BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 119—126 (1969)

The Optical Resolution and Circular Dichroism of Cobalt(III) Complexes of the $[Co(O\text{–}O)_2(O\text{–}N)]^{2-}$ Type

Kiyoshi YAMASAKI, Jinsai HIDAKA and Yoichi SHIMURA

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

(Received January 31, 1968)

Four cobalt(III) complexes of the tris-chelate type containing two dicarboxylate anions and one aminocarboxylate anion have been newly prepared and separated into their optical isomers by a chemical resolution method: they are bismalonatoglycinato-, bismalonato(L-alaninato)-, bisoxalato(L-alaninato)- and bisoxalato(β-alaninato)-cobalt(III) complexes. The diastereomeric isomers of bisoxalato(L-alaninato)cobalt(III) complex have also been separated by the solubility difference between their barium salts. The absorption spectra, circular dichroism spectra and rotatory dispersion of these complexes have been measured and discussed in relation to the splitting of the d–d transition bands. The absolute configurations of the complexes have been inferred from their circular dichroism spectra. The additivity of configurational and vicinal contributions to the optical activity has been substantiated for the bisoxalato- and bismalonato-(L-alaninato)-cobalt(III) complexes, and some considerations concerning the less stereospecific formation of the L-alaninato diastereomeric isomers have been made in relation to the additivity.

The splitting of the d–d transition bands has been studied for many types of complexes on the basis of their CD (circular dichroism) spectra and their RD (rotatory dispersion) curves.[1–6] It seems, however, that the splitting trend of the first absorption band for a bis(dicarboxylato)mono(aminocarboxylato)cobalt(III) type complex is not completely clear at the present time, because the bisoxalatoglycinatocobalt(III) complex is the only known example.[4]

Bürer pointed out that cobalt(III) complexes containing three six-membered chelate rings differ from those with three five-membered chelate rings in CD behavior of the first absorption band.[7] However, this type of problem has still not been solved. Thus it was thought desirable to study the CD spectra of complexes containing six- and five-membered chelate rings mixed.

In the present paper, the preparations and optical resolutions of four new tris-chelate complexes of the $[Co(O\text{–}O)_2(O\text{–}N)]^{2-}$ type[*1] will be reported. The CD spectra of the complexes will be compared with one another, and their absolute configurations inferred from their CD spectra. The additivity of configurational and vicinal contributions to the optical activity will be substantiated for the two L-alaninato complexes, and considered in relation to the formation ratio of the diastereomeric isomers. The solubility difference between the diastereomers containing these cobalt(III) complex ions will be briefly considered.

Experimental

Preparations of Malonato Complexes. The malonato complexes were prepared using a dark-green solution containing $[Co(mal)_3]^{3-}$.

1) $Ba[Co(mal)_2(gly)]\cdot 1.5H_2O$: To a solution containing 7.9 g of malonic acid and 11.1 g of sodium malonate in 30 m*l* of water were added 12.0 g of cobalt(II) acetate tetrahydrate, 6 m*l* of 50% acetic acid and 10 g of lead dioxide. The resulting mixture was cooled in an ice bath and mechanically stirred for about one hour. After the color of solution had changed from dark-red to dark-green, 3.7 g of glycine was added. The color of the solution gradually changed to dark-

---

[1] B. E. Douglas, R. A. Haines and J. C. Brushmiller, *Inorg. Chem.*, **2**, 1195 (1963).

[2] C. T. Liu and B. E. Douglas, *ibid.*, **3**, 1356 (1964).

[3] 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; B. J. Norman, *Inorg. Chim. Acta*, **1**, 177 (1967).

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

[5] J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962); 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); T. Komorita, J. Hidaka and Y. Shimura, to be published.

[6] J. Hidaka and Y. Shimura, This Bulletin, **40**, 2312 (1967).

[7] Th. Bürer, *Helv. Chim. Acta*, **46**, 2388 (1963).

[*1] The abbreviation (O–O) denotes a malonate(mal) or oxalate (ox) ion, and (O–N) a glycinate (gly), L-alaninate (L-ala) or β-alaninate (β-ala) ion.

blue when the resulting mixture was stirred at about 60°C for about 40 min. The dark-blue solution was placed in an ice bath for an hour, and then most insoluble material filtered off. To the filtrate, 4 m*l* of 30% aqueous solution of barium perchlorate was added, and the barium malonate deposited removed by filtration. The blue complex desired began to crystallize out when an additional 50 m*l* of barium perchlorate solution was added to the filtrate. After the solution had been cooled in an ice bath for an hour, the crude complex was filtered and washed with water, then methanol, and dried in air. 11 g.

The purification of this complex was performed as follows. Seven grams of the crude complex was added to a solution of 2.4 g of anhydrous sodium sulfate in 50 m*l* of water, and then the barium sulfate which precipitated out was filtered off. To the filtrate was added a solution of 8 g of barium perchlorate in 10 m*l* of water. After a small amount of the barium malonate deposited had been filtered off, the filtrate was kept in a refrigerator overnight. The complex which separated out was filtered and washed with an appropriate amount of water, then methanol, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 19.34; H, 2.21; N, 2.75%. Calcd for $Ba[Co(C_3H_2O_4)_2(C_2H_4NO_2)]\cdot 1.5H_2O$: C, 19.14; H, 2.20; N, 2.80%.

2) $Ba[Co(mal)_2(L\text{-}ala)]$: This complex was obtained by a procedure similar to that in 1) using L-alanine instead of glycine. The dark-green solution, containing 4.4 g of L-alanine, was kept at 60°C on a water bath with stirring for 40 min. After the mixture had been cooled to room temperature, most insoluble material was removed by filtration. Twenty grams of barium perchlorate was dissolved in the filtrate, and then the barium malonate which precipitated out was filtered off. An additional precipitate, which deposited upon adding 50 m*l* of methanol to the filtrate, was removed by filtration. The desired complex was precipitated out by adding 100 m*l* of a methanol-ethanol mixture (1 : 1) to the filtrate, and was filtered, washed with methanol and dried in a vacuum desiccator. 10 g.

The crude complex was dissolved in 40 m*l* of water, and to this solution was added 40 m*l* of methanol. After a small amount of the resulting insoluble material had been removed, 5 g of barium perchlorate was dissolved in the filtrate and 60 m*l* of methanol added to it with stirring. The fine bluish-violet crystals which deposited were filtered off, washed with methanol and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 22.14; H, 2.16; N, 2.71%. Calcd for $Ba[Co(C_3H_2O_4)_2(C_3H_6NO_2)]$: C, 22.13; H, 2.07; N, 2.87%. $[M]_{546}=-400°$, $[M]_{589}=+50°$.

Preparations of Oxalato Complexes. The oxalato complexes were prepared in the following two ways. In the first one, the binuclear complex, $Na_4[(ox)_2Co(OH)_2Co(ox)_2]\cdot 5H_2O$,[8] was used as starting material. In another one, a solution containing cobalt(II) chloride, potassium oxalate and amino acid (1 : 2 : 1) was oxidized with lead dioxide.

1) $Ba[Co(ox)_2(gly)]\cdot 0.5H_2O$: The preparation of this complex was reported by Dwyer *et al.*[4] In the present work, however, two different methods were attempted.

1-a). To a solution of 7.0 g of $Na_4[Co_2(ox)_4(OH)_2]\cdot 5H_2O$ and 1.5 g of glycine in 20 m*l* of water were added 3 g of lead dioxide and 6 m*l* of 25% acetic acid. The resulting mixture was kept on a water bath at 65°C with stirring for 20 min. After the color of solution had changed from dark-green to dark-blue, the mixture was cooled to room temperature and then lead dioxide removed by filtration. One gram of barium perchlorate was added to the filtrate, and then a small amount of the insoluble material which appeared filtered off. A further 8 g of barium perchlorate was dissolved in the filtrate and the solution cooled in an ice bath for an hour. The blue complex desired precipitated out and was filtered and dried in air. 3.4 g. The crude complex was purified as described in 1) of Preparation of Malonato Complexes.

Found: C, 15.82; H, 1.19; N, 3.00%. Calcd for $Ba[Co(C_2O_4)_2(C_2H_4NO_2)]\cdot 0.5H_2O$: C, 15.79; H, 1.11; N, 3.07%.

1-b). Twenty grams of potassium oxalate monohydrate and 4.3 g of glycine were dissolved in 40 m*l* of hot water. To the solution was added a solution containing 12.0 g of cobalt(II) chloride hexahydrate in 15 m*l* of hot water. The mixture was kept at 70°C on a water bath and 20 g of lead dioxide added, little by little. The color of solution gradually changed to dark bluish-violet within one hour. After the mixture had been cooled to room temperature, a large amount of the insoluble material which precipitated out was filtered off. The filtrate was kept in a refrigerator overnight. Additional insoluble material which deposited was filtered off, and a small amount of ethanol added to the filtrate. The blue precipitate was removed, and then the potassium salt of the desired blue complex was obtained by adding a large amount of ethanol to the filtrate. The crude product was recrystallized from water by the addition of ethanol. The crystals were filtered, washed with ethanol and ether and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 18.87; H, 1.10; N, 3.72%. Calcd for $K_2[Co(C_2O_4)_2(C_2H_4NO_2)]\cdot 3H_2O$: C, 18.61; H, 1.04; N, 3.61%.

The potassium salt can be easily changed to the barium salt with barium acetate monohydrate.

2) $K_2[Co(ox)_2(L\text{-}ala)]$: In the preparation of this complex, the same procedure as described in 1-a) was employed, but with 1.7 g of L-alanine instead of 1.5 g of glycine. After the lead dioxide had been removed, 4 g of potassium acetate was dissolved in the filtrate. To the solution was added 70 m*l* of methanol, and the slurry precipitate removed by filtration. The blue complex desired was obtained by adding a further 100 m*l* of methanol to the filtrate. Recrystallization was carried out from water by the addition of methanol. The crystals deposited were filtered, washed with methanol and acetone and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 21.18; H, 1.81; N, 3.54%. Calcd for $K_2[Co(C_2O_4)_2(C_3H_6NO_2)]$: C, 20.94; H, 1.50; N, 3.48%. $[M]_{546}=-80°$, $[M]_{589}=+440°$.

3) $Ba[Co(ox)_2(\beta\text{-}ala)]$: The β-alaninato complex was prepared using 1.7 g of β-alanine instead of 1.5 g of glycine as in 1-a). After the lead dioxide had been removed, 8 g of barium perchlorate was dissolved in the filtrate and the solution cooled in an ice bath. A small

---

[8] H. F. Holtzclaw, Jr., "Inorganic Syntheses," Vol. VIII, p. 204 (1966).

amount of the colorless insoluble material which precipitated out was filtered off, and then 10 m*l* of methanol added to the filtrate. After a small amount of the slurry precipitate which resulted had been removed, a further 30 m*l* of methanol was added to the filtrate with stirring. The barium salt of the desired blue complex which precipitated out was filtered off, washed with a water-methanol mixture(1 : 1), acetone and then ether, and dried in a desiccator. 4.7 g.

The crude complex was recrystallized two times from water by adding methanol. The crystals obtained were dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 18.14; H, 1.70; N, 3.02%. Calcd for $\mathrm{Ba[Co(C_2O_4)_2(C_3H_6NO_2)]}$: C, 18.28; H, 1.31; N, 3.04%.

Optical Resolutions. The five complexes described above were resolved using strychnium sulfate and $(+)_{546}$- or $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$ as resolving agents. The optical isomers of $[\mathrm{Co(ox)_2(\textsc{l}\text{-}ala)}]^{2-}$ were also separated without resolving agent.

i) Bismalonatoglycinatocobalt(III) Complex: *i-a) With Strychnium Sulfate.* Seven grams of strychnium sulfate pentahydrate was suspended in 40 m*l* of water and 4.0 g of $\mathrm{Ba[Co(mal)_2(gly)]\cdot 1.5H_2O}$ added. The mixture was vigorously shaken and barium sulfate which precipitated out was removed. When the filtrate was cooled in an ice bath and the vessle scrubbed with a glass rod, a pale blue diastereomer began to crystallize out. After the solution had been cooled in an ice bath for a while, the less soluble diastereomer which precipitated out was filtered off and washed with a little ice water. The diastereomer was dissolved in 5 m*l* of water and an excess of sodium perchlorate added to the solution. Then the strychnium perchlorate which precipitated out was removed. When an excess of barium perchlorate was dissolved in the filtrate and 5 m*l* of methanol added to it, the optically active barium salt of the complex crystallized out. The complex was filtered, washed with a little ice water, methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 18.54; H, 2.32; N, 2.66%. Calcd for $\mathrm{Ba[Co(C_3H_2O_4)_2(C_2H_4NO_2)]\cdot 2.5H_2O}$: C, 18.50; H,2.51; N, 2.70%. $[M]_{546}=-2400^\circ$, $[M]_{589}=-4600^\circ$.

i-b) By $(-)_{546}$-$[\mathit{Co(ox)(en)_2}]\mathit{I}$. To a solution containing 1.2 g of anhydrous sodium sulfate in 15 m*l* of hot water was added 4.0 g of $\mathrm{Ba[Co(mal)_2(gly)]\cdot 1.5H_2O}$. Then the barium sulfate which deposited was filtered off and washed with 5 m*l* of water. The washing was combined with the filtrate (solution "a"). Silver acetate (1.3 g) and $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$ (3.6 g) were shaken well in 15 m*l* of water, and the silver iodide which precipitated out was filtered off and washed with 5 m*l* of water. The washing was combined with the filtrate (solution "b"). To solution "a" was added solution "b", and the resultant solution concentrated in a vacuum desiccator over phosphorus pentoxide until the red-brown diastereomer appeared. The diastereomer was filtered off, washed with a water-methanol mixture (2 : 1) and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide. The less soluble diastereomer, $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]_2\cdot(-)_{546}$-$[\mathrm{Co(mal)_2\text{-}(gly)}]\cdot 2\mathrm{H_2O}$, was recrystallized from water by the addition of a methanol-ethanol mixture(1 : 1).

Found: C, 26.12; H, 4.63; N, 13.89%. Calcd for $[\mathrm{Co(C_2O_4)(C_2H_8N_2)_2}]_2\cdot[\mathrm{Co(C_3H_2O_4)_2(C_2H_4NO_2)}]\cdot 2\mathrm{H_2O}$: C, 26.48; H, 4.89; N, 13.90%. $[M]_{546}=-10270^\circ$, $[M]_{589}=-10390^\circ$.

The diastereomer was suspended in a small amount of water, and a slight excess of sodium iodide added to the suspension. After the mixture had been stirred well, $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$ which precipitated out was filtered off and an excess of barium perchlorate dissolved in the filtrate. The barium salt of the optically active complex was obtained by adding methanol to the solution and cooling it in an ice bath. This was filtered, washed with a water-methanol mixture (1 : 1), methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide. $[M]_{546}=-2550^\circ$, $[M]_{589}=-4700^\circ$.

ii) Bismalonato(l-alaninato)cobalt(III) Complex: *ii-a) With Strychnium Sulfate.* A small excess of strychnium sulfate pentahydrate (4.5 g) was added to a solution containing 2.5 g of unresolved $\mathrm{Ba[Co(mal)_2(\textsc{l}\text{-}ala)]}$ in 15 m*l* of water. The diastereomer obtained by a procedure similar to that of i-a) was filtered off and washed with a methanol-ether mixture (1 : 1). Recrystallization was carried out from methanol by the addition of ether. When the recrystallized diastereomer was dissolved in a small amount of water and treated with an excess of barium perchlorate, strychnium perchlorate deposited out. After it had been removed, the configurationally optically active barium salt of the complex was obtained by the addition of methanol and ether to the filtrate. The complex was filtered, washed with a methanol-ether mixture (1 : 1) and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 22.26; H, 2.32; N, 2.87%. Calcd for $\mathrm{Ba[Co(C_3H_2O_4)_2(C_3H_6NO_2)]}$: C, 22.13; H, 2.07; N, 2.87%. $[M]_{546}=+1300^\circ$, $[M]_{589}=+3200^\circ$.

ii-b) By $(+)_{546}$- *or* $(-)_{546}$-$[\mathit{Co(ox)(en)_2}]\mathit{I}$. Solution "a", containing the sodium salt of the complex (obtained from 4.9 g of unresolved $\mathrm{Ba[Co(mal)_2(\textsc{l}\text{-}ala)]}$, 1.4 g of anhydrous sodium sulfate and 15 m*l* of water), and solution "b", containing the acetate of $(+)_{546}$-$[\mathrm{Co(ox)(en)_2}]^+$ (obtained from 7.9 g of $(+)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$, 3.3 g of silver acetate and 20 m*l* of water), were mixed together. When the mixed solution was cooled in an ice bath, the less soluble diastereomer, $(+)_{546}$-$[\mathrm{Co(ox)(en)_2}]_2\cdot(-)_{546}$-$[\mathrm{Co(mal)_2(\textsc{l}\text{-}ala)}]\cdot\mathrm{H_2O}$, crystallized out. The diastereomer was recrystallized from water by the addition of methanol. The crystals were filtered, washed with methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 27.90; H, 5.05; N, 13.37%. Calcd for $[\mathrm{Co(C_2O_4)(C_2H_8N_2)_2}]_2\cdot[\mathrm{Co(C_3H_2O_4)_2(C_3H_6NO_2)}]\cdot\mathrm{H_2O}$: C, 27.93; H, 4.91; N, 13.96%. $[M]_{546}=+5450^\circ$, $[M]_{589}=+1460^\circ$.

The configurationally optically active barium salt was obtained by the same method as in i-b). It was recrystallized from water by adding a methanol-ethanol mixture (1 : 1). The fine crystals obtained were filtered, washed with methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 22.56; H, 1.93; N, 2.83%. Calcd for $\mathrm{Ba[Co(C_3H_2O_4)_2(C_3H_6NO_2)]}$: C, 22.13; H, 2.07; N, 2.87%. $[M]_{546}=-2800^\circ$, $[M]_{589}=-4400^\circ$.

When $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$ was used instead of $(+)_{546}$-$[\mathrm{Co(ox)(en)_2}]\mathrm{I}$ in the above procedure, the less soluble diastereomer obtained was $(-)_{546}$-$[\mathrm{Co(ox)(en)_2}]_2\cdot(-)_{546}$-$[\mathrm{Co(mal)_2(\textsc{l}\text{-}ala)}]\cdot 1.5\mathrm{H_2O}$.

Found: C, 27.74; H, 4.86; N, 13.54%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]_2 \cdot [Co(C_3H_2O_4)_2(C_3H_6NO_2)] \cdot 1.5H_2O$: C, 27.65; H, 4.97; N, 13.82%. $[M]_{546} = -9100°$, $[M]_{589} = -7140°$.

iii) Bisoxalatoglycinatocobalt(III) Complex: This complex has been resolved by Dwyer *et al.*[4] A slightly modified method was employed in the present study. Namely, a solution containing the sodium salt of the complex (obtained from $Ba[Co(ox)_2(gly)] \cdot 0.5H_2O$, sodium sulfate and water in the same way as in i-b)) was used instead of $Na_2[Co(ox)_2(gly)] \cdot 1.5H_2O$ as in the reported procedure. The barium salt of the $(-)_{546}$-isomer, which was obtained from the less soluble diastereomer with $(+)_{546}$-$[Co(ox)(en)_2]^+$, was dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 14.87; H, 1.77; N, 2.99%. Calcd for $Ba[Co(C_2O_4)_2(C_2H_4NO_2)] \cdot 2H_2O$: C, 14.94; H, 1.66; N, 2.90%. $[M]_{546} = -8100°$, $[M]_{589} = -1300°$.

iv) Bisoxalato(L-alaninato)cobalt(III) Complex: *iv-a) Without Resolving Agent.* Eight grams of barium perchlorate was dissolved in a solution containing the sodium salt of the complex as described in 2) of Preparation of Oxalato Complexes, and the less soluble diastereomer of the barium salt, $(+)_{546}$-$Ba[Co(ox)_2(L\text{-}ala)] \cdot 0.5H_2O$, crystallized out. After the mixture had been cooled in an ice bath for one hour, the barium salt was filtered, washed with water, methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 18.05; H, 1.53; N, 2.98%. Calcd for $Ba[Co(C_2O_4)_2(C_3H_6NO_2)] \cdot 0.5H_2O$: C, 17.93; H, 1.50; N, 2.99%. $[M]_{546} = +7100°$, $[M]_{589} = +1300°$.

iv-b) By $(+)_{546}$- or $(-)_{546}$-$[Co(ox)(en)_2]I$. This method is almost the same as i-b). A solution of 4.0 g of $K_2[Co(ox)_2(L\text{-}ala)]$ in 25 m*l* of water was used instead of solution "a" containing $Na_2[Co(mal)_2(gly)]$ in i-b). The less soluble diastereomer formed by using $(+)_{546}$-$[Co(ox)(en)_2]I$ was $(+)_{546}$-$[Co(ox)(en)_2]_2 \cdot (-)_{546}$-$[Co(ox)_2(L\text{-}ala)] \cdot H_2O$.

Found: C, 26.03; H, 4.64; N, 14.40%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]_2 \cdot [Co(C_2O_4)_2(C_3H_6NO_2)] \cdot H_2O$: C, 26.06; H, 4.57; N, 14.40%. $[M]_{546} = 0°$, $[M]_{589} = +5100°$.

By the same method as in i-b), the barium salt of the $(-)_{546}$-isomer was obtained from the diastereomer.

Found: C, 17.54; H, 1.40; N, 2.68%. Calcd for $Ba[Co(C_2O_4)_2(C_3H_6NO_2)] \cdot H_2O$: C, 17.57; H, 1.67; N, 2.93%. $[M]_{546} = -7050°$, $[M]_{589} = -500°$.

When $(-)_{546}$-$[Co(ox)(en)_2]I$ was used as a resolving agent, the less soluble diastereomer obtained was $(-)_{546}$-$[Co(ox)(en)_2]_2 \cdot (+)_{546}$-$[Co(ox)_2(L\text{-}ala)] \cdot 0.5H_2O$.

Found: C, 26.44; H, 4.83; N, 14.12%. Calcd for $[Co(C_2O_4')(C_2H_8N_2)_2]_2 \cdot [Co(C_2O_4)_2(C_3H_6NO_2)] \cdot 0.5H_2O$: C, 26.35; H, 4.54; N, 14.56%. $[M]_{546} = -6560°$, $[M]_{589} = -5280°$.

The barium salt of the $(+)_{546}$-isomer was obtained from the diastereomer. $[M]_{546} = +7100°$, $[M]_{589} = +1300°$.

v) Bisoxalato(β-alaninato)cobalt(III) Complex: Similar to the method of i-b), a mixed solution containing the sodium salt of the complex and the acetate of $(-)_{546}$-$[Co(ox)(en)_2]^+$ was cooled in an ice bath for one hour. The less soluble diastereomer deposited, $(-)_{546}$-$[Co(ox)(en)_2]_2 \cdot (-)_{546}$-$[Co(ox)_2(\beta\text{-}ala)]$, was filtered, washed with a little ice water and dried in air. Recrystallization was carried out from hot water by adding methanol and cooling in an ice bath. The crystals deposited were filtered, washed with a small amount of water, methanol and then acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

Found: C, 26.76; H, 4.72; N, 14.35%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]_2 \cdot [Co(C_2O_4)_2(C_3H_6NO_2)]$: C, 26.60; H, 4.43; N, 14.40%. $[M]_{546} = -1200°$, $[M]_{589} = -9700°$.

The optically active barium salt of the complex was obtained from the diastereomer by the same method as in i-b).

Found: C, 18.86; H, 1.32; N, 3.18%. Calcd for $Ba[Co(C_2O_4)_2(C_3H_6NO_2)]$: C, 18.28; H, 1.32; N, 3.04%. $[M]_{546} = -4900°$, $[M]_{589} = -3300°$.

Measurements. Electronic absorption spectra were measured with a Beckman DU spectrophotomer. CD spectra were recorded with a Roussel-Jouan Dichrographe and RD curves with a Yanagimoto recording spectropolarimeter, Model-185. All measurements were made in aqueous solutions at room temperature.

Results and Discussion

The d–d Transition Bands. The absorption, CD and RD curves of $(-)_{546}$-$[Co(ox)_2(gly)]^{2-}$, $(-)_{546}$-$[Co(ox)_2(\beta\text{-}ala)]^{2-}$ and $(-)_{546}$-$[Co(mal)_2(gly)]^{2-}$ are shown in Figs. 1 and 2, and those of the unresolved L-alaninato complexes, $K_2[Co(ox)_2(L\text{-}ala)]$ and $Ba[Co(mal)_2(L\text{-}ala)]$, in Fig. 3. The first absorption bands of the complexes show a vague shoulder (at about 640 mμ) at the lower energy side of the main peak. This absorption behavior coincides with the result expected from

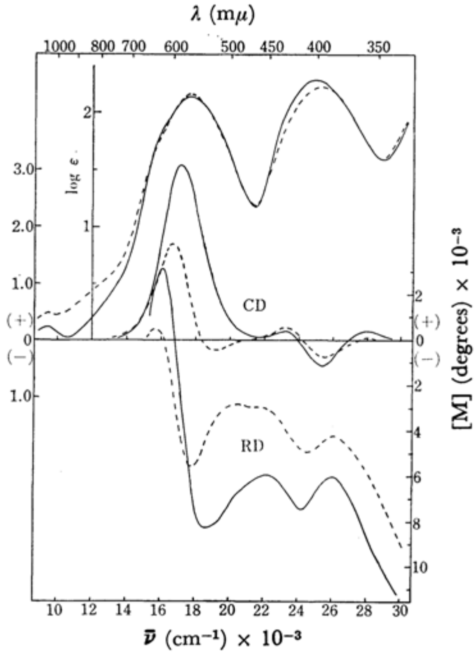

Fig. 1. Absorption, CD, and RD curves of $(-)_{546}$-$Ba[Co(ox)_2(gly)] \cdot 2H_2O$ (——) and $(-)_{546}$-$Ba[Co(ox)_2(\beta\text{-}ala)]$ (------).

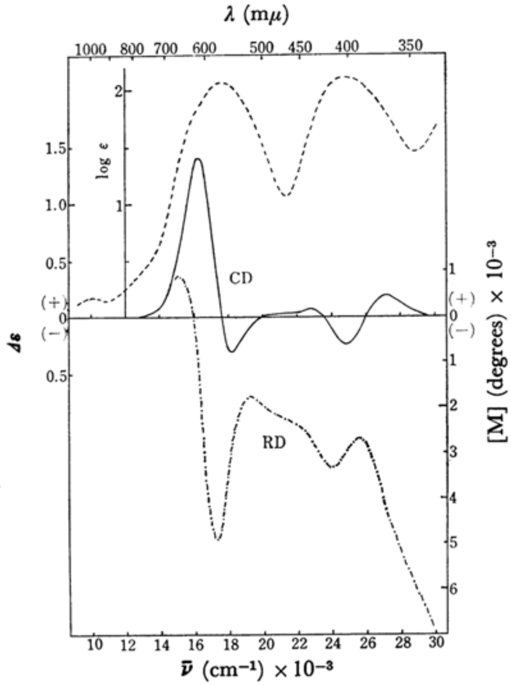

Fig. 2. Absorption (------), CD (——), and RD (—·—·—) curves of $(-)_{546}$-$Ba[Co(mal)_2(gly)]\cdot 2.5H_2O$.

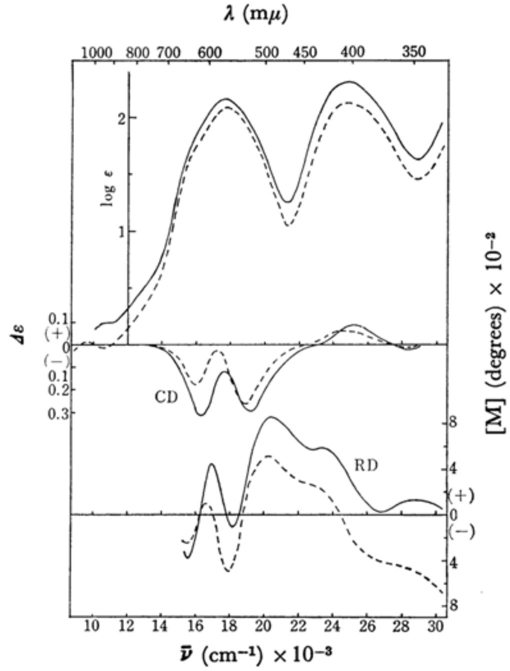

Fig. 3. Absorption, CD, and RD curves of unresolved $K_2[Co(ox)_2(\text{L-ala})]$ (——) and $Ba[Co(mal)_2(\text{L-ala})]$ (------).

a theory based on the approximation that the effective symmetry of the complexes is C_{4v}.[9] In the corresponding region, the CD cruve of $(-)_{546}$-$[Co(ox)_2(gly)]^{2-}$ shows a positive band, while the CD curves of $(-)_{546}$-$[Co(ox)_2(\beta\text{-ala})]^{2-}$ and $(-)_{546}$-$[Co(mal)_2(gly)]^{2-}$ show two bands (+ and −, listing from the lower energy side), as is seen in Figs. 1 and 2. It is noted, however, that the shape of the CD band of $(-)_{546}$-$[Co(ox)_2(gly)]^{2-}$ is not symmetrical. This trend may indicate that another weak CD band located on the higher energy side is overlapped by the main CD band at 584 mμ. This suggestion is supported by a comparison of the CD behavior with that of $(-)_{546}$-$[Co(ox)_2(\beta\text{-ala})]^{2-}$ or $(-)_{546}$-$[Co(mal)_2(gly)]^{2-}$. Moreover, the unresolved L-alaninato complexes also show two CD bands (− and −) in the corresponding region, as shown in Fig. 3. A similar consideration of the relationship between the CD and the first absorption band has been reported for aminocarboxylatobisethylenediaminecobalt(III) complexes,[2] which also belong to the same symmetry, C_1, as the present complexes. From these facts, it is indicated that all complexes treated in the present paper have at least two CD bands in the first absorption band region.

The second absorption bands of the complexes do not appear to have any splitting. However, the CD spectra of the $(-)_{546}$-isomers have three CD bands (+, − and +) in the corresponding region, though their intensities are somewhat different from one another, as seen in Figs. 1 and 2 and Table 1. From this fact, it might be thought that these three CD bands correspond to three A components under C_1 symmetry, because the true symmetry of the present complexes is C_1.

The absolute configuration Δ (left-handed screw along the pseudo-C_3 axis) has been assigned for $(-)_{546}$-$[Co(ox)_2(gly)]^{2-}$ by Dwyer *et al.*, on the basis of the CD behavior in the first absorption band region.[4] From a comparison of the net sign[10] of the CD bands in the first absorption band region with that of the CD bands of Δ-$(+)_{589}$-$[Co(en)_3]^{3+}$, the Δ configuration can be assigned to all the $(-)_{546}$-isomers in this paper, including those of the two L-alaninato complexes, and the Λ configuration to the $(+)_{546}$-isomers. The absolute configurations of the optical isomers, which formed the less soluble diastereomers with strychnium cation or optically active $[Co(ox)(en)_2]^+$, are summarized in Table 2. It is not surprising that the $(-)_{546}$-isomer of $[Co(mal)_2(\text{L-ala})]^{2-}$ forms the less soluble diastereomer with both $(-)_{546}$- and $(+)_{546}$-$[Co(ox)(en)_2]^+$, because $(+)_{546}$- and $(-)_{546}$-$[Co(mal)_2(\text{L-ala})]^{2-}$ are not antipodal with each other.

---

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

[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).

TABLE 1. ABSORPTION AND CIRCULAR DICHROISM DATA OF [Co(O–O)$_2$(O–N)]$^{2-}$ TYPE COMPLEXES

Complex ion	Absorption bands $\tilde{\nu}_{max}$ (log ε)	CD bands $\tilde{\nu}_{ext}$ ($\Delta\varepsilon$)
$(-)_{546}$-[Co(mal)$_2$(gly)]$^{2-}$	17.7 (2.06)	16.3 (+1.40) 18.2 (−0.31)
	24.7 (2.12)	22.8 (+0.06) 24.9 (−0.24) 27.2 (+0.19)
[Co(mal)$_2$(L-ala)]$^{2-}$ (unresolved)	17.8 (2.09)	16.0 (−0.18) 18.9 (−0.27)
	24.9 (2.13)	24.5 (+0.06) 28.3 (−0.01)
$(-)_{546}$-[Co(mal)$_2$(L-ala)]$^{2-}$	17.8 (2.09)	16.3 (+1.20) 18.3 (−0.44)
	24.9 (2.13)	22.9 (+0.06) 24.9 (−0.15) 27.3 (+0.26)
$(+)_{546}$-[Co(mal)$_2$(L-ala)]$^{2-}$	17.8 (2.09)	16.3 (−1.32) 17.9 (+0.03) 19.2 (−0.32)
	24.9 (2.13)	24.9 (+0.30) 27.5 (−0.18)
$(-)_{546}$-[Co(ox)$_2$(gly)]$^{2-}$	17.7 (2.14)	17.2 (+3.08)
	24.9 (2.28)	23.1 (+0.16) 25.4 (−0.44) 27.9 (+0.15)
[Co(ox)$_2$(L-ala)]$^{2-}$ (unresolved)	17.7 (2.16)	16.3 (−0.32) 19.2 (−0.30)
	24.9 (2.31)	25.3 (+0.09) 28.2 (−0.02)
$(-)_{546}$-[Co(ox)$_2$(L-ala)]$^{2-}$	17.7 (2.16)	17.4 (+2.65)
	24.9 (2.31)	23.1 (+0.13) 25.3 (−0.34) 28.1 (+0.13)
$(+)_{546}$-[Co(ox)$_2$(L-ala)]$^{2-}$	17.7 (2.16)	17.3 (−3.03)
	24.9 (2.31)	23.1 (−0.15) 25.3 (+0.52) 28.1 (−0.16)
$(-)_{546}$-[Co(ox)$_2$(β-ala)]$^{2-}$	17.7 (2.15)	16.7 (+1.69) 19.1 (−0.18)
	25.3 (2.23)	23.2 (+0.22) 25.5 (−0.30) 27.9 (+0.03)

The frequencies are given in 10^3 cm^{-1}.

TABLE 2. OPTICAL ISOMER FORMING THE LESS SOLUBLE DIASTEREOMER WITH CATION OF RESOLVING AGENT

Complex anion	Cation of the resolving agent		
	$(-)_{546}$-[Co(ox)(en)$_2$]$^+$	$(+)_{546}$-[Co(ox)(en)$_2$]$^+$	Strychnium cation
[Co(ox)$_2$(gly)]$^{2-}$	Λ-$(+)_{546}$	Δ-$(-)_{546}$	#
[Co(ox)$_2$(L-ala)]$^{2-}$*	Λ-$(+)_{546}$	Δ-$(-)_{546}$	#
[Co(ox)$_2$(β-ala)]$^{2-}$	Δ-$(-)_{546}$	Λ-$(+)_{546}$	#
[Co(mal)$_2$(gly)]$^{2-}$	Δ-$(-)_{546}$	Λ-$(+)_{546}$	Δ-$(-)_{546}$
[Co(mal)$_2$(L-ala)]$^{2-}$	Δ-$(-)_{546}$	Δ-$(-)_{546}$	Λ-$(+)_{546}$

* The isomer of this complex forming the less soluble barium salt is the Λ-$(+)_{546}$-isomer.

The resolution has not been tried.

The configurationally optically active isomers, Δ- and Λ-$[Co\text{-}(OO)_2(\text{L-ala})]^{2-}$, are not antipodal, but diastereomeric to each other, as mentioned above. It is expected, therefore, that separation of the isomers due to the solubility difference between them is possible as in the case of *trans(N)*-oxalatobis(L-alaninato)cobalt(III) complex[6] or tris-(L-alaninato)cobalt(III) complexes.[11,12] In fact, the diastereomeric barium salts, Δ- and Λ-$Ba[Co(ox)_2(\text{L-ala})]$, were completely separated only by crystallization, as described in the Experimental section, though it was unsuccessful in the case of the potassium salts. From this fact, it is pointed out that even only one asymmetric carbon atom of a ligand is effective for separation of the diastereomers, and that the possibility of separation depends merely on the solubilities of the salts employed.

Additivity of Configurational and Vicinal Effects. The CD and RD curves of Δ-$(-)_{546}$- and Λ-$(+)_{546}$-$[Co(ox)_2(\text{L-ala})]^{2-}$ are shown in Fig. 4. The two isomers are not antipodal, but diastereomeric to each other. It was reported for some cobalt(III) complexes that the configurational and vicinal contributions to CD are almost separable and additive.[2,12,13] If this is also true for $[Co(ox)_2(\text{L-ala})]^{2-}$, the following relationships will hold

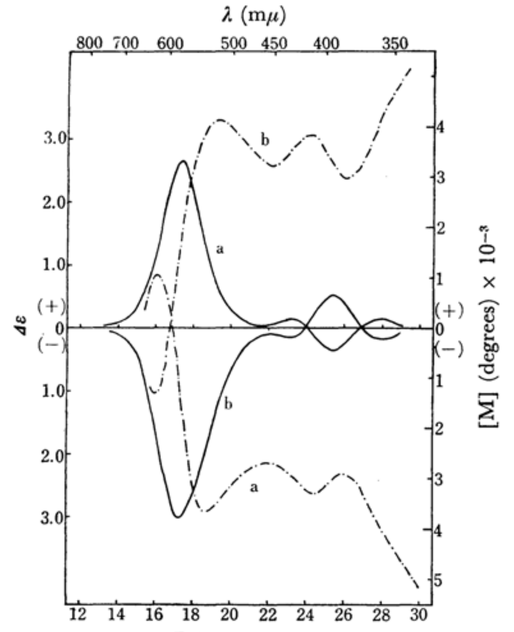

Fig. 4. CD (——) and RD (—·—) curves of Δ-$(-)_{546}$-$Ba[Co(ox)_2(\text{L-ala})]\cdot H_2O$ (a) and Λ-$(-)_{546}$-$Ba[Co(ox)_2(\text{L-ala})]\cdot 0.5H_2O$ (b).

$$\Delta\varepsilon(\text{L}) = \frac{1}{2}\left\{\Delta\varepsilon(\Delta_\text{L}) + \Delta\varepsilon(\Lambda_\text{L})\right\} \quad (1)$$

$$\Delta\varepsilon(\Delta) = \frac{1}{2}\left\{\Delta\varepsilon(\Delta_\text{L}) - \Delta\varepsilon(\Lambda_\text{L})\right\} \quad (2)$$

$$\Delta\varepsilon(\Delta) + \Delta\varepsilon(\Lambda) = 0 \quad (3)$$

The vicinal CD due to the coordinated L-alaninate, $\Delta\varepsilon(\text{L})$, and the configurational CD, $\Delta\varepsilon(\Delta)$ or $\Delta\varepsilon(\Lambda)$, can be calculated by applying the relationships (1)—(3) to the observed CD cruves for Δ-$[Co(ox)_2(\text{L-ala})]^{2-}$ and Λ-$[Co(ox)_2(\text{L-ala})]^{2-}$, namely $\Delta\varepsilon(\Delta_\text{L})$ and $\Delta\varepsilon(\Lambda_\text{L})$. The calculated cruves are shown with the observed cruves of Δ-$[Co(ox)_2(gly)]^{2-}$ (configurational effect without vicinal) and the unresolved $[Co(ox)_2(\text{L-ala})]^{2-}$(vicinal effect without configurational) in Fig. 5. The good agreement between the calculated curves and the observed ones substantiate the additivity, and indicate that the unresolved complex is the (1 : 1) mixture of Δ_L- and Λ_L-isomers. Furthermore, the observed CD curve of the reacted solution of $[Co_2(ox)_4(OH)_2]^{4-}$ with L-alanine coincides with that of the unresolved complex which was isolated from the solution. It is concluded, therefore, that this reaction is not stereospecific; in other words, equal amounts of the two diastereomers were produced in this reaction.

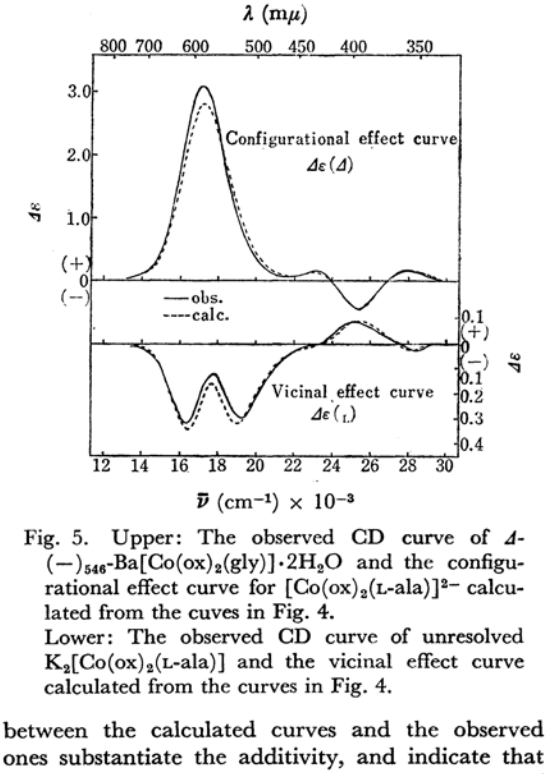

Fig. 5. Upper: The observed CD curve of Δ-$(-)_{546}$-$Ba[Co(ox)_2(gly)]\cdot 2H_2O$ and the configurational effect curve for $[Co(ox)_2(\text{L-ala})]^{2-}$ calculated from the cuves in Fig. 4.
Lower: The observed CD curve of unresolved $K_2[Co(ox)_2(\text{L-ala})]$ and the vicinal effect curve calculated from the curves in Fig. 4.

The CD and RD curves of Δ- and Λ-$[Co(mal)_2(\text{L-ala})]^{2-}$ are shown in Fig. 6. They are also a couple of diastereomeric isomers. The curves concerning the additivity are shown in Fig. 7. In this case, however, the calculated cruves of Δ- and Λ-$[Co(mal)_2(\text{L-ala})]^{2-}$ were derived from

---

[11] J. Lifschitz, *Z. phys. Chem.*, **114**, 485 (1925).

[12] B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

[13] J. I. Legg, D. W. Cooke and B. E. Douglas, *ibid.*, **6**, 700 (1967).

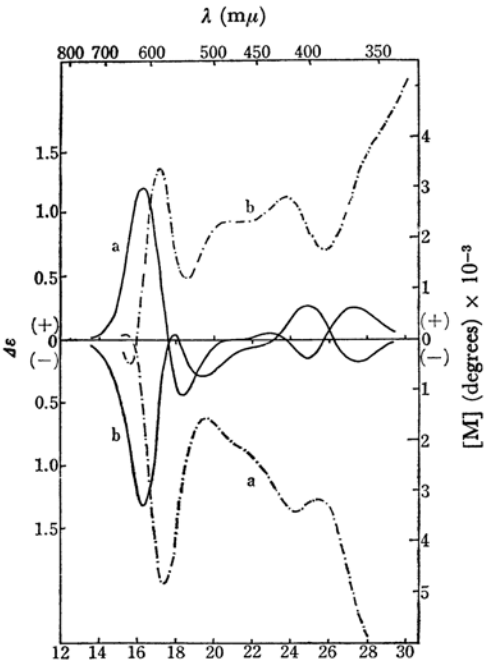

Fig. 6. CD (——) and RD (—·—) curves of Δ-$(-)_{546}$-Ba[Co(mal)$_2$(L-ala)] (a) and Λ-$(+)_{546}$-Ba-[Co(mal)$_2$(L-ala)] (b).

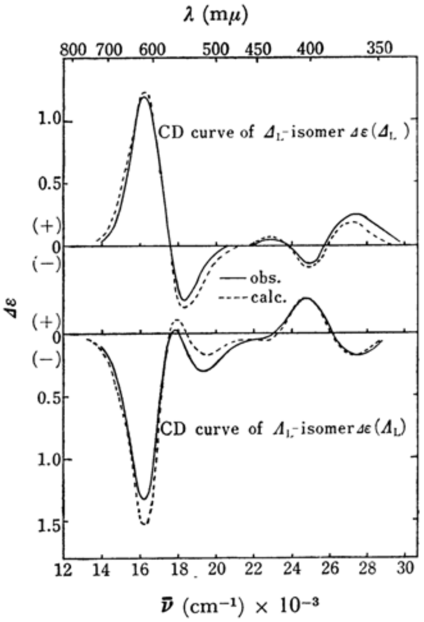

Fig. 7. Upper: The observed CD cruve of Δ-$(-)_{546}$-Ba[Co(mal)$_2$(L-ala)] and the calculated one from the curves of unresolved Ba[Co(mal)$_2$-(L-ala)] and Δ-$(-)_{546}$-Ba[Co(mal)$_2$(gly)]$\cdot$2.5H$_2$O. Lower: The observed CD curve of Λ-$(+)_{546}$-Ba-[Co(mal)$_2$(L-ala)] and the calculated one.

the curves of Δ-[Co(mal)$_2$(gly)]$^{2-}$ (configurational effect without vicinal) and the unresolved [Co(mal)$_2$-(L-ala)]$^{2-}$ (vicinal effect without configurational). The result was achieved by applying the relationships (3), (4) and (5).

$$\Delta\varepsilon(\Delta_{\rm L}) = \Delta\varepsilon(\Delta) + \Delta\varepsilon({\rm L}) \tag{4}$$

$$\Delta\varepsilon(\Lambda_{\rm L}) = \Delta\varepsilon(\Lambda) + \Delta\varepsilon({\rm L}) \tag{5}$$

The calculated cruves agree quite well with the observed ones of Δ- and Λ-[Co(mal)$_2$(L-ala)]$^{2-}$. From this result and the experimental fact that the CD curve of the reacted solution of [Co(mal)$_3$]$^{3-}$ with L-alanine coincided well with that of the unresolved complex isolated as crystals, it is pointed out that in this reaction Δ- and Λ-[Co(mal)$_2$(L-ala)]$^{2-}$ were produced in almost equal amounts, as in the case of [Co(ox)$_2$(L-ala)]$^{2-}$.

From these facts, it may be concluded that in the oxalato and malonato complexes, the coordinated L-alaninate does not have a notable stereospecific effect. This conclusion can be easily understood for the oxalato complexes, because the oxalate chelate rings are planar. This consideration is supported by the fact that almost equal amounts of Δ- and Λ-[Co(ox)$_2${(−)-pn}]$^-$ ions occur in equilibrium.[14] In the malonate system, the chelate ring of the dicarboxylate is not planar. It is expected, however, that the L-alaninate chelate ring is near-planar and hence the interaction of the CH$_3$ group with the two malonates in the one configuration is not so different from that in the other configuration. As a result, it is reasonable to consider that the energy difference between the Δ- and Λ-isomers is very small, as in the case of [Co(ox)$_2$(L-ala)]$^{2-}$. A similar result has recently been reported for the [Co(en)$_2$(L-ala)]$^{2+}$ system,[15] in which two gauche ethylenediamines are coordinated to cobalt(III) instead of the two non-planar malonates of the present complexes.

---

14) F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 661 (1963).

15) D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *ibid.*, **89**, 5133 (1967).