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Circular Dichroism Spectra of Cobalt(III) Complexes of the $[Co(O,O)_2(N)_2]^-$-Type[1]

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The $[Co(O,O)_2(N)_2]^-$-type complexes, $[Co(ox)(mal)(en)]^-$, *cis*-$[Co(CO_3)(mal)(NH_3)_2]^-$, *cis*-$[Co(ox)(mal)(NH_3)_2]^-$ and *cis*-$[Co(mal)_2(NH_3)_2]^-$, have been prepared and resolved. The CD spectra of various complexes of this type including these new complexes have been measured. The assignments of the absolute configurations have been carried out by means of the CD comparison. The CD patterns in the first absorption band region have revealed regular change with the varied O,O ligands ($O,O=CO_3^{2-}$, ox^{2-}, and mal^{2-}), and from this fact a criterion for the assignments of the absolute configurations for the complexes of the present type has been established.

It is known[2,3] that in the $[Co(O,O)_2(N,N)]^-$-type complexes, which contain two of a bidentate O-donor ligand such as oxalato (ox) or malonato (mal) and one of a bidentate N-donor ligand such as ethylenediamine (en) or trimethylenediamine (tn), the variations of the O-donor ligands cause marked changes in the CD spectra; the CD spectra of the $(+)_{546}[Co(ox)_2(en)]^-$[2] and $(+)_{546}[Co(ox)_2(tn)]^-$[3] complexes show two CD peaks of the same sign, (−, −), in the first absorption band region, while the spectra of the $(-)_{546}[Co(mal)_2(en)]^-$[2] and $(-)_{546}[Co(mal)_2(tn)]^-$[3] complexes show three CD peaks of alternating sign, (+, −, +), in the first absorption band region. On account of this change, it is difficult to correlate the absolute configurations of these complexes with the observed CD spectra. Thus, it was thought that the CD spectrum of a complex such as $[Co(ox)(mal)(en)]^-$, which is a transient intermediate between the bis(oxalato) and bis(malonato) complexes, would help in the understanding of such CD spectral changes.

From this standpoint, the preparation and optical resolution of the $[Co(O,O)_2(en)]^-$-type complexes containing a variety of O,O ligands (CO_3^{2-}, ox^{2-}, and mal^{2-}) have been conducted. The work was then extended to the corresponding diammine complexes, *cis*-$[Co(O,O)_2(NH_3)_2]^-$, and the bis(pyridine) complexes, *cis*-$[Co(O,O)_2(py)_2]^-$. The present paper deals with the CD studies of the complexes of the $[Co(O,O)_2(N)_2]^-$-type ($(N)_2=en$, $2NH_3$, and 2py).

Experimental

Preparation and Resolution. *a) Sodium Ethylenediaminemalonatooxalatocobaltate(III) Monohydrate,* $Na[Co(ox)(mal)(en)]\cdot H_2O$: To a solution of $K[Co(CO_3)(ox)(en)]\cdot H_2O$[4] (32 g, 0.1 mol, in 150 cm^3 H_2O) was added dropwise a solution of malonic acid (15 g, 0.15 mol, in 50 cm^3 H_2O) with stirring at room temperature. The mixed solution was stirred at 40 °C for 2 h. The final product was filtered and the filtrate charged on a column containing Dowex 1-X 8 resin in Cl^- form (100—200 mesh, 7×20 cm). By elution with a 0.1 M NaCl aqueous solution, three bands colored red-violet descended and the three fractions were collected. The second desired fraction was concentrated under reduced pressure and, after filtration, kept in a refrigerator. The product obtained was recrystallized from a minimum amount of warm water (*ca.* 40 °C) and the yield was 3 g. The products from the first and third fractions were $Na[Co(mal)_2(en)]$ and $Na[Co(ox)_2(en)]$, respectively. Found: C, 23.84; H, 3.36; N, 8.07%. Calcd for $Na[Co(C_2O_4)(C_3H_2O_4)(C_2H_8N_2)]\cdot H_2O$: C, 24.04; H, 3.45; N, 8.00%.

The iodide complex, $(-)_{589}[Co(ox)(en)_2]$ I (4 g, 0.01 mol) was converted into the acetate with silver acetate (2.0 g, 0.012 mol) according to the literature.[5] To a solution of this resolving agent in H_2O (40 cm^3, 40 °C) was added the above racemate (7.2 g, 0.02 mol) with constant stirring. A pink diastereoisomer containing the $(-)_{589}$-form of the malonatooxalato complex crystallized out on cooling the solution in an ice-bath (*ca.* 30 min). The crude product was recrystallized from a minimum amount of warm water (40 °C) producing fine scale-like crystals (yield 1.5 g). Found: C, 21.33; H, 4.91; N, 18.08%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_2O_4)(C_3H_2O_4)(C_2H_8N_2)]\cdot 2H_2O$: C, 21.44; H, 4.91; N, 18.19%.

When $(-)_{589}[Co(NO_2)_2(en)_2](C_2H_3O_2)$ was used as a resolving agent,[5] the same form of the complex formed the less soluble diastereoisomer.

b) Potassium Carbonatoethylenediamineoxalatocobaltate(III) Monohydrate, $K[Co(CO_3)(ox)(en)]\cdot H_2O$: This complex was prepared by the literature method,[4] and resolved with $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. The less soluble diastereoisomer containing the $(-)_{589}$-form of the carbonatooxalato complex was recrystallized from water by the addition of ethanol. Found: C, 22.85; H, 4.98; N, 14.54%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)(C_2O_4)(C_2H_8N_2)]\cdot 2.5H_2O$: C, 22.81; H, 5.05; N, 14.51%.

c) cis-Diaquaethylenediamineoxalatocobalt(III) Nitrate, cis-$[Co(ox)(en)(H_2O)_2]NO_3$: To a solution of $K[Co(CO_3)(ox)(en)]\cdot H_2O$ (13 g, 0.04 mol, in 30 cm^3 H_2O) was carefully added 6 M HNO_3 until the evolution of CO_2 ceased. The resulting solution was kept in a refrigerator overnight. The crude product thus obtained was recrystallized from warm water yielding 8 g. Found: C, 15.98; H, 3.93; N, 13.69%. Calcd for *cis*-$[Co(C_2O_4)(C_2H_8N_2)(H_2O)_2]NO_3$: C, 15.75; H, 3.96; N, 13.77%.

To a solution of this racemate (9.2 g, 0.03 mol, in 50 cm^3 H_2O, *ca.* 40 °C) was added $(+)_{546}Na[Co(ox)_2(en)]$[2] (5 g, 0.015 mol) as the resolving agent. The mixture was cooled in an ice-bath for 1 h, whereupon the less soluble diastereoisomer containing the $(+)_{589}$-form of the diaqua complex precipitated. Recrystallization from water yielded 2 g. Found: C, 20.89; H, 3.97; N, 9.93%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)(H_2O)_2]\cdot[Co(C_2O_4)_2(C_2H_8N_2)]\cdot 2H_2O$: C, 20.92; H, 4.21; N, 9.76%.

The complex, $(+)_{546}Na[Co(edta)]$[2] was also useful for the resolution of this complex, where the $(+)_{589}$-isomer also formed the less soluble diastereoisomer.

d) Potassium Dicarbonatoethylenediaminecobaltate(III) Monohydrate, $K[Co(CO_3)_2(en)]\cdot H_2O$: This complex was prepared by a modification of the procedure reported previously.[4] To a cold, green solution of tricarbonatocobaltate(III) ($Co(NO_3)_2\cdot 6H_2O$, 30 g, 0.1 mol scale) was added ethylenediamine (9 cm^3, 0.13 mol), and the mixture was then stirred at *ca.* 5 °C for half an hour. Ethanol (*ca.* 100 cm^3) was added to the solution, and the solution cooled in an ice-bath for half an hour. The solution, once filtered, was kept in a refrigerator and powdery purple crystals separated out. The material was recrystallized from warm water yielding 8 g.

This racemate was resolved with $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. The less soluble diastereoisomer containing the $(+)_{589}$-form of the dicarbonato complex was recrystallized from a minimum amount of cold water (*ca.* 10 °C). The yield was 1 g. Found: C, 21.08; H, 5.59; N, 14.64%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)_2(C_2H_8N_2)]\cdot 3H_2O$: C, 21.06; H, 5.30; N, 14.74%.

e) Lithium cis-*Diamminedicarbonatocobaltate(III)*, cis-$Li[Co(CO_3)_2(NH_3)_2]$: The preparation of this complex and the isolation of its active lithium salt have been reported in an earlier communication.[6] The active complex, $(-)_{589}Li[Co(CO_3)_2(NH_3)_2]$ was precipitated from a mixed solution of the racemic lithium salt and $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$, while the $(+)_{589}$ complex was precipitated in the presence of $(+)_{589}[Co(ox)(en)_2](C_2H_3O_2)$.

f) Potassium cis-*Diamminecarbonatooxalatocobaltate(III) Monohydrate*, cis-$K[Co(CO_3)(ox)(NH_3)_2]\cdot H_2O$: This complex was prepared according to the literature.[4] A solution of the racemate (6 g, 0.02 mol, in 50 cm^3 H$_2$O) was poured into a column of Dowex 50W-X 8 resin in Li$^+$ form (100—200 mesh, 5×10 cm) in order to convert the potassium salt into the lithium one. The effluent was added to a solution of $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$ (4 g, 0.01 mol, in 20 cm^3 H$_2$O) and the mixed solution evaporated to reduce the volume (*ca.* 15 cm^3). The concentrated solution was kept in a refrigerator until the less soluble diastereoisomer containing the $(-)_{589}$-form of the carbonatooxalato complex precipitated. Recrystallization was carried out from water. Found: C, 20.03; H, 4.40; N, 15.50%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)(C_2O_4)(NH_3)_2]\cdot 1.5H_2O$: C, 20.19; H, 4.71; N, 15.71%.

g) Potassium cis-*Diamminebis(oxalato)cobaltate(III) Monohydrate*, cis-$K[Co(ox)_2(NH_3)_2]\cdot H_2O$: This was prepared by the method in the literature.[4] The racemate was resolved with $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. The less soluble diastereoisomer containing the $(+)_{589}$-form of the bis(oxalato) complex was recrystallized from a minimum amount of warm water. Found: C, 19.45; H, 5.21; N, 13.57%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_2O_4)_2(NH_3)_2]\cdot 4.5H_2O$: C, 19.45; H, 5.06; N, 13.62%.

h) Sodium cis-*Diamminemalonatooxalatocobaltate(III) 2.5-Hydrate*, cis-$Na[Co(ox)(mal)(NH_3)_2]\cdot 2.5H_2O$: This was prepared and resolved in the same manner as that for the corresponding ethylenediamine complex. Found: C, 17.11; H, 3.73; N, 7.98%. Calcd for $Na[Co(C_2O_4)(C_3H_2O_4)(NH_3)_2]\cdot 2.5H_2O$: C, 17.25; H, 3.75; N, 8.13%. Found: C, 22.18; H, 4.95; N, 14.32%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_2O_4)(C_3H_2O_4)(NH_3)_2]\cdot 2.5H_2O$: C, 22.02; H, 4.91; N, 14.12%.

i) Potassium cis-*Diamminebis(malonato)cobaltate(III) 2.5-Hydrate*, cis-$K[Co(mal)_2(NH_3)_2]\cdot 2.5H_2O$: To a solution of *cis*-$K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (28 g, 0.1 mol, in 150 cm^3 H$_2$O) was added dropwise a solution of malonic acid (25 g, 0.25 mol, in 100 cm^3 H$_2$O) with mechanical stirring in ice. The solution was then stirred at *ca.* 40 °C until the evolution of CO$_2$ ceased. The solution was neutralized with an aqueous KOH solution and further stirred at *ca.* 50 °C for half an hour. The resulting solution was evaporated to *ca.* 100 cm^3 and the concentrated solution kept in a refrigerator overnight. The crude product thus obtained was recrystallized from warm water yielding 10 g. Found: C, 18.90; H, 3.83; N, 7.38%. Calcd for $K[Co(C_3H_2O_4)_2(NH_3)_2]\cdot 2.5H_2O$: C, 18.96; H, 3.97; N, 7.37%.

The complex was resolved with $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. The less soluble diastereoisomer containing the $(+)_{589}$-form of the bis(malonato) complex was recrystallized from warm water. Found: C, 23.55; H, 4.91; N, 13.77%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_3H_2O_4)_2(NH_3)_2]\cdot 2.5H_2O$: C, 23.69; H, 5.14; N, 13.81%.

j) Bis(ethylenediamine)oxalatocobalt(III) cis-*Diamminecarbonatomalonatocobaltate(III) Dihydrate*, $[Co(ox)(en)_2]\cdot$cis-$[Co(CO_3)(mal)(NH_3)_2]\cdot 2H_2O$: An appropriate amount of 30% HClO$_4$ was added dropwise to a solution of $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (28 g, 0.1 mol, in 100 cm^3 H$_2$O) in order to adjust the pH to 5.0 in ice. After filtration, potassium malonate (20 g, 0.1 mol) was added to the filtrate and the mixture stirred at 40 °C for 1 h. Perchloric acid (30%) was again added to adjust the pH to 1.0. The solution was then filtered and the filtrate chromatographed on a column of Dowex 50W-X 8 resin in H$^+$ form (100—200 mesh, 7×15 cm) using 0.2 M NaCl as the eluting solution. Two red-violet bands came out from the column and were collected in fractions. The first fraction was concentrated to *ca.* 50 cm^3 with simultaneous removal of NaCl precipitated by filtration. To the filtrate was added NaHCO$_3$ in order to adjust the pH to 9.0. To this solution was added an aqueous solution of $[Co(ox)(en)_2](C_2H_3O_2)$ and the mixture kept in a refrigerator until reddish brown crystals precipitated. The crude product was recrystallized from water yielding 2 g. Found: C, 21.51; H, 5.05; N, 15.05%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)(C_3H_2O_4)(NH_3)_2]\cdot 2H_2O$: C, 21.36; H, 4.87; N, 15.10%.

This complex (3 g, 0.005 mol) was ground in a mortar with water (10 cm^3) and sodium iodide (0.83 g, 0.005 mol) added. The mixture was then filtered to remove the sparingly soluble $[Co(ox)(en)_2]I$. To this filtrate was added a solution of $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$ (1.0 g, 0.0025 mol, in 15 cm^3 H$_2$O), and the mixture kept in a refrigerator. The less soluble diastereoisomer containing the $(+)_{589}$-form of the carbonatomalonato complex recrystallized yielding 0.1 g. Found: C, 20.99; H, 4.90; N, 14.90%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)(C_3H_2O_4)(NH_3)_2]\cdot 2.5H_2O$: C, 21.17; H, 5.15; N, 14.81%.

k) Potassium cis-*Dicarbonatobis(pyridine)cobaltate(III) Trihydrate*, cis-$K[Co(CO_3)_2(py)_2]\cdot 3H_2O$: This complex was prepared according to the method in the literature.[7] The optical resolution was performed with $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. The less soluble diastereoisomer containing the $(+)_{589}$-form of the dicarbonato complex was recrystallized from cold water. Found: C, 32.82; H, 4.99; N, 12.60%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(CO_3)_2(C_5H_5N)_2]\cdot 3H_2O$: C, 32.83; H, 4.89; N, 12.77%.

l) Lithium cis-*Bis(oxalato)bis(pyridine)cobaltate(III) Monohydrate*, cis-$Li[Co(ox)_2(py)_2]\cdot H_2O$: This salt was prepared by the method in the literature.[8] The resolution was carried out in the same manner as that for the corresponding dicarbonato complex. The less soluble diastereoisomer contains the $(+)_{589}$-form of the bis(oxalato) complex. Found: C, 31.67; H, 4.85; N, 11.02%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_2O_4)_2(C_5H_5N)_2]\cdot 5.5H_2O$: C, 31.63; H, 4.91; N, 11.07%.

Measurements. The absorption spectra in aqueous solution were recorded with a Hitachi 323 recording spectrophotometer. In the case of the *cis*-$[Co(CO_3)(mal)(NH_3)_2]^-$ complex, the spectrum was measured with a solution treated with a cation exchange resin in Na$^+$ form in order to remove the counter $[Co(ox)(en)_2]^+$ ion. The spectrum of the diaqua complex, after the corresponding carbonato complex was acid-hydrolyzed with 10% perchloric acid, was measured.

For the circular dichroism (CD) spectra and optical rotation measurements, a JASCO J-40CS automatic recording spectropolarimeter with a JASCO Model J-DPZ data processor for

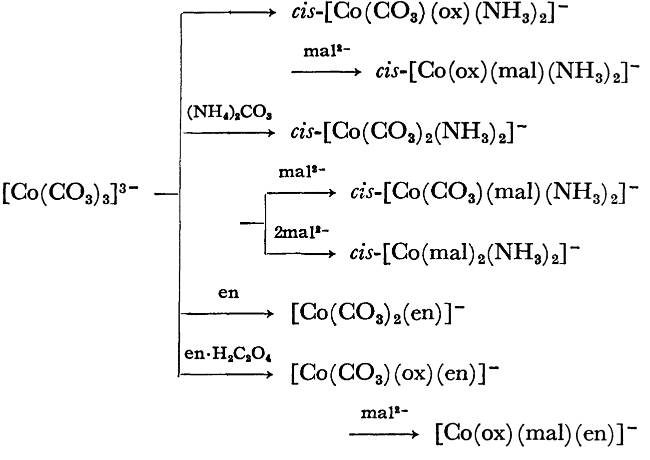
CD, and a JASCO Model DIP-SL automatic polarimeter were used, respectively, with samples converted into the same cations as those of the corresponding racemates by means of ion-exchange techniques.

Solubility measurements of the *cis*-$Li[Co(CO_3)_2(NH_3)_2]$ complex were conducted as follows; a 0.2 M aqueous solution of $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$ (20 cm^3) containing an excess of the complex to be measured was mechanically stirred at 25 °C for a minute and, after filtering, an appropriate volume of the filtrate was withdrawn with a pipet. The solution was passed through a column containing cation exchange resin (Na^+ form) and the effluent diluted to the appropriate volume. The concentration of the complex was measured at the maximum wavelength of the first absorption band (587 nm).

Gaussian Analysis. Some of the CD spectra measured were fitted to the two best gaussian on a wavelength scale using a computer. The expression of the gaussian formula employed was $E\cdot e^{-\delta(\Delta\lambda)^2}$, where E stands for the intensity of a calculated gaussian, δ a measure of the curve band-width, and $\Delta\lambda$ the difference in wavelength between the peak position of the gaussian and an arbitrary position.

Results and Discussion

Preparation and Resolution. In a previous paper,[9] it was reported that the *cis*(a),*cis*(N)-$[Coa_2(O,O)(N)_2]^-$-type complexes (a=CN^- or NO_2^-, $(N)_2$=en or $2NH_3$) could be prepared based on the *cis* substitution of the ligating carbonate ion in a starting complex by the desired ligand. The synthesis of the present *cis*-$[Co(O,O)_2(N_2)]^-$-type complexes ($(N)_2$=en or $2NH_3$) is analogous and Scheme 1 represents the pathway.



Scheme 1. Preparation of bis(dicarboxylato) complexes.

For the optical resolution of the complexes synthesized in this work, two kinds of resolving agents, $(-)_{589}$-$[Co(ox)(en)_2]^+$ and $(-)_{589}[Co(NO_2)_2(en)_2]^+$ were successfully used. The $[Co(CO_3)_2(NH_3)_2]^-$ complex, however, was an exceptional case; its active lithium salt, $(-)_{589}Li[Co(CO_3)_2(NH_3)_2]$ being precipitated from a mixed aqueous solution of the racemic lithium salt and $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$. In the presence of $(+)_{589}[Co(ox)(en)_2](C_2H_3O_2)$, the $(+)_{589}$ lithium salt was precipitated. The fact[6] that the yield of the active lithium salt was about 70% suggests that an asymmetric synthesis is achieved in the system. The complex obtained was optically labile such that its optical rotation decreased, in aqueous solution, with a half-life *ca.* 3 min at room temperature. The solubilities of the

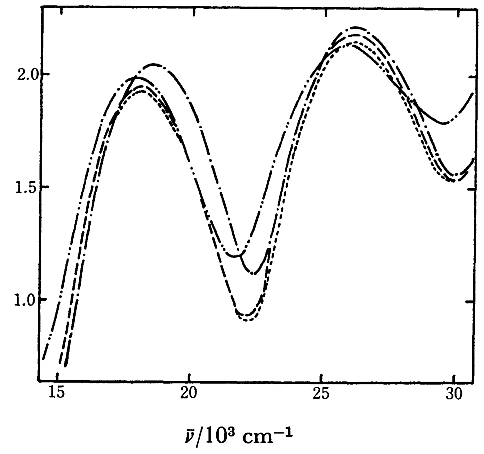


Fig. 1. Absorption spectra of —·—$[Co(ox)(mal)(en)]^-$, —··—*cis*-$[Co(CO_3)(mal)(NH_3)_2]^-$, ——*cis*-$[Co(ox)(mal)(NH_3)_2]^-$, and ------*cis*-$[Co(mal)_2(NH_3)_2]^-$.

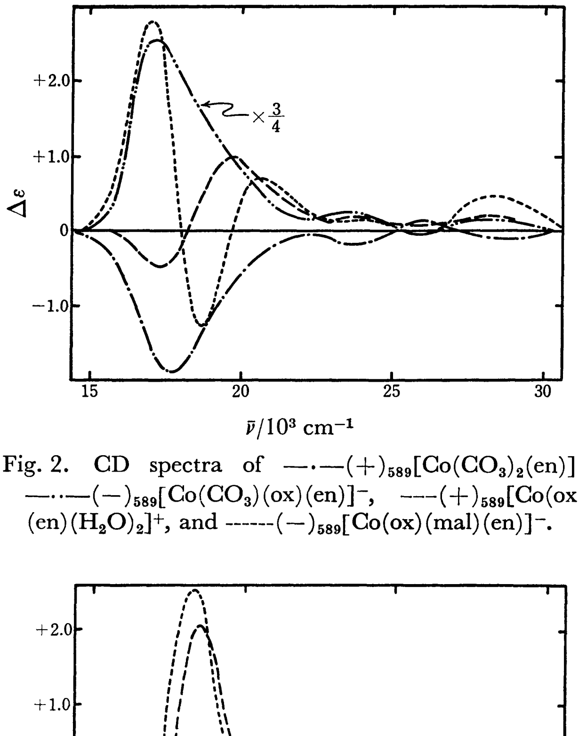


Fig. 2. CD spectra of —·—$(+)_{589}[Co(CO_3)_2(en)]^-$, —··—$(-)_{589}[Co(CO_3)(ox)(en)]^-$, ——$(+)_{589}[Co(ox)(en)(H_2O)_2]^+$, and ------$(-)_{589}[Co(ox)(mal)(en)]^-$.

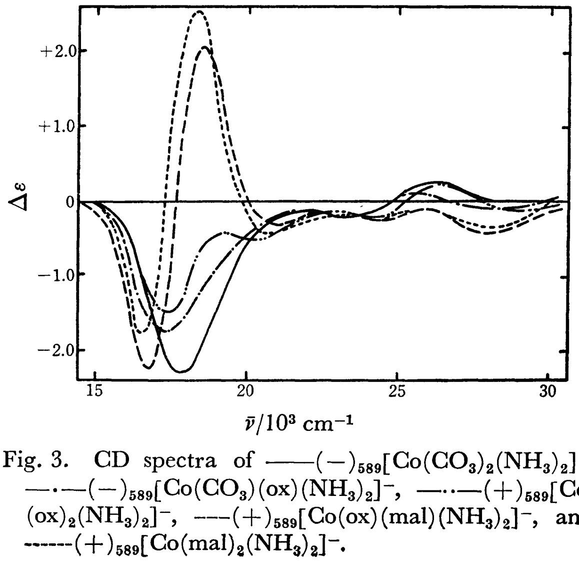


Fig. 3. CD spectra of ——$(-)_{589}[Co(CO_3)_2(NH_3)_2]^-$, —·—$(-)_{589}[Co(CO_3)(ox)(NH_3)_2]^-$, —··—$(+)_{589}[Co(ox)_2(NH_3)_2]^-$, ——$(+)_{589}[Co(ox)(mal)(NH_3)_2]^-$, and ------$(+)_{589}[Co(mal)_2(NH_3)_2]^-$.

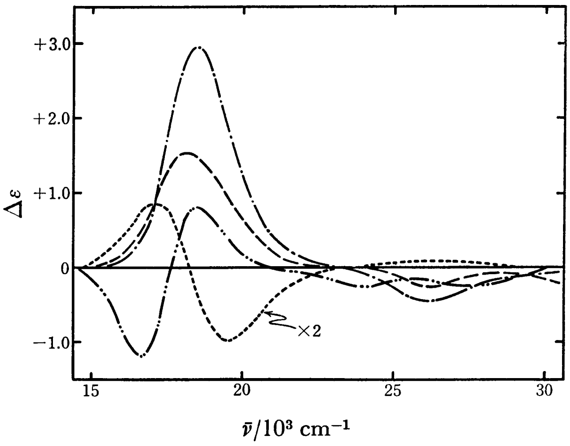


Fig. 4. CD spectra of —·—$(+)_{589}[Co(CO_3)_2(py)_2]^-$, ---$(+)_{589}[Co(ox)_2(py)_2]^-$, —··—$(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$, and ------$(-)_{589}[Co(mal)(NH_3)_2(H_2O)_2]^+$.

racemic, $(+)_{589}$ and $(-)_{589}$ lithium salts in 0.2 M $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$ aqueous solution were found to be approximately 0.35, 0.26, and 0.24 mol/l, respectively. From these facts, the poorer solubilities of the active salts than that of the racemate, the different solubilities between the enantiomeric salts, and the rapid racemization of the more soluble enantiomer are assumed as the conditions for the present asymmetric synthesis. For the documented asymmetric synthesis of metal complexes, the essential conditions are optical lability and the formation of the less soluble diastereoisomer in the presence of a resolving agent.[10]

Table 1. Spectral data and absolute configurations

Complex	Absorption	CD	Con-fign.
	$\bar{\nu}_{max}$ a) $(\log \varepsilon)$	$\bar{\nu}_{max}$ a) $(\Delta\varepsilon)$	
$(+)_{589}[Co(CO_3)_2(en)]^-$ b)	17.5(2.17)	17.6(−1.91)	Δ
	25.6(2.23)	23.5(−0.22)	
		26.8(+0.10)	
		28.8(−0.09)	
$(-)_{589}[Co(CO_3)(ox)(en)]^-$ b)	18.1(2.16)	17.2(+3.43)	Λ
	25.6(2.25)	23.9(+0.33)	
		25.9(−0.07)	
		28.3(+0.21)	
$(+)_{589}[Co(ox)(en)(H_2O)_2]^+$	18.7(1.94)	17.3(−0.47)	Λ
		19.7(+0.99)	
	26.2(2.06)	23.8(+0.16)	
		27.9(+0.18)	
$(-)_{589}[Co(ox)(mal)(en)]^-$	18.5(2.04)	17.0(+2.80)	Λ
		18.0(−1.29)	
		20.6(+0.71)	
	26.0(2.20)	23.6(+0.13)	
		25.8(−0.06)	
		27.0(+0.48)	
$(+)_{589}[Co(CO_3)_2(py)_2]^-$ c)	17.7(2.24)	18.4(+2.94)	Λ
	25.5(2.34)	26.1(−0.42)	
$(+)_{589}[Co(ox)_2(py)_2]^-$ c)	18.2(2.06)	18.2(+1.53)	Λ
	25.8(2.29)	26.2(−0.42)	

a) $\bar{\nu}_{max}$ values in $10^3\ cm^{-1}$. b) Absorption spectral data are in Ref. 4. c) Absorption spectral data are in Ref. 8.

Table 2. Spectral data and absolute configurations

Complex	Absorption	CD	Con-fign.
	$\bar{\nu}_{max}$ a) $(\log \varepsilon)$	$\bar{\nu}_{max}$ a) $(\Delta\varepsilon)$	
$(-)_{589}[Co(CO_3)_2(NH_3)_2]^-$ b)	17.3(2.13)	17.8(−2.32)	Δ
	25.4(2.40)	23.6(−0.19)	
		26.1(+0.26)	
$(-)_{589}[Co(CO_3)(ox)(NH_3)_2]^-$ b)	17.7(2.09)	17.3(−1.74)	Δ
	25.7(2.18)	23.6(−0.22)	
		25.8(+0.11)	
		28.3(−0.09)	
$(+)_{589}[Co(ox)_2(NH_3)_2]^-$ b)	18.0(2.04)	17.3(−1.52)	Δ
		20.2(−0.46)	
	26.1(2.30)	23.0(−0.11)	
		26.4(+0.26)	
		28.8(−0.08)	
$(+)_{589}[Co(ox)(mal)(NH_3)_2]^-$	18.0(1.95)	16.7(−2.25)	Δ
		18.5(+2.06)	
		20.9(−0.31)	
	26.0(2.19)	24.2(−0.23)	
		27.8(−0.42)	
$(+)_{589}[Co(mal)_2(NH_3)_2]^-$	18.0(1.92)	16.5(−1.74)	Δ
		18.3(+2.52)	
		20.6(−0.41)	
	26.0(2.14)	24.2(−0.17)	
		28.2(−0.31)	
$(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$	17.8(2.00)	16.5(−1.21)	Δ
		18.4(+0.81)	
	25.7(2.14)	23.9(−0.28)	
		27.2(−0.26)	
$(-)_{589}[Co(mal)(NH_3)_2(H_2O)_2]^+$	18.3(1.72)	17.0(+0.43)	S
		19.4(−0.49)	
	26.4(1.89)	26.1(+0.04)	

a) In $10^3\ cm^{-1}$. b) Absorption spectral data are in Ref. 4.

CD Spectra. The absorption spectra of the new complexes are shown in Fig. 1 and the CD spectra for the $[Co(O,O)_2(en)]^-$-type, $[Co(O,O)_2(NH_3)_2]^-$-type, and $[Co(O,O)_2(py)_2]^-$-type complexes are shown in Figs. 2—4, the spectral data being summarized in Tables 1 and 2. The observed CD spectra may be grouped into four types from the patterns in the first absorption band ($\bar{\nu}_I$) region; 1) only one peak, 2) two peaks of opposite sign, 3) two peaks of the same sign, and 4) three peaks of alternating sign.

The $(+)_{589}[Co(CO_3)_2(en)]^-$, $(-)_{589}[Co(CO_3)_2(NH_3)_2]^-$ and $(+)_{589}[Co(CO_3)_2(py)_2]^-$ complexes exhibit the patterns of type 1. These peaks are almost symmetrical and the maximum position of each peak shifts to the higher-frequency-side compared with the corresponding absorption maximum ($\bar{\nu}_{I\,max}$). The $(-)_{589}[Co(CO_3)(ox)(en)]^-$ and $(-)_{589}[Co(CO_3)(ox)(NH_3)_2]^-$ complexes also have only one peak, which is unsymmetrical.

The $(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$ complex exhibits the pattern of type 2. The acid hydrolysis of this carbonato complex to give the $(-)_{589}[Co(mal)(NH_3)_2(H_2O)_2]^+$ species brings about a reversal of the signs. Similar changes in CD sign has been reported with such diaqua complex species as $(+)_{589}[Co(ox)(NH_3)_2$-

$(H_2O)_2]^+$, $(+)_{589}[Co(CN)_2(NH_3)_2(H_2O)_2]^+$, and $(+)_{589}$-$[Co(NO_2)_2(NH_3)_2(H_2O)_2]^+$.[9,11]

The $(-)_{546}[Co(ox)_2(en)]^-$ [2] and $(+)_{589}[Co(ox)_2(NH_3)_2]^-$ complexes have the patterns of type 3, whereas the $(+)_{589}[Co(ox)_2(py)_2]^-$ complex has that of type 1, but its peak position is compatible with the observed $\tilde{\nu}_{I\ max}$.

The $(-)_{589}[Co(ox)(mal)(en)]^-$ and $(+)_{589}[Co(ox)(mal)(NH_3)_2]^-$ complexes have the patterns of type 4, where the dominant peak in each pattern is at the lowest-frequency-side (that is, the first peak). The patterns of $(-)_{546}[Co(mal)_2(en)]^-$,[2] $(+)_{589}[Co(mal)_2(NH_3)_2]^-$ also belong to type 4, but in these cases the middle peaks have greater intensities than the first peak intensities, or comparable ones to those.

The CD spectra in the second absorption band ($\tilde{\nu}_{II}$) region also reveal patterns of the four types; the spectra of $(+)_{589}[Co(CO_3)_2(py)_2]^-$ and $(+)_{589}[Co(ox)_2(py)_2]^-$ show one peak, the spectrum of $(-)_{589}[Co(CO_3)_2(NH_3)_2]^-$ show two peaks of opposite sign, those of $(+)_{589}[Co(ox)(mal)(NH_3)_2]^-$ show two peaks of the same sign, and those of $(+)_{589}[Co(ox)_2(NH_3)_2]^-$, $(+)_{589}[Co(CO_3)_2(en)]^-$ and $(-)_{589}[Co(ox)(mal)(en)]^-$ show three peaks of alternating sign. Further discussion can not be given about the CD spectra in the $\tilde{\nu}_{II}$ region, but it may be noted that the sign of the lowest frequency peak in this region is consistent with that of the lowest one in the $\tilde{\nu}_I$ region for complexes of the type $[Co(O,O)_2(N)_2]^-$ except for the bis(pyridine) and diaquaoxalato complexes.

Absolute Configurations. Since the absolute configuration of the $(+)_{546}[Co(ox)_2(en)]^-$ complex has been known to be Δ,[2] the absolute configuration of the $(+)_{589}[Co(ox)_2(NH_3)_2]^-$ complex is determined to be Δ, since both complexes have CD patterns of type 3. As for the complexes whose CD patterns belong to type 1, the absolute configurations are assumed to be that the $(-)$ sign refers to Δ and the $(+)$ sign to Λ compared with the $\Delta(+)_{546}[Co(ox)_2(en)]^-$ complex exhibiting the $(-, -)$ signs. The $(+)_{589}[Co(ox)(mal)(NH_3)_2]^-$, $(+)_{589}[Co(mal)_2(NH_3)_2]^-$, and $(-)_{589}[Co(ox)(mal)(en)]^-$ complexes are assigned with Δ, Δ, and Λ configurations, respectively, from a comparison of the CD patterns with that of the $(-)_{546}[Co(mal)_2(en)]^-$ complex whose absolute configuration has been shown to be Λ.[12] Douglas *et al.*[2] used the $(-)_{546}[Co(edta)]^-$ complex for the assignment of the $(+)_{546}[Co(ox)_2(en)]^-$ and $(-)_{546}[Co(mal)_2(en)]^-$ complexes as the reference. In the same manner, the $(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$ complex has tentatively been assigned to be the Δ configuration. The $(-)_{589}[Co(mal)(NH_3)_2(H_2O)_2]^+$ species derived from the above $(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$ complex may have an S[13] configuration, which is equivalent to the Δ configuration of the parent complex, since the acid hydrolysis should proceed with retention of configuration. The CD pattern of the $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$ species derived from the $(-)_{589}[Co(CO_3)(ox)(en)]^-$ complex is the same as that of the $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$ complex resolved using the $(+)_{546}[Co(ox)_2(en)]^-$ complex. Hence the Λ configuration is assigned to this diaqua complex. All the absolute configurations thus assigned are summarized in Tables 1 and 2.

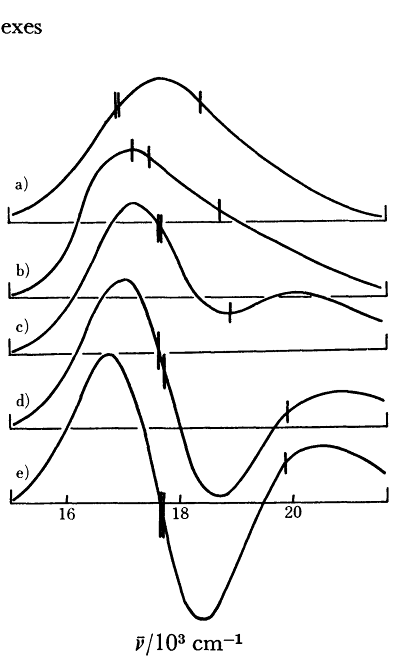


Fig. 5. CD spectral change in the $[Co(O,O)_2(en)]^-$-type complexes of Λ configuration.
a) $(-)_{589}[Co(CO_3)_2(en)]^-$, b) $(-)_{589}[Co(CO_3)(ox)(en)]^-$, c) $(-)_{546}[Co(ox)_2(en)]^-$, d) $(-)_{589}[Co(ox)(mal)(en)]^-$, e) $(-)_{546}[Co(mal)_2(en)]^-$. c) and e) Ref. 2.

In order to illustrate the changes of the CD patterns, in the $\tilde{\nu}_I$ region, with the varied O,O ligands, the patterns of the complexes having Λ configuration have been collected and are shown in Fig. 5. The peak intensity, however, is arbitarily taken in each pattern, because the discussion is limited only to the shape of the pattern. The short vertical lines on each CD curve indicate the band positions calculated by means of Yamatera's predictions:[14] δ_I(en-CO$_3$)$=5800$, δ_I(en-ox)$=4730$, and δ_I(en-mal)$=4830$ cm^{-1}.

It is clear that there are regular changes of the shapes of the patterns over the range of complexes. The CD peak for the Λ-$[Co(CO_3)_2(en)]^-$ complex is situated in a middle position of the predicted band positions, the peak for the Λ-$[Co(CO_3)(ox)(en)]^-$ complex being apart considerably from a mean position of the predicted band positions. The two CD peaks for the Λ-$[Co(ox)_2(en)]^-$ complex lie on both sides of the predicted two positions. With respect to the Λ-$[Co(ox)(mal)(en)]^-$ and Λ-$[Co(mal)_2(en)]^-$ complexes, their three CD peaks correspond incorrectly to the calculated components.

A similar change in CD pattern can be observed in the case of the Λ-$[Co(O,O)_2(NH_3)_2]^-$-type complexes, and also of the corresponding bis(pyridine) complexes although the bis(oxalato) complex exhibits only one peak.

In order to understand these regular changes of the CD patterns, an attempt has been made to analyze the patterns into Gaussian curves. Douglas *et al.*[2] resolved the CD curve of the $[Co(O,O)_2(en)]^-$ complex (O,O$=$ ox or mal) into three components with respect to both the $\tilde{\nu}_I$ and $\tilde{\nu}_{II}$ regions, and claimed an effective rhombic field for each of the complexes. In this computation, the CD curve in $\tilde{\nu}_I$ region was resolved into two com-

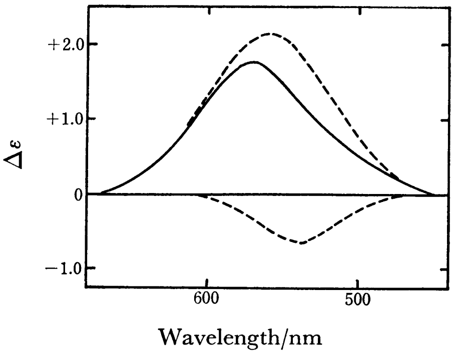


Fig. 6. Gaussian resolution of the CD spectrum of $(+)_{589}[Co(CO_3)(ox)(NH_3)_2]^-$.
——: Observed CD spectrum, ------: calculated gaussian curves.

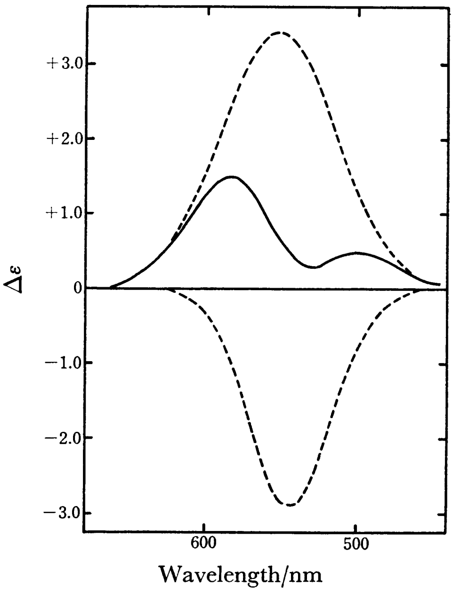


Fig. 7. Gaussian resolution of the CD spectrum of $(-)_{589}[Co(ox)_2(NH_3)_2]^-$.
——: Observed CD spectrum, ------: calculated gaussian curves.

ponents with opposite signs. The results obtained are shown in Figs. 6—8 with respect to the Λ-$[Co(O,O)_2(NH_3)_2]^-$-type complexes.

It is seen, from the Gaussian analysis, that every pattern is a resultant curve from the mutual cancellation of a (+) component at a lower frequency and a (−) component at a higher frequency. The separation between the two components is very small, unfortunately the correspondences of the peak positions of the Gaussians with the predicted band positions being too poor. However, the observed regular change in the CD spectra can be qualitatively understood from these results. It is evident that the CD sign at the shorter-wavelength is altered by the mutual cancelation, but the sign at the longest-wavelength remains unchanged. On the basis of this the absolute configurations of the $[Co(O,O)_2(N)_2]^-$-type complexes can be assigned from

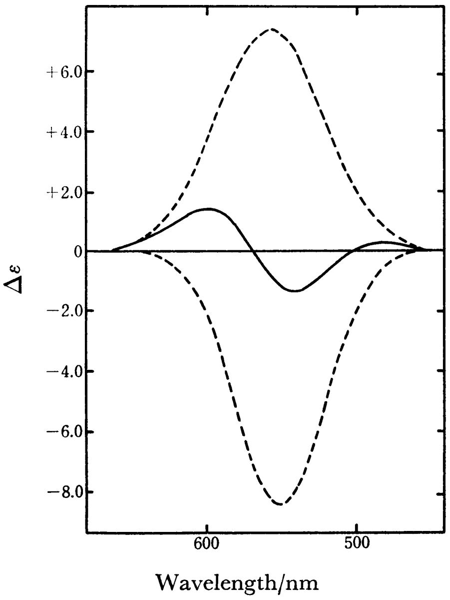


Fig. 8. Gaussian resolution of the CD spectrum of $(-)_{589}[Co(ox)(mal)(NH_3)_2]^-$.
——: Observed CD spectrum, ------ calculated gaussian curve.

the sign of the lowest-frequency peak; the (+) sign refers to Λ and the (−) sign to Δ. The results of the assignments from this criterion agree with those in Tables 1 and 2. However, this criterion is inapplicable to the $[Co(O,O)(N)_2(H_2O)_2]^+$-type complexes, where the (−) sign of the lowest-frequency peak relates to the Λ configuration of the corresponding $[Co(O,O)(CO_3)(N)_2]^-$ complex.

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