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Circular Dichroism Spectra of *cis,cis*-$[Co(OO)(N)_2(py)_2]^+$-Type Complexes

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Synopsis. Four new complexes, *cis,cis*-$[Co(OO)(NH_2C_2H_5)_2(py)_2]^+$($OO=CO_3^{2-}$, ox^{2-}, or mal^{2-}) and *cis,cis*-$[Co(ox)(NH_3)_2(py)_2]^+$, have been prepared and optically resolved. The CD patterns regularly change in the order of carbonato, oxalato, and malonato complexes, the aspect in the change being opposite to that of related *cis,cis*-$[Co(NO_2)_2(OO)(NH_3)_2]^-$-type complexes.

Many complexes of $[Co(N)_4(O)_2]^+$-type have been prepared and optically resolved. The chirality of those complexes is considered to be derived from helical distributions of chelate rings. Recently, *cis,cis*-$[Co(OO)(NO_2)_2(NH_3)_2]^-$ ($OO=CO_3^{2-}$, ox^{2-}, or mal^{2-})[1] and *cis,cis*-$[Co(CO_3)(NH_3)_2(py)_2]^+$ [2] have been prepared and resolved. These complexes are interesting, because the chirality is derived from the arrangement of three kinds of donor atoms. In this paper, the preparations and optical resolutions of *cis,cis*-$[Co(OO)(NH_2C_2H_5)_2(py)_2]^+$ and *cis,cis*-$[Co(ox)(NH_3)_2(py)_2]^+$ complexes are reported. Furthermore, the influence of the chelated OO ligands upon the CD intensity is investigated.

Experimental

Syntheses and Optical Resolutions. *a)* cis,cis-*Carbonatobis(ethylamine)bis(pyridine)cobalt(III) Chloride Trihydrate*, cis,-cis-$[Co(CO_3)(NH_2C_2H_5)_2(py)_2]Cl\cdot3H_2O$: Ethylamine (40 cm^3, 0.4 mol) was added to a solution of $[Co(CO_3)_3]^{3-}$ ($Co(NO_3)_2\cdot6H_2O$, 0.05 mol scale)[3] and the mixture stirred until the solution became blue in color. After filtration, ethanol (150 cm^3) and acetone (100 cm^3) were successively added to the filtrate in an ice-bath. The crude product precipitated was recrystallized from water. The product was *cis*-$K[Co(CO_3)_2(NH_2C_2H_5)_2]\cdot H_2O$. To a solution of the above product (30 g, 0.13 mol, in 30 cm^3 H_2O) pyridine (25 cm^3, 0.31 mol) was added and the resultant solution acidified to pH 5 with $HClO_4$ (60%). After filtration, the filtrate was stirred at room temperature for a day, whereupon some pink crystals deposited. An aqueous solution of the crystals was charged on a column of Dowex 50W-X8 resin in Na^+ form (100—200 mesh, $\phi7\times5$ cm^2). By elution with 0.3 mol/dm^3 NaCl, one red band descended. The eluate was concentrated and kept in a refrigerator. The crude product was recrystallized from warm water; yield *ca.* 7 g. Found: C, 39.31; H, 6.52; N, 12.20%. Calcd for $[Co(CO_3)(NH_2C_2H_5)_2(C_5H_5N)_2]Cl\cdot3H_2O$: C, 39.42; H, 6.57; N, 12.26%.

To a solution of the chloride (4.0 g, 0.017 mol, in 20 cm^3 H_2O) was added $(-)_{546}Ag[Co(ox)_2(en)]$ (3.7 g, 0.017 mol), and the resulting AgCl was filtered off. On concentrating the filtrate, at first, one diastereoisomeric salt of the $(-)_{589}$-carbonato complex deposited, and then another salt of the $(+)_{589}$-one deposited. Since the optical purity of the former salt could not be raised by recrystallization, the latter salt was recrystallized ten times from warm water. The yield was *ca.* 1.0 g.

b) cis,cis-*Bis(ethylamine)oxalatobis(pyridine)cobalt(III) Perchlorate Monohydrate*, cis,cis-$[Co(ox)(NH_2C_2H_5)_2(py)_2]ClO_4\cdot H_2O$: $H_2C_2O_4\cdot2H_2O$ (8 g, 0.089 mol) was added to a solution of *cis,cis*-$[Co(CO_3)(NH_2C_2H_5)_2(py)_2]Cl\cdot H_2O$ (10 g, 0.043 mol) and the mixture was stirred at 35 °C for 2 d. The solution was neutralized with $KHCO_3$. After filtration, the filtrate was charged on a column containing Dowex 50W-X8 resin in Na^+ form (100—200 mesh, $\phi4\times30$ cm^2). By elution with 0.1 mol/dm^3 $NaClO_4$, two red bands were discharged from the column (labeled E1 and E2 in the order of elution), and the desired E2 band was collected in a fraction. After concentration and filtration, the filtrate was kept in a refrigerator. The crude product was recrystallized from water. The yield was 4 g. Found: C, 37.73; H, 5.03; N, 10.85%. Calcd for $[Co(C_2O_4)(NH_2C_2H_5)_2(C_5H_5N)_2]ClO_4\cdot H_2O$: C, 37.47; H, 5.12; N, 10.93%.

This complex was partially resolved by column chromatography on SP-Sephadex C-25 ($\phi2.5\times95$ cm^2, Na^+ form) using 0.05 mol/dm^3 $K_2[Sb_2(d\text{-tart})_2]$ as an eluent.

c) cis,cis-*Bis(ethylamine)malonatobis(pyridine)cobalt(III) Perchlorate Dihydrate*, cis,cis-$[Co(mal)(NH_2C_2H_5)_2(py)_2]ClO_4\cdot2H_2O$: To a solution of *cis*-$K[Co(CO_3)_2(NH_2C_2H_5)_2]\cdot H_2O$(32 g, 0.1 mol, in 120 cm^3 H_2O) potassium malonate (17 g, 0.09 mol) was added, and the mixture acidified to pH 5 with 60% $HClO_4$ in an ice-bath. After filtration, the filtrate was stirred for 1 h, and then adjusted to pH 1 with 60% $HClO_4$. The solution was filtered and the filtrate was chromatographed on a column of Dowex 50W-X8 resin in H^+ form (100—200 mesh, $\phi7\times15$ cm^2) using 0.2 mol/dm^3 NaCl as an eluent. A univalent complex species was collected in a fraction. To the fraction was added $KHCO_3$ to adjust pH to 9 and the solution concentrated to *ca.* 50 cm^3. After filtration, pyridine (15 cm^3, 0.19 mol) was added to the filtrate followed by 60% $HClO_4$ to adjust the pH to 5 in the cold. The solution was filtered once and the filtrate stirred at room temperature for 3 d. The solution was charged on a column of Dowex 50W-X8 resin in Na^+ form (100—200 mesh, $\phi4\times30$ cm^2). By elution with 0.1 mol/dm^3 NaCl, three bands were discharged. The first eluted band was collected and concentrated to *ca.* 20 cm^3. After filtration, the filtrate was kept in a refrigerator. The product obtained was recrystallized from warm water; yield *ca.* 0.5 g. Found: C, 37.54; H, 5.52; N, 10.44%. Calcd for $[Co(C_3H_2O_4)(NH_2C_2H_5)_2(C_5H_5N)_2]ClO_4\cdot2H_2O$: C, 37.47; H, 5.56; N, 10.28%.

This complex was partially resolved on a column chromatograph of Dowex 50W-X8 resin in Na^+ form (100—200 mesh, $\phi4\times46$ cm^2) using 0.1 mol/dm^3 $K_2[Sb_2(d\text{-tart})_2]$ as eluent.

d) cis,cis-*Diammineoxalatobis(pyridine)cobalt(III) Perchlorate 2.5-Hydrate*, cis,cis-$[Co(ox)(NH_3)_2(py)_2]ClO_4\cdot2.5H_2O$: This complex was prepared in the same manner as described in *b)* except for the use of *cis,cis*-$[Co(CO_3)(NH_3)_2(py)_2]Cl\cdot H_2O$[2] (10 g, 0.027 mol) instead of *cis,cis*-$[Co(CO_3)(NH_2C_2H_5)_2(py)_2]Cl\cdot H_2O$. The yield was *ca.* 2 g. Found: C, 29.32; H, 4.34; N, 11.48%. Calcd for $[Co(C_2O_4)(NH_3)_2(C_5H_5N)_2]ClO_4\cdot2.5H_2O$: C, 29.24; H, 4.34; N, 11.58%.

The perchlorate was converted to chloride by column chromatography. The chloride was optically resolved by adding equimolar $(+)_{543}Na[Co(edta)]\cdot2H_2O$. The less soluble diastereoisomeric salt containing the $(-)_{589}$-oxalato complex was recrystallized from water.

The optical rotation, absorption and CD spectra were measured in the same manner as described in the previous

Table 1. Absorption and CD spectral data

	Absorption $\tilde{\nu}_{max}/10^3\ cm^{-1}$		CD $\tilde{\nu}_{ext}/10^3\ cm^{-1}$				$\lvert\Delta\varepsilon_1/\Delta\varepsilon_2\rvert$
	(log ε_1)	(log ε_2)	($\Delta\varepsilon_1$)	($\Delta\varepsilon_2$)	($\Delta\varepsilon_3$)	($\Delta\varepsilon_4$)	
$(+)_{589}[Co(CO_3)(NH_2C_2H_5)_2(py)_2]^+$	19.2(2.08)	27.2(2.14)	18.1(+0.61)	20.2(−0.77)	27.4(+0.26)		0.79
$(+)_{589}[Co(ox)(NH_2C_2H_5)_2(py)_2]^+$	19.2(1.98)	27.0(2.24)	18.0(+0.07)	20.0(−0.16)	28.0(+0.07)		0.44
$(+)_{589}[Co(mal)(NH_2C_2H_5)_2(py)_2]^+$	19.1(1.94)	27.0(2.13)	18.0(+0.03)	20.0(−0.13)	27.3(+0.04)		0.23
$(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$	19.4(2.06)	27.6(2.07)	18.1(−0.76)	20.3(+0.92)	27.8(−0.28)		0.83
$(-)_{589}[Co(ox)(NH_3)_2(py)_2]^+$	19.7(1.91)	27.6(2.12)	18.5(−0.80)	20.7(+1.52)	27.4(−0.46)		0.53
$(+)_{589}[Co(H_2O)_2(NH_2C_2H_5)_2(py)_2]^{3+}$	19.1(1.90)	27.0(1.97)	17.4(−0.11)	19.6(+0.24)	25.8(−0.07)	28.4(+0.02)	0.46

paper.[2] Prior to the above measurements, the samples had been converted into chlorides by means of an ion-exchange technique. The absorption and CD spectra of the diaqua complex, after the corresponding carbonato complex was acid-hydrolyzed with 10% $HClO_4$, were measured.

Results and Discussion

The absorption and CD spectral data are summerized in Table 1. The three complexes, $(+)_{589}[Co(CO_3)(NH_2C_2H_5)_2(py)_2]^+$, $(+)_{589}[Co(ox)(NH_2C_2H_5)_2(py)_2]^+$, and $(+)_{589}[Co(mal)(NH_2C_2H_5)_2(py)_2]^+$, exhibit two CD peaks with opposite sign in the first absorption band region. When the value of the extremum at the lower frequency is designated $\Delta\varepsilon_1$, and that at the higher frequency $\Delta\varepsilon_2$, the ratio, $\lvert\Delta\varepsilon_1/\Delta\varepsilon_2\rvert$, decreases in the order of the carbonato, oxalato, and malonato oomplexes, as is seen in Table 1. The two diammine complexes, $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$ [2] and $(-)_{589}[Co(ox)(NH_3)_2(py)_2]^+$, also exhibit two CD peaks, the ratio decreasing in the order of the carbonato and oxalato complexes. Such a decrease is not apparent in $[Co(OO)(en)_2]^+$ or *cis*-$[Co(OO)(NH_3)_2(en)]^+$ complexes (OO represents CO_3^{2-}, ox^{2-}, or mal^{2-}),[2] which contain tris or bis bidentate ligands and show a single CD peak in the first absorption band region. These phenomena reveal a difference between the chiral complexes due to the arrangements of three kinds of donor atoms and those due to the helical distribution of bidentate ligands. On the other hand, CD spectra of *cis,cis*-$[Co(NO_2)_2(OO)(NH_3)_2]^-$ complexes,[1] which also belong to the same type of chiral complex as the present complexes, exhibit two CD peaks in the first absorption band region. However, the ratio increases in the order of the carbonato, oxalato, and malonato complexes; the values are 0.13, 0.57, and 0.97, respectively (in the case of the malonato complex, an extremely small extremum at the lowest frequency side is neglected). Mason[4] has succeeded in explaining the rotatory strength of *all-cis*-$[Co(CN)_2(NH_3)_2(H_2O)_2]^+$ in terms of a dynamic coupling model in which ligand-polarization induced by other ligands is treated. The different behavior between CD spectra of *cis,cis*-$[Co(OO)(NH_2C_2H_5)_2(py)_2]^+$ and those of *cis,cis*-$[Co(NO_2)_2(OO)(NH_3)_2]^-$ may be explained by the dynamic coupling model rather than a static coupling model,[5] since both complexes approximately belong to the same *cis*-$[Co(O)_2(N)_4]$-type complexes. It is considered that a factor such as polarizability or formal charge on the ligands is more intimately associated with the rotatory strength of the present complexes than the ligand field strength. This is supported by the observation that the CD spectrum of $(+)_{589}[Co(NH_2C_2H_5)_2(py)_2(H_2O)_2]^{3+}$ derived from $(-)_{589}[Co(CO_3)(NH_2C_2H_5)_2(py)_2]^+$ by acid-hydrolysis shows an opposite pattern to that of the $(+)_{589}$-carbonato complex. The ligand field strength of carbonato ligand is nearly equal to that of the aqua ligand. However, the polarizability of the former ligand is very different from that of the latter one.

The absolute configuration of $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$ has been assigned *S* on the basis of the CD spectral comparison with related complexes.[2] The CD patterns of three $(+)_{589}[Co(OO)(NH_2C_2H_5)_2(py)_2]^+$ ($OO=CO_3^{2-}$, ox^{2-}, mal^{2-}) isomers are opposite to that of $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$, and the CD spectrum of $(-)_{589}[Co(ox)(NH_3)_2(py)_2]^+$ exhibits the same pattern. Consequently, the three ethylamine complexes are assignable to an *R* configuration, and the ammine complex an *S* configuration. The $(+)_{589}[Co(NH_2C_2H_5)_2(py)_2(H_2O)_2]^{3+}$ species derived from the corresponding $(+)_{589}$-carbonato complex is also assigned to *R*, since the acid-hydrolysis should proceed with retention of the configuration.

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