BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1868—1874 (1967)

Studies of the Mixed Amino-acid Complexes of Cobalt(III). II.[1] A Complete Series of $[Co(ox)_x(gly)_y(en)_z]$ Complexes

Nobuko MATSUOKA, Jinsai HIDAKA and Yoichi SHIMURA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received February 27, 1967)

Five new complexes, C_1-*cis*(O)-$[Co(gly)_2(en)]Br\cdot 3H_2O$, C_2-*cis*(O)-$[Co(gly)_2(en)]Br\cdot H_2O$, *trans*(N)-$K[Co(ox)(gly)_2]$, C_1-*cis*(N)- and C_2-*cis*(N)-$Na[Co(ox)(gly)_2]$, have been synthesized. The geometrical isomers of both the $[Co(gly)_2(en)]^+$ and the $[Co(ox)(gly)_2]^-$ complex have been separated by ion-exchange column chromatography. The geometrical structures have been determined on the basis of the visible absorption spectra and of the NMR spectra, and from a consideration of the reaction processes of derivation. The visible and near-ultraviolet absorption spectra of a complete series of the sixteen complexes of the $[Co(ox)_x(gly)_y(en)_z]$ type, have been measured and discussed.

Three geometrical isomers are expected for a $[Co(gly)_2(en)]^+$ ion, *i. e.*, the *trans*(O), C_1-*cis*(O), and C_2-*cis*(O) forms, where the prefixes C_1 and C_2 represent the symmetry of each complex.* In the first paper of this series,[1] the *trans*(O) and one of the *cis*(O) isomers were derived from the *mer*(N) and *fac*(N) isomers of the $[Co(CO_3)(gly)(en)]$ complex respectively, and their structures were determined on the basis of their visible absorption spectra mainly. It was difficult, however, to discriminate between C_1-*cis*(O) and C_2-*cis*(O) structures on the basis of only the absorption spectrum. In the present paper, the two *cis*(O) isomers will be prepared in another way and separated by ion-exchange chromatography. The C_1 and C_2 structures will then be discriminated on the basis of their proton magnetic resonance spectra.

Our success in preparing the three isomers of a $[Co(gly)_2(en)]^+$ ion prompted us to synthesize the corresponding three isomers of a $[Co(ox)(gly)_2]^-$ ion; this attempt was also rewarded by success. In consequence of these studies, a long series of sixteen $[Co(ox)_x(gly)_y(en)_z]$ complexes has been completed, where *x*, *y* and *z* are equal to 0, 1, 2 or 3, and where, of course, $x+y+z$ equals 3 (see Table 1 and Fig. 1). The oxalate, glycinate, and ethylenediamine ligands represent the most fundamental *O, O*-, *O, N*-, and *N, N*-chelate ligands respectively, all of them producing a five-membered chelate ring. Therefore, this complete series is a typical collection of complexes of the $[Co^{III}(O)_n(N)_{6-n}]$-type. The visible and ultraviolet absorption spectra of these complexes will be briefly discussed below, in reference to the well-known Yamatera's treatment.[2]

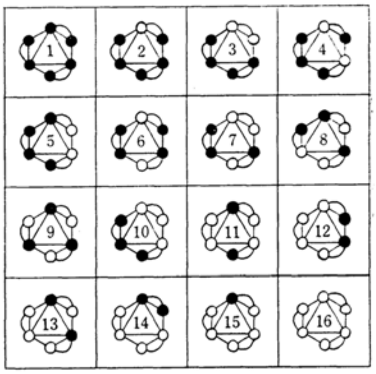

Fig. 1. Schematic representation of the geometrical structures of the $[Co(ox)_x(gly)_y(en)_z]$-type complexes.
Black circle: nitrogen
White circle: oxygen

TABLE 1. SIXTEEN MEMBERS OF A COMPLETE SERIES OF $[Co(ox)_x(gly)_y(en)_z]$ COMPLEXES

Number in Fig. 1	Composition *x*	*y*	*z*	Charge	Structure of first coordination sphere
1	0	0	3	+3	$[Co(N)_6]$
2	0	1	2	+2	$[Co(O)(N)_5]$
3	1	0	2	+1	*cis*-$[Co(O)_2(N)_4]$
4	0	2	1	+1	
5	0	2	1	+1	
6	0	2	1	+1	*trans*-$[Co(O)_2(N)_4]$
7	1	1	1	0	*mer*-$[Co(O)_3(N)_3]$
8	0	3	0	0	
9	0	3	0	0	*fac*-$[Co(O)_3(N)_3]$
10	1	1	1	0	
11	1	2	0	−1	*trans*-$[Co(O)_4(N)_2]$
12	1	2	0	−1	*cis*-$[Co(O)_4(N)_2]$
13	1	2	0	−1	
14	2	0	1	−1	
15	2	1	0	−2	$[Co(O)_5(N)]$
16	3	0	0	−3	$[Co(O)_6]$

---

* In a former paper of this series, the prefixes α and β were used instead of C_2 and C_1 respectively.

[1] Part I of this series: N. Matsuoka, J. Hidaka and Y. Shimura, This Bulletin, **39**, 1257 (1966).

[2] H. Yamatera, *ibid.*, **31**, 95 (1958).

Experimental

Preparation. *1) C_1-cis(O)-Bisglycinatoethylenediaminecobalt(III) Bromide Trihydrate:* C_1-*cis*-$[Co(gly)_2(en)]Br\cdot3H_2O$. A solution containing 10 g of cobalt(II) chloride hexahydrate in 20 m*l* of water was added to a mixed solution of 2.5 g of 98% aqueous ethylenediamine and 6.4 g of glycine in 30 m*l* of water. The solution was then oxidized by adding 10 g of lead dioxide while being heated on a water bath for 30 min. The reaction was completed by adding 10 more grams of lead dioxide while warming the solution on a water bath for an hour. After having been allowed to stand at room temperature, the solution was filtered several times at intervals because of the rather slow separation of a large amount of the precipitate. The filtrate was poured into a column (15 mm × 300 mm) of strong acid cation-exchange resin (Dowex 50W X8, 200—400 mesh, hydrogen form). After the column had been swept with water, the adsorbed band was eluted with a 0.5 N aqueous solution of potassium bromide at the rate of about 0.7 m*l* per min. At an early stage in the water-sweeping, a small quantity of non-electrolyte complexes, *mer*- and *fac*-$[Co(gly)_3]$, were eluted. By elution with 0.5 N potassium bromide three colored bands, a dark red one, a pink one, and another pink one, were eluted in this order (a small amount of +2- or +3-charged complexes remained in the column).

The firstly eluted band, the dark red one, was confirmed, by the measurement of its visible absorption spectrum, to be *trans*(O)-$[Co(gly)_2(en)]^+$. The two pink-colored bands appeared in progression, partly overlapping, so many fractions were made separately and the optical density, $D=\log(I_0/I)$, of each fraction was individually examined at a suitable wavelength. The pure species of the earlier-eluted band (C_1) has its absorption maxima at 501 mμ (λ_I) and 361 mμ (λ_{II}), with their intensities related to each other by $\log(D_I/D_{II})=-0.04$, while the pure later-eluted fraction (C_2) has its maxima at 502 mμ (λ_I) and 357 mμ (λ_{II}), with $\log(D_I/D_{II})=-0.07$. The pure earlier-eluted fractions were gathered and evaporated on a water bath. A pinkish red complex, C_1-*cis*(O)-$[Co(gly)_2(en)]Br$, contaminated with some potassium bromide, was precipitated by adding methanol. The precipitate was separated by filtration, washed with a water-methanol mixture and then with methanol, and dried in air. The crude product was recrystallized from hot water by adding methanol.

Found: C, 18.24; H, 5.87; N, 14.21%. Calcd for $C_6H_{16}O_4N_4BrCo\cdot3H_2O=[Co(gly)_2(en)]Br\cdot3H_2O$: C, 17.97; H, 5.53; N, 13.97%.

This complex was also prepared from *mer*(N)-$[Co(CO_3)(gly)(en)]$ by the following method. Two grams of *mer*(N)-$[Co(CO_3)(gly)(en)]$[1] were added to a solution of 1.2 g of glycine in 20 m*l* of water. The solution was then concentrated by evaporation on a water bath to a half of its original volume. It was cooled, filtered, and passed through a column of cation-exchange resin as described above. In this case, because of the negligible yield of the C_2 isomer, the pure complex was obtained readily.

2) C_2-cis(O)-Bisglycinatoethylenediaminecobalt(III) Bromide Monohydrate: C_2-*cis*(O)-$[Co(gly)_2(en)]Br\cdot H_2O$. This isomer was obtained from the later-eluted fraction of the pink-colored eluate, which has been described above in *1)*. After evaporating the eluate ($\lambda_I=502$ mμ, $\lambda_{II}=357$ mμ, $\log(D_I/D_{II})=-0.07$) in a vacuum, a pinkish-red compound was obtained by the same method as that used for the C_1-isomer.

Found: C, 20.58; H, 4.99; N, 15.47%. Calcd for $C_6H_{16}O_4N_4BrCo\cdot H_2O=[Co(gly)_2(en)]Br\cdot H_2O$: C, 19.74; H, 4.97; N, 15.35%.

3) Potassium trans(N)-Oxalatobisglycinatocobaltate(III): *trans*(N)-$K[Co(ox)(gly)_2]$. A solution of 19.5 g of cobalt(II) chloride hexahydrate in 50 m*l* of water was added to a solution of 21.9 g of potassium oxalate and 17.8 g of glycine in 100 m*l* of water. The mixed solution was then oxidized by adding 10 g of lead dioxide little by little, while warming the solution constantly on a water bath for 30 min. Ten grams of lead dioxide were then again added to the mixed solution, and it was concentrated to a half of its volume on a water bath. After filtering off a large amount of insoluble materials, the solution was allowed to stand at room temperature overnight. Ten crude product deposited was recrystallized from hot water by adding methanol; blue violet crystals were thus obtained.

Found: C, 20.50; H, 2.40; N, 8.35%. Calcd for $C_6H_8O_8N_2KCo=K[Co(ox)(gly)_2]$: C, 21.67; H, 2.49; N, 8.41%.

4) Sodium C_1-cis(N)-Oxalatobisglycinatocobaltate(III): C_1-*cis*(N)-$Na[Co(ox)(gly)_2]$. Ethanol was added to the filtrate obtained in 3). A crude mixture of the two reddish-violet *cis*(N)-isomers was thus precipitated. This product was dissolved in water and passed through a column (15 mm × 300 mm) containing strong base anion-exchange resin (Dowex 1 X10, 200—400 mesh, chloride form). By elution with 0.5 N sodium perchlorate, three bands, a blue violet one, a violet one, and another blue violet one, were eluted in this order. The first one, blue violet, was *trans*(N)-$[Co(ox)(gly)_2]^-$. The two *cis*(N) bands, which partly overlapped, were separated by a way similar to that described in *1)* for the separation of two isomers of *cis*(O)-$[Co(gly)_2(en)]^+$. The pure earlier-eluted *cis*(N) fraction (C_1) has its absorption maxima at 546 mμ (λ_I) and 388 mμ (λ_{II}), between whose intensities there exists the relation $\log(D_I/D_{II})=-0.09$. On the other hand, the pure later-eluted fraction (C_2) has its absorption maxima at 561 mμ (λ_I) and 385 mμ (λ_{II}), and between their intensities there is the relation $\log(D_I/D_{II})=-0.12$. The earlier eluted fraction of the violet-colored eluate was evaporated on a water bath, and methanol was added to it. The complex thus precipitated, C_1-*cis*(N)-$Na[Co(ox)(gly)_2]$, was filtered, washed with a water-methanol mixture and with methanol, and dried in air. The complex was recrystallized from hot water by adding methanol.

Found: C, 22.33; H, 3.07; N, 8.81%. Calcd for $C_6H_8O_8N_2NaCo=Na[Co(ox)(gly)_2]$: C, 22.66; H, 2.54; N, 8.81%.

5) Sodium C_2-cis(N)-Oxalatobisglycinatocobaltate(III): C_2-*cis*(N)-$Na[Co(ox)(gly)_2]$. This complex was separated from a crude mixture of the two *cis*(N) isomers as described above. A blue violet band of the C_2-isomer appeared just in the upper region of the C_1-isomer. Pure blue violet crystals were isolated by the same method as was used for the C_1-isomer.

Found: C, 22.83; H, 2.80; N, 8.70%. Calcd for $C_6H_8O_8N_2NaCo=Na[Co(ox)(gly)_2]$: C, 22.66; H, 2.54; N, 8.81%.

The other complexes used in this work were prepared according to the methods described in the available literature; some of them are recroded in Table 2.

Measurements. The electronic absorption spectra of the complexes in aqueous solutions, in the near infrared, visible and near ultraviolet region, were measured by a Beckman DU spectrophotometer. The proton magnetic resonance spectra of the complexes in deuterium oxide were measured by a Japan Electron Optics JNM 3H-60 spectrometer, using tetramethylsilane as an internal reference.

Results and Discussion

The Geometrical Configurations of Isomers of [Co(gly)$_2$(en)]$^+$. An example of the bis(amino-acidato)ethylenediaminecobalt(III) complex was first prepared in 1960 by Ogawa *et al.*3); however, they obtained only one isomer of the bis(β-alaninato) complex, *i. e.*, the *trans*(O) form, of the three geometrical isomers expected. Later Murakami *et al.*4) obtained a pink bisglycinato complex, but they did not determine its geometrical structure. Two of the three isomers of the bisglycinato complex, including the *trans*(O) isomer, were prepared in the first paper of this series1); now in this paper all three isomers have been prepared, as has been described in the Experimental section. They may be characterized as follows.

The *trans*(O)-isomer can be well characterized by the splitting of the visible *d-d* absorption band (the so-called first absorption band), as can be seen in Fig. 2. It is well known that the first band of a *trans*-[Co^{III}(O)$_2$(N)$_4$]-type complex shows a more marked splitting than the corresponding *cis*-isomer. The absorption curves of the two *cis*(O) isomers are quite similar to each other, though the maximum positions of the absorption bands are slightly different, as may be seen in Fig. 2 and Table 2. It is clear that the reaction of *mer*(N)-[Co(CO$_3$)(gly)(en)] with glycine, if it proceeds with the retention of the geometrical configuration of the [Co(gly)(en)—] part, produces only the *trans*(O) and C$_1$-*cis*(O) isomers of the [Co(gly)$_2$(en)]$^+$, complex not the C$_2$-*cis*(O) isomer. As has been described in the Experimental section, the product of this reaction consists of the *trans*(O) and one of the *cis*(O) isomers; the other *cis*(O) isomer was not detectable. The absorption curve of the C$_1$-*cis*(O) isomer thus obtained coincides with that of the *cis*(O) isomer earlier eluted from the ion-exchange chromatography of a mixture of the three isomers, mixture of which had been prepared directly from cobalt(II) chloride, ethylenediamine, and glycine. Consequently, it may be concluded that the earlier-eluted cis form is the C$_1$ isomer (No. 4 in Fig. 1), and that the later-eluted one is the C$_2$ isomer (No. 5 in Fig. 1).

A more significant foundation for the determination of these geometrical structures is provided by their NMR spectra. Since the chemical environments of the methylene protons of the two coordinated glycinate rings are equivalent in the trans and the C$_2$-*cis* isomer, but not in the C$_1$-*cis* isomer, one and two resonance lines are expected for the C$_2$-*cis* (and for the trans also) and C$_1$-*cis* isomers respectively. The resonance lines due to the methylene group of the coordinated glycinate rings are observed in the region from 3.70 to 3.40 ppm, as may be seen in Fig. 3. The earlier-eluted cis isomer exhibits two lines, at 3.60 and 3.44 ppm, while the trans and the later-eluted cis isomers

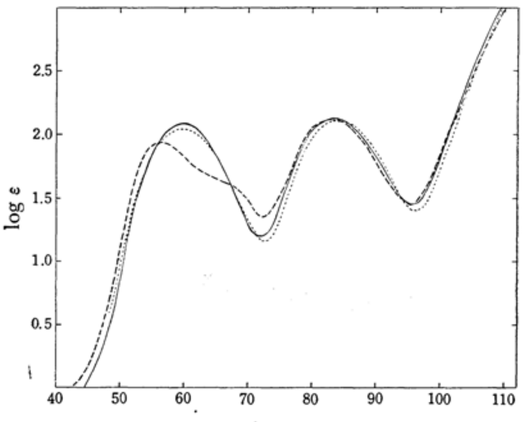

Fig. 2. Absorption spectra of three geometrical isomers of [(Co(gly)$_2$(en)]$^+$.
---- *trans*(O)-[Co(gly)$_2$(en)]I·H$_2$O
—— C$_1$-*cis*(O)-[Co(gly)$_2$(en)]Br·3H$_2$O
······ C$_2$-*cis*(O)-[Co(gly)$_2$(en)]Br·H$_2$O

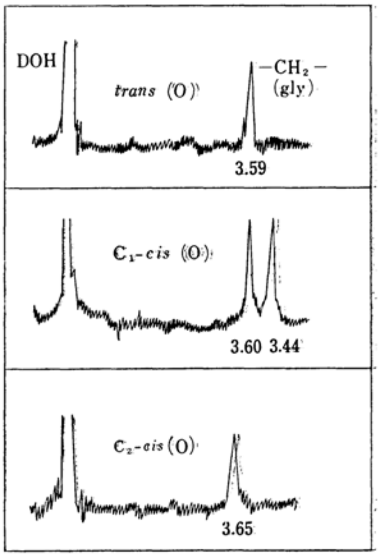

Fig. 3. NMR spectra of three geometrical isomers of [Co(gly)$_2$(en)]$^+$.

---

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

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

exhibit only one resonance line, at 3.59 and at 3.65 ppm respectively. It may be concluded, therefore, that the earlier-eluted cis species is the C_1 isomer and that the later-eluted cis species is the C_2 isomer.

As has been mentioned above, a *cis*(O) isomer was derived from the *fac*(N) isomer of the $[Co(CO_3)(gly)(en)]$ complex in the first paper of this series.1) In this case, the reaction product may contain both the *cis*(O) isomers of the bisglycinato complex, even if the reaction proceeds with the retention of the geometrical configuration of the [Co(gly)(en)—] part. However, the absorption data of the reaction product reported in the first paper almost entirely coincide with the data of the C_1 isomer in Table 2. Therefore, it may be concluded that the *cis*(O) isomer isolated in the first paper was the C_1 isomer.

The Geometrical Configurations of the Isomers of $[Co(ox)(gly)_2]^-$. Previously there has been no report on the oxalatobisglycinatocobalt(III) complexes. Two isomers of the corresponding chromium(III) complex, red and violet, were prepared by Volshtein and Molosnova,5) but they could not determine the geometrical configurations. Of the three cobalt(III) isomers which were prepared in the present study, the *trans*(N) one is well characterized by the marked splitting of its first absorption band (Fig. 4), just as in the case of the $[Co(gly)_2(en)]^+$ complex.

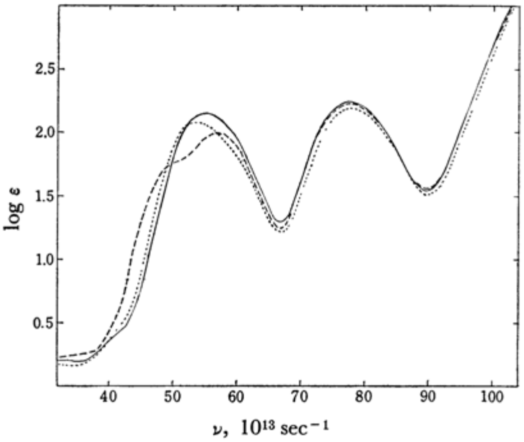

Fig. 4. Absorption spectra of three geometrical isomers of $[Co(ox)(gly)_2]^-$.
---- *trans*(N)-K$[Co(ox)(gly)_2]$
—— C_1-*cis*(N)-Na$[Co(ox)(gly)_2]$
...... C_2-*cis*(N)-Na$[Co(ox)(gly)_2]$

The assignment of the C_1 and C_2 structures for the two *cis*(N) isomers was made on the basis of the difference in their NMR spectra. The trans and the later-eluted cis isomer (C_2) show only one resonance line, at 3.70 and at 3.59 ppm respectively; on the other hand, the earlier-eluted *cis*-isomer (C_1) shows two resonance lines, at 3.58 and 3.43 ppm (Fig. 5). This NMR behavior

TABLE 2. ABSORPTION MAXIMA OF THE $[Co(ox)_x(gly)_y(en)_z]$-TYPE COMPLEXES

No.	Complex	I-Band ν_{max}* (log ε_{max})	II-Band ν_{max}* (log ε_{max})	Ref.
1	$[Co(en)_3]Br_3 \cdot H_2O$	64.4 (1.94)	88.8 (1.90)	
2	$[Co(gly)(en)_2](ClO_4)_2$	61.3 (2.00)	86.4 (2.04)	Prep. & spectrum7)
3	$[Co(ox)(en)_2]Cl$	60.1 (2.05)	84.3 (2.16)	Spectrum7)
4	C_1-*cis*(O)-$[Co(gly)_2(en)]Br \cdot 3H_2O$	59.9 (2.09)	83.1 (2.13)	
5	C_2-*cis*(O)-$[Co(gly)_2(en)]Br \cdot H_2O$	59.8 (2.04)	84.0 (2.11)	
6	*trans*-(O)-$[Co(gly)_2(en)]I \cdot H_2O$	56.6 (1.94)	83.3 (2.12)	Prep. & spectrum1)
7	*mer*(N)-$[Co(ox)(gly)(en)]$	57.7 (1.96)	81.1 (2.23)	Prep. & spectrum1)
8	*mer*(N)-$[Co(gly)_3] \cdot 2H_2O$	55.7 (2.00)	80.6 (2.18)	Spectrum6)
9	*fac*(N)-$[Co(gly)_3] \cdot H_2O$	57.7 (2.20)	80.2 (2.15)	Spectrum6)
10	*fac*(N)-$[Co(ox)(gly)(en)]$	57.7 (2.13)	81.1 (2.24)	Prep. & spectrum1)
11	*trans*(N)-K$[Co(ox)(gly)_2]$	56.6 (2.00)	77.5 (2.23)	
12	C_2-*cis*(N)-Na$[Co(ox)(gly)_2]$	53.5 (2.08)	77.7 (2.20)	
13	C_1-*cis*(N)-Na$[Co(ox)(gly)_2]$	55.0 (2.15)	77.3 (2.24)	
14	$Na[Co(ox)_2(en)] \cdot H_2O$	55.7 (2.05)	78.5 (2.25)	Prep.8)
15	$K_2[Co(ox)_2(gly)] \cdot 3H_2O$	53.6 (2.20)	75.0 (2.26)	Prep.9); Spectrum10)
16	$K_3[Co(ox)_3] \cdot 3H_2O$	49.7 (2.17)	70.9 (2.30)	Spectrum6)

* in the unit of 10^{13} sec^{-1}.

---

5) L. M. Volshtein and V. P. Molosnova, *Doklady Akad. Nauk SSSR.*, **93**, 479 (1953).; *Chem. Abstr.*, **49**, 92f (1955).

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

7) Y. Shimura and R. Tsuchida, *ibid.*, **28**, 572 (1955); **29**, 311 (1956).

8) F. P. Dwyer, I. K. Reid and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

9) F. P. Dwyer, I. K. Reid and A. M. Sargeson, *Aust. J. Chem.*, **18**, 1919 (1965).

10) K. Yamasaki, J. Hidaka and Y. Shimura, unpublished work.

and the elution order in ion-exchange chromatography are in good harmony with those of the three isomers of the $[Co(gly)_2(en)]^+$ complex. The color of the two *cis*(N) isomers of the $[Co(ox)(gly)_2]^-$ ion are quite different from each other because of the different maximum positions of the first absorption bands, 546 mμ for the violet C_1-*cis*(N) isomer and 561 mμ for the blue-violet C_2-*cis*(N) isomer.

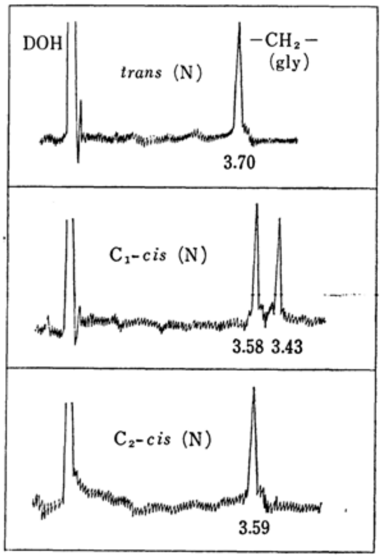

Fig. 5. NMR spectra of three geometrical isomers of $[Co(ox)(gly)_2]^-$.

The Absorption Bands of a Complete Series of the $[Co(ox)_x(gly)_y(en)_z]$ Complexes. As is shown in Table 1 and Fig. 1, sixteen complexes in all are possible in a series of $[Co(ox)_x(gly)_y(en)_z]$-type complexes; their spectra are shown in Fig. 6 and Table 2. The so-called first absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$ of an O_h complex and the corresponding transitions of the complexes of lower symmetries) are clearly split into two or three components in some of the sixteen complexes, *i. e.*, the complexes of No. 6, 7, 8, 11 and 15. On the contrary, no explicit splitting is observed in the so-called second absorption bands ($^1A_{1g} \rightarrow {}^1T_{2g}$ of an O_h complex and the corresponding transitions of the complexes of lower symmetries). The shift of the second absorption band through the series clearly obeyed "the rule of average environment"[11]; namely, the band of a mixed $[Co(O)_n(N)_{6-n}]$ complex is

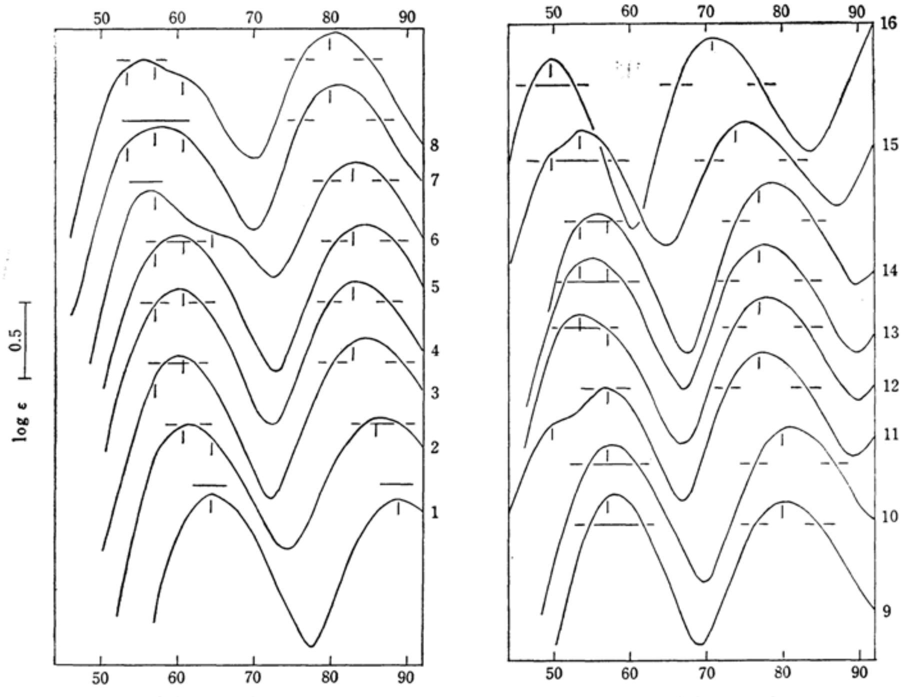

Fig. 6. Absorption spectra of all members of the $[Co(ox)_x(gly)_y(en)_z]$ series in the region of their first and second bands: the complexes are represented by numbers 1—16 same as in Table 2. Short horizontal lines show the intensity levels of $\log \varepsilon = 2.00$ for each the complexes, and short vertical lines show the calculated band positions (see Table 4).

---

11) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962), p. 109.

TABLE 3. PREDICTED SHIFTS OF THE FIRST AND SECOND ABSORPTION BANDS

Type of the complex		Components of I-band*	Weighted mean of II-band components
$[Co(N)_6]$		$\delta^{I}(N)$	$\delta^{II}(N)$
$[Co(O)(N)_5]$	a	$\frac{3}{4}\delta^{I}(N)+\frac{1}{4}\delta^{I}(O)$	$\frac{5}{6}\delta^{II}(N)+\frac{1}{6}\delta^{II}(O)$
	b	$\delta^{I}(N)$	
cis-$[Co(O)_2(N)_4]$	a	$\frac{3}{4}\delta^{I}(N)+\frac{1}{4}\delta^{I}(O)$	$\frac{2}{3}\delta^{II}(N)+\frac{1}{3}\delta^{II}(O)$
	b	$\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$	
trans-$[Co(O)_2(N)_4]$	a	$\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$	$\frac{2}{3}\delta^{II}(N)+\frac{1}{3}\delta^{II}(O)$
	b	$\delta^{I}(N)$	
mer-$[Co(O)_3(N)_3]$		$\frac{3}{4}\delta^{I}(N)+\frac{1}{4}\delta^{I}(O)$ $\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$ $\frac{1}{4}\delta^{I}(N)+\frac{3}{4}\delta^{I}(O)$	$\frac{1}{2}\delta^{II}(N)+\frac{1}{2}\delta^{II}(O)$
fac-$[Co(O)_3(N)_3]$		$\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$	$\frac{1}{2}\delta^{II}(N)+\frac{1}{2}\delta^{II}(O)$
trans-$[Co(O)_4(N)_2]$	a	$\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$	$\frac{1}{3}\delta^{II}(N)+\frac{2}{3}\delta^{II}(O)$
	b	$\delta^{I}(O)$	
cis-$[Co(O)_4(N)_2]$	a	$\frac{1}{4}\delta^{I}(N)+\frac{3}{4}\delta^{I}(O)$	$\frac{1}{3}\delta^{II}(N)+\frac{2}{3}\delta^{II}(O)$
	b	$\frac{1}{2}\delta^{I}(N)+\frac{1}{2}\delta^{I}(O)$	
$[Co(O)_5(N)]$	a	$\frac{1}{4}\delta^{I}(N)+\frac{3}{4}\delta^{I}(O)$	$\frac{1}{6}\delta^{II}(N)+\frac{5}{6}\delta^{II}(O)$
	b	$\delta^{I}(O)$	
$[Co(O)_6]$		$\delta^{I}(O)$	$\delta^{II}(O)$

* When an absorption band is split into two components, the degenerate one (truely or accidentally) is labeled *a* and another non-degenerate one *b*.

TABLE 4. ABSORPTION BAND POSITIONS CALCULATED BY USING PARAMETER VALUES $\delta^{I}(N)=64.4$, $\delta^{I}(O)=49.7$, $\delta^{II}(N)=88.8$ and $\delta^{II}(O)=70.9\times10^{13}\ sec^{-1}$

Type of complex	No. of complex	I-Band ($10^{13}\ sec^{-1}$)	II-Band ($10^{13}\ sec^{-1}$)
$[Co(N)_6]$	1	64.4	88.8
$[Co(O)(N)_5]$	2	64.4(*b*), 60.7(*a*)	85.8
cis-$[Co(O)_2(N)_4]$	3, 4, 5	60.7(*a*), 57.0(*b*)	82.8
trans-$[Co(O)_2(N)_4]$	6	64.4(*b*), 57.0(*a*)	82.8
mer-$[Co(O)_3(N)_3]$	7, 8	60.7, 57.0, 53.4	79.9
fac-$[Co(O)_3(N)_3]$	9, 10	57.0	79.9
trans-$[Co(O)_4(N)_2]$	11	57.0(*a*), 49.7(*b*)	76.9
cis-$[Co(O)_4(N)_2]$	12, 13, 14	57.0(*b*), 53.4(*a*)	76.9
$[Co(O)_5(N)]$	15	53.4(*a*), 49.7(*b*)	73.9
$[Co(O)_6]$	16	49.7	70.9

situated at $(n/6)\delta^{II}(O)+\{(6-n)/6\}\delta^{II}(N)$, where $\delta^{II}(O)$ and $\delta^{II}(N)$ are the positions of the second bands of the non-mixed complexes, $[Co(O)_6]$ and $[Co(N)_6]$ respectively.

The energy levels in octahedral and the lower-symmetry complexes belonging to the d^3 and d^6 systems have been discussed by Yamatera,(2) McClure,(12) Wentworth and Piper,(13) and Schäffer and Jørgensen,(14) using several kinds of semi-empirical parameters. In the present paper, Yamatera's parameters, somewhat modified, are used. For all the members of a $[Co(O)_n(N)_{6-n}]$ series, the energies of the first and the second absorption bands are as in Table 3. The superscripts

---

12) D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York (1961), p. 498.

13) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709, 1524 (1965).

14) C. E. Schäffer and C. K. Jørgensen, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **34**, No. 13 (1965).

I and II indicate that the parameters concern the first and the second absorption bands respectively, while the subscripts σ and π indicate the σ- and the π-contributions; there exists the relation:

$$\delta^k(\mathrm{X}) = \delta_\sigma{}^k(\mathrm{X}) + \delta_\pi{}^k(\mathrm{X}).$$

The expression for the first absorption band is fairly simple, as may be seen in Table 3, but that for the second band is more complicated. For example, the components of the second absorption band of a *cis*-$[\mathrm{Co(O)_4(N)_2}]$ complex may be expressed as follows;

$$a:\ \frac{5}{12}\delta_\sigma{}^{\mathrm{II}}(\mathrm{N}) + \frac{1}{4}\delta_\pi{}^{\mathrm{II}}(\mathrm{N}) + \frac{7}{12}\delta_\sigma{}^{\mathrm{II}}(\mathrm{O}) + \frac{3}{4}\delta_\pi{}^{\mathrm{II}}(\mathrm{O}),$$

$$b:\ \frac{1}{6}\delta_\sigma{}^{\mathrm{II}}(\mathrm{N}) + \frac{1}{2}\delta_\pi{}^{\mathrm{II}}(\mathrm{N}) + \frac{5}{6}\delta_\sigma{}^{\mathrm{II}}(\mathrm{O}) + \frac{1}{2}\delta_\pi{}^{\mathrm{II}}(\mathrm{O}).$$

If calculated as a mean of the two or three components of a complex, weighted with the degeneracy numbers of the components (2 for the *a*, 1 for the *b* or other components), the expression becomes simpler and the shift of the band obeys "the rule of average environment"; the weighted mean expressions for the second bands are presented in the last column of Table 3.

It is possible to obtain the values of $\delta^{\mathrm{I}}(\mathrm{N})$ and $\delta^{\mathrm{II}}(\mathrm{N})$ from the observed positions of the first and the second bands of the $[\mathrm{Co(en)_3}]^{3+}$ complex, and $\delta^{\mathrm{I}}(\mathrm{O})$ and $\delta^{\mathrm{II}}(\mathrm{O})$ from the data of the $[\mathrm{Co(ox)_3}]^{3-}$ complex. Substituting these parameter values into the expressions of Table 3, the band positions of all the complexes of the $[\mathrm{Co(ox)}_x\mathrm{(gly)}_y\mathrm{(en)}_z]$ series can be approximately predicted to be as shown in Table 4, where the positions of the second bands are calculated by using the weighted mean expressions. It is clear that the values in Table 4 coincide well with the observed maxima or shoulders on the curves presented in Fig. 6. This means that the nitrogen atoms of ethylenediamine and glycinate ligands are not very different, and that this is also true for the oxygen atoms of oxalate and glycinate ligands.

Recently it has been recognized that CD (circular dichroism) spectra are very useful in assigning the shifted components of *d-d* transition bands. So far the CD spectra have been measured for about half of the present sixteen complexes; those of Complexes No. 1, 2, 3, 8, 9, 14, 15, and 16 have been reported in the literature,[9,15,16] and that for No. 11 has been recently measured in this laboratory.[17] The CD spectra[16] of the $[\mathrm{Co(ox)_2(en)}]^-$ complex (No. 14), for example, showed two and three CD components in its first and second absorption bands respectively, but these splittings have never been detected in the ordinary absorption spectra, as was shown in Fig. 6. It is very promising that three split components were actually detected in the second bands of several complexes by the CD measurements. Nevertheless, a detailed discussion of the split CD components must be postponed until the CD spectra have been thoroughly measured for the complete series of sixteen complexes. Theories of the shift and split of the CD components are now very incomplete.

The authors wish to thank Assistant Professor Fukiko Yamada of Kansai University for performing the NMR measurements.

---

15) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963); A. J. McCaffery, S. F. Mason and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883; A. J. McCaffery, S. F. Mason and B. J. Norman, *ibid.*, **1965**, 5094.

16) B. E. Douglas, R. A. Haines and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963); C. T. Liu and B. E. Douglas, *ibid.*, **3**, 1356 (1964); B. E. Douglas and S. Yamada, *ibid.*, **4**, 1562 (1965).

17) J. Hidaka and Y. Shimura, This Bulletin, in Press.