The Preparation and Absorption Spectra of the Geometrical Isomers of Carbonatoglycinatodiamminecobalt(III)[1]

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Three geometrical isomers of the $[CoCO_3(gly)(NH_3)_2]$ complex, the *mer*(*cis*-diammine)-, *mer*(*trans*-diammine)-, and *fac*-isomers, have been isolated from a reaction mixture of the *cis*-$[Co(CO_3)_2(NH_3)_2]^-$ ion with glycine by means of a study of the solubility difference and by means of ion-exchange chromatography. These isomers have been characterized by the absorption spectra, the PMR spectra, and the infrared spectra. The absorption spectrum of the *mer*(*trans*)-isomer is of special interest, and there is a clear shoulder in the second absorption band region which may be due to the splitting of the second band.

Recently there has been interest in the absolute configurations of the *tris*(α-amino-acid) complexes of cobalt(III)[2–5] and also their stereoselectivities.[4,6,7] In preparing such complexes, it has been recognized that the method using the tricarbonatocobaltate(III) anion as the starting material is of use in the preparation of possible isomers for a *tris*(α-amino-acid) complex.[3,4,7,8] In the present work we undertook to use the dicarbonatodiamminecobaltate(III) anion[9,10] in the preparation of the carbonatoglycinatodiamminecobalt(III) complex. This complex, like the *tris*(amino-acid) complexes, belongs to the general type of $[CoN_3O_3]$ and is expected to have three geometrical isomers, two of *mer* and one of *fac*. We succeeded in obtaining the three isomers from a reaction mixture of the starting material with glycine by studying the solubility difference and by ion-exchange chromatography. The isomers obtained were characterized mainly by the electronic absorption and proton magnetic resonance spectra. By the way, the corresponding ethylenediamine complexes of the [Cogly(chelate)en] type (the chelate represents CO_3^{2-}, $C_2O_4^{2-}$ or the malonate ion) have already been synthesized by Matsuoka *et al.*[11]

Experimental

Preparation. In a solution of 4 g (0.015 mol) of potassium *cis*-dicarbonatodiamminecobaltate(III)[9,10] in 10 m*l* of water, an equimolar amount (1.2 g) of glycine was dissolved. The mixture was then stirred at room temperature for 10—12 hr. During this reaction, a considerable amount of fine red crystals were precipitated. The crystals were collected by filtration and recrystallized from water containing a small amount of potassium bicarbonate. A portion of the filtrate was added to a cation-exchange column containing 100—200 mesh Dowex 50W×8 resin in the sodium form (diameter, 4.5 cm; resin height, 25 cm). When water was passed through the column at a rate of about 10 m*l*/min, four red-violet bands appeared. The first band consisted of negatively-charge complexes, such as $[Co(CO_3)_2(NH_3)_2]^-$ and $[CoCO_3(gly)_2]^-$. The other three bands were isomers of the desired complex; hence, they were collected in three fractions. The fractions were conveniently numbered Nos. 1—3 in the descending order of the bands. This chromatographic separation was repeated several times in order to treat all the reacted solution. Each fraction was then concentrated to a small volume under reduced pressure at about 40°C. When a small amount of ethanol was added to the concentrate and the whole was kept in a refrigerator for one day, the desired material was precipitated. Recrystallization was done from water containing a small amount of potassium bicarbonate. The compound which had precipitated during the process of reaction was identical with that obtained from the No. 2 fraction, and the former by far exceeded the latter in yield (1 g for the former, and 0.2 g for the latter). For the other compounds, the yields were 0.4 g from the No. 1 fraction and and 0.6 g from the No. 2 fraction.

Found for the complex from No. 1: C, 14.65; H, 4.82; N, 17.12. Calcd for $[CoCO_3(C_2H_4NO_2)(NH_3)_2]\cdot H_2O$: C, 14.70; H, 4.90; N, 17.15%.

Found for the complex from No. 2: C, 13.96; H, 4.94; N, 15.96. Calcd for $[CoCO_3(C_2H_4NO_2)(NH_3)_2]\cdot 2H_2O$: C, 13.70; H, 5.30; N, 15.97%.

Found for the complex from No. 3: C, 14.60; H, 4.51; N, 17.25. Calcd for $[CoCO_3(C_2H_4NO_2)(NH_3)_2]\cdot H_2O$: C, 14.70; H, 4.90; N, 17.15%.

Measurements. The absorption spectra were usually measured with a Hitachi EPU-2A spectrophotometer, but sometimes with a Cary-14 spectrophotometer by way of precaution. The infrared spectra were measured as KBr disks with a Jasco DS-301 spectrometer (4000—700 cm^{-1}) and also with a Hitachi EDI spectrometer (700—250 cm^{-1}). The proton magnetic resonance (PMR) spectra were recorded on a JEOL C-60H spectrometer operating at 60 Mc/sec. The spectra were measured in deuterated trifluoroacetic acid, using tetramethylsilane as the internal standard. The molar conductivity was measured with a Universal Bridge BV-Z-12A, using a 5×10^{-3}M aqueous solution. The absorption spectra of a single crystal were measured through the good offices of Professor Y. Kondo of Rikkyo University.

Results and Discussion

Although the chromatographic behavior described in the experimental section was evidence for the non-

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[1] Presented in part at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.
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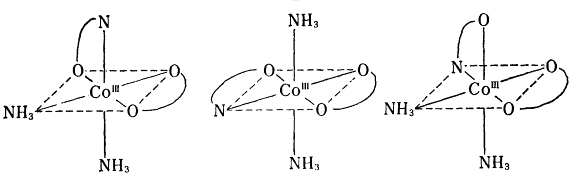
[11] N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 1257 (1966).

charged species, the molar conductivities of the isomers gave additional proof of the fact. The molar conductivity values were 6 for the isomer from the No. 1 fraction, 8 for that from No. 2 fraction, and 10 mho cm^{-1} for that from the No. 3 fraction.

Three possible geometrical isomers for the present complex are shown in Fig. 1. The first one has two NH_3 groups in the *cis* position and three N (or O) atoms in the *cis-trans* positions (a); the second one has two NH_3 in the *trans* position and three N atoms in the *cis-trans* positions (b), and the third one has two NH_3 in the *cis* position and three N atoms in the *cis-cis* positions (c). Hereafter, these will be represented as the *mer*(*cis*)-, *mer*(*trans*)-, and *fac*-isomers respectively. Furthermore, the three isomers will also be represented as No. 1, No. 2, and No. 3 isomers according to the fraction number. In order to assign these possible structures to the isolated isomers, the data from the absorption, PMR, and IR spectra were used.



(a) *mer*(*cis*) (b) *mer*(*trans*) (c) *fac*

Fig. 1. Possible isomers.

Absorption Spectra. The absorption spectra of the three isomers in aqueous solutions containing potassium bicarbonate are shown in Fig. 2. The spectrum of the No. 3 isomer shows the first absorption band (ν_1) at 56.2×10^{13} sec^{-1} (log ε=2.04) and the second band (ν_2) at 80.1×10^{13} sec^{-1} (log ε=2.13). These values are very similar to those for the known *fac*(N)-[$CoCO_3$-(gly)en][11] (ν_1=56.6 (2.17), ν_2=80.4 (2.13)). This fact indicates that the No. 3 isomer can be assigned to the *fac*-form. When the spectrum of the No. 1 isomer is compared with that of the known *mer*(N)-[$CoCO_3$-(gly)en],[11] the ν_1 and ν_2 values for the former are, in some extent, smaller than those for the latter; for the present isomer, ν_1=54.2 (2.03) and ν_2=79.5 (2.25); for comparison, ν_1=56.6 (2.07) and ν_2=81.1 (2.17). However, the spectrum is very similar to that of the familiar *mer*-[Co(gly)$_3$] isomer[12,13] and exhibits a lower intensity in the first band (half width=*ca.* 12.5×10^{13} sec^{-1}) than in the second band.[14] From these facts, the structure of this No. 1 isomer can be regarded as either one of the two *mer*-forms.

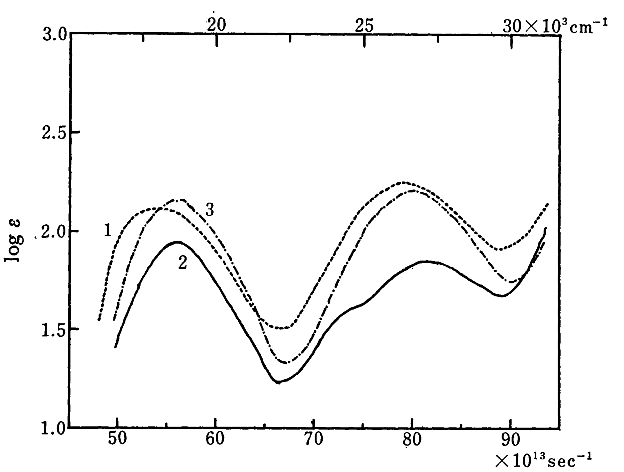


Fig. 2. Absorption spectra of the isomers in $KHCO_3$ aqueous solution.

1) *mer*(*cis*) ...... (No. 1)
2) *mer*(*trans*) —— (No. 2)
3) *fac*-isomer -·-·- (No. 3)

The absorption spectrum of the No. 2 isomer shows a shoulder in the second absorption band region (ν_1= 56.0 (1.93), sh=74.8 (1.6), ν_2=81.8 (1.85)). Apart from this shoulder, the isomer is regarded as another *mer*-from on the basis of the broadened first absorption band (half width=*ca.* 11.2×10^{13} sec^{-1}).

It is a very interesting fact that such a shoulder appears in the second absorption band region. Splittings of the first absorption band are widely observed in *mer*-isomers of the *tris*(amino-acid) complexes and also in *trans*-isomers of dihalogenotetraammine-type complexes, and can be understood with the aid of a ligand field theory, such as Yamatera's prediction.[15] The splitting of the second band has, however, never been observed in the solution spectra of cobalt(III) complexes,[16] although such splitting has been observed in the crystal spectra for some complexes of cobalt-(III).[17]

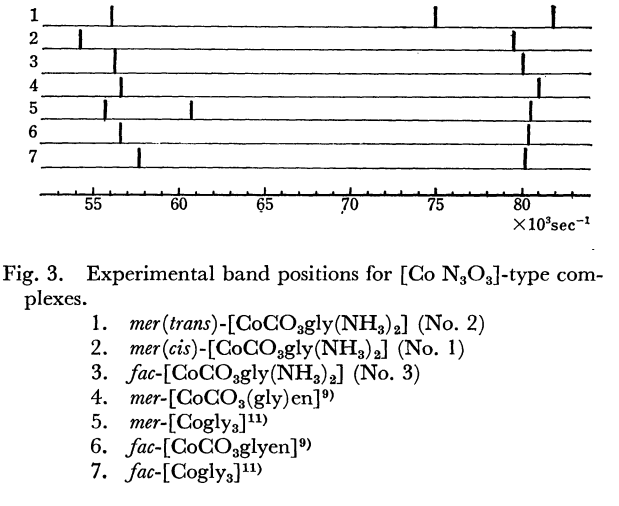


Fig. 3. Experimental band positions for [Co N_3O_3]-type complexes.

1. *mer*(*trans*)-[$CoCO_3$gly(NH_3)$_2$] (No. 2)
2. *mer*(*cis*)-[$CoCO_3$gly(NH_3)$_2$] (No. 1)
3. *fac*-[$CoCO_3$gly(NH_3)$_2$] (No. 3)
4. *mer*-[$CoCO_3$(gly)en][9]
5. *mer*-[Cogly$_3$][11]
6. *fac*-[$CoCO_3$glyen][9]
7. *fac*-[Cogly$_3$][11]

In Fig. 3 the experimental band positions for the present three and some related complexes are schematically represented. It seems to be unreasonable to regard the shoulder concerned as a component of the first band, because only a partial splitting or a braodened shape of the first band is observed in the other *mer*-isomers. When the second band maxima are compared among these isomers, it is noticed that the value (81.8) for the No. 2 isomer is considerably higher than those for the other isomers ($80—81 \times 10^{13}$ sec^{-1}).

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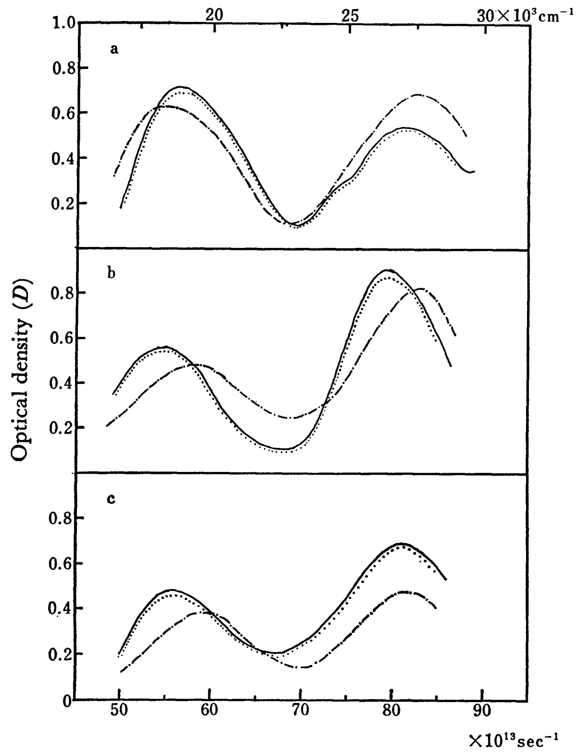

Fig. 4. Change of the spectra.
a) *mer*(*trans*)- b) *mer*(*cis*)- c) *fac*-isomer
Original soln. ——
Acidified soln. —·—
Alkalined soln. ······

Furthermore, the intensity of the ν_2 band (ε=70.5) is considerably smaller than that of the ν_1 band (ε=95.8). From these facts, we can now assume the splitting of the second band for this isomer.

When the absorption spectrum of a solution of the No. 2 isomer acidified with perchloric acid was measured (Fig. 4(a)), the above-mentioned shoulder disappeared and the ν_1 band was observed at a considerably longer wavelength (at 54.7×10^{13} sec^{-1}), contrary to expectations of the positions of the CO_3^{2-} and H_2O ligands in the spectrochemical series. When the acidified solution was again alkalined with a large amount of potassium bicarbonate, the spectrum of the resulting solution was identical with that of the original solution. The spectra for the acidified solutions of the other two isomers showed some shifts of the ν_1 bands to the shorter-wavelength side (Fig. 4(b) and (c)). The spectra for the solutions again alkalined returned to the same spectra as in the original solutions. These facts suggest a configuration retention of these isomers in the process of acid hydrolysis.

The absorption spectra of a single crystal for the No. 2 isomer are shown in Fig. 5. The dichroism of this complex is clearly observed in the first absorption band region. Both of the polarized lights are strongly absorbed in the second band region, but the relative intensities of the two maxima differ for the two directions of the light.

PMR Spectra. Because of the limited solubility of the present compounds in water and because of the instability of their aqueous solutions, the samples for the measurement were dissolved in deuterated trifluoroacetic acid. On the assumption of the configuration retention in the process of acid hydrolysis, the PMR spectra, which are shown in Fig. 6, will now be discussed.

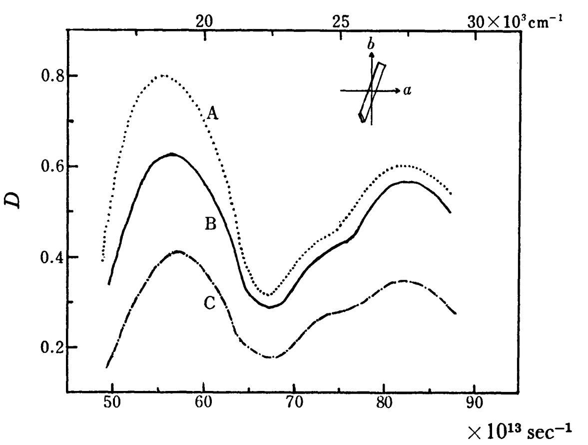

Fig. 5. Polarized single crystal spectra of *mer*(*trans*)-isomer.
A) along *a* axis ······
B) along *b* axis ($b\perp a$) —·—
C) nonpolarized light ——

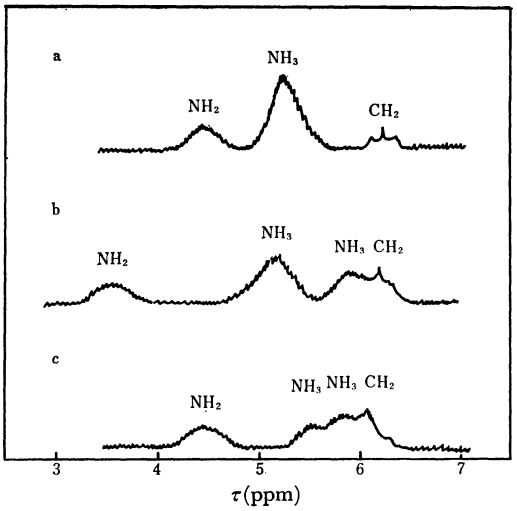

Fig. 6. PMR spectra on;
a) *mer*(*trans*)- b) *mer*(*cis*)- c) *fac*-isomer in CF_3COOD.

The spectrum on the No. 1 isomer shows two peaks due to the two NH_3 groups, at 5.1 and 5.8 ppm, and also a peak due to a NH_2 group of the chelated glycinate at 3.5 ppm (b). The integrated ratio of these three peaks is estimated to be 3:3:2, corresponding to the proton numbers concerned. This indicates the existence of two NH_3 groups in different environments; from this fact, this isomer can be identified as the *mer*(*cis*)-isomer. The spectrum on the No. 2 isomer shows two peaks, due to the NH_3 group and the NH_2 group, at 5.2 and 4.5 ppm respectively (a). From the area ratio of about 3:1, we can now judge this isomer to be the *mer*(*trans*) one. The spectrum of the No. 3 isomer exhibits one peak of the NH_2 protons at 4.6 ppm and one broad pattern at 5.7—6.4 ppm which may be resolved into three peaks due to the two different NH_3 groups and the one CH_2 group of the chelated glycinate (c). These results would seem to support the previous conclusion that this isomer is of the *fac*-form.

Infrared Absorption Spectra. The spectra of the present three isomers are shown in Fig. 7. It is clear that the carbonate ion in each isomer coordinates to central cobalt atom as a bidentate ligand, because of the presence of the characteristic sym. ν(C–O), asym. ν(C–O), and sym. ν(C=O) bands at about 1020, 1280, and 1600 cm^{-1} respectively.[18] It is also clear that the glycinate ion coordinates as a bidentate ligand, because of the presence of the band near 1600 cm^{-1} as well as the absence of the deformation band of the $-NH_3^+$ group near 1500 cm^{-1}.[19]

When the spectra in the 700—1400 cm^{-1} region are compared among the three isomers, the spectrum of the *mer*(*trans*)-isomer reveals the simplest pattern and all of the bands are attributable to the CH_2 and NH_2 waggings (1350—1300 cm^{-1}), the CH_2 twisting (1200—1180 cm^{-1}), and the NH_2 and CO_3 out-of-plane rockings (850—800 cm^{-1}). The infrared spectrum of a lower symmetry complex, in general, exhibits a more complicated pattern than that of the related higher-symmetry complex.[20,21] From this point of view, it can be said that the No. 2 isomer has a *trans* configuration with respect to the coordinated NH_3 groups, whereas the No. 1 isomer has a *cis* configuration.

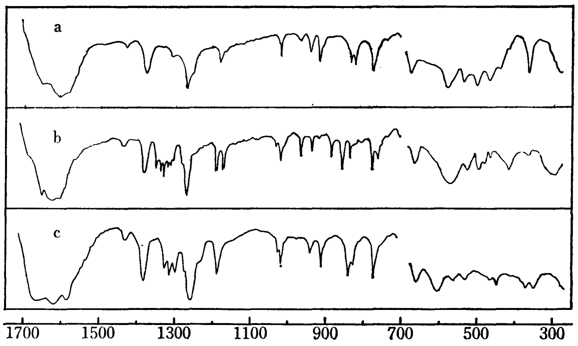

Fig. 7. Infrared spectra of;
a) *mer*(*trans*)- b) *mer*(*cis*)- c) *fac*-isomer.

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