

Dichloro(2S, 5S, 9S)- and  
(2S, 5R, 9S)-Trimethyltriethylenetetraamine Cobalt (III)

착물의 치환반응 생성물

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연세대학교 이과대학 화학과

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Dinitro, L-Alaninato, and  
S-Methyl-L-Cysteinato Cobalt (III) Complexes of  
2S, 5S, 9S- or 2S, 5R, 9S-Trimethyltriethylenetetraamine Ligands

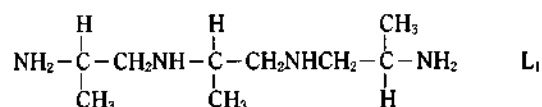
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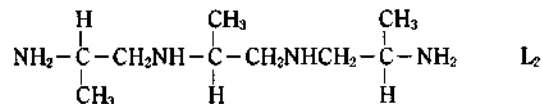
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The synthesis of the dichloro cobalt(III) complexes of 2S, 5S, 9S-trimethyltriethylenetetraamine ( $L_1$ ) and 2S, 5R, 9S-trimethyltriethylenetetraamine ( $L_2$ ) has yielded  $\Delta$ -*cis*- $\alpha$ ,  $\Delta$ -*cis*- $\beta$  and *trans* isomers for the  $L_1$  ligand while  $\Delta$ -*cis*- $\alpha$ ,  $\Delta$ -*cis*- $\beta$ , and *trans* isomers have been obtained for the  $L_2$  ligand<sup>1</sup>.

2S, 5S, 9S-Trimethyltriethylenetetraamine



2S, 5R, 9S-Trimethyltriethylenetetraamine



We wish to describe here the synthesis of the dinitro cobalt(III) complexes of  $L_1$  or  $L_2$  from the substitution reaction of the *trans*-dichlorocobalt(III) complexes of  $L_1$  or  $L_2$  with sodium nitrite as well as the synthesis of the L-alaninato and S-methyl-L-cysteinato cobalt(III) complexes of  $L_1$ . During the course of our preparation of the dinitro complexes started from the *trans*-dichlorocobalt

(III) complexes of  $L_1$  or  $L_2$ , the geometrical isomerization has occurred: the substitution reaction of the  $[\text{Co}(L_1)\text{Cl}_2]^+$  complex has yielded racemic *cis*- $\beta$ - $[\text{Co}(L_1)(\text{NO}_2)_2]^+$  composed of the  $\Delta$ -*cis*- $\beta$  and  $\Lambda$ -*cis*- $\beta$  isomers, while that of the  $[\text{Co}(L_2)\text{Cl}_2]^+$  complex gave the optically active  $\Delta$ -*cis*- $\beta$  isomer.

EXPERIMENTAL

**Measurements.** The visible absorption spectra were measured with a Shimadzu UV-240 spectrophotometer. The circular dichroism spectra were measured with JASCO J-550C automatic spectropolarimeter and the PMR spectra with a 80 MHz Varian FT-80A NMR spectrometer.

2S, 5S, 9S-Trimethyltriethylenetetraamine( $L_1$ ) and 2S, 5R, 9S-trimethyltriethylenetetraamine( $L_2$ ). The method of preparing these ligands have been described previously<sup>1</sup>.

$\Delta$ -*cis*- $\beta$ -Dinitro(2S, 5S, 9S-trimethyltriethylenetetraamine)cobalt(III) chloride,  $\Delta$ -*cis*- $\beta$ - $[\text{Co}(L_2)(\text{NO}_2)_2]\text{Cl}$ . 0.15 g ( $0.04 \times 10^{-4}$  mol) of *trans*- $[\text{Co}(L_2)\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$  was dissolved in 10 ml of absolute methanol and heated at 40°C for 10 min.  $5.57 \times 10^{-2}$  g ( $8.08 \times 10^{-4}$  mol) of  $\text{NaNO}_2$  dissolved in 40 ml of absolute methanol was added and the resultant

solution was heated at 40°C. For 2 hr. The solution was cooled to 20°C and 0.1 ml of conc. HCl was added. The solution was concentrated to 1 ml under reduced pressure. 1 ml of distilled water and 80 ml of acetone were added and the solution was stored in a refrigerator for 30 hr. Brown precipitates obtained were washed with cold acetone and dried under vacuum. Yield: 0.1 g (60%). Anal. Calcd for  $[\text{Co}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{NO}_2)_2]\text{Cl}$ : C, 28.8; H, 6.5; N, 22.4. Found: C, 28.6; H, 6.7; N, 22.1].

*Cis*- $\beta$ -dinitro(2S, 5S, 9S-trimethyltriethylenetetraamine)cobalt(III) chloride Monohydrate, *cis*- $\beta$ - $[\text{Co}(\text{L}_1)(\text{NO}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$ . This was prepared in the same way as that used to prepare  $\Delta$ -*cis*- $\beta$ - $[\text{Co}(\text{L}_2)(\text{NO}_2)_2]\text{Cl}$  using *trans*- $[\text{Co}(\text{L}_1)\text{Cl}_2]\text{Cl}$  in place of *trans*- $[\text{Co}(\text{L}_2)\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ . Anal. Calcd. for  $[\text{Co}(\text{L}_2)\text{Cl}_2]\text{Cl}$ : C, 27.5; H, 6.7; N, 21.4. Found: C, 27.7; H, 6.6; N, 22.0.

$\Lambda$ -*Cis*- $\alpha$ -L-alaninato(2S, 5S, 9S-trimethyltriethylenetetraamine)cobalt(III) Dichloride,  $\Lambda$ -*cis*- $\alpha$ - $[\text{Co}(\text{L}_1)(\text{L-ala})]\text{Cl}_2$ , (L-ala: L-alaninato). 0.17 g( $4.8 \times 10^{-4}$  mol) of  $\Lambda$ -*cis*- $\alpha$ - $[\text{Co}(\text{L}_1)\text{Cl}_2]\text{Cl}$  was dissolved in 20 ml of water at 20°C and stirred for 30 min.  $4.3 \times 10^{-2}$  g( $4.8 \times 10^{-4}$  mol) of L-alanine was added and the pH of the solution was adjusted to 8 with 10% LiOH. The solution was heated at 60°C for 2 hr. The solution was cooled to room temperature and concentrated to 1 ml under reduced pressure. 0.5 ml of conc. HCl and 50 ml of acetone were added and the solution was stored in a refrigerator for one day. Light orange precipitates were formed, which were filtered and washed with acetone and ether. Yield: 0.1 g(51%). Anal. Calcd for  $[\text{Co}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{C}_3\text{H}_7\text{NO}_2)]\text{Cl}_2$ : C, 35.5; H, 7.5; N, 17.2. Found: C, 36.1; H, 7.5; N, 17.1.

$\Lambda$ -*Cis*- $\alpha$ -S-Methyl-L-cysteinato(2S, 5S, 9S-trimethyltriethylenetetraamine)-cobalt(III) Dichloride,  $\Lambda$ -*cis*- $\alpha$ - $[\text{Co}(\text{L}_1)(\text{L-smcys})]\text{Cl}_2$ . This was prepared by the same method as that used to prepare  $\Lambda$ -*cis*- $\alpha$ - $[\text{Co}(\text{L}_1)(\text{L-ala})]\text{Cl}_2$  using S-methyl-L-cysteine in place of L-alanine. Anal. Calcd for  $[\text{Co}(\text{C}_9\text{H}_{24}\text{N}_4)(\text{C}_4\text{H}_8\text{NSO}_2)]\text{Cl}_2$ : C, 34.5; H, 7.2; N, 15.5. Found: C, 35.3; H, 7.2; N, 15.2.

*Trans*- $[\text{Co}(\text{L}_1)\text{Cl}_2]\text{Cl}$ , *trans*- $[\text{Co}(\text{L}_2)\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ .

$\Lambda$ -*cis*- $\alpha$ - $[\text{Co}(\text{L}_1)\text{Cl}_2]\text{Cl}$ . These complexes were prepared according to the methods described previously<sup>1</sup>.

## RESULT AND DISCUSSION

Yoshikawa, *et al.*<sup>2</sup> have prepared the dinitro cobalt(III) complexes of  $\text{L}_1$  and  $\text{L}_2$  from the reaction of the  $\text{L}_1$  or  $\text{L}_2$  ligand with Co(III) ion and sodium nitrite. The  $\Lambda$ -*cis*- $\beta$ ,  $\Delta$ -*cis*- $\beta$ , and  $\Lambda$ -*cis*- $\alpha$  isomers were obtained for the  $\text{L}_2$  ligand, while only the  $\Delta$ -*cis*- $\beta$  isomer was yielded for the  $\text{L}_1$  ligand.

An entirely different synthetic route was employed in this work to prepare the dinitro cobalt(III) complexes of  $\text{L}_1$  or  $\text{L}_2$  via the reaction between the *trans*-dichlorocobalt(III) complex of  $\text{L}_1$  or  $\text{L}_2$  and sodium nitrite. Geometric isomerization has been observed in our preparation: Reaction of *trans*- $[\text{Co}(\text{L}_1)\text{Cl}_2]^+$  with sodium nitrate has yielded racemic *cis*- $\beta$ - $[\text{Co}(\text{L}_1)(\text{NO}_2)_2]^+$ , while reaction of *trans*- $[\text{Co}(\text{L}_2)\text{Cl}_2]^+$  with sodium nitrite has produced optically active  $\Delta$ -*cis*- $\beta$ - $[\text{Co}(\text{L}_2)(\text{NO}_2)_2]^+$ .

Fig. 1 shows the absorption spectrum for the racemic *cis*- $\beta$ - $[\text{Co}(\text{L}_1)(\text{NO}_2)_2]^+$  as well as that for the  $\Delta$ -*cis*- $\beta$ - $[\text{Co}(\text{L}_2)(\text{NO}_2)_2]^+$  isomer. In the absor-

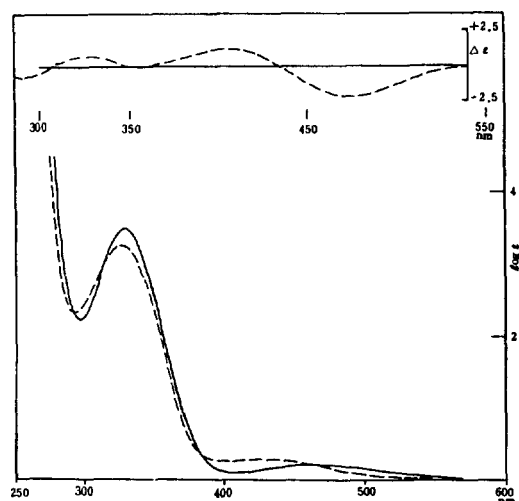


Fig. 1. CD and electronic absorption spectra of racemic-*cis*- $[\text{Co}(2\text{S}, 5\text{S}, 9\text{S-lne}_3 \text{ trien})(\text{NO}_2)_2]^+$  (—) and  $\Delta$ -*cis*- $\beta$ -(RS)- $[\text{Co}(2\text{S}, 5\text{R}, 9\text{S-me}_3 \text{ trien})(\text{NO}_2)_2]^+$  (----).

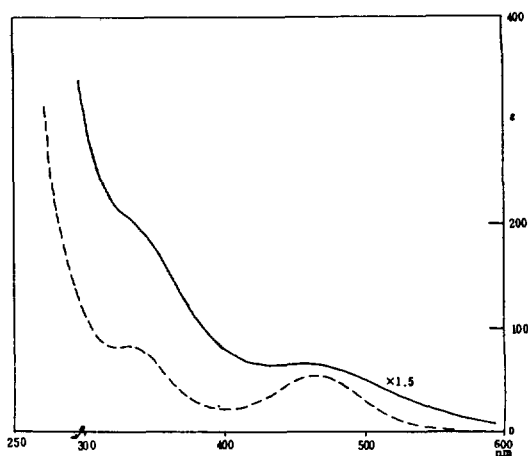


Fig. 2. Electronic absorption spectra of  $\Lambda$ -*cis*- $\alpha$ -(RR)-[Co(L)(L-ala)]<sup>2+</sup> (—) and  $\Lambda$ -*cis*- $\alpha$ -(RR)-[Co(L)(L-SMCys)]<sup>2+</sup> (----) in H<sub>2</sub>O (L=2S, 5S, 9S-me<sub>2</sub> trien)

ption spectra for the [CoN<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> system complexes the position of the second absorption in the shorter wavelength side of the *d-d* transition region is very much useful for distinguishing the *cis* and *trans* isomers<sup>2-6</sup>; in the case of the *cis* isomer the  $\lambda_{\max}$  of the second absorption band is known to appear at near 330 nm, while that of the *trans* isomer is shown at near 350 nm. Both [Co(L<sub>1</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and [Co(L<sub>2</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> show the second absorption band maxima at 328 nm and 326 nm, respectively, which indicates the fact that a *cis* isomerization from *trans* has occurred during the course of our preparation and the dinitro complexes obtained in this work have the *cis* configuration. The shapes of the absorption bands in Fig. 1 suggest that complexes have the *cis*- $\beta$  configuration.

The CD spectra of [Co(L<sub>1</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and [Co(L<sub>2</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> are shown in Fig. 2. The dinitro-L<sub>1</sub>-complex doesn't show any optical activity, which indicates that the complex is a racemate composed of  $\Delta$ -*cis*- $\beta$  and  $\Lambda$ -*cis*- $\beta$  isomers. The dominant negative band at 475 nm of the [Co(L<sub>2</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex tells that the complex has the  $\Delta$  absolute configuration<sup>7-10</sup> as shown in Fig. 2. In the case of the [Co(L<sub>1</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex  $\Lambda$  the racemic pair are  $\Delta$ -*cis*- $\beta$ -(RS)-( $\delta$   $\lambda$   $\delta$ ) and  $\Lambda$ -*cis*- $\beta$ -(SR)-( $\delta$   $\lambda$   $\delta$ ) isomers, both of which are known to be ther-

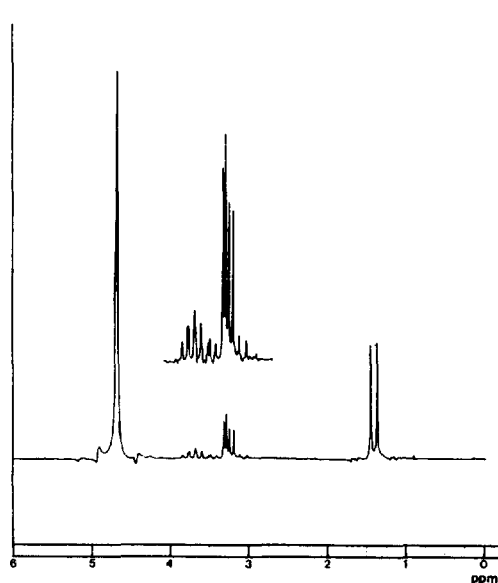


Fig. 3. PMR spectrum of  $\Lambda$ -*cis*- $\alpha$ -(RR)-[Co(2S, 5S, 9S-me<sub>3</sub> trien)(L-ala)]<sup>2+</sup> in D<sub>2</sub>O.

modynamically more stable than other geometrical or optical isomers due to much less non-bonded interaction<sup>10-12</sup>. In the case of [Co(L<sub>2</sub>)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex, on the other hand, the  $\Delta$ -*cis*- $\beta$ -(RS)-( $\delta$   $\lambda$   $\delta$ ) structure is favored in view of such thermodynamic stability, for all the methyl groups in the chelates rings take the stable equatorial position in the  $\Delta$ -*cis*- $\beta$  configuration.

The reaction of  $\Lambda$ -*cis*- $\alpha$ -[Co(L<sub>1</sub>)Cl<sub>2</sub>]<sup>+</sup> with L-alanine and S-methyl-L-cysteine gave, respectively,  $\Lambda$ -*cis*- $\alpha$ -[Co(L<sub>1</sub>)(L-ala)]<sup>2+</sup> and  $\Lambda$ -*cis*- $\alpha$ -[Co(L<sub>1</sub>)(L-smcys)]<sup>2+</sup>, the absorption spectra of which are depicted in Fig. 2. As expected, a blue shift has been observed in both complexes: the  $\lambda_{\max}$  was shifted from 537 nm to near 460 nm for band I and from 382 nm to near 380 nm for band II. In the PMR spectrum (Fig. 3) of  $\Lambda$ -*cis*- $\alpha$ -[Co(L<sub>1</sub>)(L-ala)]<sup>2+</sup> the four methyl protons appeared at 1.33 ppm as a sharp doublet, which indicates that these four methyl groups take the thermodynamically stable equatorial position. The carbonyl stretching vibration appeared at 1642 cm<sup>-1</sup> for  $\Lambda$ -*cis*- $\alpha$ -[Co(L<sub>2</sub>)(L-smcys)]<sup>2+</sup>, which showed that the amino acid coordinated to the cobalt(III) ion through the nitrogen and oxygen donor atoms. The CD spectra of both

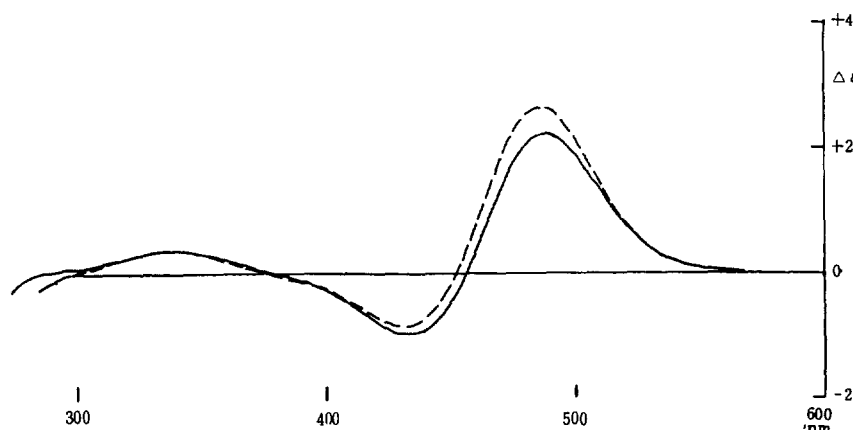


Fig. 4. CD spectra of  $\Lambda$ -cis- $\alpha$ -(RR)-[Co(L)(L-ala)]<sup>2+</sup> (—) and  $\Lambda$ -cis- $\alpha$ -(RR)-[Co(L)(L-SMCys)]<sup>3+</sup> (----) in H<sub>2</sub>O (L=2S, 5S, 9S-me<sub>2</sub> trien).

complexes (Fig. 4) show the dominant positive Cotton effect in the longer wavelength side, indicating the  $\Lambda$  absolute configuration.

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