BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2312—2317 (1967)

The Optical Resolution and Circular Dichroism of *trans*(N)-oxalatobis(amino-acidato)cobalt(III) Complexes

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(Received April 17, 1967)

Three oxalatobis(amino-acidato)cobalt(III) complexes of a *trans*(N) type have been resolved into their optically active isomers, and their visible and ultraviolet absorption spectra, circular dichroism spectra, and rotatory dispersion have been measured and discussed. The amino acids used are glycine, β-alanine, and L-α-alanine, the last named of which produces a pair of diastereomeric, not antipodal, isomers in its complex. The two diastereomeric isomers have been separated by means of the solubility difference between them. The splitting of the first absorption band of the complexes has been discussed in relation to the behavior of their CD curves. The absolute configurations of the complexes have been inferred from their CD spectra.

It has been recently recognized that CD (circular dichroism) spectra are extremely useful in assigning the split components of d-d transition bands of metal complexes.1–4) The CD spectra1) of $(+)_{546}$-Na[Co(ox)$_2$(en)], for example, show two and three components in its first and second absorption bands respectively, while these splittings have never been detected in its ordinary absorption spectrum. Furthermore, considerable progress has been made in the field of the stereospecific separation of the optical isomers of metal complexes with optically active ligands.5) These investigations have also been made on the basis of their CD spectra mainly. So far the *trans*(N)-[Co(ox)(gly)$_2$]$^-$ ion has been the only known example of a cobalt(III) complex of a *trans*(N)-oxalatobis(amino-acidato) type.6) In the present paper, the optical resolutions of this bisglycinato and the corresponding new bis(β-alaninato) complexes will be reported, and their CD and RD (rotatory dispersion) spectra will be compared with each other. Two configurationally optically active isomers of the corresponding bis(L-alaninato) complex will also be separated by means of the stereospecificity due to the coordinated L-alaninate ligands. The absolute configurations and the

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2) 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.

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

4) T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965); K. Ohkawa, J. Hidaka and Y. Shimura, This Bulletin, **39**, 1715 (1966); T. Yasui, J. Hidaka and Y. Shimura, *ibid.*, **39**, 2417 (1966).

5) a) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959); b) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1796 (1964); c) B. E. Douglas and S. Yamada, *ibid.*, **4**, 1562 (1965); d) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

6) N. Matsuoka, J. Hidaka and Y. Shimura, This Bulletin, **40**, 1868 (1967).

additivity of the configurational and vicinal CD curves of these complex ions will be discussed.

Experimental

Preparation and Resolution. *Potassium trans-(N)-Oxalatobisglycinatocobaltate(III): 1)* (±)-*trans*(N)-K[Co(ox)(gly)$_2$]. A solution of 19.5 g of cobalt(II) chloride hexahydrate in 20 m*l* of hot water was added to a solution of 21.9 g of potassium oxalate and 17.8 g of glycine in 80 m*l* of hot water. To the mixed solution, placed on a boiling water bath, 20 g of lead dioxide were gradually added; the resulting mixture was then mechanically stirred at 60°C for about one hour. The color of the solution changed from dark red to blue violet. After the mixture had been cooled to room temperature, a large amount of insoluble materials was filtered off, and the filtrate was kept in a refrigerator overnight. A large amount of the crude product deposited was then filtered off. It has been reported separately[6] that two kinds of *cis*(N)-isomers can be obtained from the filtrate in this step. A small amount of the lead salt of the complex ion, poorly soluble and light blue in color, was contaminated in the crude *trans*(N)-complex obtained. Therefore, the crude product was suspended in an appropriate amount of water, and a small amount of potassium iodide was stirred into it. The lead iodide precipitated was filtered off and washed with a little ice water. Ethanol was added to the combined filtrate and washings. The light blue complex obtained was recrystallized from water by the addition of ethanol.

Found: C, 21.32; H, 2.49; N, 8.41%. Calcd for K[Co(C_2O_4)($C_2H_4NO_2$)$_2$]: C, 21.56; H, 2.41; N, 8.38%.

2) $(+)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$]. Two grams of $(+)_{546}$-[Co(ox)(en)$_2$]I[7] were suspended in 40 m*l* of water at 50°C. After 1 g of silver acetate had been added to the suspension, the resulting mixture was vigorously shaken for 10 min. The silver iodide thus precipitated was filtered off and washed with a small amount of ice water. To the combined filtrate and washings, there was added a solution containing 2.4 g of (±)-*trans*(N)-K[Co(ox)(gly)$_2$] in 100 m*l* of warm water. After the mixed solution had been cooled to room temperature and the vessel scrubbed with a glass rod, the solution was chilled in an ice bath for about one hour. The red brown diastereomer, $(+)_{546}$-[Co(ox)(gly)$_2$]·$(+)_{546}$-[Co(ox)(en)$_2$]·H$_2$O, then crystallized out gradually. It was filtered off and washed with 5 m*l* of ice water, ethanol, and then ether. It was dried in a vacuum desiccator.

Found: C, 24.87; H, 4.59; N, 14.30; H$_2$O, 3.18%. Calcd for [Co(C_2O_4)($C_2H_4NO_2$)$_2$][Co(C_2O_4)($C_2H_8N_2$)$_2$]·H$_2$O: C, 24.83; H, 4.51; N, 14.48; H$_2$O, 3.10%.

For a 0.15% aqueous solution of the diastereomer in a 1/2 dm tube: $\alpha_{589}^{15}=(+)0.29°$, $\alpha_{546}^{15}=(+)0.52°$.

The diastereomer was suspended in a small volume of water and, after a little excess of sodium iodide had been added to the suspension, the mixed solution was sufficiently stirred. The least soluble $(+)_{546}$-[Co(ox)(en)$_2$]I deposited was filtered off and washed with 5 m*l* of a 10% sodium iodide solution. An appropriate amount of ethanol was added to the combined filtrate and washings. The light blue $(+)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$] crystallized out soon after. The product was crystallized from water by adding ethanol; washed with a water-ethanol mixture (1 : 1), ethanol, and ether, and then dried in a vacuum desiccator. $[M]_{546}^{15}=(+)1800°$.

Found: C, 22.52; H, 2.61; N, 8.81%. Calcd for Na[Co(C_2O_4)($C_2H_4NO_2$)$_2$]: C, 22.65; H, 2.53; N, 8.80%.

3) $(-)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$]. The resolution was carried out by the same method as that used for the $(+)_{546}$-*trans*(N)-isomer, but using $(-)_{546}$-[Co(ox)(en)$_2$]I instead of the $(+)_{546}$-isomer. $[M]_{546}^{15}=(-)1800°$.

Found: C, 22.48; H, 2.60; N, 8.84%. Calcd for Na[Co(C_2O_4)($C_2H_4NO_2$)$_2$]: C, 22.65; H, 2.53; N, 8.80%.

4) $(+)_{546}$- or $(-)_{546}$-*trans*(N)-K[Co(ox)(gly)$_2$]. When the filtrate from the red brown diastereomer in 2) or 3) was kept in a refrigerator overnight, a small amount of the diastereomer was found again. It was filtered off. A small amount of potassium iodide was then stirred into the filtrate, and the least soluble iodide precipitated was filtered off. The optically active potassium salt was obtained when an appropriate amount of ethanol was added, little by little, to the filtrate. The recrystallization was made from water by adding ethanol.

Found (for the $(+)_{546}$-isomer): C, 21.91; H, 2.61; N, 8.37%. Calcd for K[Co(C_2O_4)($C_2H_4NO_2$)$_2$]: C, 21.51; H, 2.41; N, 8.38%.

5) Resolution by Strychnine. In order to check the optical purity of the complexes resolved above, the resolution using strychnium sulfate pentahydrate was attempted. Two-and-a-half grams of strychnium sulfate pentahydrate were dissolved in 40 m*l* of hot water, and then 2 g of (±)-*trans*(N)-K[Co(ox)(gly)$_2$] were completely dissolved in the hot solution. The resulting solution was slowly cooled to room temperature without stirring; then it was chilled in an ice bath for about one hour. A white blue diastereomer crystallized out, plus a small amount of strychnium sulfate. It was filtered off and washed with a little ice water, ethanol, and ether, and then dried in air. This less soluble diastereomer showed a negative rotation at 589 mμ and a positive rotation at 546 mμ. The diastereomer was suspended in a little excess of a sodium iodide solution with stirring. After the least soluble strychnium iodide which was precipitated had been filtered off, an appropriate amount of ethanol was added, little by little, to the filtrate. A light blue crystalline powder was obtained. The recrystallization was then carried out as has been described above. $[M]_{546}^{15}=(+)1795°$.

Found: C, 22.60; H, 2.77; N, 8.76%. Calcd for Na[Co(C_2O_4)($C_2H_4NO_2$)$_2$]: C, 22.65; H, 2.53; N, 8.80%.

Potassium trans(N)-Oxalatobis(β-alaninato)cobaltate(III) Dihydrate: 6) (±)-*trans*(N)-K[Co(ox)(β-ala)$_2$]·2H$_2$O. A solution of 20 g of cobalt(II) chloride hexahydrate in 20 m*l* of hot water was added to a solution of 16 g of potassium oxalate and 15 g of β-alanine in 80 m*l* of hot water. The dark red solution was then oxidized by adding 15 g of lead dioxide while warming it on a water bath; the resultant mixture was mechanically stirred for about 40 min. After the mixture had been

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

cooled to room temperature, a large amount of insoluble materials was filtered off. About 80 m*l* of methanol was then added to the blue violet filtrate, and the mixture was kept in a refrigerator overnight. The *trans*(N)-complex deposited (potassium salt) was contaminated with a small amount of the lead salt of the complex ion; therefore, it was suspended in an appropriate amount of water, and the rather poorly soluble light blue lead salt was filtered off. This lead salt was again suspended in a small volume of water, and after a small excess of potassium iodide had been added to the suspension with mechanical stirring, the yellow precipitate which resulted was filtered off and washed with a little ice water. To the combined filtrate and washings, about 120 m*l* of methanol were added and the mixture was kept in a refrigerator overnight. The complex thus obtained was recrystallized from water by adding methanol; wahsed with a little ice water, methanol, and ether, and then dried in a vacuum desiccator.

Found: C, 27.01; H, 3.47; N, 7.61; H_2O, 9.23%. Calcd for $K[Co(C_2O_4)(C_4H_6NO_2)_2]\cdot 2H_2O$: C, 26.86; H, 3.35; N, 7.77; H_2O, 9.09%.

The more soluble *cis*(N)-complexes can be obtained in a similar way, as has been reported before.6)

7) $(+)_{546}$-*trans*(N)-K[Co(ox)(β-ala)$_2$]. A suspension of 3 g of $(+)_{546}$-[Co(ox)(en)$_2$]I in 20 m*l* of water was vigorously shaken with 1.3 g of silver acetate at 50°C for about 10 min. The silver iodide thus precipitated was then filtered off and washed with a little ice water. In the combined filtrate and washings there were dissolved 3 g of (±)-*trans*(N)-K[Co(ox)-(β-ala)$_2$]·2H$_2$O, after which the mixed solution was chilled in an ice bath for about four hours. The red brown diastereomer deposited, $(+)_{546}$-[Co(ox)(β-ala)$_2$]·$(+)_{546}$-[Co(ox)(en)$_2$], was filtered off; washed with a little ice water, methanol, and then ether, and dried in a vacuum desiccator.

Found: C, 28.44; H, 4.80; N, 14.01%. Cacld for $[Co(C_2O_4)(C_3H_6NO_2)_2][Co(C_2O_4)(C_2H_8N_2)_2]$: C, 28.48; H, 4.78; N, 14.23%.

For a 0.15% aqueous solution of the diastereomer in a 1/2 dm tube: $\alpha^{15}_{589}=(+)0.25°$, $\alpha^{15}_{546}=(+)0.37°$.

Two grams of the red brown diastereomer were suspended in 20 m*l* of water; after a small excess of potassium iodide had been added to the suspension, the mixture was sufficiently stirred in an ice bath. The least soluble complex, $(+)_{546}$-[Co(ox)(en)$_2$]I, was thus precipitated. It was filtered off and washed with a little ice water containing potassium iodide. About 80 m*l* of methanol were added to the combined filtrate and washings, and the mixture was chilled in an ice bath. When the vessel was scrubbed with a glass rod, a light blue complex began to crystallized within a few minutes. The crystals obtained were recrystallized from water by adding methanol. $[M]^{15}_{546}=(+)880°$.

Found: C, 26.51; H, 3.44; N, 7.65%. Calcd for $K[Co(C_2O_4)(C_3H_6NO_2)_2]$: C, 26.52; H, 3.33; N, 7.73%.

8) $(-)_{546}$-*trans*(N)-K[Co(ox)(β-ala)$_2$]. The filtrate from the diastereomer in 7) was kept in a refrigerator overnight, during which period a small amount of the diastereomer was precipitated. After the diastereomer had been filtered off, a little potassium iodide was added to the filtrate. A large amount of methanol was then added to the solution. The complex desired began to deposit when the solution was chilled in an ice bath. The recrystallization was made from water by adding methanol. $[M]^{15}_{546}=(-)870°$.

Found: C, 26.49; H, 3.41; N, 7.68%. Calcd for $K[Co(C_2O_4)(C_3H_6NO_2)_2]$: C, 26.52; H, 3.33; N, 7.73%.

This isomer, $(-)_{546}$-*trans*(N)-K[Co(ox)(β-ala)$_2$], was also obtained by the same method as that of the $(+)_{546}$-isomer by using $(-)_{546}$-[Co(ox)(en)$_2$]I as a resolving agent. It was confirmed that this method is superior to that using the filtrate in 7).

Potassium trans(N)-Oxalatobis(L-alaninato)cobaltate(III): 9) (*ΔΛ*)-, *Δ*- and *Λ*-*trans*(N)-K[Co(ox)(L-ala)$_2$]. To a solution containing 8 g of potassium oxalate and 7.5 g of L-alanine in 50 m*l* of hot water, there were added 10 g of cobalt(II) chloride hexahydrate in 20 m*l* of hot water. Twenty grams of lead dioxide were then gradually added to the dark red solution, while warming it on a water bath, after which the mixture was mechanically stirred for about 40 min. After the mixture had been cooled sufficiently, the insoluble materials were filtered off and the blue violet filtrate was kept in a refrigerator overnight. The light blue complex deposited was filtered; the complex was treated as follows, as in (1) below, and the filtrate, as in (3). (1): The light blue precipitate was recrystallized from a little hot water, washed with ice water and with a water-ethanol mixture (1 : 1), and then dried in a vacuum desiccator (Fraction A). (2): By adding ethanol to the combined filtrate and washings from the recrystallization step in (1), another portion of the light blue complex was obtained. This complex was washed with a small volume of a water-ethanol mixture (1 : 1) and with ethanol, and was then dried in a vacuum desiccator (Fraction A′). (3): The original filtrate was gradually concentrated to one-third of its original volume on a water bath, and then chilled in an ice bath. The complex deposited was filtered off and recrystallized from a little hot water (Fraction B). (4): Fraction B′ was obtained by adding an appropriate amount of ethanol to the filtrate from the recrystallization of Fraction B. It was always confirmed from the splitting pattern6) of the first absorption band that the complex obtained in each the step was the *trans*(N)-form. These fractionations were continued until the absorption spectra began to indicate the presence of the *cis*(N)-form.6) Each fraction of the *trans*(N)-complexes obtained (A, A′, B, B′, and so on) was purified by passing its aqueous solution through a column (15 mm × 300 mm) containing strong base anion-exchange resin (Dowex 1X10, 200—400 mesh, chloride form). The details of the chromatographic purification are the same as have been described in an earlier paper.6) The less soluble isomer was concentrated in the first fraction, A, while the more soluble isomer was obtained from the later fractions. Fractions A′ and B were found from their CD spectra to be mixtures of the two isomers.

For the less soluble isomer, *trans*(N)-K[Co(ox)(L-ala)$_2$], $[M]^{15}_{546}=(-)2100°$.

Found: C, 26.62; H, 3.39; N, 7.65%. Calcd for $K[Co(C_2O_4)(C_3H_6NO_2)_2]$: C, 26.52; H, 3.33; N, 7.73%.

For the more soluble isomer, *trans*(N)-K[Co(ox)-(L-ala)$_2$], $[M]^{15}_{546}=(+)660°$.

Found: C, 26.67; H, 3.43; N, 7.68%. Calcd for

$K[Co(C_2O_4)(C_3H_6NO_2)_2]$: C, 26.52; H, 3.33; N, 7.73%.

Measurements. The electronic absorption spectra of the complexes in aqueous solutions were measured by a Beckman DU spectrophotometer. The CD spectra were recorded with a Roussel-Jouan dichrographe, while the RD curves were obtained with a Yanagimoto Recording spectropolarimeter, model-185.

Results and Discussion

The optical resolution of *trans*(N)-[Co(ox)-(gly)$_2$]$^-$ was achieved by two ways, independent of each other, using optically active [Co(ox)-(en)$_2$]$^+$ or strychnium sulfate pentahydrate as the resolving agent. The CD and RD curves of $(+)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$], which was obtained from the less soluble diastereomer with $(+)_{546}$-[Co(ox)(en)$_2$]$^+$, quite agree with those of one from the less soluble diastereomers with strychnine.

The *Δ*- and *Λ*-*trans*(N)-[Co(ox)(L-ala)$_2$]$^-$ isomers are not antipodal, but diastereomeric, while the *Δ*- and *Λ*-*trans*(N)-[Co(ox)(gly)$_2$]$^-$ isomers are related to each other antipodally. It may be expected, therefore, that the solubility difference will allow the separation of the *Δ*(L-ala) and *Λ*(L-ala) isomers of the bis(L-alaninato) complex, as in the case of tris(L-alaninato)cobalt(III) complexes.[5c)] This was actually substantiated; the attempt to separate the *Δ*- and *Λ*-*trans*(N)-[Co-(ox)(L-ala)$_2$]$^-$ isomers by repeating recrystallizations succeeded, as has been described above in the "Experimental" section.

It has been known that *trans*(N)-[Co^{III}(O)$_4$-(N)$_2$]-type complexes can be well characterized by the splitting of the first absorption band. As is seen in Figs. 1—4 and Table 1, the first absorption band of the bis(β-alaninato) complex is exactly split into two bands, whereas the corresponding splitting of the bisglycinato or bis(L-alaninato) complex caused the first absorption band to have

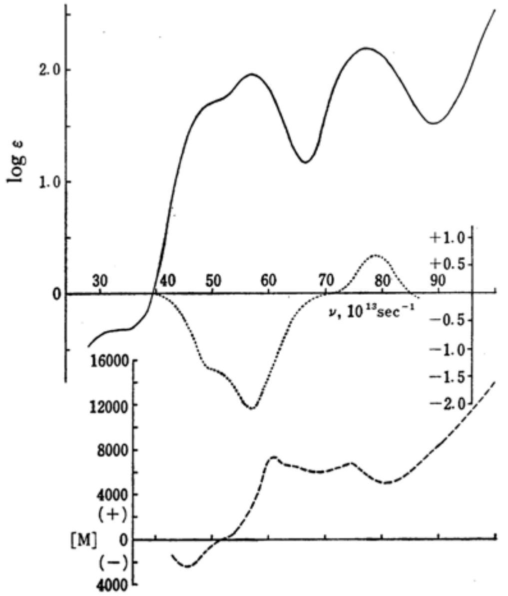

Fig. 1. Absorption (——), CD (----) and RD (—–) curves of $(+)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$].

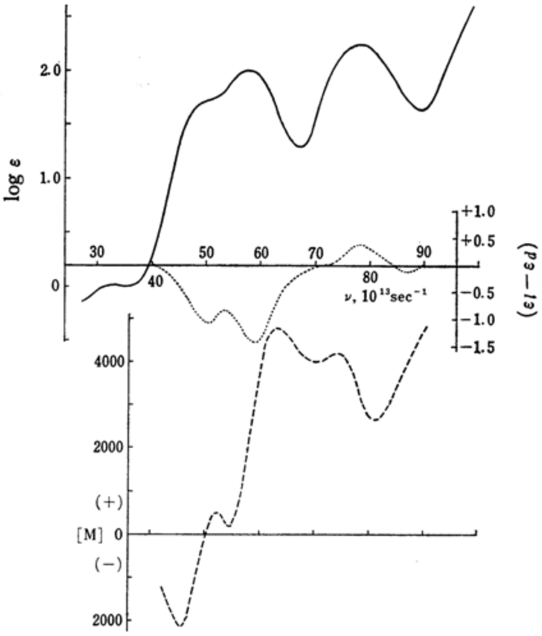

Fig. 2. Absorption (——), CD (----) and RD (—–) curves of $(+)_{546}$-*trans*(N)-K[Co(ox)(L-ala)$_2$].

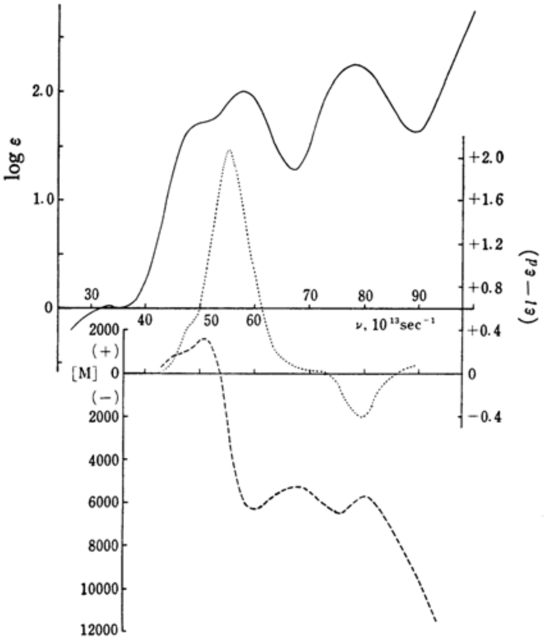

Fig. 3. Absorption (——), CD (----) and RD (—–) curves of $(-)_{546}$-*trans*(N)-K[Co(ox)(L-ala)$_2$].

TABLE 1. ABSORPTION MAXIMA OF *trans*(N)- $[Co(O)_4(N)_2]$ TYPE COMPLEXES

Complex ion	A Band		I Band		II Band		Ref.
	ν_{max}	($\log \varepsilon_{max}$)	ν_{max}	($\log \varepsilon_{max}$)	ν_{max}	($\log \varepsilon_{max}$)	
$[Co(ox)(gly)_2]^-$	*ca.* 33	($\bar{1}$.70)	*ca.* 50 56.6	(1.7) (2.00)	77.5	(2.23)	
$[Co(ox)(L\text{-}ala)_2]^-$	*ca.* 33	(0.01)	*ca.* 50 56.8	(1.7) (2.01)	77.9	(2.24)	
$[Co(ox)(\beta\text{-}ala)_2]^-$	30.0	($\bar{1}$.95)	48.0 56.5	(1.76) (2.00)	78.9	(2.12)	
$[Co(ada)_2]^-$*			50.0 61.2	(1.06) (1.72)	83.3	(1.75)	8)

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

* The abbreviation "ada" represents a divalent ammoniadiacetate anion $NH(CH_2COO)_2^{2-}$.

TABLE 2. CD DATA OF *trans*(N)-OXALATOBIS(AMINO-ACIDATO)COBALT(III) COMPLEXES

Complex ion	I Band		II Band	
	ν_{ext}	($\Delta\varepsilon_{ext}$)	ν_{ext}	($\Delta\varepsilon_{ext}$)
$(+)_{546}$-$[Co(ox)(gly)_2]^-$	*ca.* 50 56.9	(−1.4) (−2.07)	78.5	(+0.69)
$(+)_{546}$-$[Co(ox)(L\text{-}ala)_2]^-$	50.5 59.0	(−1.1) (−1.45)	78.0 87.0	(+0.35) (−0.13)
$(-)_{546}$-$[Co(ox)(L\text{-}ala)_2]^-$	*ca.* 48 55.5	(+0.44) (+2.07)	79.0	(−0.41)
$(+)_{546}$-$[Co(ox)(\beta\text{-}ala)_2]^-$	47.1 *ca.* 50 58.6	(−0.43) (−0.3) (−0.57)	71.4 79.6	(−0.13) (+0.71)

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

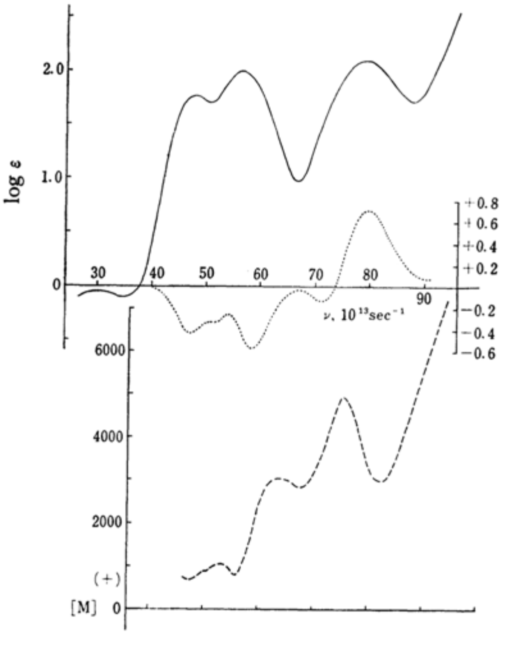

Fig. 4. Absorption (——), CD (----) and RD (— —) curves of $(+)_{546}$-*trans*(N)-K$[Co(ox)(\beta\text{-}ala)_2]$.

a shoulder on the longer wavelength side. Thus a sub-band (at 625 mμ) of the bis(β-alaninato) complex is situated at a longer wavelength than a shoulder of the bisglycinato or bis(L-alaninato) complex. Now, it has been generally recognized that an effective field symmetry rather than a true molecular symmetry determines the splitting of the first absorption band. In the present case, it can be said that the first absorption bands of these *trans*(N)-$[Co(ox)(am)_2]^-$[*1]-type complex ions show a pattern of the tetragonal splitting. As may be seen in Fig. 1, the CD behavior of $(+)_{546}$-*trans*(N)-$[Co(ox)(gly)_2]^-$ appears to be also in support of the tetragonal splitting pattern. A similar relationship is also suitable for the pattern of $(+)_{546}$- or $(-)_{546}$-*trans*(N)-$[Co(ox)(L\text{-}ala)_2]^-$, as may be seen in Figs. 2 and 3 and Table 2. However, the true symmetry of a *trans*(N)-$[Co(ox)(am)_2]^-$-type complex ion belongs to C_2; therefore, its CD band may be expected to be split into three components. In fact, the three negative CD peaks are observed in the CD curve of $(+)_{546}$-*trans*(N)-$[Co(ox)(\beta\text{-}ala)_2]^-$, as may be seen in Fig. 4 and Table 2. It may be assumed, therefore, that the CD curve of $(+)_{546}$-*trans*(N)-$[Co(ox)(gly)_2]^-$ in its first absorption band region also consists of three CD components, two of which existed very close together.

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8) J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962).

[*1] The abbreviation "am" represents a glycinate, L-α-alaninate, or β-alaninate ion.

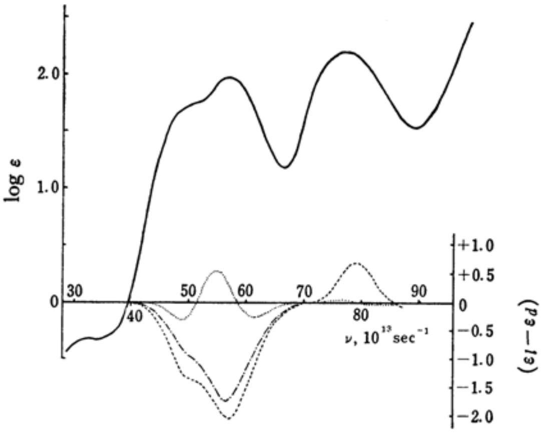

Fig. 5. Absorption (——) and CD (----) curves of $(+)_{546}$-*trans*(N)-Na[Co(ox)(gly)$_2$], and configurational (—·—) and vicinal (……) CD *trans*(N)-K[Co(ox)(L-ala)$_2$].

It has been known that the configurational and the vicinal effects can be separated and are additive for the cobalt(III) complexes which have optically active amino-acid in their coordination spheres.[5b,9] The treatment reported for the tris(L-alaninato)cobalt(III) complexes[9] was applied to the CD curves of the *Δ*- and *Λ*-*trans*(N)-[Co(ox)(L-ala)$_2$]$^-$ isomers. In the curve of the "vicinal effect," which was induced in the d-d transition bands by the coordinated L-alaninate ions, three CD components of its first absorption band were found, as may be seen in Fig. 5. The configurational curve has two CD peaks in this region. There is a rather good correspondence between the configurational curve for the L-alaninato complexes and that of the resolved *trans*(N)-Na[Co(ox)(gly)$_2$]. From a comparison of the net sign of the CD bands in the first absorption band region to that of the CD bands of *Δ*(+)-[Co(en)$_3$]$^{3+}$, it is possible to assign an absolute configuration, *Λ*[10], for the $(+)_{546}$-isomers of these *trans*(N)-oxalatobis(amino-acidato) complexes.

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[9] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1350 (1964).

[10] J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966); C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).