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Magnetic Circular Dichroism Spectra of Amino Acid Complexes of the $[\mathrm{Co^{III}(N)_5(O)}]^{n+}$ Type

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Synopsis. MCD spectra of amino acid complexes of $[\mathrm{Co(NH_3)_5(OCOCHRNH_3)}]^{3+}$, $[\mathrm{Co(NH_2CHRCO_2)(NH_3)_4}]^{2+}$, and $[\mathrm{Co(NH_2CHRCO_2)(en)_2}]^{2+}$ types have been measured. The complexes belonging to a given type show nearly identical MCD curves irrespective of variation in their natural CD patterns. The complexes of D-, L-, and DL-alanine show identical MCD spectra.

In connection with our previous study[1] on magnetic circular dichroism (MCD) spectra of a series of racemic tris(chelate)cobalt(III) complexes, it seems worthwhile to investigate MCD spectra of optically active cobalt(III) complexes. Larcher and Gabriel compared MCD spectra of mono- and bis(L-valinato)nickel(II) complexes with their natural CD spectra.[2] We have made a comparison of the MCD and natural CD spectra of α-amino acid complexes of the $[\mathrm{Co^{III}(N)_5(O)}]^{n+}$ type, the result of which are reported here. The complexes studied are classified into three types, namely, a pentaammine type $[\mathrm{Co(NH_3)_5(OCOCHRNH_3)}]^{3+}$, in which the carboxylate end of amino acid ligand is attached to the central cobalt ion,[3] and a tetraammine and a bis(ethylenediamine) type, $[\mathrm{Co(NH_2CHRCO_2)(NH_3)_4}]^{2+}$ and $[\mathrm{Co(NH_2CHRCO_2)(en)_2}]^{2+}$, which contain the amino carboxylato ligand as chelate one. The natural CD spectra of a large part of these complexes were investigated previously in our laboratory.[4] The following abbreviations are used for the amino acid ligands: Hgly for glycine, Hala alanine, Hser serine, and Hphe phenylalanine.

Experimental

Preparations. The pentaammine (chloride or perchlorate) and tetraammine (sulfate) complexes were prepared by the methods described in previous papers.[3-5] The bis(ethylenediamine) complexes were prepared as follows.

$[\mathrm{Co(gly)(en)_2]Br_2\cdot H_2O}$ and $[\mathrm{Co(DL\text{-}ala)(en)_2]Br_2\cdot H_2O}$: A solution containing glycine (0.4 g) (or DL-alanine, 0.5 g) and $[\mathrm{Co(NH_3)(en)_2(OH_2)]Br_3}$ (2.5 g) in 20 $\mathrm{cm^3}$ of water was evaporated together with powdered activated charcoal (0.1 g) to about 5 $\mathrm{cm^3}$ at 80 °C on a water-bath. The solution was cooled to room temperature, filtered, and 1 $\mathrm{cm^3}$ of methanol was added. After mixture was kept in a refrigerator overnight, the orange red deposit was filtered, washed with methanol and ether, and dried in air. The crude complex was dissolved in 5 $\mathrm{cm^3}$ of water (*ca.* 50 °C). The solution was filtered, and kept in a refrigerator overnight after 3 $\mathrm{cm^3}$ of methanol had been added. The crystalline powder deposited was filtered, washed with methanol and ether, and dried in air. The pure complex was obtained by repeated crystallizations. Found: C, 16.93; H, 5.28; N, 16.50%. Calcd for $\mathrm{C_6H_{20}N_5O_2Br_2Co\ H_2O}$: C, 16.72; H, 5.14; N, 16.25%. Found: C, 18.60; H, 5.44; N, 15.53%. Calcd for $\mathrm{C_7H_{22}N_5O_2Br_2Co\cdot H_2O}$: C, 18.89; H, 5.44; N, 15.74%.

Measurements. The CD and MCD spectra were recorded with a JASCO MOE-1 spectropolarimeter. The MCD measurements were made in a magnetic field of 1.5 T(= 15000 G). The MCD intensity is expressed in terms of the molar circular dichroism per unit magnetic field in the direction of the light beam, $\Delta\varepsilon_M$, which has the units of $\mathrm{cm^{-1}\cdot mol^{-1}\ dm^3\ T^{-1}}$. The visible and near-ultraviolet absorption spectra were measured using a Shimadzu UV-200 spectrophotometer. All measurements were made at room temperature in aqueous solutions.

Results and Discussion

Figure 1 shows the observed curves of absorption, natural CD and MCD spectra of $[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$ and the related complexes. The MCD spectrum of the optically active complex is observed in overlap with the natural CD. Therefore the true MCD spectrum ($\Delta\varepsilon_M$ curve) was obtained by calculating the difference between the observed MCD and the natural CD curves, assuming that the natural CD and MCD are additive. The MCD spectra which are obtained in this manner are shown in Fig. 2. The MCD extremum data of the complexes studied are shown in Table 1. It is most

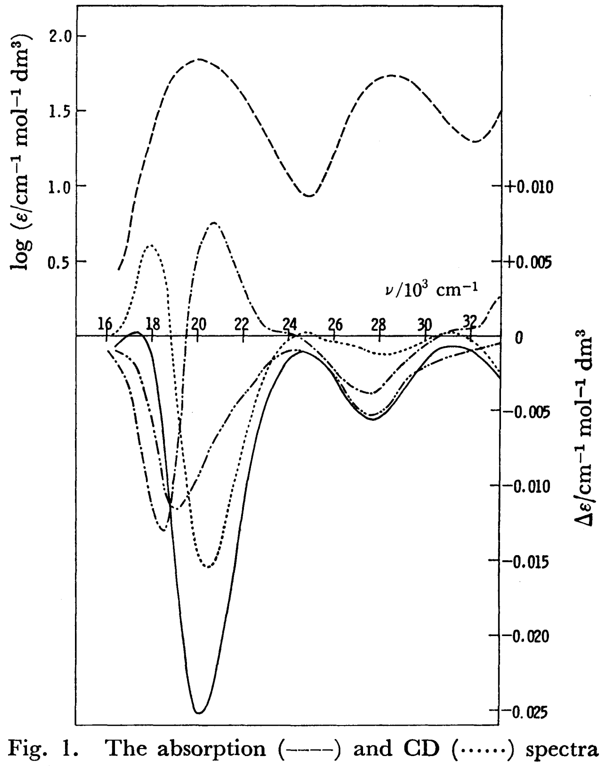

Fig. 1. The absorption (——) and CD (······) spectra of $[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$, and overlapped curves of CD and MCD in a magnetic field of 1.5 T of $[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$ (——), $[\mathrm{Co(NH_3)_5(D\text{-}Hala)}]^{3+}$ (—·—), and $[\mathrm{Co(NH_3)_5(DL\text{-}Hala)}]^{3+}$ (—··—).

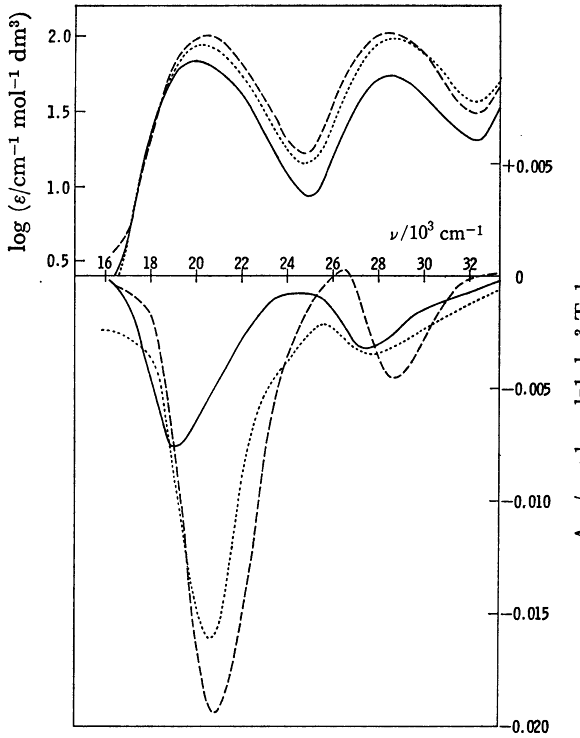

Fig. 2. The absorption and MCD spectra of $[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$ (——), $[\mathrm{Co(L\text{-}ala)(NH_3)_4}]^{2+}$ (······), and $[\mathrm{Co(DL\text{-}ala)(en)_2}]^{2+}$ (– – –).

remarkable that the D-, L- and DL-alanine complexes show strictly identical MCD spectra.

The MCD spectra of all the pentaammine type complexes are very similar, *viz.*, a negative band which may be mainly due to Faraday B term appears each in the first and the second absorption band region. Such a behavior in MCD is quite different from that in natural CD, which show a variety of patterns.[4] The natural CD curve of $[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$ has two extrema, 18000 (+0.005) and 20600 cm^{-1} (−0.015), in the first d-d band region. In the same region the tetraammine complex $[\mathrm{Co(L\text{-}ala)(NH_3)_4}]^{2+}$ has three extrema, 18200 (−0.036), 19700 (+0.11), and 21900 cm^{-1} (−0.32). The $\Delta\varepsilon_M$ intensity in the first d-d band region is greater than that in the second band region as was also observed for tris(chelate) complexes.[1] The intensity increases in the order of pentaammine$<$tetraammine$<$bis(ethylenediamine) in both first and second band regions; this order is parallel to the increase of absorption intensity.

The pentaammine complex ion belongs approximately to the C_{4v} symmetry, and in the first absorption band region two components, $^1E \leftarrow {}^1A_1$ and $^1A_2 \leftarrow {}^1A_1$, are expected in 19600 and 21000 cm^{-1}, respectively, as is seen in Table 2. The observed MCD peak is located at 19100 cm^{-1}. Therefore the MCD peak is primarily due to the Faraday B term of the E transition. The fact that the peak is in longer wavelength than the expected position of the E transition may be rationalized in terms of the swamping of the Faraday A term having a negative wing in the longer wavelength region. In the tetraammine and bis(ethylenediamine) complexes the longer wavelength component (^1E in C_{4v} symmetry) splits into two components by the lowering of symmetry, and the Faraday A term is not expected. The MCD peaks of complexes of these types appeared near the mean position of the split components as is seen in Table 2. Thus it is concluded that the negative MCD peaks of these complexes are mainly due to the composed B terms of split components.

Table 1. Absorption maximum and MCD extremum data (Wave numbers are given in 10^3 cm^{-1})

Complex ion	Absorption band ν (log ε)	MCD band ν ($\Delta\varepsilon_M$)
$[\mathrm{Co(NH_3)_5(Hgly)}]^{3+}$	20.0(1.83) 28.6(1.74)	19.0(−0.007) 27.6(−0.003)
$[\mathrm{Co(NH_3)_5(L\text{-}Hala)}]^{3+}$ [a]	20.0(1.84) 28.6(1.74)	19.0(−0.007) 27.5(−0.003)
$[\mathrm{Co(NH_3)_5(L\text{-}Hser)}]^{3+}$ [b]	20.0(1.83) 28.6(1.73)	19.1(−0.009) 27.5(−0.003)
$[\mathrm{Co(NH_3)_5(L\text{-}Hphe)}]^{3+}$ [c]	20.0(1.83) 28.7(1.74)	19.2(−0.012) 27.5(−0.003)
$[\mathrm{Co(NH_3)_5(\beta\text{-}Hala)}]^{3+}$	19.8(1.87) 28.3(1.76)	19.0(−0.008) 27.4(−0.004)
$[\mathrm{Co(gly)(NH_3)_4}]^{2+}$	20.3(1.89) 28.5(1.98)	20.4(−0.013) 28.2(−0.003)
$[\mathrm{Co(L\text{-}ala)(NH_3)_4}]^{2+}$ [a]	20.3(1.90) 28.7(1.94)	20.4(−0.015) 28.1(−0.003)
$[\mathrm{Co(gly)(en)_2}]^{2+}$	20.3(2.02) 28.5(2.05)	20.8(−0.020) {26.0(+0.0003) {28.6(−0.005)
$[\mathrm{Co(DL\text{-}ala)(en)_2}]^{2+}$	20.3(2.00) 28.5(2.02)	20.8(−0.020) {26.2(+0.0003) {28.8(−0.005)

a) The complex of D or DL ligand also shows the identical spectra. b) The L-leucine and L-threonine complexes show the MCD spectra nearly identical to that of the L-serine complex. c) The L-valine and L-proline complexes show the MCD spectra nearly identical to that of the L-phenylalanine complex.

Table 2. Splitting of the first d-d band

Complex	Calcd position of component[a]			MCD peak observed
	E (C_{4v})	A_2 (C_{4v})	Weighted mean	
$[\mathrm{Co(NH_3)_5(OCOCHRNH_3)}]^{3+}$	19.6	21.0	20.1	19.1
$[\mathrm{Co(NH_2CHRCO_2)(NH_3)_4}]^{2+}$	19.8, 19.9	21.1	20.3	20.4
$[\mathrm{Co(NH_2CHRCO_2)(en)_2}]^{2+}$	20.1, 20.1	21.4	20.5	20.8

a) The following values of Yamatera's parameters[6] are used: $\delta(\mathrm{NH_3}) = 0$ (the first band of hexaammine complex is in 21000 cm^{-1}), δ(en) = δ(N, amino carboxylate) = +400 cm^{-1}, δ(O, chelated amino carboxylate) = −4660 cm^{-1}, and δ(O, unidentate amino acid) = −5500 cm^{-1}, the latter two values of which were calculated from the data of the $E_g(D_{4h})$ bands of *trans*(*O*)-$[\mathrm{Co(gly)_2(en)}]^+$ (18870 cm^{-1}) and *trans*(*O*)-$[\mathrm{Co(en)_2(L\text{-}Hala)_2}]^{3+}$ (18450 cm^{-1}).

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