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N, N′-Dimethylethylenediamine-N, N′-di-α-butyric acid의 세자리 리간드 아미노산 코발트(III) 착물

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Trifunctional Amino Acid - Co(III) Complexes of N,N' - Dimethylethylenediamine -N,N' - di - a - butyric Acid

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요 약. N, N′-dimethyethylenediamine-N, N′-di-α-butyric acid(dmedba)와 세자리 아미노산과의 코발트(III) 착물인 [Co(dmedba)(*L*-aa)] (*L*-aa=S-methyl-*L*-cysteine, *L*-methionine, *L*-glutamic acid, *L*-aspartic acid)는 *s-cis*-[Co(dmedba)Cl_2]$^-$ 착물과 아미노산과의 반응으로부터 얻었다. 아미노산들은 [Co(dmedda)(*L*-dd)] 착물과 같이 아민과 카르복실그룹을 통하여 배위되었다. 이 착물들의 구조는 ^{1}H-NMR, IR, UV 스펙트럼 데이타와 원소분석으로 확인하였다.

ABSTRACT. Cobalt(III) complexes of N,N' - dimethylethylenediamine - N,N' - di - α - butyric acid (dmedba) and trifunctional aminoacids, [Co(dmedba)(*L* - aa)] (*L* - aa = S - methyl - *L* - cysteine, *L* - methionine, *L* - glutamic acid, *L* - aspartic acid) have been prepared from the reaction between the *s* - *cis* - [Co (dmedba) Cl_2]$^-$ complex and the amino acid. The amino acids have been found to coordinate through the amine and carboxylate groups just like [Co(dmedda)(*L* - aa)]. The complexes obtained in this work were characterized by their proton magnetic resonance, infrared and visible absorption spectral data along with the elemental analyses.

INTRODUCTION

Recently, cobalt(III) complexes of the N,N'-dimethylethylenediamine-N,N'-di-α butyrate (dmedba) have been obtained in the *s-cis* geometry only.[1] The flexible quadridentate dmedba is an ONNO type ligand like the ethylenediamine-N,N'-diacetate ion (edda) except that the former has both the C-ethyl and N-methyl substitution. The cobalt(III) complexes of dmedba have been obtained in the *s-cis* geometry only, while those of edda have been isolated in both geometries, *uns-cis* and *s-cis*.[2,3]

The trifunctional amino acids such as S-methyl-*L*-cysteine (*L*-smc), *L*-methionine (*L*-met), *L*-glutamic acid (*L*-glu), and *L*-aspartic acid (*L*-asp) have been of particular interest because only two of three functional groups present in those amino acids can bind to the cobalt(III) complexes of dmdba. In this work, we have undertaken to study the dmedba-cobalt(III) complexes of the trifunctional amino acids, [Co(dmedba) (*L*-aa)],

(*L*-aa=S-methyl-*L*-cysteine, *L*-methionine, *L*-glutamic acid, *L*-aspartic acid), to observe the mode of coordination resulting from the reaction between the $[Co(dmedba)Cl_2]^-$ complex and trifunctional amino acids.

The sulfur containing amino acids of S-methyl-*L*-cysteine and *L*-methionine are interesting ligands to study. They contain three donor atoms (nitrogen, oxygen and sulfur atoms), which will show different donor properties, for the nitrogen atom of the amino group and the oxygen atom of the carboxylate group are hard bases, while the sulfur atom of the thioether group is a soft base.

On the other hand, the *L*-glutamic acid and *L*-aspartic acid are also interesting ligands to study because they can form, when coordinated to a methal ion, either a five-of sis-membered chelate ring, and even a seven-membered chelate ring in the case of glutamic acid depending on the mode of coordination.

EXPERIMENTAL

Physical measurements. Electronic absorption spectra were obtained with a Hitachi U-3200 Spectrophotometer. ^{1}H-NMR spcetra were recorded on a Bruker AW-80 Spectrometer. Infrared spectra were taken with a Hitachi 270-30 Spectrophotometer. Elemental analyses were performed by Korea Advanced Institute of Science and Technology.

Praparation of *s-cis*-(S-methyl-*L*-cysteinato)(N,N'-dimethylethylenediamine-N,N'-di-α buthy-rato)cobalt(III), *s-cis*-[Co(dmedba)(*L*-smc)]. A solution containing 0.58g (1.5 mmol) of *s-cis*-$[Co(dmedba)Cl_2]^-$ in 30 m*l* of water was heated at 60°C for 20 min. To this solution was added a solution containing 0.20g (1.5 mmol) of S-methyl-*L*-cysteine in 10 m*l* of water. The pH of the solution was adjustd to 8.5 by addition of 1.0*N* NaOH aqueous solution. After 0.1g of activated charcoal was added to the solution, the mixture was mechanically stirred at 60@C for 8 h. The charcoal and insoluble matrial were removed by filtration and washed with hot water. The combined filtrate and washings were concentrated to ca. 5 m*l* with a rotary evaporator. The resulting violet solution was poured into a column containing cation-exchange resin (Dowex 50W-X4, 200-400 mesh, H^+ form). The mixture of products absorbed at the top of the column and pink impurities were eluted with water. Only one fraction was obtained, which was concentrated to a small volume when ethanol and ether were added to the solution. The resulting crystals were collected washed with ethanol, and then dried. Yield: 0.31g (48%) Anal.Calcd. for CoC_{16} $H_{30}O_6N_3S$: C,42.6; H,6.7; N,9.3 Found: C,42.8; H,6.8; N,9.2

Preparation of *s-cis*-(*L*-Methionine)(N,N'-dimethylenediamine-N,N'-di-α-butyrato)cobalt(III), *s-cis*-[Co(dmedba)(*L*-met]. This complex was prepared and separated into only one isomer *via* the same procedure as that used for [Co(dmedba)(*L*-smc)] using *L*-methionine in place of S-methyl-*L*-cysteine. the reaction solution was concentrated and chromatographed on an cation-exchange column. The complex was eluted with distilled water. The substance was concentrated to a small volume, and to this solution was added ethanol and ether. The resulting crystals were collected, washed with ethanol, and then dried. Yield: 0.073g (10%) Anal. Calcd. for $CoC_{17\ 32}$ O_6N_3S: C, 43.9; H, 6.9; N, 9.0 Found: C, 43.5; H, 6.8; N, 9.1

Preparation of *s-cis*-(*L*-Hydrogen glutamato) (N,N'-dimethylethylenediamine-N,N'-di-α-butyrato)cobalt(III), *s-cis*-[Co(dmedba)(*L*-asp)]. The complex was prepared in the same way as that used ffor [Co(dmedba)(*L*-smc)] using *L*- glutamic acid. Yield: 0.12g (17%) Anal. Calcd. for CoC_{17} $H_{30}O_8N_3 \cdot 3H_2O$: C, 39.5; H, 6.9; N, 8.1 Found: C, 39.5; H, 6.7; N, 8.2

Preparation of *s-cis*-(*L*-Hydrogen aspartato)(N,N'-dimethylethylenediamine-N,N'-di-

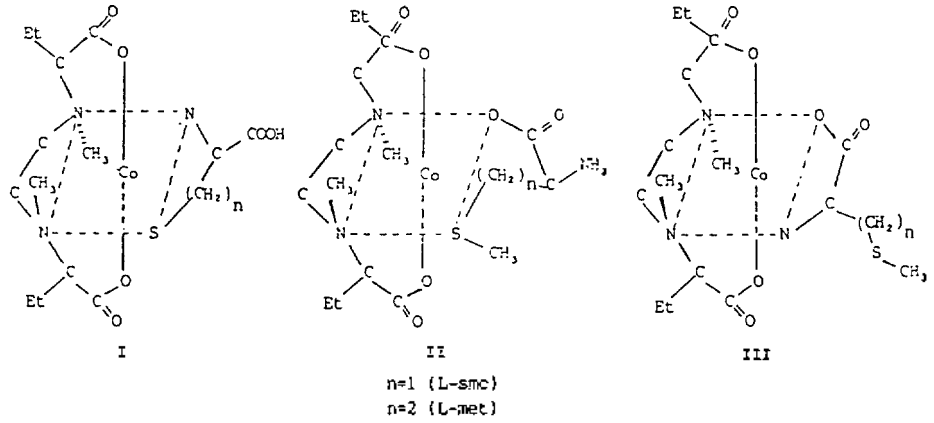

Fig. 1. The geometrical isomers of [Co(dmedba)(L aa)] where aa is s methyl L cysteine and L methionine.

butyrato) cobalt(III), *s-cis*-[Co(dmedba) (*L*-sap)]. The complex was prepared in the same way as that used for [Co(dmedba)(*L*-smc)] using *L*-aspartic acid. Yield: 0.19g(28%) Anal. Calcd. for $CoC_{16}H_{28}O_8N_3 \cdot {}_2O$: C, 41.1; H, 6.4; N, 9.0 Found: C, 41.5; H, 6.3; N, 8.9

RESULTS AND DISCUSSION

The trifunctional amino acid cobalt(III) complexes of dmedba have been prepared from the reaction between the *s-cis*-$[Co(dmedba)Cl_2]^-$ complex and one of the amino acids used here, S-methyl-*L*-cysteine, *L*-methionine, *L*-glutamic acid, or *L*-aspartic acid.

In the system [Co(dmedba)(*L*-aa)] (*L*-aa = S-methyl-*L*-cysteine, *L*-methionine) there are three geometrical isomers which result from different modes of coordination of the amino acid, each capable for existing in diastereomeric pairs as shown in *Fig.* 1: N,S chelation (I), S,O chelation (II), and N,O chelation (III). Infrared spectra of both *s-cis*-[Co(dmedba)(*L*-smc)] and s-cis-[Co (dmedba)(*L*-met)] (*Table* 1) show a cordinated-COO at 1650 cm^{-1} indicating the fact that the complexes prepared in this work rules out structure I.[9]

The electronic absorption spectra are particularly helpful in distinguishing the coordinating donor atoms of N,O, and S. The visible spectra of

Table 1. The COO stretching frequencies of the cobalt (III) complexes (in cm^{-1})

Compound	(C=O)[a]	(C-O)[a]
Dmeda	1600	1410
$[Co(dmedba)Cl_2]^-$	1645	1380
[Co(dmedba)(L asp)]	1720[b], 1650	1375
[Co(dmedba)(L glu)]	1720[b], 1650	1378
[Co(dmedba)(L smc)]	1650	1370
[Co(dmedba)(L met)]	1650	1370

[a]These correspond to $_aCOO^-$ and $_sCOO^-$ of the symmetrical COO group. [b]Uncoordinated COOH stretching band.

Table 2. Electronic absorption spectral data for aqueous solution of the cobalt(III) complexes

Compound	absorption maxima nm (, M^{-1} cm^{-1})
$[Co(dmedba)Cl_2]^-$	588(81), 412(53)
[Co(dmedba)(L asp)]	545(101), 385(119)
[Co(dmedba)(L glu)]	545(108), 384(132)
[Co(dmedba)(L smc)]	546(95), 375(149)
[Co(dmedba)(L met)]	542(64), 366(154)

[Co(dmedba)(*L*-aa)] complexes are shown in *Fig.* 2. and all of the spectral data are summarized in *Table* 2. The band I and II, which are due to the d-d transitions occure at 546 and 375 nm.[10] The band at longer wavelength is assigned to the transition $^1A_{1g} \longrightarrow {}^1T_{1g}$, and the one at shorter wavelength to $^1A_{1g} \longrightarrow {}^1T_{2g}$. If an S atom is coordinated, the visible spectra of both $[CoCN_3\ O_2S]$

Table 3. Resonance frequency assignment from the ^1H NMR of coblat(III) complexes

Compound	N-CH_3 (ppm)	v
dmedba	2.20	
[Co(dmedba)(L asp)]	2.26 2.52	0.26
[Co(dmedba)(L glu)]	2.26 2.52	0.26
[Co(dmedba)(L smc)]	2.25 2.50	0.25
[Co(dmedba)(L met)]	2.25 2.50	0.25

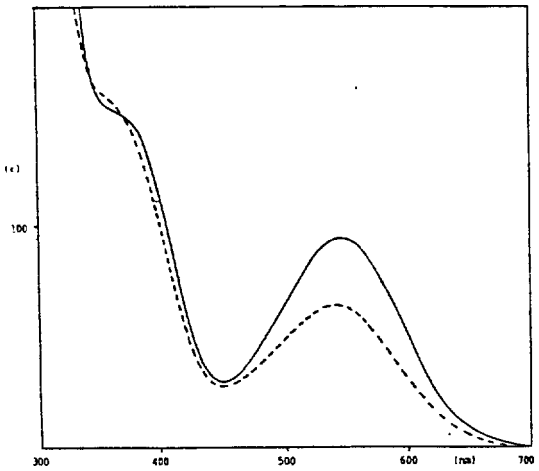

Fig. 2. Electronic absorption spectra of [Co (dmedba)(L smc)] (——) and [Co(dmedba)(L met)] (----).

and $[Co(N_3O_3S)]$ (structure I, II in *Fig.* 1) would have shown the band I at much longer wavelengths (~600 nm) than those observed in this work, reflecting the relative position of the groups in the spectrochemical series, $-S^- < amine < - Co_2^-$.[11,12] Therefore, structure I, II in *Fig.* 1. are elliminated, and in the [Co(dmedba)(*L-aa*)] complex the coordination of the S-methyl-cysteine and *L*-methionine ligand takes place through the amine and carboxylate groups (structure III).

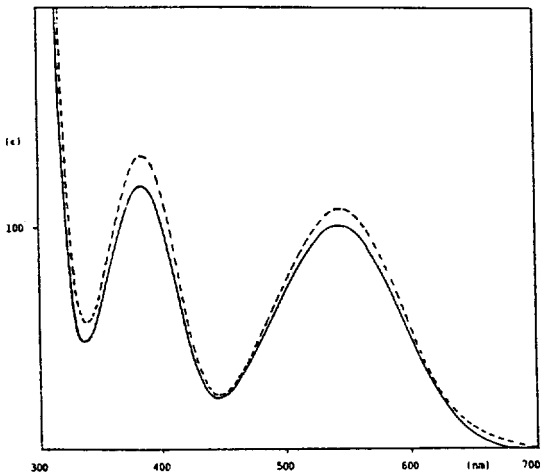

Fig. 3. The ^1H NMR spectrum of [Co (dmedba)(L smc)] in D_2O.

The fact that the [Co(dmedba)(*L*-aa)] (*L*-aa = S-methyl-*L*-cysteine, *L*-methionine) complexes prepared in this work have the structure III shown in the ^1H-NMR spectra of these complexes. The methyl protons at the sulfur atom are shown as a singlet at 1.8 ppm, and the single hydrogen on the α-carbon atom and two hydrogens on the α-carbon atom in the R ring are shown at 3.2-3.9 ppm. The methyl protons attached to the -carbon atoms are shown as a triplet at 0.9 ppm.

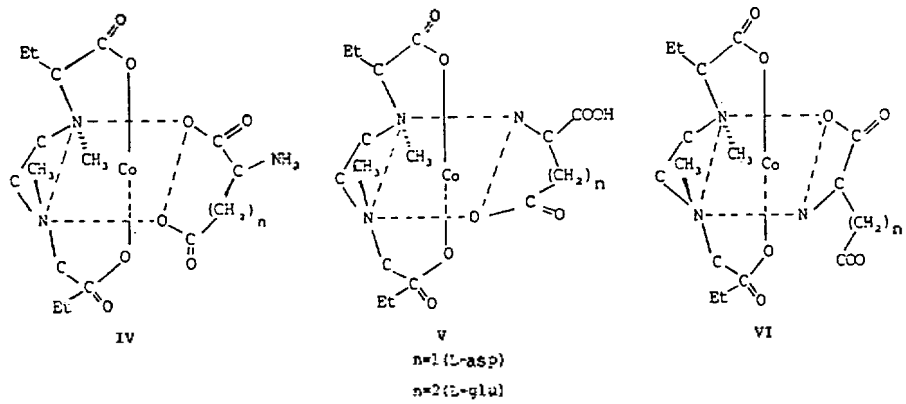

Fig. 4. The geomerical isomers of [Co(dmedba)(L aa)] where aa is aspartic or glutamic acid.

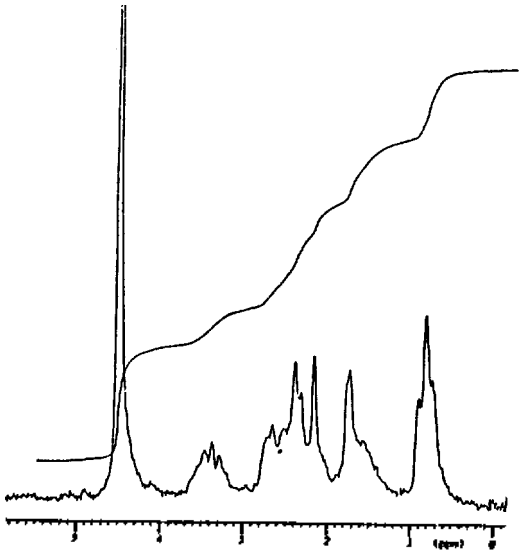

Fig. 5. Electronic absorption spectra of [Co (dmedba)(L asp)] (——) and [Co(dmedba)(L glu)] (---).

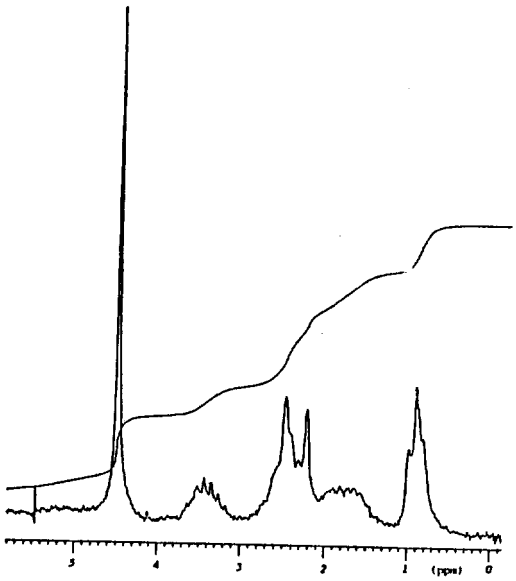

Fig. 6. The ^{1}H NMR spectrum of s cis [Co (dmedba)(L glu)] in D_2O.

In the *s-cis*-[Co(dmedba)(aa)] (aa = *L*-aspartic acid and *L*-glutamic acid) there are three possible geometrical isomers resulting from different modes of coordination of the amino acids (*Fig.* 4). Structure IV would not occur because of the excessively large chelate rings seven membered ring (*L*-asp) and eight membered ring (*L*-glu), and then infrared spectra of both complexes show an uncoordinated -COOH at 1720 cm^{-1} and a coordinated -COO at 1650 cm^{-1} indicating the fact that the complexes prepared in this work have either structure V or structure VI. The electronic absorption spectra are not helpful in distinguishing the structure V and VI because the two structures are the CoN_3O_3 type (*Fig.* 5).

^{1}H-NMR spectrum of the complexes give strong evidence for the existence of a five-membered chelating in the complex (structure VI). In the ^{1}H-NMR spectrum of [Co(dmedba)(*L*-glu)] (*Fig.* 6) the methyl protons at the nitrogen donor atoms show two peaks between 2.26 and 2.52 ppm. The occurrence of two bands is probably due to nonequivalent chemical environment of the two N-methyl protons. The similarity in the chemical shift of the N-methyl protons in the complexes of *L*-glutamic acid, *L*-aspartic acid, S- methyl-*L*-cysteine, and *L*-methionine may result from the protons being in the same chemical environment in these complexes as would be expected if the complexes have a five-membered chelate ring. Our assignment that *s-cis*-[Co (dmedba)(*L*-asp)] and *s-cis*-[Co(dmedba)(*L*-glu)] have structure VI is substantiated by the observation that the glutamic and aspartic acids are coordinated exclusively *via* the fivemembered glycinate ring in the [Co(tmdda)(*L*-aa)] and [Co(dmedda) (*L*-aa)] complexes. (*L*-aa = *L-glu, L-asp*).[13~15]

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REFERENCE

1. J. S. Jung, C. H. Kim and M. J. Jun, *polyhedron.*, 7, 529 (1988).

2. M. Mori, M. Shibata, E. Kyuno and F. Maruyama, *Bull. Chem. Soc. Jpn.*, **35**, 75 (1962).
3. K. Kuroda and K. Watanabe, *ibid.*, **44**, 2520 (1971)
4. K. Kuroda, *Chem. Lett.*, 197 (1972).
5. L. Halloran and J. I. Legg, *Inorg. Chem.*, **13**, 2193 (1974).
6. J. Daboroski and D. Cooke, *J. Am. Chem. Soc.*, **92**, 1097 (1970).
7. W. Jordan and J. I. Legg and J. Steele, *Inorg. Chem.*, **13**, 955 (1974).
8. P. F. Coleman, J. I. Legg and J. Steele, *ibid.*, **9**, 937 (1970).
9. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; John Wiley and Sons: New York, (1977).
10. B. E. Douglas, C. A. Hollingsworth, "Symmetry in Bonding and Structure an Introduction"; Academic Press: London, (1985).
11. J. E. Huheey, "Inorganic Chemistry"; Harper & Row: New York, (1983).
12. V. M. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969).
13. M. Okabayashi, K. Igi and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **52**, 753 (1979).
14. J. I. Legg and J. Steele, *Inorg. Chem.*, **10**, 2177 (1971).
15. J. S. Jung, C. Kim and M. J. Jun, *Inorg. Chim. Acta.*, **145**, 185 (1988).