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Metal Complexes of Amino Acids. IV.[1] The Circular Dichroism of Tetrammine Cobalt(III) Complexes Containing Two Unidentate L-Amino Acid Ligands

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The preparation of a large number of pentammine and tetrammine cobalt(III) complexes containing L-amino acids as unidentate ligands were given in previous papers,[1,2] and the studies on the so-called vicinal effect due to the coordinated L-amino acids by means of rotatory dispersion (RD) and circular dichroism (CD) were reported.

From these studies, it was shown that the magnitude of inversive dispersion of RD and the intensity of CD in the d→d transition band region are enhanced by the sterical restriction of the conformational mobility of the coordinated L-amino acid. As a supplement to these studies, some new tetramminebis(amino-acid)cobalt(III) complexes are described in the present paper. The following abbreviations are used for the amino acid ligands: glyH = $CH_2(COO^-)NH_3^+$, alaH = $CH_3CH(COO^-)NH_3^+$, β-alaH = $CH_2(COO^-)CH_2NH_3^+$, sarH = $CH_2(COO^-)(NH_2CH_3)^+$, and proH = $CH(COO^-)CH_2CH_2CH_2NH_2^+$.

Experimental

***cis*-Tetrammine(β-alanine)(L-alanine)cobalt(III) Perchlorate and *cis*-Tetrammine(sarcosine)(L-alanine)cobalt(III) Perchlorate: *cis*-[$Co(NH_3)_4$(β-alaH)(L-alaH)]$(ClO_4)_3$ and *cis*-[$Co(NH_3)_4$(sarH)(L-alaH)]$(ClO_4)_3$.** The crude complexes were obtained by a method similar to that employed in the preparation of *cis*-[$Co(NH_3)_4$(glyH)(L-alaH)]$(ClO_4)_3 \cdot 2H_2O$.[2] Purification was carried out by reprecipitation from their methanol solutions with dropwise addition of ether. These purple complexes are readily soluble in water and acetone, but insoluble in ether. The elemental analyses were made after dehydrating them on phosphorus pentoxide in a vacuum desiccator.

Found: C, 11.78; H, 4.37; N, 13.64%. Calcd for $C_6H_{26}N_6O_{16}Cl_3Co$: C, 11.94; H, 4.35; N, 13.93%.

Found: C, 12.02; H, 4.30; N, 13.67%. Calcd for $C_6H_{26}N_6O_{16}Cl_3Co$: C, 11.94; H, 4.35; N, 13.93%.

***cis*-Tetramminebis(L-proline)cobalt(III) Perchlorate: *cis*-[$Co(NH_3)_4$(L-proH)$_2$]$(ClO_4)_3$.** A solution of *cis*-[$Co(NH_3)_4(OH_2)_2$]$(ClO_4)_3$[3] and the calculated amount of L-proline in a small amount of water was warmed on a water-bath at 65°C for about seven hours. After the resulting solution had been kept for two days at room temperature, a large amount of methanol-ether mixture (2 : 1) was added to it. Purification of the crude product obtained was made from the methanol solution by the addition of ethanol-ether mixture (2 : 1). This was dehydrated on phosphorus pentoxide in a vacuum desiccator.

Found: C, 18.05; H, 4.54; N, 12.81%. Calcd for $C_{10}H_{30}N_6O_{16}Cl_3Co$: C, 18.32; H, 4.62; N, 12.82%.

The preparation of the other complexes studied has

1) Part III of this series: T. Yasui, J. Hidaka and Y. Shimura, This Bulletin, **39**, 2417 (1966).

2) J. Fujita, T. Yasui and Y. Shimura, *ibid.*, **38**, 654 (1965).

3) M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **260**, 65 (1949).

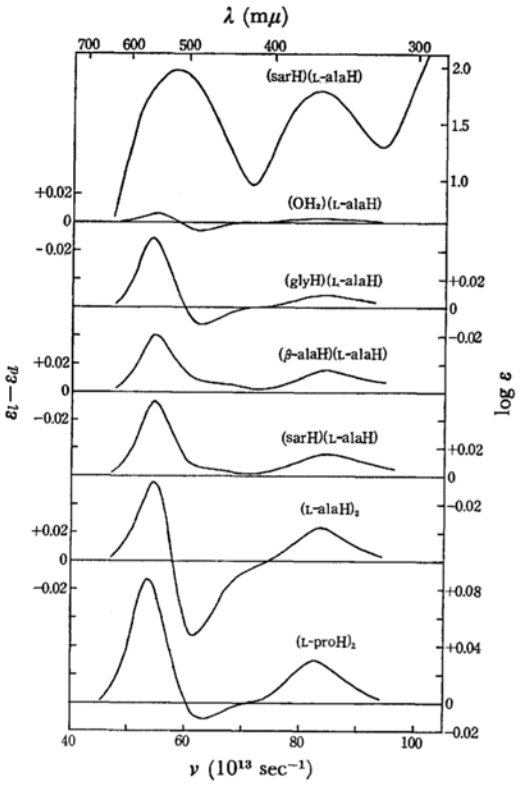

Fig. 1. Absorption and CD curves of the *cis*-[$Co^{III}(N)_4(O)_2$] type complexes containing one or two unidentate amino acid ligands.

already been reported.[2] The CD curves were obtained by a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. and the absorption spectra by a Shimadzu QR-50 spectrophotometer; the measurements were made in aqueous solutions at room temperature. The CD curves are shown in Fig. 1 and their extremum data are listed in Table 1.

Discussion

The analytical results and the absorption spectra of the complexes obtained obviously indicate that the amino acid ligands are coordinated to the cobalt(III) ion with the oxygen atom of the carboxyl group, and that the two oxygen donor atoms are situated at the *cis* positions of an octahedron. Therefore all of the complexes studied here have a general type of coordination, namely *cis*-[$Co(N)_4(O)_2$] structure.

In the first absorption band region, the CD bands of the *cis*-[$Co(OH_2)(NH_3)_4$(L-alaH)]$^{3+}$ complex are very weak in contrast to those of the other complexes (Fig. 1). The CD bands of the [$Co(NH_3)_5$(L-alaH)]$^{3+}$ complex, which contains only one L-alanine ligand, is also very weak.[1] If the aquo ligand in the (aquo)(L-alanine) complex is replaced by another amino acid ligand, the CD bands are considerably intensified (Fig. 1). In these complexes, the two amino acids in *cis* positions should take conformations somewhat restricted by the mutual interaction between them. The interaction between the L-alanine and the aquo ligands in the (aquo)(L-alanine) complex will be less than that between the two amino acid ligands in a bis(amino-acid)tetrammine complex. Thus the enhancement of the CD intensity may be attributed to the sterical restriction of the conformational mobility of the L-alanine ligand.

The *cis*-[$Co(N)_4(O)_2$] structure has a symmetry of C_{2v}, and two CD components are expected in the region of the first absorption band of these complexes. Indeed they show the two CD bands; the longer wavelength bands of all the complexes are positive in their signs. A positive CD band is also commonly observed in the second absorption band region for each L-amino acid complex. These CD bands of the bis(amino-acid) complexes will

Table 1. Absorption and CD data of the tetrammine complexes of [$Co^{III}(N)_4(O)_2$] type (the extremum positions are given in 10^{13} sec^{-1})

Ligand in *cis* positions	I Band		II Band	
	ν^{AB}_{max} (log ε_{max})	ν^{CD}_{ext} $(\varepsilon_l-\varepsilon_d)_{ext}$	ν^{AB}_{max} (log ε_{max})	ν^{CD}_{ext} $(\varepsilon_l-\varepsilon_d)_{ext}$
(OH₂)(L-alaH)	59.2 (1.86)	53.6 (+0.006)	84.0 (1.72)	83.3 (+0.002)
		61.2 (−0.006)		
(glyH)(L-alaH)	58.0 (1.97)	53.7 (+0.048)	82.4 (1.78)	83.3 ($+0.007_4$)
		61.8 (-0.013_5)		
(β-alaH)(L-alaH)	57.8 (1.98)	54.0 ($+0.040_5$)	82.6 (1.79)	84.5 ($+0.014_5$)
		ca. 62 (+0.007)		
(sarH)(L-alaH)	58.1 (1.97)	54.0 (+0.054)	82.5 (1.78)	85.7 ($+0.016_5$)
		ca. 62 (+0.006)		
(L-alaH)₂	58.2 (1.96)	53.6 (+0.057)	82.8 (1.77)	82.2 ($+0.025_6$)
		60.6 (−0.054)		
(L-proH)₂	58.0 (1.97)	54.0 (+0.089)	82.8 (1.79)	82.5 (+0.032)
		63.1 (-0.010_2)		

be useful in determining the absolute configurations of amino acids. It has already been reported that the complexes of *trans*-$[Co(en)_2(L\text{-amino-acid})_2]^{3+}$ type have positive CD signs in the longer wavelength component of the first absorption band, and also in the second absorption band. Dunlop and Gillard[4] proposed the use of the complexes of $[Co(NH_3)_5(OCOR)]^{n+}$ type for the determination of absolute configuration of the $RCOO^-$, and this was criticized by Hawkins and Lawson.[5] The latter authors stated that the pentammine type complexes with the L-ligands impose a positive sign to the $^1A_1 \rightarrow {}^1E$ and a negative sign to the $^1A_1 \rightarrow {}^1A_2$ transition in the first absorption band region. Almost all of the pentammine type complexes, however, show only one component in the first absorption band region.[1,5] It seems that the bis(amino-acid) type complexes are more suitable for the determination of the absolute configurations of amino acids.

4) J. H. Dunlop and R. D. Gillard, *Tetrahedron*, **23**, 349 (1967).

5) C. J. Hawkins and P. J. Lawson, *Chem. Commun.*, **1968**, 177.