

지방족디아민과 에틸렌디아민-트리아세테이트를 포함하는  
코발트(III)錯物에 관한 연구(제1보). 수용액 중에서  
[Co(EDTA)]<sup>-</sup>錯物에 트리메틸렌디아민의 반응

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Cobalt(III) Complexes Containing Ethylenediamine-Triacetate  
and Aliphatic Diamine (I). The Reaction of Ethylenediamine-  
tetraacetatocobaltate(III) with Trimethylenediamine  
in Aqueous Solution

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**要約.** 수용액 중에서 ethylenediamine-tetraacetatocobaltate(III) 錯物에 트리메틸렌디아민(tn)을 반응시켜 얻어지는 [Co(tn)(HEDTRA)]Cl·2H<sub>2</sub>O 錯物을 수소이온형陽이온교환수지, Dowex 50W-X8을 이용하여 분리하였다. EDTRA<sup>3-</sup>(ethylenediamine-triacetate) 리간드는 유리 식초산 가지를 갖고 4 자리 형태로 코발트(III) 이온에 配位되어 있으며, 원소분석, UV, IR, NMR 등 분광학적 방법을 이용하여 얻어진 錯物은 가능한한 기학적 이성질체 중에서 *trans*(O-O)(1) 형태의 구조를 가지고 있음을 확인하였다.

**ABSTRACT.** Cobalt(III) complex containing ethylenediamine-triacetate and trimethylenediamine has been isolated from the reaction of ethylenediamine-tetraacetatocobaltate(III) with trimethylenediamine in aqueous solution by Dowex 50W-X8, cation exchange resin in H<sup>+</sup> form.

The ethylenediamine-triacetate(EDTRA<sup>3-</sup>) ligand coordinates to the cobalt(III) ion as a quadridentate with a free acetate branch. It has been observed that the complex has *trans*(O-O)(1) structure via the elemental analysis, UV, IR and NMR data.

INTRODUCTION

It was reported that [Co(EDTA)]<sup>-</sup> (EDTA: ethylenediamine-tetraacetate ion) reacts easily with ethylenediamine to form [Co(en)<sub>3</sub>]<sup>3+</sup> (en: ethylenediamine) at room temperature.<sup>1,2</sup> Re-

cently we have reported on the cobalt(III) complexes containing both EDTA and ethylenediamine as intermediates for the replacement of the EDTA from the [Co(EDTA)]<sup>-</sup> complex by ethylenediamine.<sup>3</sup> Although numerous examples of cobalt(III) complexes containing a

quinquedentate ethylenediamine-triacetate have been reported by Blackmer *et al.*<sup>4-6</sup> only a few studies have been reported on the quadridentate ethylenediamine-triacetatocobalt(III) complex<sup>3</sup>.

In the present study, we have isolated the cobalt(III) complexes containing the quadridentate ethylenediamine-triacetate and trimethylenediamine (tn) from the reaction of  $[\text{Co}(\text{EDTA})]^-$  with trimethylenediamine in aqueous solution using Dowex 50W-X8, cation exchange resin in  $\text{H}^+$  form. The structure of the complex has been characterized by elemental analysis, UV, IR and NMR data.

## EXPERIMENTAL

**Preparation of *trans*(O—O)(1)-[Co(tn)-(HEDTRA)]Cl·2H<sub>2</sub>O.**  $\text{Na}[\text{Co}(\text{EDTA})] \cdot 4\text{H}_2\text{O}$  (0.1 mol) was dissolved in 1.0 litre of water and 0.15 mol of trimethylenediamine was added. The solution was warmed for 60 minutes on water bath at 50°C and then was cooled at room temperature. The solution was acidified ( $\text{pH} \approx 2$ ) with hydrochloric acid, diluted to 20 litre with water and poured on a column ( $\phi 5 \times 60$  cm) of Dowex 50W-X8, cation exchange resin in  $\text{H}^+$  form. The column was washed with water, and the adsorbed band was eluted with 0.15 M hydrochloric acid. A large amount of  $[\text{Co}(\text{tn})_3]^{3+}$  remaining on the top of the column and three separate bands were obtained. In this reaction, as in the case of  $[\text{Co}(\text{en})(\text{HEDTRA})] \text{Cl} \cdot 3\text{H}_2\text{O}$ ,<sup>3</sup> *trans*(O—O)(1)-[Co(tn)(H<sub>2</sub>EDTA)]<sup>+</sup> in the first band, and *trans*(O—O)(1)-[Co(tn)-(EDDA)]<sup>+</sup> in the third band were also confirmed by both the column chromatography and the UV absorption spectra, but the amounts were too little to be isolated. The second red band was evaporated to almost dryness under reduced pressure at 50°C. The product was recrystallized from small amount of water.

*Anal.* Calcd for  $[\text{Co}(\text{tn})(\text{HEDTRA})] \text{Cl} \cdot$

$2\text{H}_2\text{O}$ . ( $\text{C}_{11}\text{H}_{26}\text{N}_4\text{O}_8\text{ClCo}$ ): C, 30.25; H, 6.00; N, 12.83.

Found: C, 30.40; H, 5.58; N, 12.40.

**pH Titration.** The pH titration of the complex with concentration of  $5.00 \times 10^{-3} \text{M}$  and ionic strength of 0.10 ( $\text{NaClO}_4$ ) was carried out using a 0.05 M NaOH solution mixed with 0.05 M  $\text{NaClO}_4$  at  $25.0 \pm 0.1^\circ\text{C}$  in nitrogen gas.

**Spectral Measurement** The pH titration curve was investigated by a Metrohm AG CH-9100 (Switzerland) pH meter. The infrared spectrum was obtained using the KBr-disk method with a Perkin-Elmer model 267. The visible and ultra violet absorption spectra were recorded with a Hitachi model 124 spectrophotometer. The NMR spectrum was checked with a Varian HA-100 spectrometer in deuterium oxide solution containing sodium 3-(trimethylsilyl)-1-propane-sulfonate (TMS) as the internal standard. All spectral measurement were made at room temperature.

## RESULTS AND DISCUSSION

The isolation of the isomers of the mixed ethylenediamine-EDTA cobalt(III) complexes has been known to be difficult because the  $[\text{Co}(\text{EDTA})]^-$  reacts easily with ethylenediamine to form  $[\text{Co}(\text{en})_3]^{3+}$  at room temperature.<sup>1</sup> In recent years, however, new mixed ligand cobalt(III) complexes containing ethylenediamine-triacetate, ethylenediamine-tetracetate and ethylenediamine have been isolated by the reaction of  $[\text{Co}(\text{EDTA})]^-$  with ethylenediamine in dilute aqueous solution.<sup>3</sup> In this work, the isolation and characterization of the cobalt(III) complex containing mixed ligand trimethylenediamine-ethylenediamine-triacetate from the reaction of  $[\text{Co}(\text{EDTA})]^-$  with trimethylenediamine has been carried out in a similar way to a previous report<sup>3</sup>. We have been able to isolate only one isomer out of the four possible geometric isomers

shown in Fig. 1. The main purpose of this work is to find out the mode of coordination of HEDTRA ligand to cobalt(III) ion, about which will be discussed in the following section. As far as the conformation of the trimethylenediamine ligand is concerned, it is thought that the trimethylenediamine ligand takes a chair conformation judging from the literature report.<sup>7,8</sup> Saito *et al.* reported that the trimethylenediamine ligand takes chair conformations in  $[\text{Co}(\text{tn})_3]^{3+}$ .<sup>7</sup> From the conformational analysis of six-membered diamine chelate rings, Gollogly and Hawkins showed that the six-membered 1,3-diaminopropane(tn) chelate ring would take a symmetrical chair conformation in the simple monooctahedral complex.<sup>8</sup> Although there is a chance that the trimethylenediamine ligand may take a skew-boat conformation, we feel that the preferred conformation for trimethylenediamine in  $[\text{Co}(\text{tn})(\text{HEDTRA})]^+$  is a chair form (the boat conformation will be least stable because of the ring strain). Assuming that the trimethylenediamine ligand takes a chair conformation, there are four possible geometric isomers as

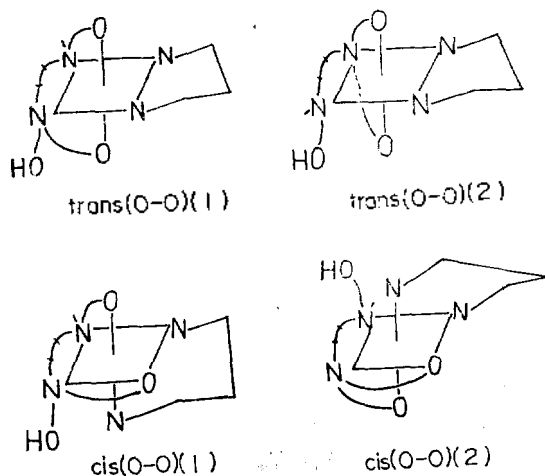


Fig. 1. The four possible geometric isomers of the  $[\text{Co}(\text{tn})(\text{HEDTRA})]^+$  complex.  $\text{N} \text{---} \text{N}$  = trimethylenediamine,  $\text{O} \text{---} \text{N} \text{---} \text{N} \text{---} \text{O}$  Or  $\text{HO} \text{---} \text{N} \text{---} \text{N} \text{---} \text{O}$  = HEDTRA.

shown in Fig. 1.

The analytical data have shown that the isomer has the  $[\text{Co}(\text{tn})(\text{HEDTRA})]\text{Cl} \cdot 2\text{H}_2\text{O}$  formula. The coordination style of the trimethylenediamine-ethylenediamine-triacetate to the cobalt(III) ion was studied by means of the pH titration. The isolated product should have a free-COOH group to be subjected to pH titration, which is well indicated in Fig. 2.

The IR spectrum of the complex exhibits a medium band at around  $1730 \text{ cm}^{-1}$  which is characteristic of the free -COOH group and a broad absorption band of the coordinate EDTRA ligand at  $1650 \text{ cm}^{-1}$  as shown in Fig. 3. The existence of the two absorptions typically associated with a EDTRA, namely, the C=O stretch which commonly occurs in the  $1730 \sim 1750$

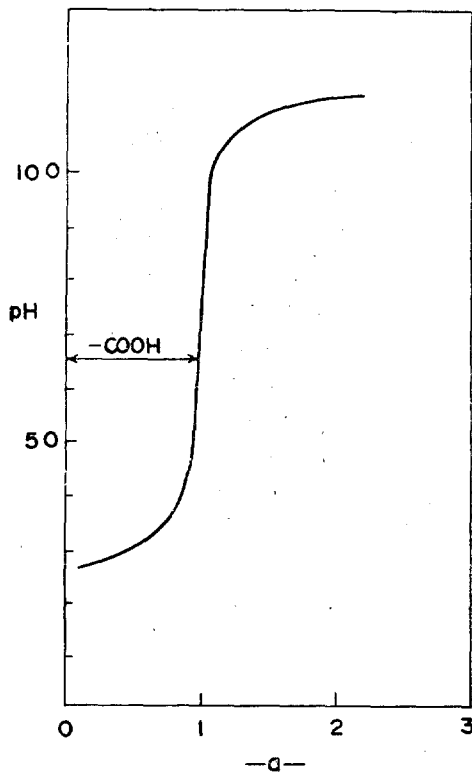


Fig. 2. pH Titration curve for the  $[\text{Co}(\text{tn})(\text{HEDTRA})]\text{Cl} \cdot 2\text{H}_2\text{O}$  complex. -a- is the equivalent weight of NaOH corresponding to the free -COOH group in HEDTRA.

$\text{cm}^{-1}$  region, and the band of the absorption at  $1650\text{ cm}^{-1}$  arising from the complexed carbonyl group appears through out the series of cobalt(III) complexes<sup>3,9</sup>. The presence of an uncoordinated carboxylic acid group by the IR spectrum is in good agreement with the pH titration results. Geometric isomers of the *cis* and *trans* are usually investigated by the electronic absorption spectra. In the present study, however, the *trans*(O—O)(1) and *trans*(O—O)(2) isomers or the *cis*(O—O)(1) and *cis*(O—O)(2) isomers (Fig. 1) are  $\text{N}_4\text{O}_2$  systems with the differences too subtle to be interpreted from the electronic absorption spectra.

The *cis*(O—O)(2) isomer has two acetate groups on the tertiary nitrogen coordinated *cis* to each other. Such coordination is difficult because of the distance of the coordinated oxygen of the acetate group<sup>6,10</sup>. In the cobalt(III) complexes with EDDA type and ethylenediamine ligand, the first absorption band indicates that the *cis* isomer has more symmetry than the *trans* isomer. The absorption spectrum of the complex prepared in this work has the characteristic feature of the *trans*(O—O) isomer, namely, a large split in the first band region (Fig. 4), similar to those of other cobalt(III) complexes<sup>11</sup>, which rules out the possibility of the *cis*(O—O)(1) configuration of the complex prepared. The *trans*(O—O)(2) isomer has two acetate groups coordinated *trans* to each other on a tertiary nitrogen. Such a form was reported in the  $[\text{Co}(\text{NO}_2)(\text{R-PDTRA})]^-$  complex<sup>12</sup> (R-PDTRA=R-1,2-propanediamine-triacetate ion) and the  $[\text{Co}(\text{en})(\text{R-H}_2\text{PDTA})]^+$  complex<sup>3</sup> (R-PDTA=R-1,2-propanediamine-tetraacetate ion). In the complex with ethylenediamine-triacetate ligand, however, such coordination is difficult because of the interaction between the free acetate group and the coordinated out-of-plane acetate groups. Furthermore, even though the

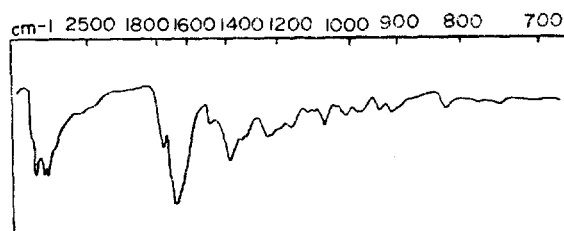


Fig. 3. IR spectrum of the  $[\text{Co}(\text{tn})(\text{HEDTRA})]\text{Cl}\cdot 2\text{H}_2\text{O}$  complex in KBr disk.

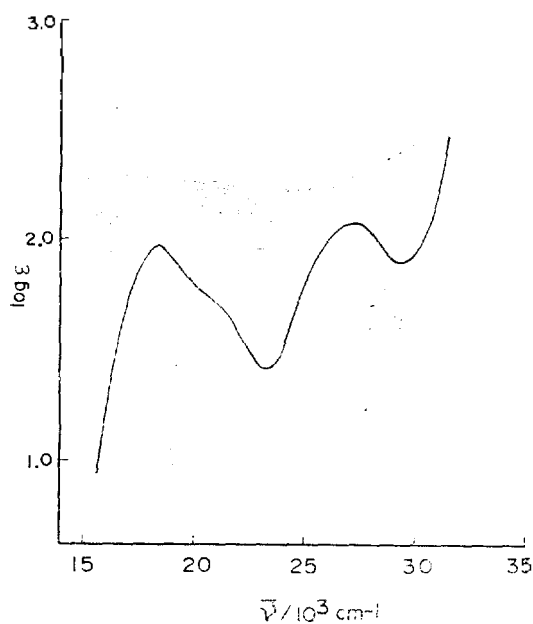


Fig. 4. UV absorption spectrum of the  $[\text{Co}(\text{tn})(\text{HEDTRA})]^+$  complex in water.

*trans*(O—O)(2) isomer can be formed with EDTRA, it is readily converted to the *trans*(O—O)(1) form.<sup>4</sup> Therefore, the complex prepared is thought to have the *trans*(O—O)(1) configuration.

The NMR spectroscopic study was utilized to elucidate the structure further. The nitro cobalt(III) complex of R-1,2-propanediamine-triacetate shows two AB acetate protons with 18Hz coupling constant of the acetate group in the out-of-plane position in the case of *trans*(O—O)(1) isomer, while the *trans*(O—O)(2) isomer shows two AB acetate protons with 17.0 and

16.0 Hz coupling constants of the acetate group in the out of-plane position<sup>12</sup>.

The 100 MHz NMR spectrum of the red complex obtained in this work (Fig. 5) exhibits two AB patterns due to the acetate protons with coupling constants of 18.0 Hz. The protons of the free acetate, the ethylenediamine-triacetate, and the trimethylenediamine are in an overlapping state. This type of spectra have been observed for the compounds with similar acetate rings of cobalt(III) complexes<sup>3</sup>. In [Co(EDTA)] and its related complexes, it is reported that the magnitude of the geminal coupling constant for the in-plane acetate protons is about 16 Hz,

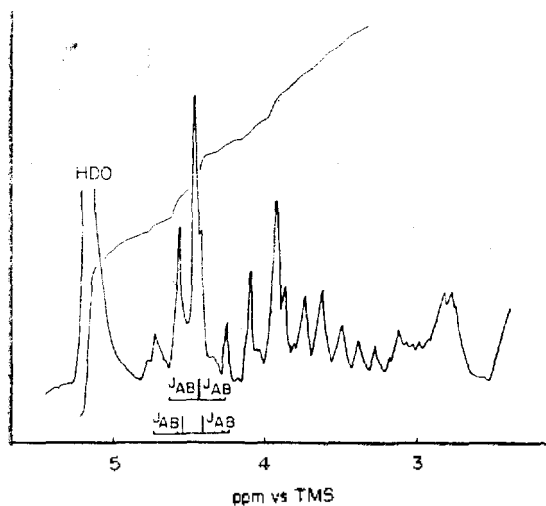


Fig. 5. NMR spectrum (100 MHz) of the [Co(m)-(HEDTRA)]<sup>+</sup> complex in D<sub>2</sub>O. The TMS denotes sodium 3-(trimethylsilyl)-1-propane-sulfonate

while that for the out-of-plane acetate protons is about 18 Hz<sup>3</sup>. Therefore, this NMR study and other data obtained lead to the conclusion that the red complex prepared in this work has the *trans* (O—O) (1) structure.

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