The Rotatory Dispersion of Cobalt(III) Ammine Complexes Containing Amino Acid as a Unidentate Ligand

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Although several studies[1-4] have been made of the rotatory dispersion of metallic complexes in which the asymmetric center is not around the metal ion but is only at the atom in the coordinated ligand, most of these studies have been made on planar-type complexes such as copper(II) alaninate. For octahedral complexes, Jaeger[5] has prepared the molecular complex $[Co(NO_2)_3NH_3(d\text{-chxn})]$** and shown that this complex exhibits an anomalous dispersion in the region of the first absorption band. A similar study has been reported by Mathieu[6] on a similar complex, $[Co(NO_2)_3NH_3(d\text{-pn})]$. Recently, Shimura[7] has prepared the complex $[Co(NH_3)_4(\text{L-leuc})]^{2+}$, which has a much simpler structure than those of the above type, and has observed an anomalous dispersion which consists of two inversive dispersions in the vicinity of its first absorption band. Through these experiments, the existence of the so-called "vicinal effect"[1,2] between the central metal ion and the asymmetric atom in the ligand has been proved.

It should be noted, however, that the previous investigations were made with complexes containing an optically active reagent as a chelate ligand. The chelate ligand sometimes takes the gauche form upon coordination, which may result in another optically active structure. In order to study the vicinal effect in more detail, it would be desirable to measure the rotatory dispersion of the complex coordinating with a unidentate optically active ligand. Unfortunately, no complexes of such type are known. It was decided at first, therefore, to prepare cobalt(III) complexes in which amino acid is coordinated as a unidentate ligand.

In the present paper, the preparation and the absorption studies of a large number of pentammine and tetrammine cobalt(III) complexes containing both optically active and inactive amino acids will be described. The rotatory dispersion and the circular dichroism of the optically active complexes will also be measured, and the results will be discussed from the standpoint of the structure of these complexes.

Experimental

Preparation. — *Pentammineglycinecobalt(III) Perchlorate Monohydrate:* $[Co(NH_3)_5(glyH)](ClO_4)_3\cdot H_2O$. — An aqueous solution containing 5 g. of aquopentamminecobalt(III) perchlorate[8] and 2 g. (excess) of glycine in 50 ml. of water was gradually evaporated on a water bath at 75—80°C to a volume of about 20 cc. The dark red solution obtained was kept in a refrigerator overnight. The orange-pink crystals formed were filtered and washed with a water-ethanol (1 : 1) mixture and then with absolute ethanol. This was recrystallized by dissolving it in warm water and then cooling it in a refrigerator. Recrystallization from a cold aqueous solution was also effected by the addition of 30% perchloric acid.

Pentamminecobalt(III) Perchlorates of β-Alanine, DL-α-Alanine, L-α-Alanine and γ-Aminobutylic Acid: $[Co(NH_3)_5(\beta\text{-alaH})](ClO_4)_3$, $[Co(NH_3)_5(\text{DL-}\alpha\text{-alaH})](ClO_4)_3\cdot H_2O$, $[Co(NH_3)_5(\text{L-}\alpha\text{-alaH})](ClO_4)_3\cdot 2H_2O$ and $[Co(NH_3)_5(\gamma\text{-ambutH})](ClO_4)_3\cdot$ — These complexes were prepared by the same method as the glycine complex described above, using β-alanine, DL-α-alanine, L-α-alanine and γ-aminobutylic acid respectively. These complexes are more soluble in water than is the glycine complex.

Pentammine-L-phenylalanine-cobalt(III) Perchlorate Monohydrate: $[Co(NH_3)_5(\text{L-phalaH})](ClO_4)_3\cdot H_2O$.— To 50 ml. of an aqueous solution containing 5 g. of aquopentamminecobalt(III) perchlorate 2 g. (a slight excess) of L-phenylalanine was added. The mixture was warmed on a water bath at 80°C until the amino acid was dissolved. The dark red solution

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1) I. Lifschitz, *Z. phys. Chem.*, **105**, 27 (1923); **114**, 485 (1925).

2) P. Pfeiffer and W. Christeleit, *Z. physiol. Chem.*, **247**, 262 (1937); **248**, 197 (1937).

3) P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzner and H. Thielert, *J. prak. Chem.*, **150**, 261 (1938).

4) I. Lifschitz and F. L. M. Schouteden, *Rec. Trav. Chim.*, 58, 411 (1939).

5) F. M. Jaeger, *Bull. soc. chim. France*, [5] **4**, 1201 (1937).

** The following abbreviations will be used: chxn = $C_6H_{10}(NH_2)_2$, 1,2-diaminocyclohexane; pn = $NH_2CH(CH_3)CH_2NH_2$; leuc = $NH_2CH(COO^-)CH_2CH(CH_3)_2$; glyH = $NH_3^+CH_2COO^-$; gly = $NH_2CH_2COO^-$; β-alaH = $NH_3^+CH_2CH_2COO^-$; α-alaH = $NH_3^+CH(CH_3)COO^-$; α-ala = $NH_2CH(CH_3)COO^-$; phalaH = $C_6H_5CH_2CH(NH_3^+)COO^-$; γ-ambutH = $NH_3^+CH_2CH_2CH_2COO^-$; bet = $(CH_3)_3N^+CH_2COO^-$.

6) J.-P. Mathieu, *Ann. de Phys.*, [11] 19, 335 (1944).

7) Y. Shimura, This Bulletin, **31**, 315 (1958).

8) O. Hassel and G. B. Naess, *Z. anorg. Chem.*, **174**, 24 (1928).

obtained was then evaporated on a water bath at 75—80°C to a volume of about 20 cc. and cooled in ice. The red crystals obtained were filtered and washed with a water-ethanol (1 : 1) mixture and then with absolute ethanol. Fine crystalline needles were obtained from a cold aqueous solution by adding 30% perchloric acid.

Glycinatopentamminecobalt(III) Perchlorate: $[Co\,gly(NH_3)_5](ClO_4)_2$. — Three grams of pentamminеglycinecobalt(III) perchlorate monohydrate was dissolved in 20 ml. of 30% aqueous ammonia. To the dark red solution obtained ethanol was then added. Upon cooling in ice, the dark red crystals formed were filtered and washed with a water-ethanol (1 : 1) mixture and then with absolute ethanol. This complex was recrystallized from 3% aqueous ammonia by adding ethanol.

DL-α-Alaninato-pentamminecobalt(III) Perchlorate Monohydrate: $[Co(\text{DL-}\alpha\text{-ala})(NH_3)_5](ClO_4)_2 \cdot H_2O$. — The dark red crystals of this complex were obtained by the method described above for the glycinato complex, but using $[Co(NH_3)_5(\text{DL-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$ instead of $[Co(NH_3)_5(glyH)](ClO_4)_3 \cdot H_2O$.

Tetrammine-bis(glycine)cobalt(III) Perchlorate: $[Co(NH_3)_4(glyH)_2](ClO_4)_3$. — To 30 ml. of an aqueous solution containing 5 g. of diaquotetramminecobalt(III) perchlorate[9] a slight excess of glycine (1.8 g.) was added. The resulting solution was gradually evaporated on a water bath at 75—80°C to a volume of about 10 ml. After cooling, the drop-by-drop addition of absolute ethanol to this solution resulted in the formation of purple crude crystals, which were then filtered and washed with ethanol. These crystals were recrystallized by dissolving them in the minimum amount of water and then adding ethanol and a few drops of concentrated perchloric acid. Purple crystals were obtained after the solution had been kept in a refrigerator overnight.

Tetrammine-bis(DL-α-alanine)-, and Tetrammine-bis(L-α-alanine)cobalt(III) Perchlorates: $[Co(NH_3)_4(\text{DL-}\alpha\text{-alaH})_2](ClO_4)_3$ *and* $[Co(NH_3)_4(\text{L-}\alpha\text{-alaH})_2](ClO_4)_3 \cdot 2H_2O$.—Purple crystals of these complexes were prepared by the same method as the bis(glycine) complex described above, but using 2 g. of DL-α-alanine and L-α-alanine respectively instead of glycine.

Aquotetrammineglycinecobalt(III) Perchlorate Monohydrate: $[Co(OH_2)(NH_3)_4(glyH)](ClO_4)_3 \cdot H_2O$. — To an aqueous solution of 5 g. of diaquotetramminecobalt(III) perchlorate in 50 ml. of water 1 g. of glycine was added. The purple red solution obtained was warmed on a water bath at 80°C for 15 min. and cooled in ice. Pink-colored crystals were precipitated by adding concentrated perchloric acid; the crystals were then filtered and washed with ethanol. This complex was recrystallized from a cold aqueous solution by adding concentrated perchloric acid.

Aquotetrammine-DL-α-alanine- and Aquotetrammine-L-α-alaninecobalt(III) Perchlorates: $[Co(OH_2)(NH_3)_4(\text{DL-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$ *and* $[Co(OH_2)(NH_3)_4(\text{L-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$. — These complexes were prepared and recrystallized by the method which has been described above for the aquo-glycine complex, but using 1.2 g. of DL-α-alanine and L-α-alanine respectively instead of glycine. These complexes were more soluble in water than the corresponding

TABLE I. CHEMICAL ANALYSIS OF THE COMPLEXES

Complex	Co, %		H_2O, %		C, %		H, %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$[Co(NH_3)_5(glyH)](ClO_4)_3 \cdot H_2O$	10.91	11.00	3.33	3.36	4.76	4.49	4.22	4.14
$[Co(NH_3)_5(\beta\text{-alaH})](ClO_4)_3$	10.70	11.09	—	—	6.83	6.78	4.35	4.17
$[Co(NH_3)_5(\text{DL-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$	10.71	10.72	3.10	3.28	6.43	6.56	4.52	4.40
$[Co(NH_3)_5(\text{L-}\alpha\text{-alaH})](ClO_4)_3 \cdot 2H_2O$	10.14	10.38	6.42	6.35	6.77	6.35	4.49	4.62
$[Co(NH_3)_5(\text{L-phalaH})](ClO_4)_3 \cdot H_2O$	9.24	9.42	2.97	2.88	17.66	17.28	4.58	4.51
$[Co(NH_3)_5(\gamma\text{-ambutH})](ClO_4)_3$	10.76	10.80	—	—	9.11	8.81	4.47	4.43
$[Co(NH_3)_5bet](ClO_4)_3$	10.47	10.53	—	—	10.91	10.73	4.68	4.68
$[Co\ gly(NH_3)_5](ClO_4)_2$	14.27	14.13	—	—	6.03	5.76	4.64	4.59
$[Co(\text{DL-}\alpha\text{-ala})(NH_3)_5](ClO_4)_2 \cdot H_2O$	13.26	13.12	3.91	4.01	8.44	8.02	5.20	5.16
$[Co(OH_2)(NH_3)_4(glyH)](ClO_4)_3 \cdot H_2O$	11.04	10.98	3.27	3.36	4.65	4.48	3.94	3.95
$[Co(OH_2)(NH_3)_4(\text{DL-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$	10.99	10.70	3.07	3.27	6.89	6.55	4.01	4.21
$[Co(OH_2)(NH_3)_4(\text{L-}\alpha\text{-alaH})](ClO_4)_3 \cdot H_2O$	10.72	10.70	2.96	3.27	6.43	6.55	4.11	4.21
$[Co(NH_3)_4(glyH)_2](ClO_4)_3$	10.19	10.24	—	—	8.77	8.35	3.95	3.85
$[Co(NH_3)_4(\text{DL-}\alpha\text{-alaH})_2](ClO_4)_3$	9.55	9.76	—	—	12.27	11.94	4.54	4.34
$[Co(NH_3)_4(\text{L-}\alpha\text{-alaH})_2](ClO_4)_3 \cdot 2H_2O$	9.25	9.21	5.62	5.63	13.70	11.27	4.89	4.73
$[Co(NH_3)_4(glyH)(\text{L-}\alpha\text{-alaH})](ClO_4)_3 \cdot 2H_2O$	9.42	9.42	5.74	5.76	11.66	9.60	4.60	4.51
$[Co(NH_3)_4(bet)_2](ClO_4)_3$	8.81	8.93	—	—	18.07	18.21	5.25	5.19
$[Co(\text{L-}\alpha\text{-ala})(NH_3)_4]SO_4$	18.70	18.94	—	—	11.43	11.58	5.97	5.83

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9) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

glycine complex.

Tetrammineglycine-L-α-alaninecobalt(III) Perchlorate Dihydrate: $[Co(NH_3)_4(glyH)(L\text{-}\alpha\text{-}alaH)](ClO_4)_3\cdot 2H_2O$.—To an aqueous solution containing 5 g. of aquotetrammineglycinecobalt(III) perchlorate dissolved in the minimum amount of water 0.9 g. of L-α-alanine was added. The reddish-violet solution obtained was warmed on a water bath at 80°C for 15 min. After it had cooled as a clear, dark violet solution, ethanol was added, resulting in the slow formation of purple crystals. These were filtered and washed with ethanol. Recrystallization from a concentrated aqueous solution was effected by the addition of ethanol and of a few drops of concentrated perchloric acid. Purple crystals were obtained after the solution had been kept in a refrigerator overnight.

Pentamminebetaine- and Tetrammine-bis(betaine)-cobalt(III) Perchlorates: $[Co(NH_3)_5bet](ClO_4)_3$ and $[Co(NH_3)_4(bet)_2](ClO_4)_3$.—These betaine complexes were prepared by the method described in the literature[10] and were recrystallized several times from the aqueous solutions.

L-α-Alaninato-tetramminecobalt(III) Sulfate: $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]SO_4$.—This complex was prepared by the method given by Shimura[11] for the preparation of DL-α-alaninato-tetramminecobalt(III) sulfate. The corresponding D-α-alaninato complex was also prepared by this method.

The results of the chemical analysis for all the complexes prepared are given in Table I.

Spectral Measurements.—Visible and ultraviolet absorption spectra were obtained by using a Shimadzu QR-50 spectrophotometer in the 30 to 150×10^{13} sec^{-1} range. Infrared spectra were obtained with a Hitachi EPI-2G infrared spectrophotometer. The rotatory dispersion measurements were made by a Rudolph photoelectric spectropolarimeter, Model 200S-80. A Roussel-Jouan dichrograph in University of Pittsburgh, U. S. A., was used to obtain the circular dichroism spectra. All the measurements were made in aqueous solutions and at room temperature.

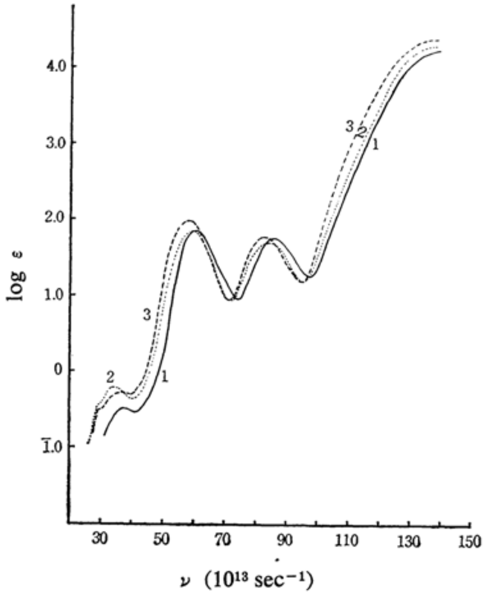

Fig. 1. Absorption spectra of
1, —— $[Co(NH_3)_5(glyH)](ClO_4)_3\cdot H_2O$;
2, ······ cis-$[Co(NH_3)_4(OH_2)(glyH)](ClO_4)_3\cdot H_2O$;
3, - - - cis-$[Co(NH_3)_4(glyH)_2](ClO_4)_3$.

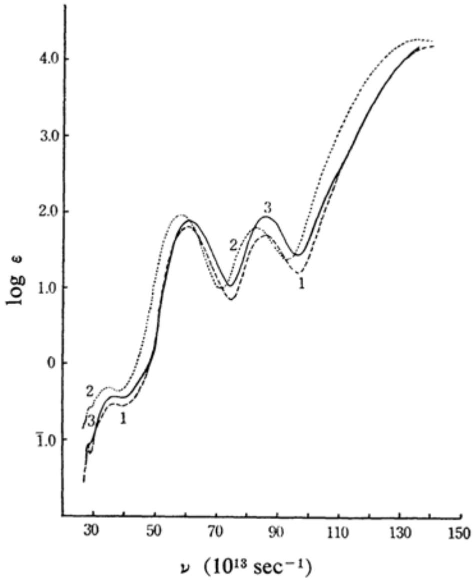

Fig. 2. Absorption spectra of
1, - - - $[Co(NH_3)_5(L\text{-}\alpha\text{-}alaH)](ClO_4)_3\cdot 2H_2O$;
2, ······ cis-$[Co(NH_3)_4(L\text{-}\alpha\text{-}alaH)_2](ClO_4)_3\cdot 2H_2O$;
3, —— $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]SO_4$.

Results

Table II lists the numerical data for the A, the first and the second absorption bands obtained in the present measurements. The data for the complexes which contain DL-α-alanine are not listed in this table, because they are exactly identical with those of the corresponding L-α-alanine complexes. Some typical absorption curves of the spectra are shown in Figs. 1 and 2. Figures 3—9 show the rotatory dispersion, the circular dichroism and the absorption curves of different complexes.

Discussion

Amino Acid in Unidentate Coordination.—It has been well known that an amino acid usually coordinates to a metal as a chelate ligand with its amino and carboxyl groups. In some particular complexes, however, the ligand amino acid is considered to act as a

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[10] J. V. Quagliano, S. Kida and J. Fujita, *J. Am. Chem. Soc.*, **84**, 724 (1962).

[11] Y. Shimura, This Bulletin, **31**, 173 (1958).

TABLE II. SUMMARY OF ABSORPTION DATA

The frequencies are given in 10^{13} sec^{-1}, and the intensities by log ε in parentheses.

Complex	A	I	II
[Co(NH$_3$)$_5$(glyH)](ClO$_4$)$_3$·H$_2$O	37 ($\bar{1}$.5)	60.0(1.84)	85.6(1.74)
[Co(NH$_3$)$_5$(β-alaH)](ClO$_4$)$_3$	37.5($\bar{1}$.5)	60.2(1.83)	85.3(1.72)
[Co(NH$_3$)$_5$(L-α-alaH)](ClO$_4$)$_3$·2H$_2$O	37 ($\bar{1}$.5)	60.0(1.83)	85.7(1.73)
[Co(NH$_3$)$_5$(L-phalaH)](ClO$_4$)$_3$·H$_2$O	37 ($\bar{1}$.5)	60.0(1.83)	85.8(1.74)
[Co(NH$_3$)$_5$(γ-ambutH)](ClO$_4$)$_3$	37.5($\bar{1}$.5)	60.0(1.89)	85.2(1.79)
[Co(NH$_3$)$_5$bet](ClO$_4$)$_3$	38 ($\bar{1}$.5)	59.8(1.84)	85.0(1.73)
cis-[Co(OH$_2$)(NH$_3$)$_4$(glyH)](ClO$_4$)$_3$·H$_2$O	34.5($\bar{1}$.8)	58.8(1.84)	84.0(1.69)
cis-[Co(OH$_2$)(NH$_3$)$_4$(L-α-alaH)](ClO$_4$)$_3$·H$_2$O	35 ($\bar{1}$.9)	59.3(1.86)	83.6(1.72)
cis-[Co(NH$_3$)$_4$(glyH)$_2$](ClO$_4$)$_3$	35 ($\bar{1}$.7)	58.2(1.98)	82.8(1.76)
cis-[Co(NH$_3$)$_4$(L-α-alaH)$_2$](ClO$_4$)$_3$·2H$_2$O	34.5($\bar{1}$.7)	58.2(1.97)	82.6(1.82)
cis-[Co(NH$_3$)$_4$(glyH)(L-α-alaH)](ClO$_4$)$_3$·2H$_2$O	35.5($\bar{1}$.7)	58.3(1.95)	82.7(1.78)
cis-[Co(NH$_3$)$_4$(bet)$_2$](ClO$_4$)$_3$	35 ($\bar{1}$.7$_5$)	58.5(1.97)	82.7(1.78)
[Co(L-α-ala)(NH$_3$)$_4$]SO$_4$	36.5($\bar{1}$.5$_5$)	60.8(1.89)	86.5(1.94)

unidentate ligand,[12-15] although no such complexes of cobalt(III) have been isolated. In the present study, the analytical values of the complexes prepared clearly indicate that the amino acids in these complexes coordinate to the cobalt(III) ion as a unidentate ligand. With respect to the amino acids concerned, there are two possible ways of bonding to the cobalt ion as a unidentate ligand. One is to be coordinated to the cobalt with the oxygen atom of the carboxyl group, and the other, with the nitrogen atom of the amino group. In the present case, the results of the absorption measurements suggest that the coordination of amino acid corresponds to the former way. The maximum frequencies and intensities of the first and the second bands of the unidentate amino acid complexes are almost the same as those of the betaine complexes in which the ligand betaine undoubtedly coordinates to the cobalt(III) ion with its carboxyl group (see Table II). Other evidence of the cobalt-oxygen linkage in the unidentate amino acid complexes lies in their infrared spectra. All the unidentate amino acid complexes except for the [Co gly(NH$_3$)$_5$](ClO$_4$)$_2$ and [Co(DL-α-ala)(NH$_3$)$_5$](ClO$_4$)$_2$·H$_2$O complexes show the C–O stretching band of the coordinated carboxyl group at about 1650 cm^{-1}.[10,16] and the deformation band of –NH$_3^+$ group at about 1500 cm^{-1}.[17] The [Co gly(NH$_3$)$_5$](ClO$_4$)$_2$ and [Co(DL-α-ala)(NH$_3$)$_5$](ClO$_4$)$_2$·H$_2$O complexes, which are prepared in alkaline media, do not show the –NH$_3^+$ deformation band. This indicates that the structure of the amino group is the –NH$_2$ form caused by the neutralization with alkali. All these facts lead to the conclusion that the carboxyl group is more favored than the amino group in the unidentate coordination to the cobalt(III) ion.

An attempt to prepare a complex in which the unidentate amino acid is coordinated to the cobalt(III) ion with its amino group was not successful. In the reaction of aquopentamminecobalt(III) perchlorate with amino acid, the treatment above 85°C or the addition of activated charcoal always produced complexes containing amino acid as a chelate ligand, with the evolution of ammonia gas.

In the tetrammine-bis(amino-acid)cobalt(III) ion two geometrical isomers, cis and trans, are possible, but only one species for each tetrammine complex has been obtained in the present preparation. As Figs. 1 and 2 show, the first bands of all the tetrammine complexes exhibit no splittings. The tetrammine complex with two oxygen atoms in trans positions may be expected to show distinct splittings of the first absorption band.[18] Thus, it has been concluded that all the tetrammine complexes prepared here correspond to the cis isomers. The first band of the bis(acetato)tetramminecobalt(III) complex, which has a structure similar to that of the unidentate amino acid complexes, shows a remarkable splitting in the trans isomer, but no splitting in the cis isomer.[19]

The first and the second absorption bands of the pentammine(amino-acid)cobalt(III) complexes shifted to a longer wavelength than

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[12] A. Nakahara, J. Hidaka and R. Tsuchida, This Bulletin, **29**, 925 (1956).

[13] R. W. Green and K. P. Ang, *J. Am. Chem. Soc.*, **77**, 5482 (1955).

[14] L. M. Volshtein and M. F. Mogilevkina, *Doklady Akad. Nauk S. S. S. R.*, **104**, 418 (1955).

[15] L. M. Volshtein and N. S. Velikanova, *Zhur. Neorg. Khim.*, **1**, 48 (1956).

[16] K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York (1958).

[18] H. Yamatera, This Bulletin, **31**, 95 (1958).

[19] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

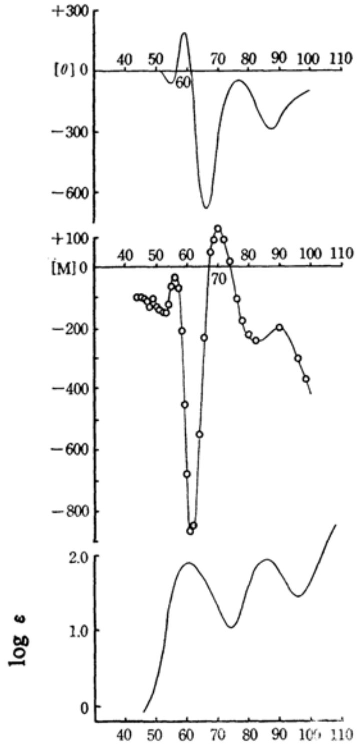

Fig. 3. Circular dichroism, rotatory dispersion and absorption of $[Co(L\text{-}\alpha\text{-ala})(NH_3)_4]SO_4$.

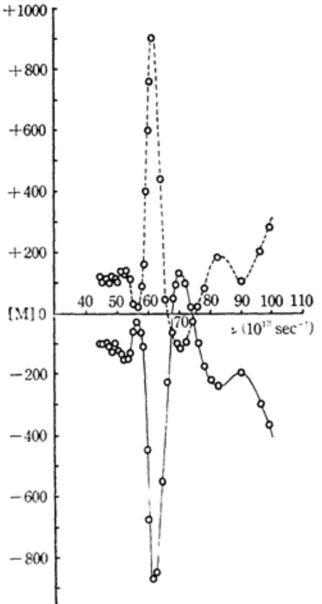

Fig. 4. Rotatory dispersion of:
—— $[Co(L\text{-}\alpha\text{-ala})(NH_3)_4]SO_4$, and - - - $[Co(D\text{-}\alpha\text{-ala})(NH_3)_4]SO_4$.

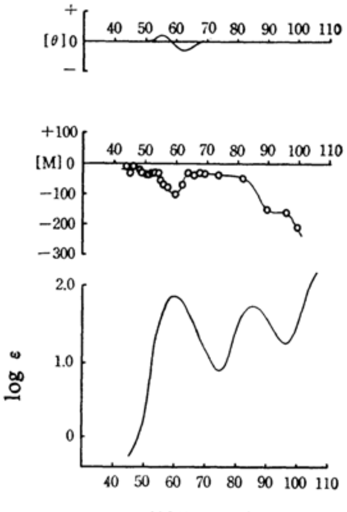

Fig. 5. Circular dichroism, rotatory dispersion and absorption of $[Co(NH_3)_5(L\text{-}\alpha\text{-alaH})](ClO_4)_3 \cdot 2H_2O$.

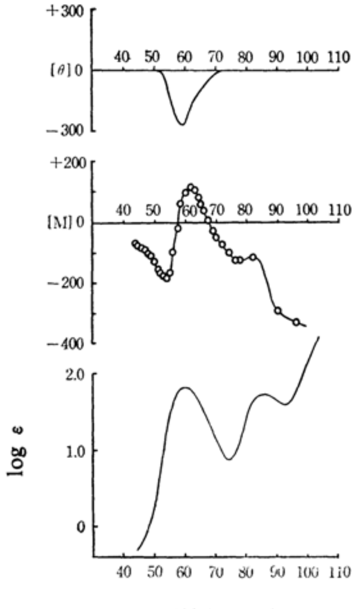

Fig. 6. Circular dichroism, rotatory dispersion and absorption of $[Co(NH_3)_5(L\text{-phalaH})](ClO_4)_3 \cdot H_2O$.

those of the aquopentamminecobalt(III) complex.[20] As Fig. 1 shows, the same relation may be seen to result from the replacement of the water molecule by amino acid in a series of complexes, $[Co(NH_3)_4(glyH)_2]^{3+}$, $[Co(NH_3)_4(OH_2)(glyH)]^{3+}$ and $[Co(NH_3)_4$-

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[20] Y. Shimura and R. Tsuchida, This Bulletin, 29, 311 (1956).

$(OH_2)_2]^{3+}$. The first and the second bands of the last complex have been observed at 59.4 and $84.6\times10^{13}\,sec^{-1}$ respectively.[20] From these spectral results, it has been concluded that the position of the unidentate amino acid in the spectrochemical series[20,21] is behind OH_2, but higher than CH_3COO^- or CO_3^{2-}.

Rotatory Dispersion and Circular Dichroism.—As has been mentioned above, Shimura[7] measured the rotatory dispersion of the complex, $[Co(L\text{-}leuc)(NH_3)_4]^{2+}$ which contains only one optically active chelate ligand. The shape and the magnitude of the anomalous dispersion of this complex in the region of its first absorption band are very similar to those of $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$, which has been measured in the present study in order to compare with the dispersion of the unidentate amino acid complexes. Shimura has also shown, by curve analysis, that the first band of $[Co(L\text{-}leuc)(NH_3)_4]^{2+}$ exhibits two inversive dispersions, one of which shows a positive Cotton effect and the other, a negative Cotton effect. A similar result is obtained by the analysis of the rotatory dispersion curve of $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$. The circular dichroism of $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$, on the other hand, indicates that the first band should have another weak, negative Cotton effect on the longer wavelength side adjacent to the above-mentioned two strong Cotton effects and, moreover, one negative Cotton effect in the region of the second absorption band (see Fig. 3). In the rotatory dispersion curve of $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$, some indications of the inversive dispersion are seen at 55 and $87\times10^{13}\,sec^{-1}$. In order to establish these small anomalous dispersions, the rotatory dispersion of $[Co(D\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$ has been measured. As may be seen in Fig. 4, the dispersion curve of this complex is almost antipodal to that of the corresponding L-α-alaninato complex. It may be concluded, therefore, that the first absorption band of the $[Co(L\text{-}\alpha\text{-}ala)(NH_3)_4]^{2+}$ complex shows three inversive dispersions and the second band, one or more additional inversive dispersions.

The rotatory dispersion curve of the unidentate amino acid complex $[Co(NH_3)_5(L\text{-}\alpha\text{-}alaH)]^{3+}$, on the other hand, shows a very weak anomalous dispersion in its first band compared with that of the chelate complex (see Fig. 5). The magnitude of the partial molar rotation of the former is about 1/10 that of the latter. The circular dichroism of $[Co(NH_3)_5(L\text{-}\alpha\text{-}alaH)]^{3+}$ is also so weak that quantitative measurement was impossible. The circular dichroism curve given in Fig. 5 is only qualitative. In the rotatory dispersion curve of $[Co(NH_3)_5(L\text{-}phalaH)]^{3+}$ (Fig. 6), a more distinct anomalous dispersion than that of the corresponding L-α-alanine complex is observed in the region of the first band, although the magnitude of this dispersion is still very weak compared with those of the chelate amino acid complexes. The difference in the magnitude of anomalous dispersion between the unidentate and the chelate amino acid complexes might be caused by: 1) the difference in the distance from the asymmetric carbon atom to the cobalt ion, Co-O-C-C*- for the unidentate complex, but Co-O-C-C*- and Co-N-C*- for the chelate complex; 2) the conformational difference (that is, the conformation of the amino acid in the chelate complex is fixed by the formation of the chelate ring, but in the unidentate complex the amino acid can rotate about the Co-O bond axis), or 3) the difference in the electronic states of the complex ions caused by the coordination of the different atoms or by the different structures.

In order to study the points above-mentioned in more detail, the rotatory dispersion of three tetrammine complexes of $[Co\,N_4O_2]$ type have been measured. As Fig. 7 shows, the anomalous dispersion of *cis*-$[Co(NH_3)_4(L\text{-}\alpha\text{-}alaH)_2]^{3+}$ in its first band is rather remarkable compared with that of $[Co(NH_3)_5(L\text{-}\alpha\text{-}alaH)]^{3+}$. The

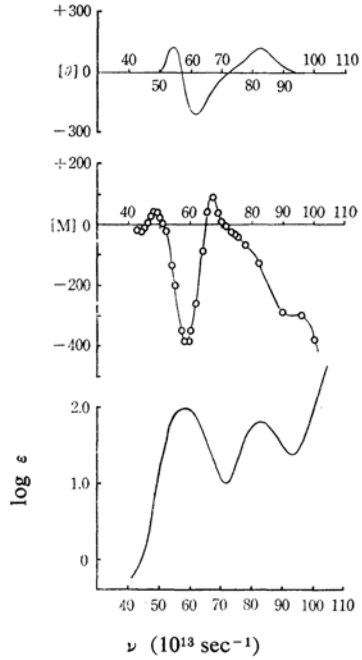

Fig. 7. Circular dichroism, rotatory dispersion and absorption of *cis*-$[Co(NH_3)_4(L\text{-}\alpha\text{-}alaH)_2](ClO_4)_3\cdot2H_2O$.

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[21] R. Tsuchida, ibid., 13, 388, 436 (1938).

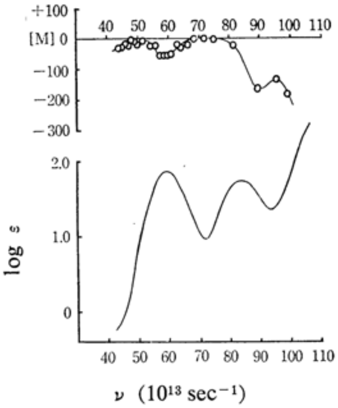

Fig. 8. Rotatory dispersion and absorption of cis-[Co(OH_2)(NH_3)$_4$(L-α-alaH)](ClO_4)$_3\cdot H_2O$.

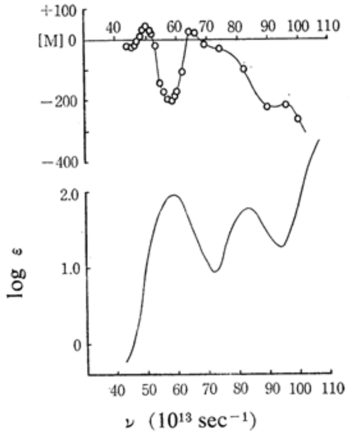

Fig. 9. Rotatory dispersion and absorption of cis-[Co(NH_3)$_4$(glyH)(L-α-alaH)](ClO_4)$_3\cdot 2H_2O$.

magnitude of the inversive dispersion in the former is estimated to be almost four times larger than that in the latter. This fact seems to suggest that the magnitude of the anomalous dispersion is not proportional to the number of the optically active ligands. This might be caused by the difference in the conformational mobility of the coordinated amino acid. The difference in the types of the complexes ([Co N_5O] and [Co N_4O_2]) does not seem to be important in this case. In cis-[Co(NH_3)$_4$(L-α-alaH)$_2$]$^{3+}$, two amino acids in the cis positions should take a conformation somewhat restricted by the mutual interaction, in contrast with the fact that the amino acid in [Co(NH_3)$_5$(L-α-alaH)]$^{3+}$ should be rather free from the interaction with the coordinated ammonia molecules. The anomalous dispersion of cis-[Co(OH_2)(NH_3)$_4$(L-α-alaH)]$^{3+}$, in which the conformational mobility of the amino acid is similar to that of [Co(NH_3)$_5$(L-α-alaH)]$^{3+}$, is as weak as that of [Co(NH_3)$_5$(L-α-alaH)]$^{3+}$. The anomalous dispersion of cis-[Co(NH_3)$_4$(glyH)(L-α-alaH)]$^{3+}$, on the other hand, shows a shape very similar to that of cis-[Co(NH_3)$_4$(L-α-alaH)$_2$]$^{3+}$, but its magnitude is almost half that of the latter (see Figs. 7 and 9). This fact indicates that the L-α-alanine cis-[Co(NH_3)$_4$(glyH)(L-α-alaH)]$^{3+}$ is in the same conformational state as those in cis-[Co(NH_3)$_4$(L-α-alaH)$_2$]$^{3+}$ as a result of the effect of the glycine coordinated in the adjacent cis position. Therefore, the proportionality of the magnitudes of the anomalous dispersions to the number of optically active ligands holds in this case.

From all these observations, including the fact that the first band of the chelate complex [Co(L-α-ala)(NH_3)$_4$]$^{2+}$ exhibits a strong anomalous dispersion, it may be concluded that the magnitude of the anomalous dispersion of the optically active α-amino acid complex in its first absorption band depends mainly on the conformational mobility of the optically active ligand.

As a further investigation, the measurement of the rotatory dispersion for $trans$-[Co(NH_3)$_4$(L-α-alaH)$_2$]$^{3+}$ will be an interesting subject, since the steric condition in the trans complex will be quite different from those in the cis isomers. Several attempts to prepare the trans complex, however, have been unsuccessful.

Summary

Fifteen new cobalt(III) ammine complexes containing amino acids as unidentate ligands have been prepared. The infrared, visible and ultraviolet absorption spectra of these complexes indicate that the oxygen of the carboxyl group acts as a donor atom. The circular dichroism and the rotatory dispersion of the unidentate complexes of the optically active α-amino acids and such chelate amino acid complexes as [Co(L-α-ala)(NH_3)$_4$]$^{2+}$ have been measured. The results suggest that the magnitude of the anomalous dispersion of the α-amino acid complex in the region of its first absorption band seems to depend mainly on the conformational mobility of the optically active ligand in the coordination sphere.

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