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# The Circular Dichroism Spectra of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$, *cis*-$[Co(NO_2)_2(CO_3)_2]^{3-}$, and Related Bis(dicarboxylato) Complexes

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Five kinds of *cis*-$[Co(CN)_2(OO)_2]^{3-}$ and *cis*-$[Co(NO_2)_2(OO)_2]^{3-}$ complexes ($OO=CO_3^{2-}$, $ox^{2-}$, $mal^{2-}$) have been optically resolved. As to the dicarbonato complexes, one enantiomer has been obtained in a yield far exceeding 50% because of the rapid racemization. When the carbonato ligand is replaced with an oxalato or malonato ligand, the complex becomes inert for racemization and a new Cotton peak with an opposite sign appears at the lower frequency in the first-absorption-band region. The CD spectral change is different from the change observed in *cis*-$[Co(a)_2(OO)_2]^-$ complexes ($a=NH_3$, py, en/2), suggesting the intimate participation of the unidentate ligands in determining the signs of the Cotton peaks.

It is known that the variation in the size of a dicarboxylato chelate ring causes a marked change in the CD spectra.[1–6] For example, a $[Co(CO_3)_2(en)]^-$ complex exhibits a single Cotton peak in the first-absorption-band region, while $[Co(ox)_2(en)]^-$ and $[Co(mal)_2(en)]^-$ complexes exhibit two and three Cotton peaks respectively. Such a spectral change has been utilized to assign a single Cotton peak observed in the *cis*-$[Co(a)_2(CO_3)_2]^-$ complex ($a=NH_3$, py, or en/2).[6] When the carbonato ligand is replaced with an oxalato or malonato ligand, a new Cotton peak with an opposite sign appears at a higher frequency in the first-absorption-band region. Therefore, the single Cotton peaks in the dicarbonato complexes have been assigned to the $A_{1g}\rightarrow E_g$ transition component in a holohedrized[7] $D_{4h}$ symmetry, since this component lies at a lower frequency in the *cis*-$[Co(N)_2(O)_4]$-type complexes.

This paper deals with the optical resolutions of *cis*-$[Co(CN)_2(OO)_2]^{3-}$ and *cis*-$[Co(NO_2)_2(OO)_2]^{3-}$ complexes ($OO=CO_3^{2-}$, $ox^{2-}$, and $mal^{2-}$). These dicyano and dinitro complexes have previously been synthesized, and only *cis*-$[Co(CN)_2(CO_3)(ox)]^{3-}$ and *cis*-$[Co(CN)_2(ox)_2]^{3-}$ complexes have been optically resolved.[8,9] The CD spectral changes in the *cis*-$[Co(CN)_2(OO)_2]^{3-}$ and *cis*-$[Co(NO_2)_2(OO)_2]^{3-}$ complexes will be investigated and compared with those in the *cis*-$[Co(a)_2(OO)_2]^-$ complexes ($a=NH_3$, py, and en/2).

## Experimental

*1) Optical Resolution of* cis-$[Co(CN)_2(CO_3)_2]^{3-}$. This complex was prepared and crystallized by adding $(+)_{589}$-$[Co(en)_3]Br_3$ and an appropriate amount of ethanol according to the method in the literature.[8] Since the dicyano complex racemized rapidly in an aqueous solution, the CD spectrum was measured by the following procedure. The brown-violet crystals[8] were quickly dissolved into a cold 0.5 mol dm$^{-3}$ $NaHCO_3$ solution. The solution was poured onto a column of Dowex 50W-X8 ($\phi$ 1 cm × 1 cm, in $Na^+$ form) and then discharged rapidly by air-pressing the top of the column. The effluent was submitted to the measurement of the CD spectrum within the range of 50—100 nm at 5 °C. The procedure should be done as fast as possible and repeated several times to cover the region of the d-d transition bands. Each time needed to separate the complex cation was recorded in order to correct the spectrum. The separation of the cation was carried out at *ca.* 10 s, and the spectrum was recorded at a speed of 100 nm min$^{-1}$. Since no change in the absorption spectrum was observed after the measurement of the CD spectrum, the metal concentration was evaluated from the absorption spectral data. The height of the Cotton peak at 459 nm decreased to half after *ca.* 27 s at 5 °C in a 0.5 mol dm$^{-3}$ $NaHCO_3$ solution. The deposited brown-violet crystals contained the $(+)^{CD}_{589}$-dicyano isomer.

*2) Preparation and Optical Resolution of* cis-$[Co(CN)_2(mal)_2]^{3-}$. This complex was prepared by a literature method with only a slight modification.[8] Malonic acid (25 g, 0.35 mol) and potassium hydrogencarbonate (25 g, 0.25 mol) were dissolved in 30 cm$^3$ of warm water, and the solution was stirred vigorously until the evolution of $CO_2$ gas ceased. The resultant solution was added to a deep red solution of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$[8] which had been prepared by using a green solution of tricarbonatocobaltate(III) (0.05 mol scale).[10] The mixed solution was adjusted to pH 5 by acetic acid and stirred at room temperature for 3 h.

After filtration, the filtrate was poured onto a column of QAE Sephadex A-25 in the $Cl^-$ form ($\phi$3 cm × 15 cm). By elution with 0.6 mol dm$^{-3}$ KCl, red and orange bands were discharged from the column, in that order. The effluent of the orange band was concentrated to a small volume (*ca.* 10 cm$^3$) with the simultaneous removal of the precipitated KCl. An appropriate amount of an acetone solution of $(+)_{589}$-$[Co(en)_3](ClO_4)_3$ was added to the concentrate. After the removal of the deposited $KClO_4$, small amount of ethanol was added to the filtrate. The precipitated resolving agent was repeatedly removed, and a red diastereoisomeric salt containing the $(+)^{CD}_{546}$-dicyano complex was finally obtained. The yield was very poor. The salt was dissolved in water, and the solution was passed through a short column of Dowex 50W-X8 ($\phi$ 1 cm × 2 cm, in $Na^+$ form). The absorption spectral data of the effluent were identical with those of the literature.[8] The CD spectrum was measured by using the effluent, and the metal concentration was estimated from the absorption spectral data. The enantiomer was enough inert for racemization for the CD spectrum to be measured.

*3) Optical Resolution of* cis-$[Co(NO_2)_2(CO_3)_2]^{3-}$. This complex was prepared according to the method in the literature.[9] Into a cold solution of $K_3[Co(NO_2)_2(CO_3)_2]\cdot H_2O$ (2 g, 5 mmol, in 200 cm$^3$ $H_2O$) we stirred, in turn, a solution of $(-)_{589}[Co(gly)(en)_2]Cl_2$[11] (1.6 g, 5 mmol, in 50 cm$^3$ $H_2O$) and acetone (20 cm$^3$) under iced conditions. The *cis*-$[Co(NO_2)_2(CO_3)_2]^{3-}$ complex was deposited as a less-soluble pink diastereoisomeric salt. Found: C, 18.17; H, 5.26; N, 18.63%. Calcd for $[Co(gly)(en)_2]_3\cdot[Co(NO_2)_2(CO_3)_2]_2\cdot 7.5H_2O$: 18.39; H, 5.26; N, 18.52%.

The dinitro complexes was also racemized rapidly in an aqueous solution, and the CD spectrum was measured by a method similar to that used for *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$. The Cotton peak at 521 nm decreased in intensity to half after *ca.* 80 s at 5 °C in a 0.5 mol dm$^{-3}$ $NaHCO_3$ solution. No change in the absorption spectrum was observed after the measurement of the CD spectrum. The diastereoisomeric salt contained the $(-)^{CD}_{589}$-dinitro isomer.

*4) Optical Resolution of* cis-*[Co(NO$_2$)$_2$(CO$_3$)(ox)]$^{3-}$.* Into a solution of *cis*-$K_3[Co(NO_2)_2(CO_3)(ox)]$[9] (4 g, 0.01 mol, in 300 cm$^3$ $H_2O$) we stirred a solution of $(+)_{589}[Co(en)_3]Cl_3$ (2 g, 5 mmol, in 50 cm$^3$ $H_2O$) at room temperature. Red diastereoisomeric salt was soon deposited. The salt was sparingly soluble in water, but it could not be recrystallized. Purification was carried out by the following method. The salt and the ion-exchange resin (Dowex 50W-X8, $Na^+$ form) were mixed in water, and the mixture was stirred for 20 min. The resin was filtered out, and the filtrate containing the $(-)^{CD}_{589}$-isomer of the dinitro complex was mixed with a solution containing an equimolar amount of $(+)_{589}[Co(en)_3]Cl_3$. The red salt was soon obtained. This procedure was repeated until the $\Delta\varepsilon$ value at 490 nm became constant. The CD spectrum was measured by using the solution from which the resin had been removed by filtration; the metal concentration was evaluated from the absorption spectral data. The rate of the racemization of the enantiomer was very slow compared with that of *cis*-$[Co(NO_2)_2(CO_3)_2]^{3-}$.

*5) Derivation of Optically Active* cis-*[Co(NO$_2$)$_2$(ox)$_2$]$^{3-}$.* Into a solution of an optically active $[Co(NO_2)_2(CO_3)(ox)]^{3-}$ isomer (5 mmol in 100 cm$^3$ $H_2O$) we successively stirred potassium oxalate (35 g, 0.21 mol) and oxalic acid (1 g, 0.01 mol) under iced conditions; the pH of the solution thereupon became *ca.* 4. After stirring for 3 h, the solution was filtered and the filtrate was poured onto a column of QAE Sephadex A-25 ($\phi$2.5 cm × 15 cm, in $Cl^-$ form). The band containing a univalent species was discharged by elution with 0.6 mol dm$^{-3}$ KCl, and then the desired tervalent complex species was eluted with 1 mol dm$^{-3}$ KCl. The absorption spectrum of the eluate was identical with that in the literature.[9] The eluate was also subjected to the measurement of its CD spectrum, while the metal concentration was evaluated from the absorption spectral data. The enantiomer was enough inert for racemization for the CD spectrum to be measured. The $(-)^{CD}_{589}[Co(NO_2)_2(ox)_2]^{3-}$ isomer was derived from the $(-)^{CD}_{589}[Co(NO_2)_2(CO_3)(ox)]^{3-}$ isomer.

*Measurement.* The absorption and CD spectra were measured with a Hitachi 323 recording spectrophotometer and a JASCO J40-C automatic recording spectropolarimeter respectively.

The CD spectrum of $(-)^{CD}_{589}[Co(CN)_2(ox)(H_2O)_2]^-$ was measured by acidifying a solution of $(-)^{CD}_{589}[Co(CN)_2(CO_3)(ox)]^{3-}$[8] to pH 2 with perchloric acid. The spectrum was reformed to that of the parent complex on the addition of $KHCO_3$.

## Results and Discussion

*Optical Resolution of the Labile Complex.* A series of *cis*-$[Co(CN)_2(OO)_2]^{3-}$ complexes (OO$=$$CO_3^{2-}$, $ox^{2-}$, $mal^{2-}$) has been prepared, and the optical resolutions have been successfully done for the *cis*-$[Co(CN)_2(CO_3)(ox)]^{3-}$ and *cis*-$[Co(CN)_2(ox)_2]^{3-}$ complexes by using $(+)_{589}[Co(en)_3]Br_3$ as a resolving agent.[8] The attempt to measure the CD spectrum of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$ has resulted in failure, although the anion was easily crystallized with a $(+)_{589}[Co(en)_3]^{3+}$ cation. This failure is attributable to a rapid racemization of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$ in an aqueous solution. In this study, the separation of the complex cation from the solution of the diastereoisomeric salt was done as fast as possible. A CD spectral measurement was carried out within a narrow range of wavelengths and was repeated several times under the same conditions to cover the first-absorption-band region. Since the half-life of the optical activity (*ca.* 27 s at 5 °C) is shorter than the time needed to record a CD spectrum, the recorded curve does not afford a correct CD spectrum. The curves were corrected by extrapolating the ellipticity recorded at each wavelength to that at the time when the diastereoisomeric salt had been dissolved. The corrected spectrum was reproducible with a deviation of *ca.* 4%. A dominant positive extremum appeared at 21800 cm$^{-1}$ and a weak positive plateau, at 17500 cm$^{-1}$, in the first-absorption-band region.

The *cis*-$[Co(NO_2)_2(OO)_2]^{3-}$ complexes (OO$=$$CO_3^{2-}$, $ox^{2-}$) have been prepared, but their optical resolutions have not been reported.[9] The *cis*-$[Co(NO_2)_2(CO_3)(ox)]^{3-}$ complex was optically resolved with $(+)_{589}[Co(en)_3]Br_3$, while the *cis*-$[Co(NO_2)_2(ox)_2]^{3-}$ complex was not resolved by using resolving agents. The optically active bis(oxalato) isomer was derived from the optically resolved $[Co(NO_2)_2(CO_3)(ox)]^{3-}$. The rates of the racemization of the two dinitro complexes were very slow, so the recorded CD spectra did not need to be corrected. The $[Co(NO_2)_2(CO_3)_2]^{3-}$ complex was rapidly racemized in an aqueous solution. The half-life of the optical activity was *ca.* 80 s at 5 °C. The recorded CD spectral curves were also corrected by the method described in the case of *cis*-$[Co(CN)_2(CO_3)_2]^{3-}$. The corrected spectrum exhibits two extrema, with opposite signs, at 16400 and 19200 cm$^{-1}$, the extremum at the lower frequency being extremely weak.

It is characteristic that almost the whole of the dicarbonato complex in a solution could be deposited as a less-soluble diastereoisomeric salt by adding excess amounts of a resolving agent and an organic solvent; the crop of the crystals and the rate of crystallization were controlled by the amount of organic solvent added, but the optical purity was independent of the conditions. Moreover, the $\Delta\varepsilon$ value of the dominant peak in each dicarbonato complex is comparable with that in the corresponding carbonatooxalato complex, as is shown in Table 1. The high-yield resolution of the dicarbonato complexes can be explained by a so-called second-order asymmetric process.[12,13]

As to the *cis*-$[Co(NH_3)_2(CO_3)_2]^-$ complex, $Li(-)_{589}[Co(NH_3)_2(CO_3)_2]$ has been deposited in the presence of $(-)_{589}[Co(ox)(en)_2]^+$, with the yield far exceeding 50%.[14] However, the $[Co(CN)_2(CO_3)_2]^{3-}$ and $[Co(NO_2)_2(CO_3)_2]^{3-}$ complexes crystallized as diastereoisomeric salts. The present dicarbonato complexes racemize more rapidly than the $[Co(NH_3)_2(CO_3)_2]^-$ complex.

*CD Spectra of Bis(dicarboxylato) Complexes.* The CD spectral data for the enantiomers obtained from the less-soluble diastereoisomeric salts are listed in Table 1. The CD spectral changes in a series of *cis*-$[Co(CN)_2(OO)_2]^{3-}$ complexes are illustrated in Fig. 1. Except for the dicarbonato complex, the dicyano complexes exhibit two Cotton peaks, with opposite signs, in the first-absorption-band region. It is found that the peak observed on a lower-frequency side apparently increases in intensity as the member of the

Table 1. Absorption and CD spectral data

| Complex | Absorption[a] | | CD | |
|---|---|---|---|---|
| | $\tilde{\nu}/10^3\mathrm{cm}^{-1}$ | (log $\varepsilon$) | $\tilde{\nu}/10^3\mathrm{cm}^{-1}$ | ($\Delta\varepsilon$) |
| $(+)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(CO_3)_2}]^{3-}$ | 18.3 | (1.96) | 17.5 | (+0.18) |
| | 22.5 | (2.03) | 21.8 | (+1.47) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(CO_3)(ox)}]^{3-}$ | 18.7 | (1.90) | 19.3 | (−0.66)[a] |
| | 23.0 | (2.07) | 22.9 | (+2.17) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(ox)_2}]^{3-}$ | 18.8 | (1.84) | 19.1 | (−1.74)[a] |
| | 23.4 | (2.14) | 23.5 | (+3.03) |
| $(+)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(mal)_2}]^{3-}$ | 18.7 | (1.60) | 18.2 | (+0.40) |
| | 23.3 | (2.08) | 23.4 | (−0.24) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(ox)(H_2O)_2}]^{-}$ | 18.5 | (1.70) | 18.0 | (−0.71) |
| | 23.8 | (2.08) | 23.5 | (+0.52) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(CO_3)_2}]^{3-}$ | 18.3 | (2.24) | 16.4 | (+0.04) |
| | | | 19.2 | (−3.00) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(CO_3)(ox)}]^{3-}$ | 18.7 | (2.26) | 17.2 | (−0.45) |
| | | | 20.4 | (+2.93) |
| $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(ox)_2}]^{3-}$ | 19.1 | (2.13) | 18.0 | (−0.39) |
| | | | 20.9 | (+0.87) |

a) Cited from Refs. 9 and 10.

chelate ring increases.

It is troublesome to decide whether the Cotton peaks of a complex with $C_2$ symmetry indicate three transition components or two transition components. Both interpretations have been applied to the *cis*-$[\mathrm{Co\text{-}(a)_2(mal)_2}]^{-}$ ($\mathrm{a} = \mathrm{NH_3}$, en/2, and tn/2) complexes which exhibit three Cotton peaks with alternating signs.[1,6] However, Gaussian analyses of both situations have given splittings of the transition components incompatible with the predictions from an angular overlap model.[15] Since the *cis*-$[\mathrm{Co(CN)_2(mal)_2}]^{3-}$ complex, in which the transition components are considered to be well separated from one another, exhibits two extrema, we will analyze the CD spectra of the dicarboxylato complexes with two transition components.

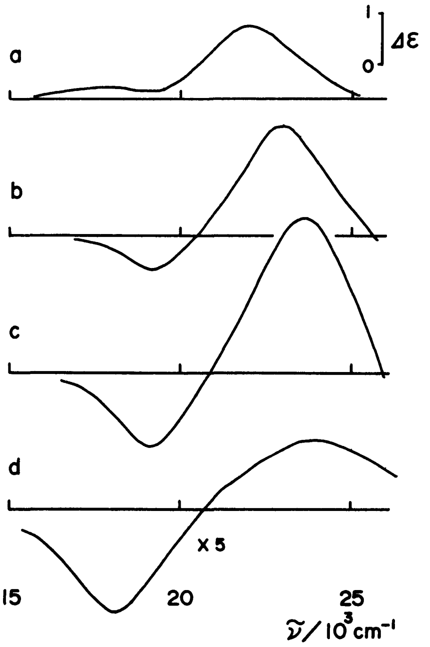

Fig. 1. CD Spectra of; a) $(+)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(CO_3)_2}]^{3-}$, b) $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(CO_3)(ox)}]^{3-}$, c) $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(ox)_2}]^{3-}$, d) $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(CN)_2(mal)_2}]^{3-}$.

The angular overlap model also predicts that two of the three transition components in an octahedral parentage band will almost entirely degenerate in these dicarboxylato complexes with a holohedrized $D_{4h}$ symmetry,[7] while the remaining one will separate well from the two components. In this situation, the Cotton peak, which increases in intensity on a lower-frequency side with the replacement of the OO chelate from $\mathrm{CO_3}^{2-}$ to $\mathrm{ox}^{2-}$ or $\mathrm{mal}^{2-}$, can be assigned to the $A_{1g} \rightarrow E_g(D_{4h})$ component, while the dominant Cotton peak in *cis*-$[\mathrm{Co(CN)_2(CO_3)_2}]^{3-}$ is attributed to $A_{1g} \rightarrow A_{2g}(D_{4h})$. Similar CD spectral changes were observed in the *cis*-$[\mathrm{Co(NO_2)_2(OO)_2}]^{3-}$ complexes, as is shown in Fig. 2. The negative Cotton peak at a lower frequency also increases in intensity with the change from $\mathrm{CO_3}^{2-}$ to $\mathrm{ox}^{2-}$.

These spectral changes are different from those in the *cis*- $[\mathrm{Co(a)_2(OO)_2}]^{-}$ complexes ($\mathrm{a} = \mathrm{NH_3}$, py, and en/2), in which a new component has been observed on a

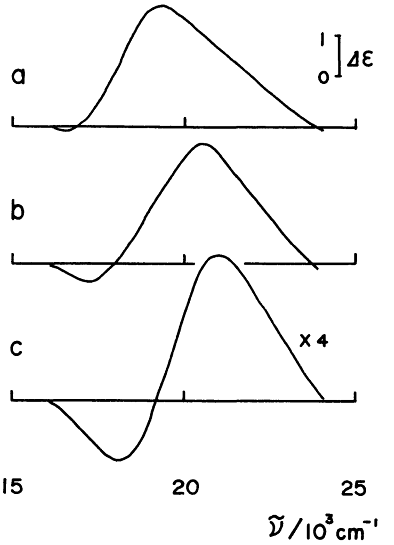

Fig. 2. CD spectra of; a) $(+)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(CO_3)_2}]^{3-}$, b) $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(CO_3)(ox)}]^{3-}$, c) $(-)^{\mathrm{CD}}_{589}[\mathrm{Co(NO_2)_2(ox)_2}]^{3-}$.

higher-frequency side with the replacement from $CO_3^{2-}$ to $ox^{2-}$ or $mal^{2-}$ and in which a single Cotton peak in each dicarbonato complex has been assigned to $A_{1g} \rightarrow E_g(D_{4h})$.[6] This difference is considered to be caused by the difference between the charges of the unidentate ligands. The unidentate a is neutral, while the cyano and nitro ligands are anionic.

Similar CD spectral changes with the ligand replacement from $CO_3^{2-}$ to $2H_2O$ have been reported in *cis*-$[Co(N)_2(O)_4]$-[6] and *cis*-$[Co(N)_4(O)_2]$-type complexes.[16] The $(+)_{589}[Co(CO_3)(mal)(NH_3)_2]^-$ and $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$ complexes exhibit (−) and (+) Cotton peaks from a lower frequency in the first-absorption-band region. When the $(-)_{589}$-$[Co(mal)(NH_3)_2(H_2O)_2]^+$ and $(-)_{589}[Co(NH_3)_2(py)_2$-$(H_2O)_2]^{3+}$ complexes are derived from these optically active carbonato complexes, two Cotton peaks, with (+) and (−) signs, from a lower frequency are observed. This phenomenon has been explained in terms of a crystal-field model of the rotatory strength in transition-metal complexes: the spectral change is ascribed to a change in the effective charge on donor atoms according to aquation.[17] Therefore, the CD spectral changes in the dicyano and dinitro complexes are regarded as the second piece of evidence indicating an intimate relation between the effective charge of donor atoms and the Cotton signs.

When a $(-)^{CD}_{589}[Co(CN)_2(ox)(H_2O)_2]^-$ complex was derived from the $(-)^{CD}_{589}[Co(CN)_2(CO_3)(ox)]^{3-}$ complex, no drastic change in the CD spectrum was observed. However, a decrease in the negative Cotton peak at a lower frequency, compared with that of the parent carbonato complex, was detected.

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