

## Ethylenediamine-N, N'-di-S- $\alpha$ -Propionic Acid 의 코발트 (III) 착물

田球鏞<sup>†</sup> · 朴潤燁 · 韓昌倫 · 崔承洛

연세대학교 이과대학 화학과

(1985. 1. 23 접수)

### Cobalt (III) Complex of Ethylenediamine-N, N'-di-S- $\alpha$ -Propionic Acid

Meo-Jin Jun<sup>†</sup>, Yoon Bong Park, Chang Yun Han,  
and Sung Rack Choi

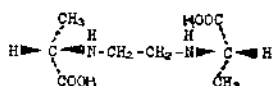
Department of Chemistry, Yonsei University, Seoul 120, Korea

(Received January 23, 1985)

**요 약.** 네자리 리간드인 ethylenediamine-N, N'-di-S- $\alpha$ -propionic acid(eddp)의 디클로르 코발트(III) 착물을 공기산화법에 의하여 합성하였다. eddp 리간드는 코발트(III) 이온에 매우 입체선택적으로 배위하여  $\Delta$ -S-*cis* 이성체만을 형성함이 관찰되었다. 합성된 착물의 구조는 원소분석, 적외선 분광분석법, 핵자기 공명 및 흡수스펙트럼으로 확인되었으며 특히 착물의 절대배열은 핵자기공명 스펙트럼으로 확인하였다.

**ABSTRACT.** Dichloro cobalt (III) complex of a flexible tetradentate ligand of ethylenediamine-N, N'-di-S- $\alpha$ -propionic acid (eddp) has been prepared via the air-oxidation technique. Only  $\Delta$ -*cis* isomer has been yielded showing high stereoselectivity of the eddp ligand. Elemental analysis, ir, nmr and electronic absorption spectra have been used to characterize the complex and the absolute configuration of the complex is assigned by means of the nmr spectroscopy.

Ethylenediamine-N, N'-di-S- $\alpha$ -propionic acid (SS-eddp), whose configuration is shown below, was first prepared by Liu and coworkers in 1968<sup>1</sup>.



SS-eddp ligand is a flexible tetradentate of  $N_2O_2$  system and can occupy four coordinate sites with three geometric isomers possible, *s-cis* (symmetric-*cis*), *uns-cis* (unsymmetric-*cis*), and *trans*. Both *s-cis* and *uns-cis* geometric isomers can have either  $\Delta$  or  $\Lambda$  absolute configuration and, therefore, there are five possible isomers in  $[Co(SS-eddp)_2]^{2+}$  type complexes as shown in

Fig. 1.

Liu and coworkers have prepared cobalt (III) complexes of SS-eddp,  $[Co(SS-eddp)L]^{2+}$  type complexes, where L is ethylenediamine (en), R-propylenediamine (R-Pn), or S-alanine (s-ala).<sup>1</sup> The  $[Co(SS-eddp)-(en)]^{2+}$  complex has yielded  $\Delta$ -*s-cis*,  $\Lambda$ -*s-cis*, and  $\Delta$ -*uns-cis*, and  $\Lambda$ -*uns-cis* isomers. No *trans* isomer has been yielded. Recently, rhodium(III) complexes of SS-eddp of the type  $[Rh(SS-eddp)L]^{2+}$  (L =  $Cl_2$ , en, R- or S-alanine, glycine) have been prepared.<sup>2-4</sup> The dichloro complex of  $[Rh(SS-eddp)Cl_2]^+$  has yielded only  $\Delta$ -*s-cis* and  $\Lambda$ -*uns-cis* isomers out of the possible five isomers

depicted in Fig. 1. The ethylenediamine rhodium (III) complex of SS-eddp has also yielded only  $\Delta$ -*s-cis* and  $\Lambda$ -*uns-cis* isomers.

The purpose of this work is to find out what isomers would be obtained in the dichloro cobalt (III) complex of SS-eddp. As mentioned earlier, the ethylenediamine cobalt(III) complex of SS-eddp has produced both  $\Lambda$ - and  $\Delta$ -*s-cis* isomers as well as  $\Delta$ -*uns-cis* isomers, while both dichloro and ethylenediamine rhodium(III) complexes have yielded only  $\Delta$ -*s-cis* and  $\Lambda$ -*s-cis* isomers. The dichloro cobalt(III) complex of SS-eddp has not been reported.<sup>5</sup> It will be shown that only one isomer,  $\Delta$ -*s-cis* isomer, has been yielded and proton magnetic resonance spectroscopy is mainly used to assign the absolute configuration of the dichloro cobalt(III) complex of SS-eddp.

### EXPERIMENTAL

Physical measurements. Electronic absorption spectra were obtained with a Shimadzu UV-240 spectrophotometer. Pmr spectra were recorded on Varian EM 360L spectrometer. Infrared spectra

were taken with a Shimadzu IR-435 spectrophotometer. Elemental analyses were performed by Micro-Tech Analytical Lab., Skokie, Illinois, U. S. A.

Ethylenediamine-N, N'-di-S- $\alpha$ -propionic acid (SS-EDDP). This was prepared by the method reported.<sup>1</sup> *Anal.* Calcd for  $C_8H_{16}N_2O_4$ ; C, 46.90; H, 7.89; N, 13.70. Found: C, 46.71; H, 7.76; N, 13.45.

Preparation of Hydrogen Dichloro (ethylenediamine-N, N'-di- $\alpha$ -propionato)cobaltate(III). In 35ml water, ethylenediamine-N, N'-di-S- $\alpha$ -propionic acid (1.02 g), sodium hydroxide (0.4g), and cobalt(II) chloride hexahydrate (1.15g) were added in this order. The brown solution was aerated with carbon-dioxide free air for 5 h. Eighty milliliters of concentrated hydrochloric acid were added to the oxidation product, and then the mixture was concentrated on a steam bath, with continuous stirring, to about 30ml. The color changed to a dark bluish green; at the same time a dark green precipitate appeared. After cooling, the precipitate was collected on a filter, and washed with concentrated hydrochloric acid, methanol, and ether. More of the green compound was obtained from the filtrated solution by adding small amount of conc-HCl and evaporating the solution. Yield, 0.45g. *Anal.* Calcd for H [Co(SS-EDDP)Cl<sub>2</sub>]·H<sub>2</sub>O; C, 27.37; H, 4.88; N, 7.98. Found: C, 27.39; H, 4.61; N, 8.05.

### RESULTS AND DISCUSSION

The pmr spectrum of SS-eddp ligand is shown in Fig. 2. The methyl protons are shown at 1.65 ppm as a doublet and the  $\alpha$ -carbon proton resonates at  $\delta$ 3.5 as a quartet. Fig. 3 shows infrared spectra of both SS-eddp ligand and dichloro cobalt (III) complex of SS-eddp. The free ionized carboxylate group in the ligand is shown at 1580cm<sup>-1</sup>, and the coordinated car-

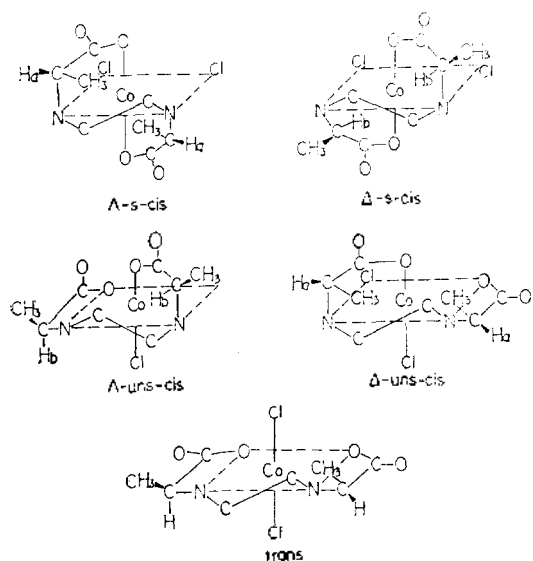


Fig. 1. Possible isomers of [Co(SS-eddp)Cl<sub>2</sub>].

boxylate at  $1620\text{cm}^{-1}$  in the complex.<sup>6</sup>

Only one isomer, *s-cis* isomer, has been yielded during the process of our preparation. Attempts to isolate other isomers including ion-exchange chromatography, if any, have been failed. In the electronic absorption spectrum of the complex (Fig. 4) the band I and band II, which are due to the d-d transitions in the octahedral  $\text{CoN}_2\text{O}_2\text{Cl}_2$  system, appear between 400~650nm. The shape of the first band is nearly symmetrical, indicating an *s-cis* isomer. If the complex has the *trans* configuration, a large split in the band I region should be observed.<sup>7-9</sup> If the complex has a *uns-cis* geometry, two atoms of the same kind (Cl-Cl, N-N, O-O) are at the *cis* positions, and a very intense absorption would be expected, since the ligand field around the central atom is highly unsymmetrical.

The pmr spectrum of the dichloro cobalt(III) complex of SS-eddp (Fig. 5) clearly indicates that the  $[\text{Co}(\text{SS-eddp})\text{Cl}_2]^-$  prepared in this work has an *s-cis* geometry. A single methyl (a) doublet is nicely shown at 1.6ppm and a single  $\text{CH}(\text{H}_b)$  quartet is clearly seen at  $\delta 3.5$

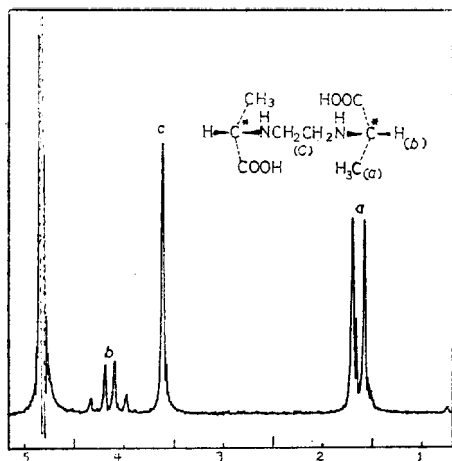


Fig. 2. 60-MHz H NMR spectrum of ethylenediamine-N,N'-di-S- $\alpha$ -propionic acid in  $\text{D}_2\text{O} + \text{HCl}$ .

ppm. If the complex is an *uns-cis* geometry, the same methyl (a) should show two doublets and the  $\text{CH}(\text{H}_b)$  proton should show two quartets, because the two carboxylate arms are not equivalent in the *uns-cis* geometry. An *s-cis* configuration is, therefore, assigned to the

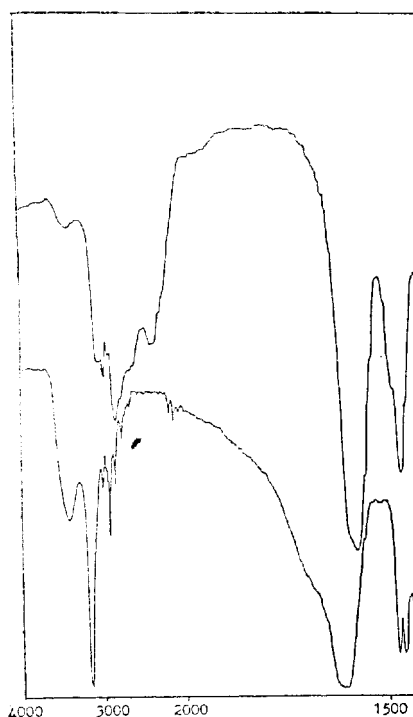


Fig. 3. Infrared absorption spectra of ethylenediamine-N,N'-di-S- $\alpha$ -propionic acid and  $\text{H}(\text{Co}(\text{SS-EDDP})\text{Cl}_2)\cdot\text{H}_2\text{O}$ .

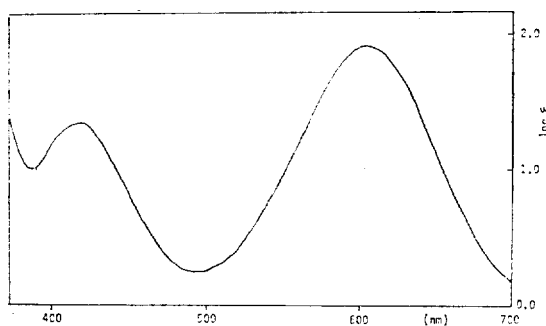


Fig. 4. Electronic absorption spectra of  $\text{H}(\text{Co}(\text{SS-EDDP})\text{Cl}_2)\cdot\text{H}_2\text{O}$ .

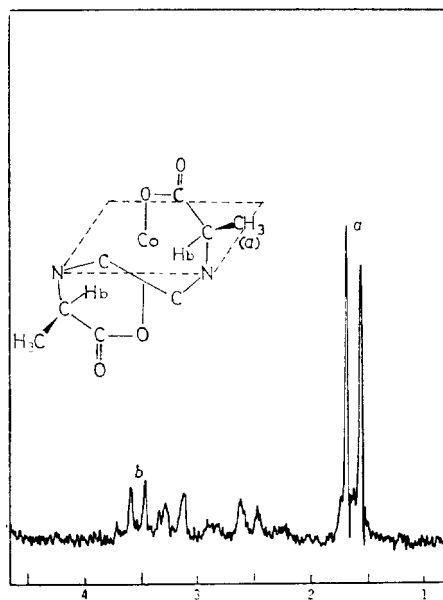


Fig. 5. 60-MHz  $^1\text{H}$  NMR spectrum of  $\Delta$ -*cis*- $\alpha$ -H  $[\text{Co}(\text{SS-EDDP}) \text{Cl}_2] \text{H}_2\text{O}$  in  $\text{D}_2\text{O}$ .

isomer obtained in this work.

Fig. 6. shows portions of the nmr spectra of *s-cis*- $[\text{Co}(\text{edda})(\text{en})]^+$ , *A-s-cis*- $[\text{Co}(\text{SS-eddp})(\text{en})]^+$ , *A-s-cis*- $[\text{Co}(\text{SS-eddp})(\text{en})]^+$ ,  $\Delta$ -*s-cis*- $[\text{Co}(\text{SS-eddp})(\text{en})]^+$ , and  $\Delta$ -*s-cis*- $[\text{Co}(\text{SS-eddp})\text{Cl}_2]^-$ , where edda is ethylenediaminediacetic acid. The chemical shifts of the protons of edda (labeled  $\text{H}_a$  and  $\text{H}_b$ ) can be distinguished because of the magnetic anisotropic shielding of the C-N bond.<sup>1,10,11</sup> The  $\text{H}_b$  protons are situated almost directly over the C-N bond of the ethylenediamine backbone ring and are shielded by it, while the  $\text{H}_a$  protons are not affected by this bond.<sup>10</sup> Thus, the  $\text{H}_a$  protons resonate at lower fields than the  $\text{H}_b$  protons.

On the basis of argument described above, the absolute configuration of the *s-cis* isomer of the complex obtained in this work can be assigned from the known absolute configuration of SS-eddp. Only an  $\text{H}_a$  proton signal is exhibited in *A-s-cis* isomer at about 4.0 ppm, while only an  $\text{H}_b$  proton signal in  $\Delta$ -*s-cis* isomer at

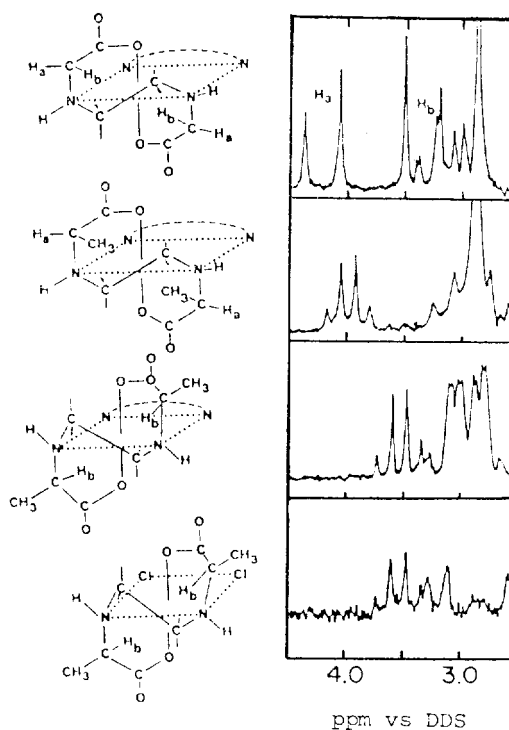


Fig. 6. 60 MHz  $^1\text{H}$  NMR spectra of (from top to bottom) *s-cis*- $[\text{Co}(\text{EDDA})(\text{en})]^+$ , *A-s-cis*- $[\text{Co}(\text{SS-EDDP})(\text{en})]^+$ ,  $\Delta$ -*s-cis*- $[\text{Co}(\text{SS-EDDP})(\text{en})]^+$ , and  $\Delta$ -*s-cis*- $[\text{Co}(\text{SS-EDDP})\text{Cl}_2]^-$ . Stereochemical representations are shown at the left.

about 3.5 ppm. The *s-cis*- $[\text{Co}(\text{SS-eddp})\text{Cl}_2]^-$  is showing only the  $\text{H}_b$  quartet at 3.5 ppm, and, therefore, a  $\Delta$  absolute configuration is assigned to this complex.

It is quite interesting to find out that only *s-cis* isomer has been yielded during the preparation of dichloro cobalt (III) complex of SS-eddp. In octahedral complexes of the type  $[\text{M}(\text{edda-type})(\text{L})_2]^{n+}$ , *s-cis* isomer is exclusively favored when L is a unidentate ligand, while *uns-cis* isomer is also formed in low yield when L is a bidentate ligand.<sup>5</sup> Octahedral complexes of  $[\text{Co}(\text{SS-eddp})(\text{L})]^{n+}$  have yielded both *s-cis* and *uns-cis* isomers when L is a bidentate ligand such as en and amino acid.<sup>1,5</sup> Dichloro cobalt(III) complex of SS-eddp prepared in this

work is so far the only octahedral complex of the type  $[\text{Co}(\text{SS-eddp})(\text{L})_2]^{3+}$  where L is a unidentate ligand, and, like complexes of eddatype ligands, *s-cis* isomer is turned out to be exclusively favored. Although non-bonding interaction has been cited for such preference for *s-cis* isomer<sup>5</sup>, it is not totally clear at this point why *s-cis* configuration is exclusively favored in the complexes of  $[\text{Co}(\text{SS-eddp})(\text{L})_2]^{3+}$ , when L is occupied by a unidentate ligand. More works are being done for this direction.

#### REFERENCES

1. L. N. Schoenberg, D. W. Cooke and C. F. Liu, *Inorg. Chem.*, **7**, 2386 (1968).
2. M. Sheridan, M. J. Jun, and C. F. Liu, *Inorg. Chem.*, **23**, 1485 (1984).
3. M. Sheridan, M. J. Jun and C. F. Liu, *Inorg. Chim. Acta*, **69**, 183 (1983).
4. M. Sheridan, M. J. Jun and, C. F. Liu, *Polyhedron*, **1**, 659 (1982).
5. D. J. Radanovic, *Coord. Chem. Reviews*, **54**, 159-261 (1984).
6. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," John Wiley and Sons., New York, 3rd Ed. 1978.
7. H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).
8. P. C. Harrington, S. Linke, and M. Alexander, *Inorg. Chem.*, **12**, 168 (1973).
9. V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **6**, 2168 (1967).
10. J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).
11. W. A. Freeman, *J. Coord. Chem.*, **7**, 197 (1978).