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전이금속착물의 구조와 그 반응성 (I). 암민류를 포함하는 Ethylenediamine-triacetatocobalt(III) 착물의 합성과 기하이성질현상

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Structure and Chemical Reactivity of the Transition Metal Complexes (I). Synthesis and Geometrical Isomerism of the Ethylenediamine-triacetatocobalt(III) Complexes with Ammine or Diamines

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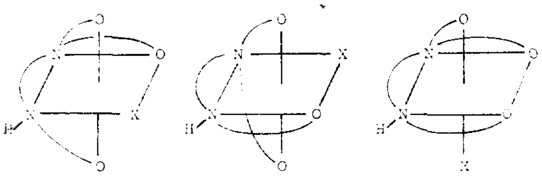
요 약. 한자리 리간드로써 암민, 에틸렌디아민, 트리메틸렌디아민 등을 포함하는 ethylenediamine-triacetatocobalt (III) 착물을 합성하고, Dowex 50W-X8, 수소이온형 양이온교환수지를 사용하여 각각 한 종류의 이성질체를 분리하였으며, 원소분석, pH 적정, 적외선분광법, 핵자기공명 및 전자흡수스펙트럼으로 가능한 기하이성질체중에서 *cis*-equatorial 형이라고 추정하였다. 여러자리 리간드를 동시에 포함하는 meridional 형의 $[CoN_3O_3]$계에서 나타난 제 1 흡수띠는 크게 분열된 양상을 보여주었고, 에틸렌디아민, 트리메틸렌디아민 등이 코발트(III) 이온에 한자리 리간드로 배위되었다는 사실도 확인하게 되었다.

ABSTRACT. Ethylenediamine-triacetatocobalt (III) complexes with an ammine, an ethylenediamine, and a trimethylenediamine as the unidentate ligand were prepared, and were isolated as only one isomer for each case by the Dowex 50W-X8, cation exchange resin in H^+ form. The geometrical isomer of these complexes have been assigned *cis*-equatorial form in the three possible geometrical isomers from the elemental analysis, pH titration, IR, NMR, and electronic absorption spectrum. It was found that the $[CoN_3O_3]$ system of the meridional form with multidentate ligand have the first absorption band of the largely splitting pattern, and that the diamines (ethylenediamine, trimethylenediamine) have coordinated to the central cobalt(III) ion as a unidentate ligand.

INTRODUCTION

When a pentadentate ligand such as ethylenediamine-triacetate(EDTRA) forms a cobalt(III) complex together with a unidentate ligand(X) in the sixth position, there are three possible geometrical isomers which are described as *cis*-equatorial, *trans*-equatorial, and *cis*-polar, depending on the coordination of unidentate ligand(X) and acetate ring in the EDTRA as shown in *Fig.* 1. Blackmer *et al.*[1] first prepared only one isomer in the three possible geometrical isomers of the cobalt (III) complexes with EDTRA and unidentate(X), [Co(EDTRA)(X)]



cis-equatorial trans-equatorial cis-polar

Fig. 1. Three possible geometric isomers of [Co(EDTRA)X] complex.

($X=Cl^-$, NO_2^-, H_2O). Sudmeier[2] *et al* have disclosed that structure of these complexes exists as *cis*-equatorial isomer by the NMR spectra which have the three different AB acetate patterns in the EDTRA. Bell and Blacker[3] were also confirmed that K[Co(EDTRA)(NO_2)] complex has a similar structure by the X-ray analysis. On the other hand, a similar type to *trans*-equatorial form have been reported in the K[Co(R-PDTRA)(NO_2)][4] and [Co(R-H_2PDTA)(en)] Cl[5] complexes.

In the present study, three new cobalt (III) complexes of the [CoN_3O_3] type containing a pentadentate EDTRA and an ammine, an ethylenediamine and a trimethylenediamine as the unidentate ligand were prepared to determine geometrical structure by the electronic absorption spectra. [Co(EDTRA)(X)] ($X=NH_3$, enH^+, tnH^+) have obtained only one isomer in the three possible geometrical isomers. The compositions of these complexes have been determined by the elemental analysis, and the geometrical structure of this isomer have been assigned on the base of pH titration, and IR NMR, and electronic absorption spectra.

EXPERIMENTAL

Ammine ethylenediamine-triacetatocobalt(III), [Co(EDTRA)(NH_3)] $0.5H_2O$

Sodium ethylenediamine-triacetate (Na_3EDTRA) solution which was prepared by a method similar to N-methyl-ethylenediamine-triacetate[6] was treated with 46.0g(0.1 mol) of [Co$(NH_3)_5$$H_2O$] $(ClO_4)_3$[7] in 100m*l* of water. This solution was reacted at 70°C for 6 hrs to remove the excess ammonia. This solution was filtered, and the reddish violet filtrate was diluted with water to 4 *l* and then acidified (pH=5) with concentrated HCl. The reddish violet solution was passed through a column of Dowex 50W-X8, cation exchange resin in H^+ form and then through a column of Dowex 1-X8, anion exchange resin in Cl^- form again to obtain the neutral complex, [Co(EDTRA)(NH_3)]. The reddish violet effluent with Cl^- was evaported to almost dryness by rotary evaporator under reduced pressure at 50°C. The residue was again dissolved in 100m*l* of water, and treated with silver oxide to remove chloride ion. Silver chloride was filtered, and the filtrate was evaporated to a small volume. This solution was poured carefully on a column (3×6cm) of Dowex 50W-X8, cation exchange resin in H^+ form, and then eluted with water. Elution with water gave only one band. This effluent was obtained to reddish violet crystal by evaporation under reduced pressure below 40°C, and the product was recrystallized from a small volume of water. It was dried in a vacuum desiccator over P_2O_5 and NaOH. Anal. Found: Reddish violet complex; C, 30.35; H, 4.28; N, 13.44 %, Calcd for [Co(EDTRA)(NH_3)] $0.5H_2O$ ($C_8H_{15}N_3O_{6.5}Co$) C, 30.39; H, 4.78; N, 13.29 %, yield 15 % (4.7g)

Hydrogen-ethylenediamine ethylenediamine-triacetatocobalt(III) chloride, [Co(EDTRA)(en-H)] Cl 1.5 HCl.

Ethylenediamine(3.6g, 6×10^{-2}mol) was added to 12.3g(4×10^{-2}mol) of [Co(EDTRA)(H_2O)][1] in 100m*l* of DMSO solution. This solution was reacted at room temperature for 12 hrs. This reddish violet solution was diluted with water to 1*l*, and then acidified to pH 2～3 with concentrated HCl. This solution was passed through a column of Dowex 50W-X 8, cation exchange resin in H^+ form to obtain the univalent complex. This column was washed with water, and then the adsorbed band was eluted with 0.3 M HCl. We obtained reddsh violet effluent of univalent complex except the other complexes. The reddish violet effluent was poured carefully on a Dowex 50W-X8, cation exchange resin in H^+ form again. This column was separated into the three bands, reddish violet, red, and red by elution with 0.15M HCl. The first effluent of reddish violet was concentrated until an oily residue. We obtained the reddish violet complex by addition of an ethanol to this oily residue. It can be considered that the red complexes in the other bands have [Co (HEDTRA) (en)] Cl and [Co(EDDA) (en)]$^+$ with bidentate ethylenediamiue[5]. Anal Found: Reddish violet complex, C, 27.30; H, 5.31; N, 12.53%, Calcd for [Co (EDTRA) (enH)]Cl 1.5HCl ($C_{10}H_{21.5}N_4O_6Cl_{2.5}Co$) C, 27.21; H, 4.91; N, 12.70 %, yield 10 % (4.49g).

Hydrogen-trimethylenediamine ethylenediamine-triacetatocobalt(III) chloride [Co(EDTRA) (tnH)]Cl HCl.

Although this complex was prepared by a method similar to that for [Co(EDTRA) (enH)] Cl, but we have not obtained the data of elemental analysis because of the strong absorptive power of water

Measurement. The titration curve was investigated by a Metrohm AG CH-9100 (switzerland) pH meter. The pH titration of the [Co(EDTRA) (enH)]Cl 1.5 HCl and [Co(EDTRA) (tnH)]Cl HCl with concentration of $5.00\times10^{-3}M$ and ionic strength of 0.10 ($NaClO_4$) was carried out by using a $0.05M$ NaOH solution mixed with $0.05M$ $NaClO_4$ at 25.0±0.1°C. Elemental analysis were performed by Perkin-Elmer Model 240. The infrared spectrum was obtained by using KBr disc method with a Perkin-Elmer 1330 infrared spectrophotometer. Visible and Ultraviolet absorption spectra were recorded with a Hitachi model 320 spectrophotometer. The NMR spectrum were measured with a Varian HA-100 spectrometer in a deuterium oxide solution containing sodium 3-(trimethylsily)-1-propane sulfonate (TMS) as the internal standard. All measurements were made at room temperature.

RESULTS AND DISCUSSION

Three new [CoN_3O_3] type complexes of the reddish violet containing both multidentate ethylenediamine-triacetate (EDTRA) and an ammine, an ethylenediamine, and a trimethylenediamine as the unidentate ligand have been prepared and isolated by the ion exchange resin (Dowex 50W-X8, H^+ form) column chromatography. The complexes obtained by this experiment were isolated only one isomer for each species. The analytical and spectral data indicate that the complexes have [Co(EDTRA) (NH_3)] $0.5H_2O$, [Co(EDTRA) (enH)]Cl 1.5 HCl and [Co(EDTRA) (tnH)]Cl HCl, respectively. The IR spectra (*Fig.* 2) of the obtained complexes exhibit a broad and strong intensity band at around 1650cm^{-1}. In general, the IR spectra of the EDTA-cobalt(III) complexes[8] have a broad and strong intensity band at around 1650 cm^{-1} which is characteristic band of the coordinated carboxlylate group in the EDTA. These complexes (*Fig.* 2) have no band which is characteristic peak of the uncoordinated-COOH in the EDTRA at around 1750cm^{-1}. Therefore, we are estimated that multidentate EDTRA in the complexes have been coordinated to cobalt (III) ion as the pentadentate ligand. pH titration curves (*Fig.* 3) of the [Co (EDTRA) (enH)]Cl 1.5 HCl and [Co(EDTRA) (tnH)]Cl HCl indicated that an ethylenediamine and a

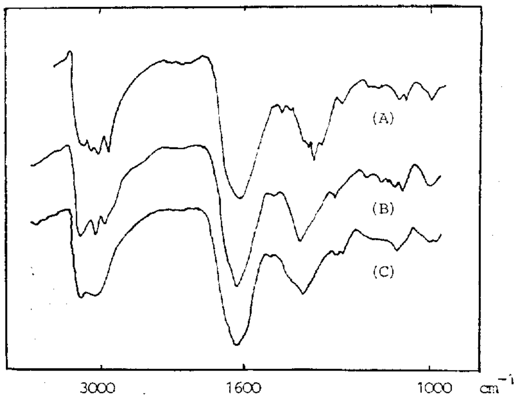


Fig. 2. IR spectra of the [Co(EDTRA)(NH_3)] 0.5H_2O (A), [Co(EDTRA)(enH)] Cl 1.5HCl(B) and [Co(EDTRA)(tnH)] Cl HCl (C).

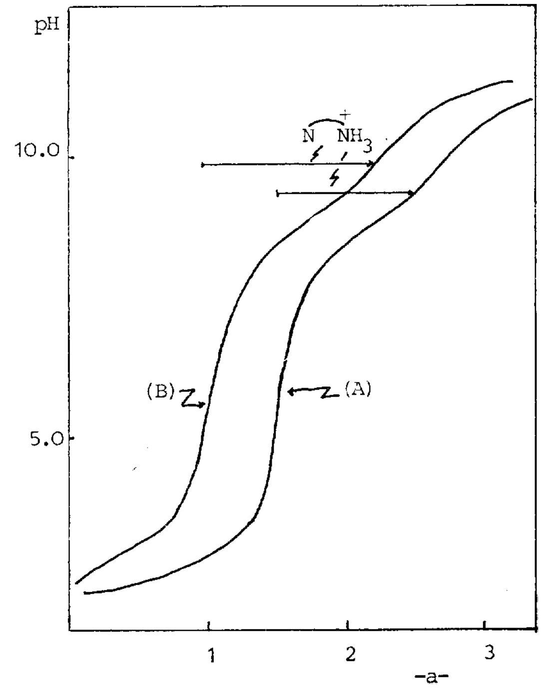


Fig. 3. pH titration curves of [Co(EDTRA) (enH)] Cl 1.5HCl (A) and [Co(EDTRA)(tnH)] Cl HCl (B). -a- is the equivalent weight of NaOH.

trimethylenediamine in the complex have been coordinated to the cobalt(III) ion as a unidentate ligand. The absence of an uncoordinated carboxylic acid in the complexes by the IR spectra is in good agreement with the pH titration result. From these results, it was found that the diamines (en, tn) have been coordinated to the cobalt(III) ion as a unidentate ligand. The similar cobalt(III) complexes containing an ethylenediamine as the unidentate ligand have been reported in the [Co(R-HPDTA)(enH)]Cl^5, [Co$(NH_3)_5$ (enH)]$X_4{}^9$, and [CoCl$(en)_2$(enH)]$^{3+}$ [10]. These complexes belong to [CoN_3O_3] system with respect to the configuration of the nitrogen and oxygen atom in the EDTRA and a nitrogen atom of the unidentate ammine, ethylenediamine, and trimethylenediamine. These complexes belong to only one isomer in the three possible geometrical isomers of the [Co(EDTRA)(X)] type (*Fig.* 1). The purpose of this work is to find out the coordination mode of EDTRA to cobalt(III) ion and the geometrical isomerism of the [CoN_3O_3] system by the electronic absorption spectrum. *Fig.* 4 and *Table* 1 show the electronic absorption spectra of three obtained complexes. The first absorption band of these complexes showed similar pattern with a largely splitting. The geometrical configuration of these [CoN_3O_3] system have the facial and meridional form[11] as shown in *Fig.* 4. If the complexes of [CoN_3O_3] system with multidentate ligand have the meridonal form, the first absorption band of the complexes has been expected to cause a splitting or broading pattern[11]. The proposed absorption region (*Table* 2) of the first absorption band of the obtained [CoN_3O_3] system have been calculated by the Yamatera theory[11]. From these data, the geometrical isomer of the three obtained complexes can be assigned to meridional form. This assignment would be supported by the first absorption spectrum of the equatorial-skew-ammine N-methyl-TRDTRA-cobalt(III) complex with meridional form[12]. However, the geometrical isomers of the obtained complexes have *cis*-equatorial and *trans*-equatorial types

Table 1. Electronic absorption data of the complexes

Complex	Colour	Maximum position, nm ($\bar{\nu}/10^3\mathrm{cm}^{-1}$)	
		First band	Second band
$[\mathrm{Co(EDTRA)(NH_3)}]$	red violet	510(19.61)	370
$[\mathrm{Co(EDTRA)(enH)}]\mathrm{Cl}$	red violet	560^{sh} (17.68), 505(19.80)	375
$[\mathrm{Co(EDTRA)(tnH)}]\mathrm{Cl}$	red violet	560^{sh} (17.86), 500(20.00)	375
$[\mathrm{Co(EDTRA)(NO_2)}]^+$	red violet	584^{sh} (17.10), 492(20.30)	Ref. 1

^{sh} shoulder.

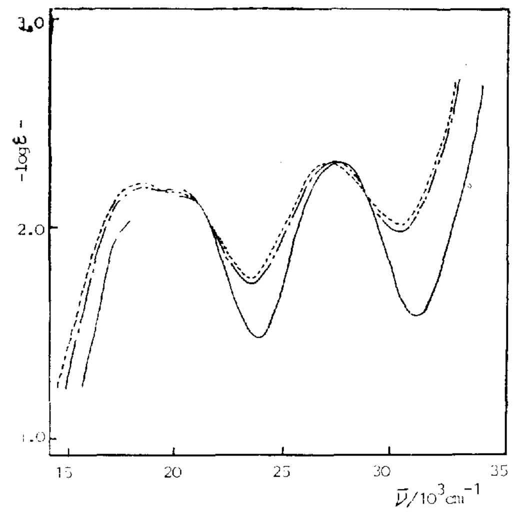


Fig. 4. Electronic absorption spectra of $[\mathrm{Co(EDTRA)(NH_3)}]$ (—), $[\mathrm{Co(EDTRA)(enH)}]\mathrm{Cl}$ (--) and $[\mathrm{Co(EDTRA)(tnH)}]$ Cl (---).

Table 2. Proposed absorption region of the first *d–d* absorption band in $[\mathrm{Co(EDTRA)(NH_3)}]$

(N, N, X)		Meridional type	Facial type
		(+X, +Z, −X)	(+X, +Z, +Y)
first *d–d* band	$d_{xy} \longrightarrow d_{x^2-y^2}$	$\frac{1}{4}(\mathrm{N})+\frac{1}{4}(\mathrm{X})$	$\frac{1}{4}(\mathrm{N})+\frac{1}{4}(\mathrm{X})$
	$d_{yz} \longrightarrow d_{y^2-z^2}$	$\frac{1}{4}(\mathrm{N})$	$\frac{1}{4}(\mathrm{N})+\frac{1}{4}(\mathrm{X})$
	$d_{zx} \longrightarrow d_{z^2-x^2}$	$\frac{1}{2}(\mathrm{N})+\frac{1}{4}(\mathrm{X})$	$\frac{1}{2}(\mathrm{N})$
$\mathrm{X=NH_3}$		18.9cm^{-1} 17.8 20.1	18.9cm^{-1} 19.0

$\delta=\delta_\sigma-\delta_\pi$ reference is $[\mathrm{Co(ox)_3}]^{3-}$ ($16.6\times10^3\mathrm{cm}^{-1}$).
$\delta(\mathrm{N})=4800\mathrm{cm}^{-1}$ at $[\mathrm{Co(en)_3}]^{3+}$ ($21.4\times10^3\mathrm{cm}^{-1}$).
$\delta(\mathrm{NH_3})=4400\mathrm{cm}^{-1}$ at $[\mathrm{Co(NH_3)_6}]^{3+}$($21.0\times10^3\mathrm{cm}^{-1}$).

as the meridional form. The difference between *cis*-and *trans*-equatorial type, although both are $[\mathrm{N_3O_3}]$ system, is too subtle to be interpreted from the only electronic absorption spectra. In this case, the *trans*-equatorial isomer has two acetate groups coordinated *trans* to each other on a tertiary nitrogen of EDTRA. A similar form to this was reported in the $\mathrm{K[Co(R\text{-}PDTRA)(NO_2)]}$[4] and $[\mathrm{Co(R\text{-}H_2PDTA)(en)}]\mathrm{Cl}$[5]. In the cobalt (III) complexes with EDTRA ligand, however, such coordination is difficult because of the change of conformation of the ethylenediamine moiety in EDTRA and bond direction of the acetate with *trans* in EDTRA. Furthermore, even though the *trans*-equatorial isomer can be formed with EDTRA, it is readily to the *cis*-equatorial form[4]. Therefore, these complexes are thought to have the *cis*-equatorial configuration. This assignment of the $[\mathrm{Co(EDTRA)(NH_3)}]$ complex has been supported by the NMR spectrum in *Fig*. 5. and *Table* 3. The NMR spectrum of $[\mathrm{Co(EDTRA)(NH_3)}]$ complex shows different acetate AB patterns with coupling constants, 16.0, 18.2, and singlet. In the $[\mathrm{Co(EDTA)}]$ and its related complexes[2], it was reported that the magnitude of the geminal coupling constant for the protons of the in-plane acetate of EDTA is about 16Hz, and that for the protons of the out-of plane of EDTA is about 18Hz or singlet. It was found that the geometrical isomer of the $[\mathrm{Co(EDTRA)(NH_3)}]$ has *cis*-equatorial form with two acetate ring of

Table 3. Chemical shifts (ν_A, ν_B in ppm) and coupling constants (J_{AB} in Hz) for acetate protons of [Co(EDTRA)(NH_3)] $0.5H_2O$ in D_2O (100 MHz)

Complex	out-of-plane			in-plane		
	J_{AB}	ν_A	ν_B	J_{AB}	ν_A	ν_B
[Co(EDTRA)(NH_3)]$0.5\ H_2O$	18.2	3.99	3.18	16.0	4.07	3.87
	singlet	4.08				

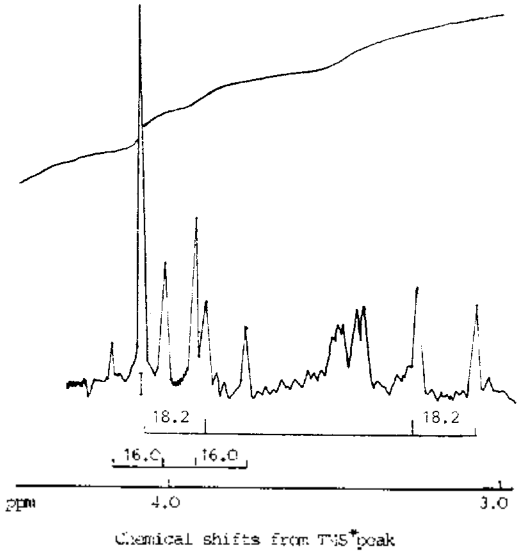


Fig. 5 NMR spectrum of Co(EDTRA)(NH_3) $0.5H_2O$ in D_2O Values: The coupling constants for acetate protons.

the out-of plane and a acetate ring of the in-plane in EDTRA by means of NMR spectral data. On the basis of the results described above, the three complexes of the [CoN_3O_3] system obtained in this work can be assigned to *cis*-equatorial form with meridional type from the chracterization of the electronic absorption spectra.

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