BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1257—1261 (1966)

Studies of the Mixed Amino-acid Complexes of Cobalt(III). I. The Geometrical Isomers of the [Co en gly (chelate)] Series

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(Received October 28, 1965)

Five new complexes of the [Co en gly (chelate)] type, i. e., *mer(N)*- and *fac(N)*-[Co en gly CO_3], *mer(N)*- and *fac(N)*-[Co en gly ox] and *mer(N)*-[Co en gly malo], have been derived from a new dinitro complex, *cis*-[Co en gly $(NO_2)_2$], through an intermediate complex, [Co en gly Cl (OH_2)]Cl. The geometrical structures of these complexes have been determined on the basis of the processes of their derivation and their absorption spectra. Two new bisglycinato complexes, *trans(O)*- and *cis(O)*-[Co en gly_2]I·H_2O, have been prepared from *mer(N)*- and *fac(N)*-[Co en gly CO_3] respectively.

Recently the mixed amino-acid complexes of cobalt(III) have been recognized as interesting in relation to the optical rotatory dispersion or the circular dichroism studies of metal complexes, and several reports have appeared.[1-6] However, only a few mixed amino-acid complexes have been known; they belong to the [Co^{III} N_4O_2]- or the [Co^{III} N_3O_3]-type. In particular, we know of extremely few examples of pairs of geometrical isomers, for example, the *trans(O)*- and *cis(O)*-isomers of a [Co N_4O_2] complex or the *mer(N)*- and *fac(N)*-isomers of a [Co N_3O_3] complex.

In the present paper, five new complexes of the [Co en gly (chelate)] type, including two pairs of geometrical isomers, and a pair of the *trans(O)*- and *cis(O)*-isomers of [Co en gly_2]X, will be reported on. All of these new complexes will be derived from a new starting material, [Co en gly $(NO_2)_2$]. The absorption spectra of these complexes will then be discussed in the same way as in a previous paper.[7]

Experimental

Preparation.—*1) Dinitroglycinatoethylenediaminecobalt(III):* [$Co(NO_2)_2$ gly en].—A solution containing 25 g. of potassium nitrite in 30 ml. of water was added to a solution containing 20 g. of cobalt(II) chloride hexahydrate in 20 ml. of water, and then 7 g. of glycine in 40 ml. of water and 6 g. of 93% aqueous ethylenediamine were added to the solution in this order. The dark brown solution was oxidized by bubbling air in for about ten hours, whereupon the desired complex separated as yellow precipitates. The crude complex was filtered and washed with a small quantity of water, and then with ethanol, and dried in air. This complex is sparingly soluble in water at room temperature, moderately soluble in hot water, and insoluble in methanol, ethanol, acetone and benzene. The pure crystals were obtained by recrystallization from hot water. Yield, 18 g.

Found: C, 17.33; H, 4.44; N, 24.30. Calcd. for [$Co(NO_2)_2(C_2H_4NO_2)(C_2H_8N_2)$]: C, 16.85; H, 4.24; N, 24.57%.

The following three complexes, 2—4), were prepared by the same method as above using racemic alanine and racemic propylenediamine.

2) Dinitroalaninatoethylenediaminecobalt(III): [$Co(NO_2)_2$ ala en].—Found: C, 20.21; H, 4.64; N, 23.26. Calcd. for [$Co(NO_2)_2(C_3H_6NO_2)(C_2H_8N_2)$]: C, 20.08; H, 4.72; N, 23.41%.

3) Dinitroglycinatopropylenediaminecobalt(III): [$Co(NO_2)_2$ gly pn].—Found: C, 20.29; H, 4.66; N, 23.39. Calcd. for [$Co(NO_2)_2(C_2H_4NO_2)(C_3H_{10}N_2)$]: C, 20.08; H, 4.72; N, 23.41%.

4) Dinitroalaninatopropylenediaminecobalt(III): [$Co(NO_2)_2$ ala pn].—Found: C, 23.06; H, 5.06; N, 22.26. Calcd. for [$Co(NO_2)_2(C_3H_6NO_2)(C_3H_{10}N_2)$]: C, 23.01; H, 5.15; N, 22.36%.

5) Potassium Dinitrobisglycinatocobaltate(III): K[Co $(NO_2)_2$ gly_2]. Potassium nitrite (50 g.) in 70 ml. of water and glycine (26 g.) in 150 ml. of water were added in this order to a solution containing 40 g. of cobalt(II) chloride hexahydrate in 50 ml. of water. The dark brown solution was then oxidized by bubbling air in for about three hours. After the addition of 200 ml. of ethanol, the solution was kept in a refrigerator overnight. The yellow brown crystals were filtered and recrystallized from hot water. They were dried by heating at 105°C. Yield, 30 g.

Found: C, 13.99; H, 2.85; N, 17.13. Calcd. for K[$Co(NO_2)_2(C_2H_4NO_2)_2$]: C, 14.21; H, 2.38; N, 16.57%.

6) Chloroglycinatoaquoethylenediaminecobalt(III) Chloride: [Co Cl gly (OH_2) en]Cl.—The ground sample of the [Co $(NO_2)_2$ gly en] complex (20 g.) was suspended in 50 ml. of concentrated hydrochloric acid and warmed on a water bath. The yellowish suspension began to dissolve with the bubbling of nitrogen dioxide, and the mixture became violet. After the bubbling of gas had ceased, the violet solution was cooled to room temperature. The violet crystalline complex deposited was then filtered and washed with diluted hydrochloric acid (1 : 1) and dried in air. This complex is soluble in water, with an accompanying aquation but insoluble in ethanol and methanol. Yield, 14 g.

Found: C, 16.86; H, 5.06; N, 14.79. Calcd. for [Co Cl $(C_2H_4NO_2)OH_2(C_2H_8N_2)$]Cl: C, 17.03; H, 5.00; N, 14.90%.

7) Diisothiocyanatoglycinatoethylenediaminecobalt(III): [Co $(NCS)_2$ gly en].—To a solution of 2 g. of potassium thiocyanate in 20 ml. of water, 2 g. of [Co Cl gly (OH_2) en]Cl was added, and the mixture was warmed on a water bath. The color of the solution changed from violet to dark red, and the red crystals began to deposit. After the solution had been cooled to room temperature, the crystals were separated and washed with a little water, and then with ethanol, and dried in air. This complex is insoluble in water, ethanol and methanol. Yield, 2 g.

Found: C, 23.54; H, 3.97; N, 22.22. Calcd. for [$Co(NCS)_2(C_2H_4NO_2)(C_2H_8N_2)$]: C, 23.30; H, 3.91; N, 22.65%.

8) The mer(N) or Violet Form of Carbonatoglycinatoethylenediaminecobalt(III) Monohydrate: *mer(N)*-[Co CO_3 gly en]·H_2O. — In 100 ml. of water 10 g. of [Co Cl gly (OH_2) en]Cl and 10 g. of potassium hydrogen carbonate were dissolved; the mixture was then heated on a water bath for an hour. The solution was cooled to room temperature, and 50 ml. of ethanol was added to it. Some violet crystals began to separate in this step. After the solution had been kept in a refrigerator overnight, a large amount of the violet crystals, which were contaminated with a little amount of the reddish violet *fac(N)*-form, was obtained. The pure violet needles were obtained by recrystallization from hot water, washed with ethanol, and dried in air. This complex is insoluble in methanol and ethanol. Yield, 6.8 g.

Found: C, 22.14; H, 5.24; N, 15.23. Calcd. for [Co $CO_3(C_2H_4NO_2)(C_2H_8N_2)$]·$H_2O$: C, 22.15; H, 5.20; N, 15.50%.

9) The fac(N) or Red Form of Carbonatoglycinatoethylenediaminecobalt(III): *fac(N)*-[Co CO_3 gly en]. — Five grams of [Co Cl gly (OH_2) en]Cl were dissolved in a solution of 5 g. of potassium hydrogen carbonate

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[1] Y. Shimura, This Bulletin, **31**, 173, 315 (1958).

[2] M. Ogawa, Y. Shimura and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 72 (1960).

[3] M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J. W. Kang, ibid., **83**, 734 (1962).

[4] C. T. Liu and B. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[5] J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, **1964**, 2822.

[6] J. Fujita, T. Yasui and Y. Shimura, This Bulletin, **38**, 654 (1965).

[7] N. Matsuoka, Y. Shimura and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 1637 (1961).

in 100 ml. of water. The solution was heated on a water bath for an hour and then cooled to room temperature. After about 20 ml. of methanol had been added to the solution, it was allowed to stand for about ten hours. The crude complex deposited as reddish violet crystals. This was recrystallized from water by the usual procedure. Yield, 0.2 g.

Found: C, 23.62; H, 4.98; N, 16.71. Calcd. for [Co $CO_3(C_2H_4NO_2)(C_2H_8N_2)$]: C, 23.73; H, 4.78; N, 16.60%.

10) The mer(N) or Violet Form of Oxalatoglycinatoethylenediaminecobalt(III): mer(N)-[Co ox gly en].—In 20 ml. of warm water 4 g. of potassium oxalate and 5 g. of [Co Cl gly (OH_2) en]Cl were dissolved, and the mixture was heated on a water bath. After about 5 min. the desired complex gradually separated as reddish-violet needle crystals. This was recrystallized from hot water. Yield, 4 g.

Found: C, 25.66; H, 4.33; N, 14.98. Calcd. for [Co $(C_2O_4)(C_2H_4NO_2)(C_2H_8N_2)$]: C, 25.63; H, 4.30; N, 14.95%.

This complex was also prepared from *mer(N)*-[Co CO_3 gly en] and oxalic acid.

11) The fac(N) or Red Form of Oxalatoglycinatoethylenediaminecobalt(III): fac(N)-[Co ox gly en].—This complex was prepared from *fac(N)*-[Co CO_3 gly en] and oxalic acid by the same method as that used for *mer(N)*-[Co ox gly en]. The pure complex was obtained as a pink powder. Yield, 0.1 g. from 0.5 g. of the carbonato complex.

Found: C, 25.54; H, 4.29; N, 14.89. Calcd. for [Co $(C_2O_4)(C_2H_4NO_2)(C_2H_8N_2)$]: C, 25.63; H, 4.30; N, 14.95%.

12) mer(N)-Malonatoglycinatoethylenediaminecobalt(III): mer(N)-[Co malo gly en].—To a solution of 2.5 g. of malonic acid in 50 ml. of water, 5 g. of *mer(N)*-[Co CO_3 gly en] was added and heated on a water bath. After the bubbling of carbon dioxide had finished, the solution was heated for more about one hour. It was then cooled and allowed to stand overnight. Reddish-violet crystals were recrystallized from water. Yield, 3.8 g. The same product was also obtained from the *fac(N)* carbonato complex.

Found: C, 28.42; H, 4.80; N, 14.18. Calcd. for [$Co(C_3H_2O_4)(C_2H_4NO_2)(C_2H_8N_2)$]: C, 28.49; H, 4.78; N, 14.24%.

13) trans(O)-Bisglycinatoethylenediaminecobalt (III) Iodide Monohydrate: trans(O)-[Co gly_2 en]I·H_2O.—Two grams of *mer(N)*-[Co CO_3 gly en] was added to a solution containing 1.2 g. of glycine in 20 ml. of water. The solution was evaporated to 5 ml. on a water bath at about 70°C and filtered in hot. The filtrate was cooled to room temperature. After a calculated amount of potassium iodide had been added to the solution, dark red crystals began to separate. The mixture was kept in a refrigerator overnight. The recrystallization was made from water by the usual procedure.

Found: C, 17.78; H, 4.51; N, 13.61. Calcd. for [Co $(C_2H_4NO_2)_2(C_2H_8N_2)$]I·$H_2O$: C, 17.48; H, 4.40; N, 13.62%.

14) cis(O)-Bisglycinatoethylenediaminecobalt(III) Iodide Monohydrate: cis(O)-[Co gly_2 en]I·H_2O.—This complex was obtained by the same method as that used for the *trans(O)*-isomer, using *fac(N)*-[Co CO_3 gly en] instead of the *mer(N)*-isomer. After a little red precipitate produced by the addition of a calculated amount of potassium iodide had been filtered off, a small quantity of ethanol was added to the filtrate; the solution was then kept in a refrigerator overnight. The pinkish red powder deposited was recrystallized from water.

Found: C, 17.46; H, 4.34; N, 13.80. Calcd. for [$Co(C_2H_4NO_2)_2(C_2H_8N_2)$]I·$H_2O$: C, 17.48; H, 4.40; N, 13.62%.

Measurements.—The absorption spectra were measured by a Beckman DU spectrophotometer at room temperature. The concentrations of the solutions varied from 1.0×10^{-2} to 0.5×10^{-4} F.

Results and Discussion

As a representative absorption spectrum of the complexes of the dinitro(amino-acidato)diamine type, the curve of [Co en gly$(NO_2)_2$], which was used as the starting compound in the preparations of the [Co en gly (chelate)] series, is shown in Fig. 1, in which the curve of a new bisglycinato complex, K[Co gly_2 $(NO_2)_2$], is also plotted. Previously one of the present authors[8] showed that the so-called nitro specific band of a *trans*-dinitrocobalt(III) complex was located at about 350—335 mμ, while, on the other hand, the band of the corresponding *cis*-dinitro complex was located at about 335—320 mμ. Judging from the positions of the nitro specific band of the present complexes, which are at 325 and 332 mμ for [Co en gly $(NO_2)_2$] and K[Co gly_2 $(NO_2)_2$] respectively, it may be considered that the two coordinated NO_2^- ligands of both the complexes are in the *cis* positions.

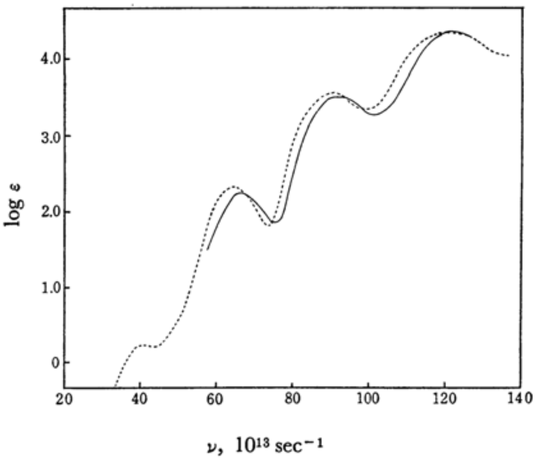

Fig. 1. Absorption curves of ——[Co en gly $(NO_2)_2$] and ······K[Co $gly_2(NO_2)_2$].

By warming up the starting complex, [Co en gly $(NO_2)_2$], with concentrated hydrochloric acid, the two coordinated NO_2^- ligands are easily freed from the cobalt(III) ion without the decomposition of the two chelate rings, while the two glycine

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[8] Y. Shimura, *J. Am. Chem. Soc.*, **73**, 5079 (1951).

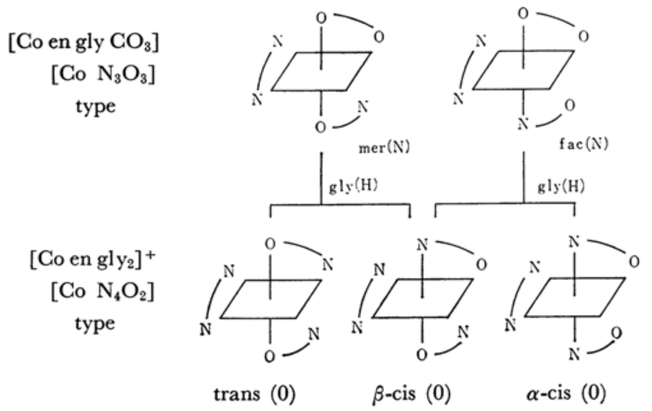

Fig. 2. Geometrical isomers of [Co en gly CO$_3$] and [Co en gly$_2$]$^+$.

TABLE I. ABSORPTION DATA OF THE COMPLEXES OF THE [Co N$_3$O$_3$] TYPE

Complex	A-band ν_{max} (log ε_{max})	I-band ν_{max} (log ε_{max})	II-band ν_{max} (log ε_{max})
mer(N)-[Co en gly CO$_3$]	31.0 (0.04) 34.9 (0.01)	56.6 (2.07)	81.1 (2.17)
fac(N)-[Co en gly CO$_3$]	33.0 (0.17)	56.6 (2.17)	80.4 (2.13)
mer(N)-[Co en gly ox]	ca. 35 (0.15)	57.7 (1.96)	81.1 (2.23)
fac(N)-[Co en gly ox]		57.7 (2.13)	81.1 (2.24)
mer(N)-[Co en gly malo]		58.3 (1.95)	80.6 (2.13)
mer(N)-[Co gly$_3$]9)	29.8 ($\bar{1}$.82)	55.7 (2.00)	80.6 (2.18)
fac(N)-[Co gly$_3$]9)	33.0 (0.02)	57.7 (2.20)	80.2 (2.15)

The frequencies are given in 10^{13} sec^{-1}.

rings of K[Co gly$_2$ (NO$_2$)$_2$] are decomposed by such treatment. The complex salt resulting from the treatment of [Co en gly (NO$_2$)$_2$] is quantitatively obtained as a violet crystalline powder. The analytical data show that this complex has one water molecule which is not removed even by heating at 105°C for a few days. It may be assumed that this water molecule is coordinated to the cobalt(III) ion.

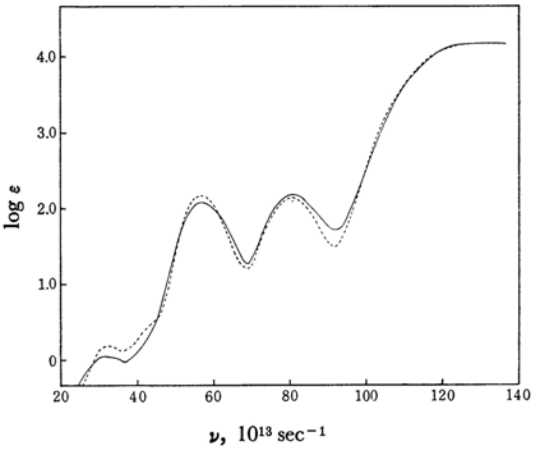

Fig. 3. Absorption curves of —— *mer(N)*- and ······ *fac(N)*-[Co en gly CO$_3$].

From the reaction of [Co en gly Cl (OH$_2$)]Cl with potassium hydrogen carbonate, two kinds of the carbonato complex, the violet form and the red form, are obtained. Now, the [Co en gly (CO$_3$)] complex may be expected to have two geometrical isomers, *mer(N)* and *fac(N)*, as is seen in Fig. 2. The absorption curves and the numerical data of both the isomers are shown in Fig. 3 and Table I. The first absorption band of the violet isomer is broader in shape and lower in intensity than that of the red isomer. It has been well established that the first band of a *mer(N)*-isomer of the complex of the [Co N$_3$O$_3$] type is broadened by the overlap of the split three absorption components and that the degenerate first band of a *fac(N)*-isomer is higher in intensity than that of the *mer(N)*-isomer.7) Consequently, it may be concluded that the violet isomer of [Co en gly CO$_3$] is a *mer(N)*-form, and the red one, a *fac(N)*-form.

As is shown in Fig. 4 and Table I, the absorption curves of the two isomers of [Co en gly ox] show the same trends in the first bands as those of the *mer(N)*- and *fac(N)*-isomers of [Co en gly CO$_3$]. Furthermore, the violet oxalato isomer is derived from *mer(N)*-[Co en gly CO$_3$], and the red one, from *fac(N)*-[Co en gly CO$_3$]. These facts confirm

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9) J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963).

TABLE II. ABSORPTION DATA OF BIS(AMINO-ACIDATO) SERIES

Complex ion	A-band ν_{max} (log ε_{max})	I-band ε_{max} (log ε_{max})	II-band ν_{max} (log ε_{max})
trans(O)-[Co en gly_2]$^+$	31.6 ($\bar{1}$.90)	$\begin{cases}56.6\ (1.94)\\66.0\ (1.64)\end{cases}$	83.3 (2.12)
cis(O)-[Co en gly_2]$^+$	37.0 ($\bar{1}$.90)	59.8 (2.09)	83.3 (2.13)
trans(O)-[Co en (β-ala)$_2$]$^+$ [2]		$\begin{cases}55.2\ (2.00)\\65.8\ (1.61)\end{cases}$	82.8 (1.94)

The frequencies are given in 10^{13} sec^{-1}.

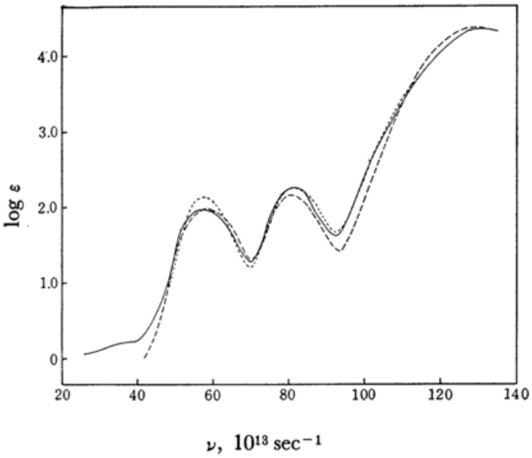

Fig. 4. Absorption curves of —— *mer(N)*- and ······ *fac(N)*-[Co en gly ox] and ---- *mer(N)*-[Co en gly malo].

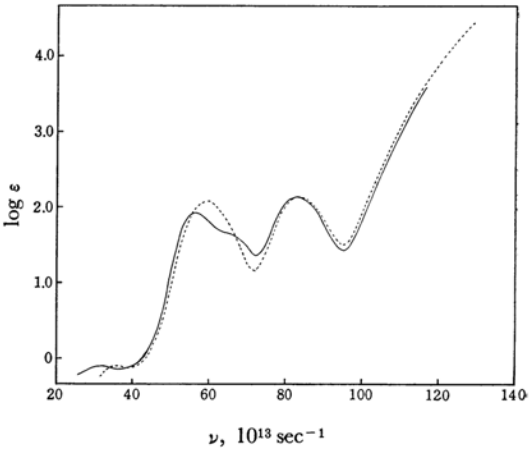

Fig. 5. Absorption curves of —— *trans(O)*- and ······ *cis(O)*-[Co en gly_2]I·H_2O.

that the violet [Co en gly ox] is of the *mer(N)* - form, and the red one, of the *fac(N)*-form.

The complexes which are derived from *mer(N)*- and *fac(N)*-[Co en gly CO_3] by the reaction with malonic acid are identical. From the fact that the first band of this complex agrees with that of *mer(N)*-[Co en gly ox], as is seen in Fig. 4, the *mer(N)* structure is assigned to this complex.

Three geometrical isomers, *trans(O)*-, *β-cis(O)*- and *β-cis(O)*-forms,* are expected for the [Co en gly_2]$^+$ ion. The *trans(O)*- and *α-cis(O)*-[Co en gly_2]$^+$ ions will be derived from *mer(N)*-[Co en gly CO_3] if the substitution reaction of the CO_3^{2-} ligand by the gly^- ion proceeds with the retention of the geometrical configuration of the [Co en gly —] part, while the *α-cis(O)*- and the *β-cis(O)*-[Co en gly_2]$^+$ ions are derived from *fac(N)*-[Co en gly CO_3], as is shown in Fig. 2. In fact, the dark red complex is derived from *mer(N)*-[Co en gly CO_3], accompanied by a small quantity of a pinkish red complex, while from *fac(N)*-[Co en gly CO_3] the pinkish red complex, which is more soluble than the dark red one, is derived. The first absorption band of the dark red complex splits into two distinct components (Fig. 5 and Table II). This splitting pattern agrees well with the data[2,10] of the other *trans(O)*-[Co N_4O_2] complexes and with the pattern which is to be expected for the *trans* form from the semi-empirical molecular orbital calculations.[11] The first absorption band of the pinkish red complex is normal in shape; it may reasonably be considered that the pinkish red complex is *cis(O)*-[Co en gly_2]$^+$. It is difficult, however, on the basis of only the absorption spectrum, to discriminate between *α-cis(O)*- and *β-cis(O)*-structures.

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* The prefix α denote that the two nitrogen atoms of the coordinated amino-acid ions occupy the *trans*-positions, and prefix β the *cis*-positions.

[10] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

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