadecyl mercaptan (ODM) in ethanol. The substrate was subsequently rinsed with neat ethanol to remove unbound ODM. The Langmuir-Blodgett (LB) stearic acid monolayers were then deposited onto the substrate with a computerized home-made LB trough.[2] After spreading 5×10^{-3} M stearic acid (STA) in chloroform onto the water subphase containing 10^{-2} M $CdCl_2$, chloroform was allowed