

Co(III) Glycine Methyl Ester 착물에 관한 연구 (제1보).

착물의 합성과 구조규명

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Co(III) Complexes of Glycine Methyl Ester (I).

Preparation and Characterization

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요 약. 팔면체 구조를 갖는 Co(III) glycine methyl ester 착물을 합성하고 원소분석과 적외선 스펙트럼 및 핵자기공명스펙트럼을 이용하여, 이들 착물의 구조에 관하여 고찰하였다. 이들 중 $[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$ 착물은 양이온 교환수지인 Dowex 50W-X8을 이용하여 분리하였으며, 가능한 기하학적 이성질체는 $\text{C}_1\text{-cis}(0-0)$, $\text{C}_2\text{-cis}(0-0)$, $\text{trans}(0-0)$ 형태의 구조를 가지고 있음을 확인하였다.

ABSTRACT. Octahedral Co(III) complexes of the glycine methyl ester have been prepared and characterized by elemental analysis, infrared, and NMR spectrum. Co(III) glycine methyl ester complex has been isolated from the reaction of glycine and glycine methyl ester in aqueous solution by cation exchange resin, Dowex 50W-X8 (hydrogen form). It has been observed that the complexes have $\text{C}_1\text{-cis}(0-0)$, $\text{C}_2\text{-cis}(0-0)$, $\text{trans}(0-0)$ geometry.

INTRODUCTION

The preparation of Co(III) complexes containing glycinato ligand has been extensively studied.¹⁻⁵ Since they undergo ligand exchange reactions relatively slowly, the isomerism, mode of reaction and general properties of octahedral complexes have been studied.⁶⁻⁷

The origin of attractive intermolecular interactions and the factors determine the geometry of Co(III) glycinato complexes have been sought after using numerous experimental techni-

ques.⁸⁻¹² Co(III) glycinato complexes are remarkably inert in aqueous or acid solutions^{13,14}. When acid or aqueous solutions of these complexes were irradiated with 254 or 313 nm light corresponding to LMCT bands, on oxidation-reduction decomposition occurred.¹⁵⁻¹⁷

In this work, we report the synthesis and isolation of the Co(III) complexes containing the glycine methyl ester complexes in aqueous solution using Dowex 50W-X8, a cation exchange resin in H^+ form. The geometric structure of the complex has been characterized by

elemental analysis, IR and NMR data.

EXPERIMENTAL

Preparation of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{CH}_3)\text{Cl}]\text{Cl}_2$. The complexes were prepared by the similar method of Alexander and Busch.² The crude product was taken up in a minimum of hot water (50~60°C) and recrystallized on cooling after the addition of a few drops of concentrated hydrochloric acid.

Elemental analysis. Calcd(%) for $\text{Co}(\text{C}_7\text{H}_{23}\text{N}_5\text{O}_2\text{Cl}_3)\text{H}_2\text{O}$; C, 21.4, H, 6.41, N, 17.8 Found(%) C, 21.5H, 6.53 N, 17.2

Preparation of $[\text{Co}(\text{gly})_2(\text{glycine methyl ester})\text{Cl}]\text{Cl}_2$. A solution containing 10g(0.042 mole) of Co(II) chloride hexahydrate in 20 ml of water was added to mixed solution of 5.15g (0.041 mole) of glycine methyl ester hydrochloride and 6.4 g(0.085 mole) of glycine in 30 ml of water. The solution was then oxidized by bubbling oxygen through the solution while being heated in a water bath for one and half hours. After having been allowed to stand at room temperature, the solution was filtered several times at intervals. The solution was acidified (pH \approx 2) with hydrochloric acid, diluted to 2 liter with water and poured on a column (ϕ 15 \times 300 mm) of Dowex 50W-X8 cation exchange resin(200~400 mesh, hydrogen form). The column was washed with water and the adsorbed band was eluted with 0.15 M hydrochloric acid. A dark reddish violet, a violet and another violet band were eluted in

that order. The first eluted band, a dark reddish violet color, was characterized by the NMR spectrum. The two violet band was separated by filtration, washed with methanol, then with absolute ethanol, and ether and dried in vacuum over $\text{Mg}(\text{ClO}_4)_2$. The crude product was recrystallized from hot water by adding methanol.

Elemental analysis. Calcd(%) for $\text{Co}(\text{C}_7\text{H}_{15}\text{N}_3\text{O}_6\text{Cl}_3)\text{H}_2\text{O}$; C, 20.0 H, 4.04 N, 10.0 Found (%) C, 20.1 H, 3.92 N, 9.70

Preparation of $[\text{Co}(\text{ox})_2(\text{glycine methyl ester})\text{Cl}]\text{Cl}$. Cobalt(II) chloride hexahydrate was mixed with the glycine methyl ester hydrochloride and 10.72 g(0.085 mole) of oxalic acid in 30 ml of water as mentioned in the previous section. The crude product was recrystallized from hot water by adding methanol.

Elemental analysis. Calcd(%) for $\text{Co}(\text{C}_7\text{H}_7\text{NO}_{10}\text{Cl}_3)\text{H}_2\text{O}$; C, 18.7 H, 2.01 N, 3.12 Found (%) C, 18.8 H, 1.89 N, 3.32

Spectral Measurements and Physical Data.

The infrared spectra were recorded on a Perkin-Elmer Model 267 using potassium bromide pellets. NMR spectra were measured by a Varian T-60A spectrometer in deuterium oxide solution against tetramethylsilane external standard. All spectral measurement were made at room temperature. Elemental analysis were carried out at the Korea Institute of Science and Technology, on a F & M Scientific Cooperation C. H. N Analyser Model 180.

Table 1. The important infrared bands of Co(III) complexes (cm^{-1}).

Complexes	N-H stretching	C=O stretching	CH ₂ twisting, rocking
$[\text{Co}(\text{en})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$	3100s	1745vs	850w
	3200s	1750vs	1150s
$[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$	3300s	1745vs	820w
	3350s	1750vs	1140s
$[\text{Co}(\text{ox})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$	3300m	1610vs	860w

RESULTS AND DISCUSSION

The method of preparation of bidentate ligand, ethylenediamine, glycinato, oxalato complexes is identical, with the exception that

used by Alexander and Busch² in the preparation the unsubstituted glycine methyl ester.

The infrared spectra of the glycine methyl ester Co(III) complexes are shown in Table 1.

There appears a very sharp and intense band

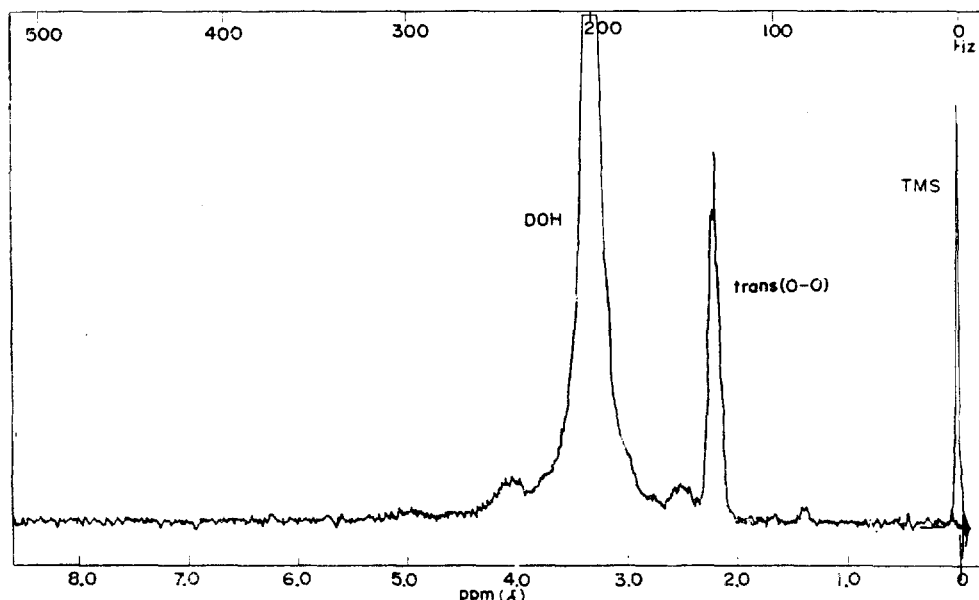


Fig. 1. NMR spectrum of *trans*(0-0)-(Co(gly)₂(glycinemethylester)Cl)Cl₂ complex in D₂O.

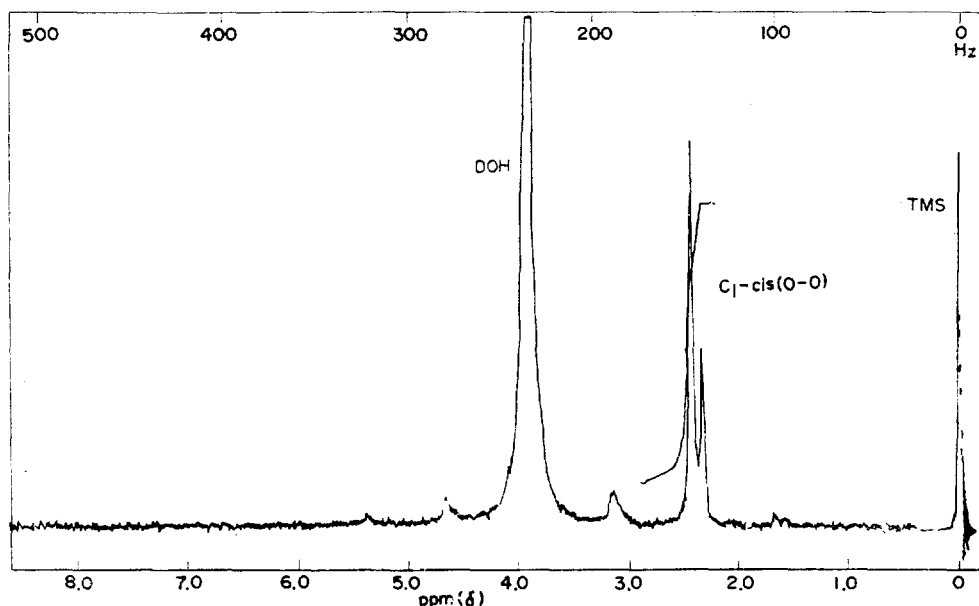


Fig. 2. NMR spectrum of C₁-*cis*(0-0) [Co(gly)₂(glycinemethylester)Cl]Cl₂ complex in D₂O.

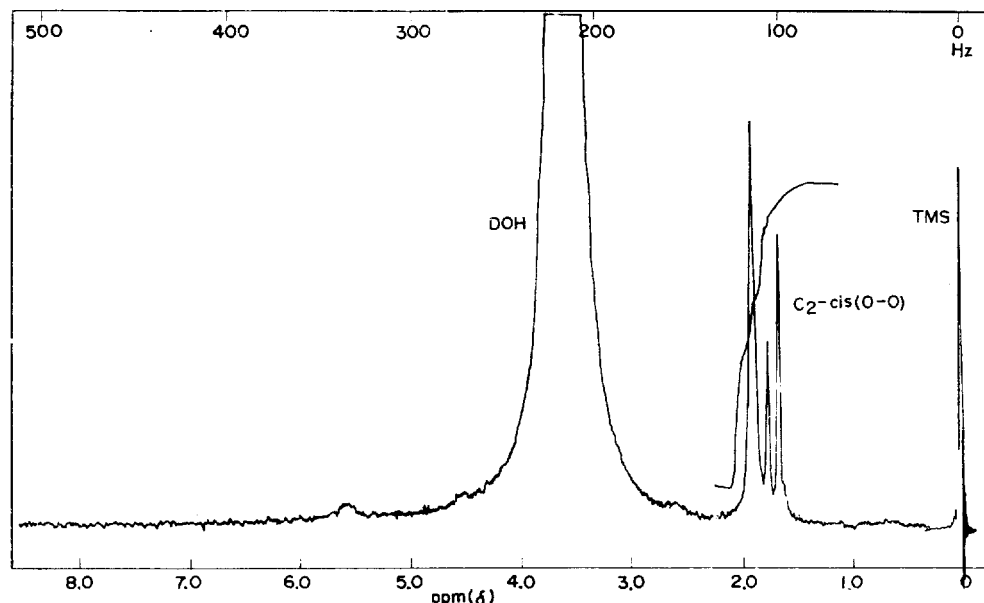


Fig. 3. NMR spectrum of C_2 -cis(0-0) $[\text{Co}(\text{gly})_2(\text{glycinemethylester})\text{Cl}]\text{Cl}_2$ complex in D_2O .

at $1745 \pm 5 \text{ cm}^{-1}$ which is attributed to the stretching mode of the carbonyl group of the ester in ethylenediamine and glycinato ligands. This is slightly higher in frequency than that of the uncoordinated esters. The higher frequency has also been attributed to the inductive effect of positive charge on the amino group.¹⁸ The carbonyl stretching band indicates that the ester is coordinating simply as a monodentate ligand.¹⁹ The CH_2 twisting and rocking at $850 \sim 1150 \text{ cm}^{-1}$, and NH stretching at $3100 \sim 3350 \text{ cm}^{-1}$ bands are apparent as shown in Table 1.

The NMR spectra provide more concrete information on the structure of the complexes and the NMR spectra of the Co(III) glycine methyl ester complexes are shown in Fig. 1, 2, 3.

The methylene proton signals of the chelated glycine appear in the region of $3.3 \sim 3.7 \text{ ppm}$. The *trans*(0-0) isomer exhibits a single resonance at 2.21 ppm while the *cis*- C_1 (0-0) isomer shows two lines at 2.40 ppm and the *cis*- C_2 (0-0) isomer gives a triplet at 1.85 ppm²⁰. The

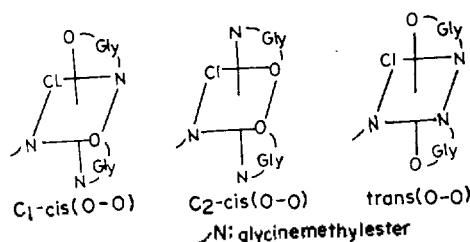


Fig. 4. The possible geometric isomers of the Co(III) glycinemethylester complex.

geminal coupling constant for the *trans* isomer is about 6 Hz while that of the *cis* isomer is 3 Hz by first order analysis. This suggests that the methylene protons of the three glycines are present in different chemical environments in each isomer. The methylene protons of the chelated glycine located in the plane would be observed at the lower field than the methylene protons of the other chelated glycine which is not in the plane. From the NMR spectra, it is evident that there are three geometric isomers and these isomers are shown in Fig. 4.

The NMR study and other experimental results obtained confirm the possible geometric

isomers of $[\text{Co}(\text{gly})_2(\text{glycinemsthylyster})\text{Cl}]\text{Cl}_2$ complexes.

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