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Synthesis and Circular Dichroism Spectra of *mer*(*N*)-*cis*(*NH*$_3$)-[Co(OO)(NH$_3$)$_2$(py)(H$_2$O)]$^+$ and *mer*(*N*)-[Co(OO)(en)(py)(H$_2$O)]$^+$ Complexes

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Synopsis. The *mer(N)-cis(NH$_3$)*-[Co(OO)(NH$_3$)$_2$(py)(H$_2$O)]$^+$ and *mer*(*N*)-[Co(OO)(en)(py)(H$_2$O)]$^+$ complexes (OO=ox^{2-} or mal^{2-}) have been prepared and optically resolved. The CD spectra are different. The difference seems to be due to the additional optical activity derived from the helical arrangement of two bidentate ligands in the latter ethylenediamin complexes.

Recently, the complexes of *cis,cis,cis*-[Co(a)$_2$(b)$_2$(c)$_2$],[1,2] *cis,cis*-[Co(a)$_2$(b)$_2$(CC)],[2] *fac*(*D*)-[Co(a)(b)(c)(DDD)],[3] and *fac*(*a*)-[Co(a)$_3$(b)(CD)] types,[4] which derive their dissymmetry mainly from the distribution of donor atoms, have been prepared in our laboratory. In this note, novel complexes, *mer*(*N*)-*cis*(*NH*$_3$)-[Co(OO)(NH$_3$)$_2$(py)(H$_2$O)]$^+$, and related complexes, *mer*(*N*)-[Co(OO)(en)(py)(H$_2$O)]$^+$ (OO=ox^{2-} ormal^{2-}), are reported. The CD spectra of these complexes are of interest in investigating the optical activity of *mer*-[Co(N)$_3$(O)$_3$] chromophore.

Experimental

Preparation and Optical Resolution. *a)* mer(N)-cis(NH$_3$)-*Diammineaquaoxalatopyridinecobalt(III) Perchlorate*, mer(N)-cis-(NH$_3$)-[*Co(ox)(NH$_3$)$_2$(py)(H$_2$O)*]*ClO$_4$*: To a solution of *cis*-K[Co(CO$_3$)(ox)(NH$_3$)$_2$]·H$_2$O[5] (20 g, 0.067 mol, in 200 cm^3 H$_2$O) was added pyridine (17 cm^3, 0.21 mol), and the solution was adjusted to pH 5.5 with 60% HClO$_4$ in an ice-bath. After filtration, the filtrate was stirred at room temperature for 0.5 h. The crude product which deposited was recrystallized from warm water. The yield was *ca.* 5 g. Found: C, 22.26; H, 3.47; N, 10.84%. Calcd for [Co(C$_2$O$_4$)(NH$_3$)$_2$(C$_5$H$_5$N)(H$_2$O)]ClO$_4$: C, 22.26; H, 3.48; N, 11.13%.

The perchlorate was converted into chloride by using a column of Dowex 50W-X8 in Na$^+$ form. To a solution of the chloride (6 g, 0.02 mol, in 90 cm^3 H$_2$O) was added (+)$_{546}$-K[Co(edta)]·2H$_2$O (4 g, 0.01 mol) with mechanical stirring, and the whole was kept in an ice-bath. The less-soluble diastereoisomeric salt containing the (−)$_{589}$-oxalato complex was recrystallized five times from water. The final yield was *ca.* 1.5 g. Found: C, 31.17; H, 4.31; N, 10.16%. Calcd for [Co(C$_2$O$_4$)(NH$_3$)$_2$(C$_5$H$_5$N)(H$_2$O)][Co(C$_{10}$H$_{12}$N$_2$O$_8$)]·2H$_2$O: C, 30.87; H, 4.43; N, 10.59%.

b) mer(N)-*Aquaethylenediamineoxalatopyridinecobalt(III) Chloride*, mer(N)-[*Co(ox)(en)(py)(H$_2$O)*]*Cl*: Pyridine (24 cm^3, 0.3 mol) was added to a solution of K[Co(CO$_3$)(ox)(en)]·H$_2$O[5] (32.5 g, 0.1 mol, in 100 cm^3 H$_2$O), and pH of the solution was adjusted to 5.5 with 60% HClO$_4$. After filtration, the filtrate was stirred at room temperature for a day. The solution, once filtered, was chromatographed on a column of Dowex 50W-X8 in Na$^+$ form (5 cm × 30 cm) using a 0.15 mol/dm^3 NaCl solution. The red-violet band which descended was collected. After concentrating the effluent to *ca.* 30 cm^3, followed by filtering, the filtrate was kept in a refrigerator. The crude product thus obtained was recrystallized from warm water. The yield was 5.5 g. Found: C, 31.83; H, 4.45; N, 12.36%. Calcd for [Co(C$_2$O$_4$)(C$_2$H$_8$N$_2$)(C$_5$H$_5$N)(H$_2$O)]Cl: C, 31.97; H, 4.39; 12.46%.

Optical resolution was performed by using (+)$_{546}$Na[Co(edta)]·2H$_2$O in a way similar to that in *a*). The less-soluble diastereoisomeric salt of the (−)$_{589}$-oxalato complex was recrystallized from water. Found: C, 33.95; H, 4.42; N, 10.48%. Calcd for [Co(C$_2$O$_4$)(C$_2$H$_8$N$_2$)(C$_5$H$_5$N)(H$_2$O)][Co(C$_{10}$H$_{12}$N$_2$O$_8$)]·H$_2$O: C, 34.09; H, 4.33; N, 10.46%.

c) mer(N)-cis(NH$_3$)-*Diammineaquamalonatopyridinecobalt(III) Chloride Monohydrate*, mer(N)-cis(NH$_3$)-[*Co(mal)(NH$_3$)$_2$(py)(H$_2$O)*]*Cl·H$_2$O*: A solution containing a *cis*-[Co(CO$_3$)(mal)(NH$_3$)$_2$]$^-$ complex, which had been prepared according to the literature method[5] (*cis*-K[Co(CO$_3$)$_2$(NH$_3$)$_2$]·H$_2$O, 27 g, 0.1 mol scale), was treated in the same manner as *b*). By elution with 0.15 mol/dm^3 NaCl, red-violet and pink bands successively descended. The aimed red-violet band was collected, and the effluent was concentrated to *ca.* 20 cm^3. After filtration, the filtrate was kept in a refrigerator. The product thus obtained was recrystallized from warm water. The yield was *ca.* 0.2 g, Found: C, 27.62; H, 5.01; N, 12.35%. Calcd for [Co(C$_3$H$_2$O$_4$)(NH$_3$)$_2$(C$_5$H$_5$N)(H$_2$O)]Cl·H$_2$O: C, 27.79; H, 4.92; N, 12.15%.

This complex was partially resolved by means of chromatography on a column of Dowex 50W-X8 in Na$^+$ form (100—200 mesh, 2 cm × 30 cm), using 0.1 mol/dm^3 K$_2$[Sb$_2$(*d*-tart)$_2$] as the eluent. The earlier eluted species was the (+)$^{\mathrm{CD}}_{500}$-isomer.

d) mer(N)-*Aquaethylenediaminemalonatopyridinecobalt(III) Chloride Trihydrate*, mer(N)-[*Co(mal)(en)(py)(H$_2$O)*]*Cl·3H$_2$O*: This complex was prepared by the same way as described in *c)* except for the use of a [Co(CO$_3$)(mal)(en)]$^-$ complex,[5] which had been prepared from K[Co(CO$_3$)$_2$(en)]·H$_2$O (30 g, 0.1 mol scale). The yield was *ca.* 0.3 g. Found: C, 29.47; H, 5.75; N, 10.77%. Calcd for [Co(C$_3$H$_2$O$_4$)(C$_2$H$_8$N$_2$)(C$_5$H$_5$N)(H$_2$O)]Cl·3H$_2$O: C, 29.45; H, 5.64; N, 10.31%.

This complex was partially resolved in a way similar to that in *c)*, except for the use of a long column (2 cm × 60 cm). The earlier eluted species was the (+)$_{589}$-isomer.

Measurement. The absorption spectra were measured with a Hitachi 323 spectrophotometer. The CD spectra were recorded on a JASCO J-40CS automatic recording spectropolarimeter. Samples were converted into the chloride by an ion-exchange technique, and the $\Delta\varepsilon$ values were evaluated from the absorption spectral data. For the measurements of the optical rotation, a JASCO DIP-SL automatic polarimeter was used.

Results and Discussion

For the [Co(OO)(NH$_3$)$_2$(py)(H$_2$O)]$^+$ complexes four geometrical isomers are possible: (a) *mer(N)-cis(NH$_3$)*, (b) *mer(N)-trans(NH$_3$)*, (c) *fac(N)-cis(py, H$_2$O)*, and (d) *fac(N)-trans(py, H$_2$O)*. On the other hand, for the [Co(OO)(en)(py)(H$_2$O)]$^+$ complexes, three geometrical isomers are possible: (e) *mer(N)*, (f) *fac(N)-cis(py, H$_2$O)*, and (g) *fac(N)-trans(py, H$_2$O)*. Among these isomers, (a), (c), (e), and (f) are resolvable into enantiomeric pairs. All complexes prepared in the present work could be resolved as described in the Experimental section.

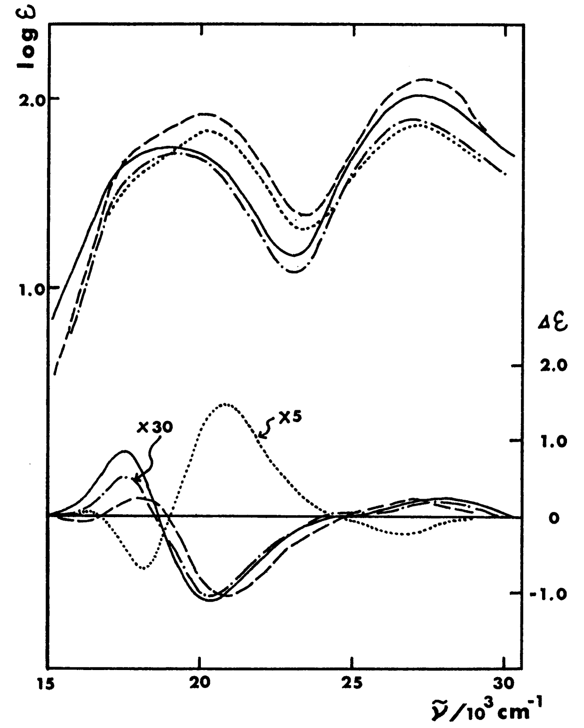

Fig. 1. Absorption and CD Spectra.
——: *mer*(*N*)-*cis*(*NH*$_3$)-$(-)_{589}[\mathrm{Co(ox)(NH_3)_2(py)(H_2O)}]^+$, ----: *mer*(*N*)-$(-)_{589}[\mathrm{Co(ox)(en)(py)(H_2O)}]^+$, —·—·: *mer*(*N*)-*cis*(*NH*$_3$)-$(-)^{\mathrm{CD}}_{500}$ $[\mathrm{Co(mal)(NH_3)_2(py)(H_2O)}]^+$, ······: *mer*(*N*)-$(+)_{589}[\mathrm{Co(mal)(en)(py)(H_2O)}]^+$

As shown in Fig. 1, the first absorption bands of the $[\mathrm{Co(OO)(NH_3)_2(py)(H_2O)}]^+$ complexes are broad, and those of the $[\mathrm{Co(OO)(en)(py)(H_2O)}]^+$ complexes exhibit obvious shoulders, suggesting that these complexes have *mer*-$[\mathrm{Co(N)_3(O)_3}]$ chromophores. On this basis, the present $[\mathrm{Co(ox)(NH_3)_2(py)(H_2O)}]^+$ and $[\mathrm{Co(mal)(NH_3)_2(py)(H_2O)}]^+$ complexes can be assignable to *mer(N)-cis(NH*$_3$*)* isomers, and the $[\mathrm{Co(ox)(en)(py)(H_2O)}]^+$ and $[\mathrm{Co(mal)(en)(py)(H_2O)}]^+$ complexes to *mer(N)* isomers.

The CD spectra of the diammine complexes exhibit two Cotton peaks with opposite signs in the first absorption band region. The peaks at the higher-frequency side are dominant: 17300 cm^{-1} ($\Delta\varepsilon=0.90$) and 20300 cm^{-1} ($\Delta\varepsilon=-1.07$) for the $(-)_{589}[\mathrm{Co(ox)(NH_3)_2(py)(H_2O)}]^+$ complex, and 17600 cm^{-1} ($\Delta\varepsilon=0.017$) and 20400 cm^{-1} ($\Delta\varepsilon=-0.035$) for the $(-)^{\mathrm{CD}}_{500}[\mathrm{Co(mal)(NH_3)_2(py)(H_2O)}]^+$ complex. On the other hand, the CD spectra of the ethylenediamine complexes exhibit three peaks with alternating signs, the peaks at the lowest frequency being extremely weak compared with the dominant peaks at the highest frequency: 16100 cm^{-1} ($\Delta\varepsilon=-0.03$), 18000 cm^{-1} ($\Delta\varepsilon=0.26$), and 20800 cm^{-1} ($\Delta\varepsilon=-1.05$) for the $(-)_{589}[\mathrm{Co(ox)(en)(py)(H_2O)}]^+$ complex, and 16200 cm^{-1} ($\Delta\varepsilon=0.016$), 18200 cm^{-1} ($\Delta\varepsilon=-0.09$), and 20800 cm^{-1} ($\Delta\varepsilon=0.28$) for the $(+)_{589}[\mathrm{Co(mal)(en)(py)(H_2O)}]^+$ complex.

The CD spectral shapes are little affected by the change of a five-membered oxalato chelate to a six-membered malonato chelate, while a large difference in CD spectral shapes is observed between the diammine and the corresponding ethylenediamine complexes. It is considered that the optical activity of $[\mathrm{Co(OO)(NH_3)_2(py)(H_2O)}]^+$ is mainly derived from an arrangement of four kinds of ligating atoms, two O donors in OO and aqua, and two N donors in ammine and pyridine. On the other hand, that of $[\mathrm{Co(OO)(en)(py)(H_2O)}]^+$ is mainly derived from two sources, one of which is an arrangement of four kinds of donor atoms, and the other is a helical distribution of two chelate rings. Therefore, the CD spectral difference between the diammine and ethylenediamine complexes, which is clearly observable at the lower frequency side, may be attributed to the additional optical activity derived from the helical distribution of the chelates.

Dividing the optical activity between the two sources is justified by the CD spectral comparison between the *all-cis*-$[\mathrm{Co(C)_2(N)_2(O)_2}]$ complexes, which have a rhombic crystal field like the present complexes.[1] A CD spectrum of *all-cis*-$[\mathrm{Co(CN)_2(H_2O)_2(NH_3)_2}]^+$ resembles that of *cis,cis*-$[\mathrm{Co(CN)_2(H_2O)_2(en)}]^+$. On the other hand, a spectrum of *cis,cis*-$[\mathrm{Co(CN)_2(ox)(NH_3)_2}]^-$ is different from that of *cis*-$[\mathrm{Co(CN)_2(ox)(en)}]^-$; the former exhibits two extrema in the first absorption band region, and the latter, three extrema. From these comparisons, the chiral environments are considered not to be derived by the ethylenediamine chelate itsel but to be derived by forming a ring pair with the oxalate chelate.

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