3544 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3544—3548 (1972) [Vol. 45, No. 12

Characterization of the Geometrical Isomers of the Carbonato(or oxalato)-aminoacidatodiammine Complexes of Cobalt(III)[1]

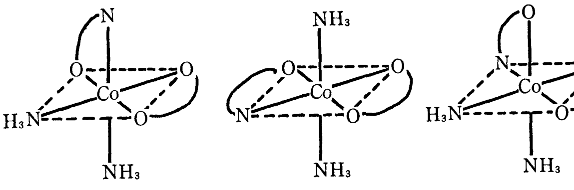
Kiyoshi Nakai, Shuji Kanazawa, and Muraji Shibata

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received April 12, 1972)

Three geometrical isomers of the $[CoCO_3(aa)(NH_3)_2]$-type complex (aa stands for the α-alaninate, β-alaninate or valinate ion)—the *mer(cis*-diammine)-, *mer(trans*-diammine)- and *fac*-isomers—have been prepared. Three similar isomers of the $[Co\ ox(gly)(NH_3)_2]$ and $[Co\ ox(\beta\text{-ala})(NH_3)_2]$ complexes have been obtained by reactions of the corresponding carbonato complexes with an oxalate. In addition, the corresponding three isomers of a related $[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$ complex have been prepared. The isomers thus obtained have been characterized by their absorption, PMR, and IR spectra. Of the *mer(trans)* isomers of the present complexes, those of the carbonato-α-alaninato and carbonatovalinato complexes revealed clear shoulders in their second absorption bands. Through the present study, some relationships between the appearance of such a shoulder in the *mer(trans*-diammine) isomer and the ring size of chelates have been deduced.

In a previous paper,[2] we reported that three possible geometrical isomers of the $[CoCO_3(gly)(NH_3)_2]$ complex could be isolated from a reaction mixture of the *cis*-$[Co(CO_3)_2(NH_3)_2]^-$ complex with glycine, and that an isomer characterized as the *mer(trans)* form showed an interesting absorption spectrum with a clear shoulder in the second absorption band. Here, *mer(trans)* represents the isomer which has two NH_3 groups in the *trans* positions and three N (or O) atoms in the *cis-trans* positions (Fig. 1).



mer-cis (NH_3) *mer-trans* (NH_3) *fac*

Fig. 1. Possible geometrical isomers.

The present work was first undertaken in order to obtain complexes by using α-alanine, valine, and β-alanine instead of the glycine used in the previous work. Then the work was proceeded in obtaining the related glycinatodiammine and β-alaninatodiammine complexes containing oxalate ion in place of the carbonate ion. In each preparation three geometrical isomers of a desired complex were obtained. In addition, three isomers of the $[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$ complex were obtained through the acid hydrolysis of each isomer of the corresponding carbonato complex.

As to the *mer(trans)* isomers, the absorption spectra of the carbonato-α-alaninato and carbonatovalinato complexes showed a shoulder such as that observed for the previous glycinato complex, while the spectra for the carbonato-β-alaninato, oxalatoglycinato, and oxalato-β-alaninato complexes revealed no shoulder. On the other hand, a shoulder was observed on the shorter-wave-length-side of the first band for the oxalato-β-alaninato and diaquoglycinato complexes.

Experimental

Preparation. The procedure for the preparation of the $[CoCO_3(aa)(NH_3)_2]$-type complexes (where aa stands for the α-alaninate, β-alaninate, or valinate ion) was essentially the same as that for the glycinato complex previously reported.[2] In that preparation of the glycinato complex, the *mer(trans)* isomer was precipitated during the reaction between the *cis*-$[Co(CO_3)_2(NH_3)_2]^-$ and glycine, while no precipitate was obtained in the present preparation. The reacted solution, therefore, was directly chromatographed in order to separate geometrical isomers of a desired complex.

The formation ratio among the three isomers for the carbonato complexes, *mer(cis)* : *mer(trans)* : *fac*, was determined spectrophotometrically with the fractions obtained in chromatographic separation. The results obtained were: 4.4 : 1.0 : 1.5 for the α-alaninato complex, 5.1 : 1.0 : 1.4 for the valinato complex, and 6.0 : 1.0 : 0.6 for the β-alaninato complex.

The $[Co\ ox(gly)(NH_3)_2]$ complex was prepared as follows. To a suspension of the *mer(trans)*-$[CoCO_3(gly)(NH_3)_2]$ complex (1.5 g, 0.005 mol) in water (20 m*l*), we added 60% perchloric acid (ca. 1 m*l*) under an iced condition; the mixture was then stirred for about 30 min under the same conditions in order to complete the acid hydrolysis. Then, potassium oxalate (2 g, 0.01 mol) was added to the solution, and it was neutralized with an aqueous solution of potassium hydroxide, whereby potassium perchlorate was precipitated. After the removal of the precipitates by filtration, the filtrate was stirred for 30 minutes at room temperature. The resulting solution was then chromatographed in the same manner as the carbonato complexes. During the addition of water to a column of Dowex 50W-X8 (Na-form), three bands were separated. After each band had been collected in a fraction, the fraction was concentrated and kept in a refrigerator. Very fine crystals were obtained from each concentrate.

The oxalato-β-alaninato complex could be obtained by a similar preparation, using the carbonato-β-alaninato complex as the starting material.

When an isomer of the carbonatoglycinato complex was treated with a saturated solution of oxalic acid, very fine crystals were deposited. This compound was the corresponding isomer of the $[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$ complex.

The results of the elemental analyses for the complexes obtained in the present work are given in Table 1.

Measurements. The absorption, infrared (IR), and

---

[1] Presented at the 26th Annual Meeting of the Chemical Society of Japan, April 3rd, 1972, Hiratsuka.

[2] S. Kanazawa and M. Shibata, This Bulletin, **48**, 2424 (1971).

Table 1. The analytical data of the present complexes

Compound	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
mer(cis)-[CoCO$_3$(α-ala)(NH$_3$)$_2$]·H$_2$O	18.09	18.54	5.28	5.45	16.09	16.22
mer(trans)-[CoCO$_3$(α-ala)(NH$_3$)$_2$]	20.36	19.93	5.00	5.00	16.83	17.43
fac-[CoCO$_3$(α-ala)(NH$_3$)$_2$]	19.73	19.93	4.94	5.00	17.16	17.43
mer(cis)-[CoCO$_3$(val)(NH$_3$)$_2$]	26.69	26.77	6.03	6.11	15.46	15.61
mer(trans)-[CoCO$_3$(val)(NH$_3$)$_2$]·0.5H$_2$O	25.85	25.90	5.71	6.17	17.16	17.43
fac-[CoCO$_3$(val)(NH$_3$)$_2$]	26.62	26.77	5.91	6.11	15.48	15.61
mer(cis)-[CoCO$_3$(β-ala)(NH$_3$)$_2$]	19.51	19.93	5.15	5.00	17.21	17.43
mer(trans)-[CoCO$_3$(β-ala)(NH$_3$)$_2$]·0.5H$_2$O	19.33	19.21	4.96	5.24	17.07	16.80
fac-[CoCO$_3$(β-ala)NH$_3$)$_2$]	19.67	19.93	5.09	5.00	17.84	17.43
mer(cis)-[Co ox(gly)(NH$_3$)$_2$]·2H$_2$O	16.63	16.50	4.51	4.86	14.35	14.44
mer(trans)-[Co ox(gly)(NH$_3$)$_2$]	18.84	18.83	4.05	3.96	16.55	16.48
fac-[Co ox(gly)(NH$_3$)$_2$]·H$_2$O	17.93	17.59	4.65	4.44	15.07	15.39
mer(cis)-[Co ox(β-ala)(NH$_3$)$_2$]	22.86	22.40	4.55	4.14	15.30	15.68
mer(trans)-[Co ox(β-ala)(NH$_3$)$_2$]·1.5H$_2$O	20.67	20.34	5.20	5.13	13.99	14.24
fac[Co ox(β-ala)(NH$_3$)$_2$]·1.5H$_2$O	20.57	20.34	5.00	5.13	14.26	14.24
mer(cis)-[Co(gly)(NH$_3$)$_2$(OH$_2$)$_2$]·C$_2$O$_4$	16.77	16.50	4.66	4.87	14.94	14.44
mer(trans)-[Co(gly)(NH$_3$)$_2$(OH$_2$)$_2$]·C$_2$O$_4$·0.5H$_2$C$_2$O$_4$	17.72	17.86	4.68	4.51	12.22	12.50
fac-[Co(gly)(NH$_3$)$_2$(OH$_2$)$_2$]·C$_2$O$_4$·0.5H$_2$C$_2$O$_4$	17.90	17.86	4.53	4.51	12.15	12.50

proton magnetic resonance (PMR) spectra were measured with the same instruments as were used in a previous work.[2] Since it had been reported in the previous paper that the geometrical configuration of an isomer of the carbonato complex was retained in the process of acid hydrolysis, the PMR spectra were measured in a mixture of D$_2$O and D$_2$SO$_4$ (1 : 1 v/v), using sodium 3-(trimethylsilyl)-propanesulfonate as the internal or external reference.

Results and Discussion

Characterization of Isomers. The absorption spectra of the three isomers for each complex are shown in Figs. 2—7, while the numerical data are listed in Table 2, in which the data for the known [CoCO$_3$(gly)(NH$_3$)$_2$] complex are also included for the sake of comparison.

In the cases of α-alaninato and valinato complexes, the isomers obtained from the first fractions in

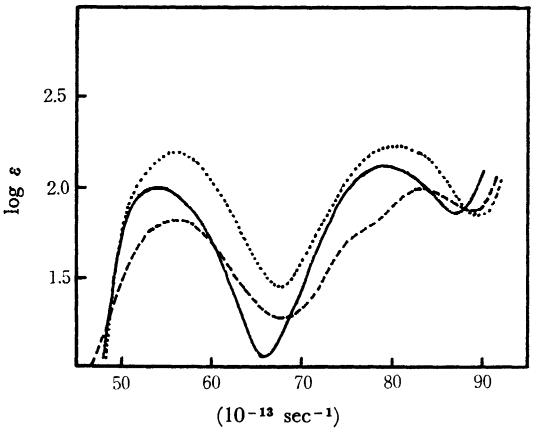


Fig. 2. Absorption spectra of the three isomers of the [Co(CO$_3$)(α-ala)(NH$_3$)$_2$] in KHCO$_3$ aq.
—— *mer(cis)*, ---- *mer(trans)*, ···· *fac*

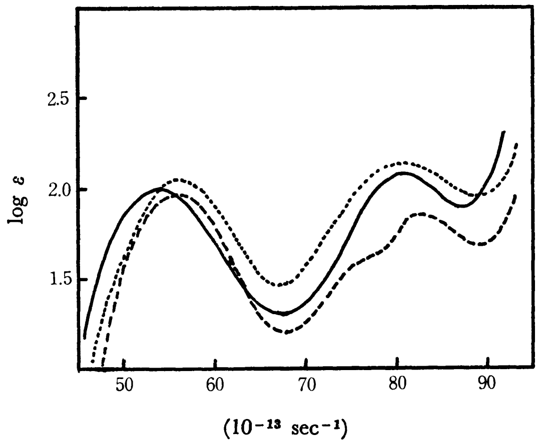


Fig. 3. Absorption spectra of the three isomers of the [Co(CO$_3$)(val)(NH$_3$)$_2$] in KHCO$_3$ aq.
—— *mer(cis)*, ---- *mer(trans)*, ···· *fac*

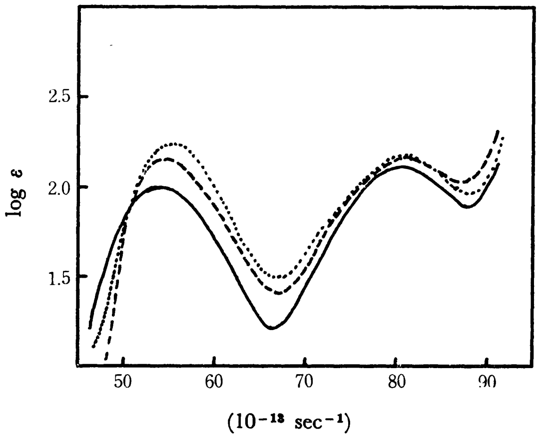


Fig. 4. Absorption spectra of the three isomers of the [Co(CO$_3$)(β-ala)(NH$_3$)$_2$] in KHCO$_3$ aq.
—— *mer(cis)*, ---- *mer(trans)*, ···· *fac*

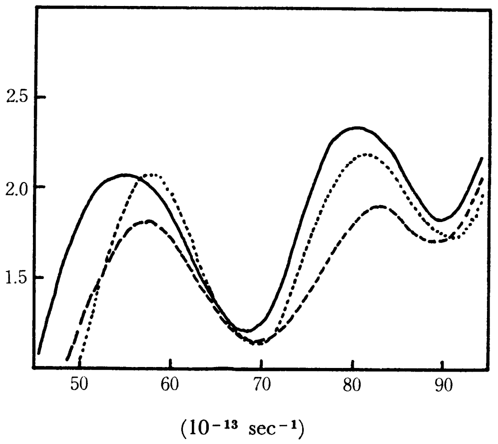


Fig. 5. Absorption spectra of the three isomers of the $[Co(ox)(gly)(NH_3)_2]$ in ca. 10% $HClO_4$.
—— *mer(cis)*, ---- *mer(trans)*, ···· *fac*

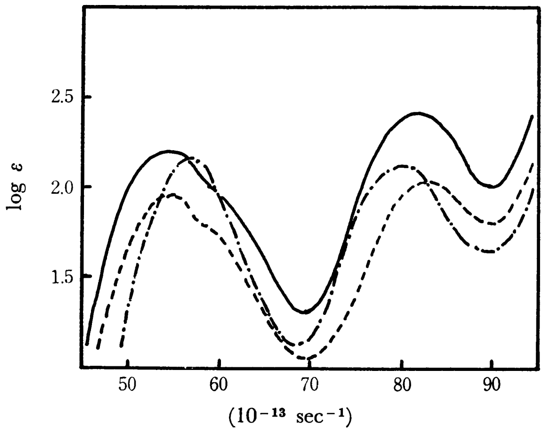


Fig. 6. Absorption spectra of the three isomers of the $[Co(ox)(\beta\text{-ala})(NH_3)_2]$ in *ca.* 10% $HClO_4$.
—— *mer(cis)*, ---- *mer(trans)*, –·–·– *fac*

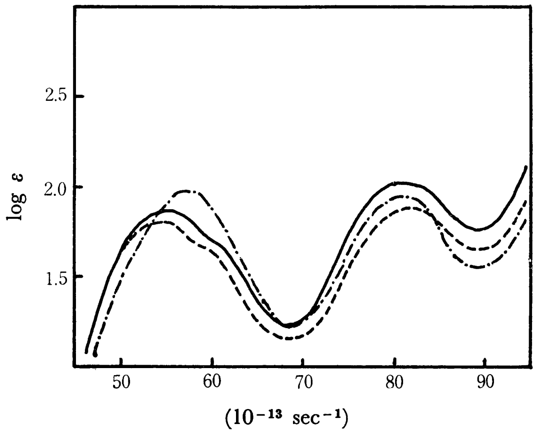


Fig. 7. Absorption spectra of the three isomers of the $[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$ in *ca.* 10% $HClO_4$.
—— *mer(cis)*, ---- *mer(trans)*, –·–·– *fac*

TABLE 2. THE SPECTRAL DATA OF THE PRESENT COMPLEXES

Compound	ν_1[a] (log ε)	Half width(ν_1)	ν_2[a] (log ε)
mer(cis) Isomers			
$[CoCO_3(\alpha\text{-ala})(NH_3)_2]$	54.5(1.97)	17.7	79.3(2.11)
$[CoCO_3(val)(NH_3)_2]$	54.0(1.97)	13.6	80.3(2.08)
$[CoCO_3(gly)(NH_3)_2]$	54.2(2.13)	12.5	79.5(2.25)
$[CoCO_3(\beta\text{-ala})(NH_3)_2]$	54.0(1.99)	11.7	80.0(2.10)
$[Co\ ox(gly)(NH_3)_2]$	54.8(2.06)	12.0	80.0(2.34)
$[Co\ ox(\beta\text{-ala})(NH_3)_2]$	54.5(2.18) *ca.* 60 sh	12.8	81.0(2.39)
$[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$	55.8(1.85) *ca.* 60 sh	13.0	80.8(2.02)
mer(trans)-Isomers			
$[CoCO_3(\alpha\text{-ala})(NH_3)_2]$	56.5(2.00)	11.0	72.5 sh 82.0(2.04)
$[CoCO_3(val)(NH_3)_2]$	56.3(1.90)	11.8	72.0 sh 82.0(1.80)
$[CoCO_3(gly)(NH_3)_2]$	56.0(1.93)	11.2	72.0 sh 81.8(1.85)
$[CoCO_3(\beta\text{-ala})(NH_3)_2]$	54.8(2.11)	11.0	80.5(2.15)
$[Co\ ox(gly)(NH_3)_2]$	56.5(1.78)	13.4	82.0(1.88)
$[Co\ ox(\beta\text{-ala})(NH_3)_2]$	53.8(1.94) *ca.* 60 sh	10.4	81.5(2.04)
$[Co(gly)(NH_3)_2(OH_2)_2]^{2+}$	54.0(1.79) *ca.* 59 sh	13.3	82.8(1.83)
fac-Isomers			
$[CoCO_3(\alpha\text{-ala})(NH_3)_2]$	56.2(2.15)	11.2	81.2(2.20)
$[CoCO_3(val)(NH_3)_2]$	56.2(2.04)	11.0	80.8(2.13)
$[CoCO_3(gly)NH_3)_2]$	56.2(2.16)	10.0	80.1(2.22)
$[CoCO_3(\beta\text{-ala})(NH_3)_2]$	55.8(2.17)	10.2	80.0(2.18)
$[Co\ ox(gly)(NH_3)_2]$	57.0(2.06)	9.5	81.0(2.21)
$[Co\ ox(\beta\text{-ala})(NH_3)_2]$	57.0(2.13)	9.4	80.0(2.12)
$[Co(gly)(NH_3)_2(OH_2)_2]^{2}+$	57.5(1.96)	12.0	81.0(1.93)

a) $\times 10^{13}$ sec^{-1}

their chromatographic separations exhibit absorption spectra very similar to that for the *mer(cis)* isomer of the glycinato complex. The same situation holds between the isomers of the third fractions of the present complexes and the *fac* isomer of the glycinato complex. Each spectrum for the isomers of the second fractions clearly shows a shoulder in the second absorption band, similar to the spectrum for the *mer(trans)* isomer of the glycinato complex. However, the intensity of the second band of the α-alaninato complex is rather larger than that of the first band, contrary to the cases of the corresponding isomers of the glycinato and valinato complexes (Figs. 2 and 3). From these similarities in absorption spectra, *mer(cis)*, *mer(trans)*, and *fac* structures (Fig. 1) could be assigned to the isomers isolated, according to the order of elution.

For the carbonato-β-alaninato complex, the *mer* and *fac* assignments to the isomers can easily be done from the shapes of the first absorption bands, but *cis* and *trans* assignments for the two *mer*-isomers are difficult because their spectra resemble each other very much (Fig. 4). However, from the order of elution, it may be assumed that the *mer(cis)* isomer is the compound obtained from the first fraction. Further confirmation is provided by PMR spectral studies to be described later.

As to the oxalatoglycinatodiammine complex, the isomer obtained from the second fraction shows its first and second absorption maxima at considerably shorter wavelengths compared with the isomer obtained from the first fraction (Fig. 5). Apart from the disappearance of a shoulder, this hypsochromic shift of the absorption bands in the former isomer corresponds well to that in the *mer(trans)* isomers of the carbonato-α-aminoacidato complexes. Thus, the *mer* isomer of the second fraction may be regarded as the *mer(trans)* isomer.

As to the oxalato-β-alaninato complex, the two *mer* isomers show similar spectra; it is impossible to determine their geometrical configurations by means of the electronic spectra (Fig. 6). Therefore, the confirmation is based on the PMR spectral data.

In the previous paper, it was reported that the configuration of each isomer of the carbonatoglycinato complex was retained during acid hydrolysis. The electronic spectrum of each isomer of the aquo complex isolated as an oxalate in the present work is consistent with the previous observation (Fig. 7).²⁾

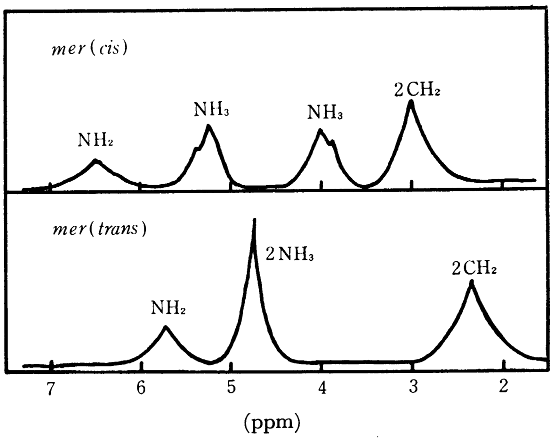


Fig. 8. PMR spectra of the *mer*-isomers of the [Co(CO_3)(β-ala)(NH_3)$_2$] in D_2O/D_2SO_4.

The PMR spectra of the two *mer* isomers of the carbonato-β-alaninato complex are shown in Fig. 8. The isomer tentatively identified as the *cis* isomer, based on the order of elution, shows four peaks, at 6.5, 5.3, 4.0, and 3.0 ppm, with an integrated ratio of ca. 2 : 3 : 3 : 4. As is indicated in the figure, this ratio corresponds to the NH_2 group of the chelated β-alaninate, the two NH_3 groups in different environments, and the two CH_2 groups of the β-alaninate undistinguishable from each other. On the other hand, the isomer assigned tentatively to the *trans* isomer shows three peaks, at 5.7, 4.8, and 2.7 ppm, with a ratio of ca. 2 : 6 : 4. This ratio corresponds to the NH_2 group, the two NH_3 groups in equivalent environments, and the two CH_2 groups respectively. From these results, the previous assignments are now ascertained.

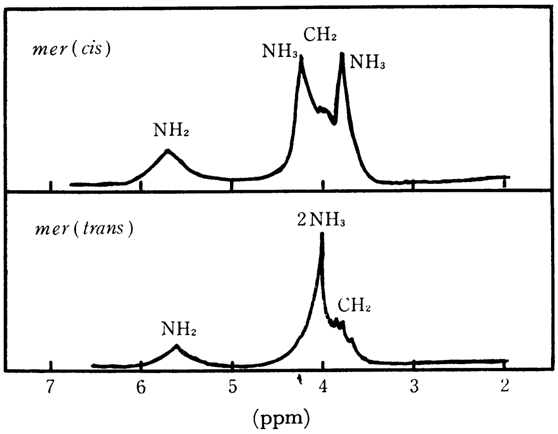


Fig. 9. PMR spectra of the *mer*-isomers of the [Co(ox)(gly)(NH_3)$_2$] in D_2O/D_2SO_4.

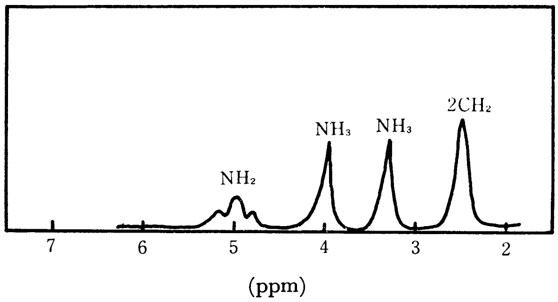


Fig. 10. PMR spectrum of the *mer(cis)*-[Co(ox)(β-ala)(NH_3)$_2$].

The PMR spectra of the two *mer*-isomers of the oxalatoglycinato complex are shown in Fig. 9. The spectrum of the isomer assumed to be *cis* exhibits four peaks; the one observed at 5.7 ppm is due to the NH_2 group of the chelated glycinate, while the other three peaks, close together between 3.5 and 4.5 ppm, are due to the complexed NH_3 groups and the CH_2 group of the glycinate. The integrated ratio of these peaks is estimated to be ca. 2 : 3 : 2 : 3, ranging from lower to higher fields. Provided that the two peaks at 4.3 and 3.8 ppm are due to the NH_3 groups in different environments, the above ratio corresponds to the proton numbers concerned. Thus, the PMR results also support the assignment of the *cis* configuration to this isomer. On the other hand, the spectrum of the other *mer* isomer exhibits three peaks, at 5.6, 4.0, and 3.8 ppm, with a ratio of ca. 2 : 6 : 2. Since the middle peak, with the highest value, is attributable to the two NH_3 groups in equivalent situations, the *mer(trans)* configuration is assigned to this isomer.

The PMR spectrum of the *mer*-isomer of the oxalato-β-alaninato complex obtained from the first fraction is shown in Fig. 10. The isomer exhibits four peaks, at 5.2, 4.0, 3.3, and 2.5 ppm, with a ratio of ca. 2 : 3 : 3 : 4. This result suggests that the two coordinated NH_3 groups are in different environments and that, therefore, this isomer may be assigned the *mer(cis)* configuration. Though the PMR spectrum of the other *mer*-isomer was not measured, it is certain from the above-mentioned analogue of the configurational determination that this isomer has the *mer(trans)* configuration.

The PMR spectrum of each isomer for the present diaquo complex is essentially the same as that in the previous work.²⁾

The evidence for the chelation of a carbonate ion in the β-alaninato complex was supported by the IR spectral data—that is, by the observation of the bands near 1600 (ν_s(C=O)), 1270 (ν_s(C-O)+δ(O-C=O)), 1030 (ν_s(C-O)), and 760 cm^{-1} (in-plane def. of

CO_3^{2-}).[3] The evidence for the chelation of an oxalate ion in the oxalato complexes was also supported by the observation of characteristic bands at 1710 and 1680 (ν_{as}(C=O)), 900 (ν_s(C–O)+δ(O–C=O)), 1400 (ν_s(C–O)+ν(C–C)), and 1260 cm^{-1} (ν_s(C–O)+δ(O–C=O)).[3] In the IR spectra of the aquo-complex, the existence of an oxalate ion as the counterion was also supported by the absorption near 1700 cm^{-1}; the band of oxalic acid of crystallization is also observed in this region.

Mer(trans) *Isomers.* As has been mentioned in the foregoing discussion, the absorption spectra of the *mer(trans)* isomers for the α-alaninato and valinato complexes, like that for the glycinato complex, show shoulders in their second absorption bands. A similar shoulder in the second absorption band has been found in a few complexes: Jørgensen[4] cited the spectra for the [Co edta(OH)]$^{2-}$ and [Cr edta(OH)]$^{2-}$ species. Furlani *et al.*[5] stated that such effects upon the second absorption band for the [Cr edta(OH)]$^{2-}$ species could be due to a lower symmetry caused by a distortion of the octahedron. Emmenegger and Schwarzenbach[6] reported a similar splitting in the spectrum of the [Co penten(OH)]$^{2+}$ complex (penten=*N,N,N′,N′-tetrakis*(α-aminoethyl)ethylenediamine). Recently, Igi *et al.*[7] have reported that the second absorption bands for the [Co(guH)(en)$_2$]$^{3+}$ and [Co(gu)(en)$_2$]$^{2+}$ complexes (guH stands for a guanylurea) split into two components.

It should be noticed that even though the second absorption band exhibits a remarkable splitting for the present *mer(trans)* isomer, the first absorption band shows nothing remarkable. In addition, it is a noteworthy fact that the half-width of the first band for the *mer(trans)* isomer of a carbonato-α-aminoacidato complex is less than that for the *mer(cis)* isomer of the same complex (Table 1).

For the *mer(trans)* isomer of the carbonato-β-alaninato complex, both the first and second absorption maxima are at considerably lower wavelengths than those for the same isomer of a carbonato-α-aminoacidato complex. Moreover, no shoulder is found in the second band region for this isomer of the β-alaninato complex.

When the absorption spectral data are compared between the *mer(trans)* isomers of the carbonatoglycinato and oxalatoglycinato complexes, their maxima are at almost the same positions, though the carbonato ligand lies in a lower position in the spectrochemical series than the oxalato ligand, and no shoulder is observed for the isomer of the oxalato complex. When the same comparison is made between the *mer(cis)* and *mer(trans)* isomers of the oxalato complex, a considerable hypsochromic shift is observed in the latter isomer. This feature is the same as in the case of the corresponding carbonato complex.

As to the absorption spectrum of the *mer(trans)* isomer of the oxalato-β-alaninato complex, both the first and second bands are observed at rather longer wavelengths than those of the corresponding oxalatoglycinato complex, and a shoulder appears in the shorter wavelength-side of the first absorption band. Comparing this spectrum with that of the *mer(cis)* isomer, both the first and second bands are observed at almost the same positions.

From an X-ray study of the [CoCO$_3$(NH$_3$)$_4$]$^+$ complex,[8] it has been pointed out that the bond lengths between the complexed NH$_3$ groups lying at the *trans* positions to the carbonate chelate and the central cobalt are longer than those between the other NH$_3$ groups lying at the *cis* positions, and that the ∠NCoN with N atoms of the NH$_3$ groups in the *trans* positions is larger than the other N–Co–N angles. Thus, we can now expect that the two NH$_3$ groups lying at the *trans* positions to the carbonate chelate behave as weaker ligands than the NH$_3$ groups at the *cis* positions. Moreover, such an effect will more strongly appear when a rigid five-membered chelate ring is in a co-plane with the carbonate chelate ring. Thus, it can be expected in regard to the present carbonato-α-aminoacidato complex, that the α-aminoacidate chelate lying on a co-plane with the carbonate chelate behaves as a somewhat weaker ligand than the same chelate forming a spiral with the carbonate chelate. The remarkable differences in absorption spectrum between a *mer(trans)* and the corresponding *mer(cis)* isomer may be related to the different effects of the carbonate chelates upon the α-aminoacidate chelates. The absorption spectrum of the *mer(cis)* isomer of a carbonato-α-amino acidato complex can be understood with the aid of a ligand field theory, such as in Yamatera's prediction,[9] but the spectrum of the *mer(trans)* isomer of the same complex can not be interpreted at present.

As a result of the present work, we can say the following thing: 1) An octahedral cobalt(III) complex consisting of a five-membered α-aminoacidate ring, two ammonia groups in *trans* positions, and a four-membered carbonate ring reveals a shoulder which is considered to be one component of the split second absorption band, while, when the five-membered aminoacidate ring is replaced by a six-membered one, or when the four-membered carbonate ring is replaced by a five-membered oxalate ring, no such shoulder appears. 2) The half-width of the first absorption band of the *mer(trans)* is less than that of the *mer(cis)* isomer for a carbonato-α-aminoacidato complex. 3) A *mer(trans)* isomer containing a five-membered aminoacidate and a carbonate or an oxalate chelate ring shows its first and second absorption maxima at shorter wavelengths than the *mer(cis)* isomer of the same complex.

---

[3] K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," John Wiley and Sons Inc., New York (1966).

[4] C. K. Jørgensen, *Acta. Chem. Scand.*, **9**, 1362 (1955).

[5] C. Furlani, G. Morpurgo, and G. Sartori, *Z. Anorg. Allg. Chem.*, **363**, 1 (1960).

[6] F. P. Emmenegger and G. Schwarzenbach, *Helv. Chim. Acta*, **99**, 625 (1966).

[7] K. Igi, T. Yasui, J. Hidaka, and Y. Shimura, This Bulletin **44**, 426 (1971).

[8] G. A. Barclay and B. F. Haskins, *J. Chem. Soc.*, **1962**, 586.

[9] H. Yamatera, This Bulletin, **31**, 95 (1958).