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THE SIX GEOMETRICAL ISOMERS OF BIS(4-AMINO-2-AZA-BUTANECARBOXYLATO)COBALT(III) ION, $[Co(edma)_2]^+$

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All of the six geometrical isomers possible in $[Co(edma)_2]^+$ complex ion (edma: 4-amino-2-aza-butanecarboxylato or ethylenediaminemonoacetato) were isolated in crystal and the five racemates were resolved into optically active isomers by a column chromatographic method. The visible absorption, ^{13}C-NMR, and CD spectra were measured and the geometrical structures were assigned.

The bis(4-amino-2-aza-butanecarboxylato)cobalt(III) ($[Co(edma)_2]^+$) provides six geometrical isomers, as Fig. 1 shows. It is expected that this type complex presents useful informations to the studies of kinetics and stereochemistry of cobalt(III) complexes. However, there are no reports that all of the six isomers were isolated. Previously, Fujii et al.$^{1)}$ isolated two geometrical isomers of red and orange colors and assigned them to trans(O) and cis(O), respectively, but they did not identify which of the six possible isomers shown in Fig. 1. Igi and Douglas$^{2)}$ proved by optical resolution that the structure of the red isomer is C_2-trans(O). In the present letter, we will describe the preparation and structural assignments for the six isomers of the title complex.

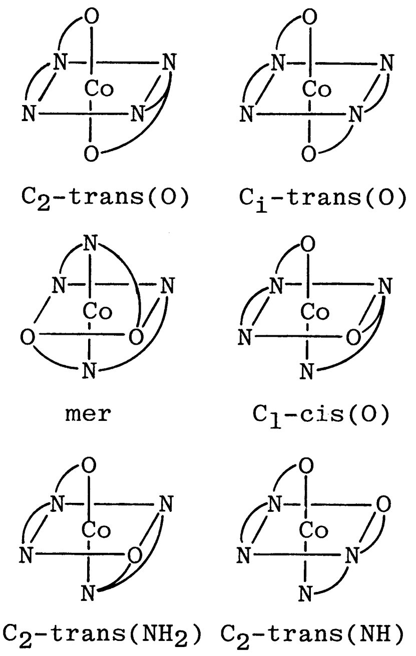
C_2-trans(O) C_i-trans(O)
mer C_1-cis(O)
C_2-trans(NH_2) C_2-trans(NH)

Fig. 1. Possible Structures of $[Co(edma)_2]^+$ Ion.

The six geometrical isomers of $[Co(edma)_2]X$ complex were prepared by the following method. To a suspension of $Na_3[Co(CO_3)_3]\cdot 3H_2O^{3)}$ (3.62 g, 0.01 mol) in 60 cm^3 of warm water (50°C), 4.54 g (0.02 mol) of 4-amino-2-aza-butanecarboxylic acid dihydrochloride dihydrate ($Hedma\cdot 2HCl\cdot 2H_2O$)$^{1)}$ was gradually added with stirring. The suspended matter dissolved with evolution of CO_2 gas. The solution was kept in a water bath (60°C) for 30 min with stirring. After cooled to room temperature, the solution was charged on the top of a SP-Sephadex column (4.7 cm × 50 cm, K^+ form) and the column was flushed with water to elute out neutral and anionic complexes. A red-orange band was transfered to another SP-Sephadex column

(4.7 cm X 90 cm, K^+ form) using 0.1 mol·dm^{-3} KCl solution as an eluent. The band was separated into three bands of red-orange (el. 1), orange-red (el. 2), and pinkish-orange (el. 3) colors by two recycled developments on the same column. The eluate from el. 1 was concentrated under reduced pressure and then methanol was added to the concentrated solution. After removal of potassium chloride deposited, the solution was concentrated again. Orange crystals (E-2) obtained by adding methanol to the concentrated solution were recrystallized from hot water. To the filtrate of E-2 was added a large amount of methanol. Red crystals (E-1) deposited were filtered and recrystallized from hot water. The eluate from el. 2 containing three isomers (E-3, 4, and 5) was treated by the same procedure as described for el. 1 to remove an excess of potassium chloride. Red crystals (E-4) was obtained by adding methanol to the concentrated solution. Recrystallization was carried out from water by addition of methanol. The filtrate of E-4 was passed through a short column of QAE-Sephadex (Br^- form) to convert the chloride salt to the bromide one. The bromide solution was evaporated under reduced pressure. The E-3 and 5 isomers were obtained fractionally as brownish-orange and orange crystals, respectively, by adding methanol dropwise to the concentrated solution. These isomers were recrystallized from water by adding methanol. The E-6 isomer was obtained from el. 3 by the same way as described for E-2. Recrystallization was carried out from hot water. Elemental analyses of the six isomers are shown in Table 1.

Table 1. Elemental Analyses

Isomer		C, % Found(Calcd)	H, % Found(Calcd)	N, % Found(Calcd)
E-1	$[Co(edma)_2]Cl\cdot 2H_2O$	26.31(26.35)	6.05(6.08)	15.35(15.36)
E-2	$[Co(edma)_2]Cl\cdot 2H_2O$	26.14(26.35)	6.04(6.08)	15.34(15.36)
E-3	$[Co(edma)_2]Br$	25.54(25.75)	4.88(4.86)	14.80(15.01)
E-4	$[Co(edma)_2]Cl\cdot 2H_2O$	25.59(26.35)	5.98(6.08)	15.27(15.36)
E-5	$[Co(edma)_2]Br\cdot H_2O$	24.27(24.57)	5.03(5.15)	14.03(14.33)
E-6	$[Co(edma)_2]Cl\cdot H_2O$	27.70(27.72)	5.74(5.82)	16.17(16.16)

Optical resolutions of the racemic complexes except for E-2 (achiral complex) were carried out by the following method. An aqueous solution containing a racemate was poured into a SP-Sephadex column (K^+ form). The adsorbed band was chromatographed using 0.1 mol·dm^{-3} K_2Sb_2(d-tart)$_2$ solution as an eluent. After the band had been separated completely into two, the eluent was replaced by 0.1 mol·dm^{-3} KCl or KBr solution. The optically active isomer was obtained as a chloride or bromide salt by treating each eluate with the same way as used in the case of the racemate. Similarly, an examination of optical resolution was performed for E-2, but no optical active isomer was obtainable.

It is known that the first absorption band of a trans(O)-$[Co(O)_2(N)_4]$ type complex shows a more marked split than that of the corresponding cis(O)-isomer.4) As Fig. 2a shows, the splitting bands are observed for E-1 (red isomer) and E-2 (orange isomer). These observations suggest that both the isomers belong to a trans(O) type complex. However, two configurations are possible for the trans(O) type complex; chiral configuration of C_2-trans(O) and achiral configuration of C_i-trans(O) (Fig. 1). As described above, only the E-1 isomer was optically resolved. Therefore, we can conclude that the structures of the E-1 and 2 isomers are C_2-trans(O) and C_i-trans(O), respectively. This assignment to red isomer (E-1) quite agrees with that reported by Igi and Douglas.[2)]

The E-3, 4, 5, and 6 isomers did not show such marked split in the first absorption band as the E-1 and 2 isomers did (Fig. 2a and 2b). Accordingly, it is suitable to assign the former isomers to cis(O).

The structure of E-3 can be assigned to mer on the basis of the following observations. The molar absorption coefficient of E-3 is much larger than those of other cis(O) isomers.[5)] The ^{13}C-NMR shifts of the NH_2-CH_2- and -CH_2-NH-CH_2- carbons in E-3 are located at lower and higher magnetic fields, respectively, than those of other cis(O) isomer (Table 2). A similar shift behavior has been observed for the bis and mixed ligand complexes containing ida and dien; the -CH_2-NH-CH_2- carbon resonances of ida and dien meridionally coordinated to cobalt(III) are located at higher field than those of ida and dien facially coordinated.[6,7)]

It is apparent from ^{13}C-NMR data that E-4 has the C_1-cis(O) structure, because the two edma ligands in E-4 exhibit nonequivalent resonance pattern (Table 2).

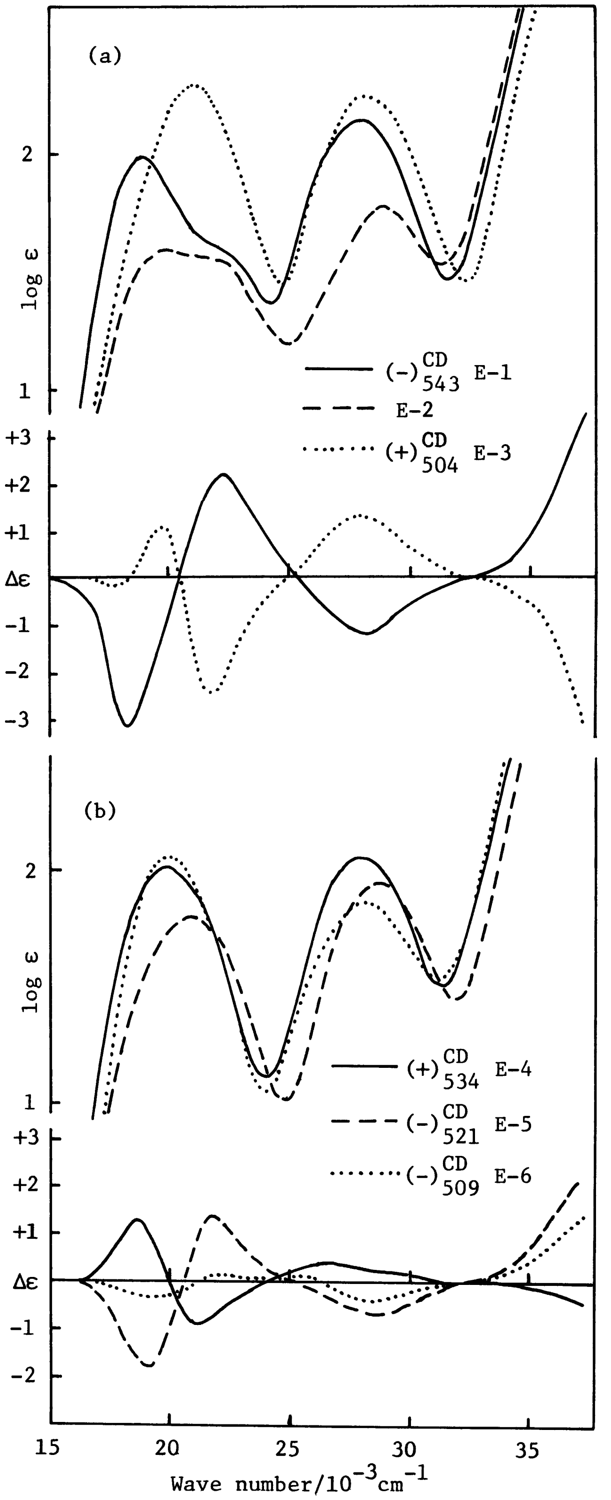

Fig. 2. Absorption and CD Spectra of $[Co(edma)_2]^+$ Ions.

Recently, Juranic et al.[8)] investigated the influence of magnetic anisotropy of cobalt(III) ion on ^{1}H and ^{13}C chemical shifts of the glycinato ligand in the

[Co(ox)$_x$(gly)$_y$(en)$_z$] series complexes. They pointed out that the trans influence on chemical shifts is more pronounced when different ligators are facing the glycinato ligand, and that the ^{13}C chemical shifts of the α- and carboxyl-carbons of glycinato ligand are moved toward a lower field when oxygen is in the trans position in relation to the field when nitrogen is in the trans position. If the above rule is applied to the present edma complexes, the structural assignments to E-5 and 6 are possible. As shown in Table 2, the ^{13}C chemical shift (δ = 43.37) of the NH$_2$-CH$_2$- carbon in E-5 is located at lower field than that (δ = 40.79) in E-6. The low field shift in E-5 can be attributed to the carboxyl-oxygen in the trans position to the NH$_2$ group. According to this consideration, the structures of E-5 and 6 are tentatively assigned to C$_2$-trans(NH) and C$_2$-trans(NH$_2$), respectively.

Table 2. ^{13}C-NMR Chemical Shift$^{a)}$ (ppm) of Six Isomers

Isomer	NH_2-$\underline{C}H_2$---	---$\underline{C}H_2$-NH-$\underline{C}H_2$---	---$\underline{C}OO^-$
E-1	41.76	55.36	185.61
		56.28	
E-2	42.25	55.50	185.42
		56.58	
E-3	47.51	52.48	184.73
		54.04	
E-4	40.59	55.99	184.30
	43.52	57.16	185.65
		57.16$^{b)}$	
		57.79	
E-5	43.37	55.36	185.71
		57.16	
E-6	40.79	56.53	184.44
		58.53	

a) Chemical shifts were measured relative to dioxane (internal standard, δ = 67.40 (CH$_3$)$_4$Si) in D$_2$O solution. (b) Overlapped signal.

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