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# Metal Complexes of Amino Acids. III.[1] The Circular Dichroism of Cobalt(III) Ammine and Ethylenediamine Complexes with L-Amino Acids

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In order to study the vicinal effect of the L-amino acid coordinated in a complex on the central metal ion, a number of cobalt(III) L-amino acid complexes of three types were prepared, i. e., $[Co(NH_3)_5(L\text{-}amH)]X_3$, $[Co(L\text{-}am)(NH_3)_4]SO_4$, and *trans*-$[Co\ en_2(L\text{-}amH)_2]X_3$, where L-amH denotes an L-amino acid, and where X is Cl, Br, or I. The circular dichroism (CD) and the rotatory dispersion (RD) spectra of their aqueous solutions were measured in the wavelength range from 650 to 300 m$\mu$. In the region of the first absorption band, both the $[Co(NH_3)_5(L\text{-}amH)]^{3+}$ and the *trans*-$[Co\ en_2(L\text{-}amH)_2]^{3+}$ ions show one or two CD bands to be expected in complexes of the $C_{4v}$ symmetry with a structure of the $[Co\ N_5O]$-type and of the $D_{4h}$ symmetry with a structure of the *trans*-$[Co\ N_4O_2]$-type respectively. The positions of the CD bands observed in the *trans* complexes coincide well with the maxima of the split components, Ia and Ib, of the first absorption band. The CD spectra of different $[Co(L\text{-}am)(NH_3)_4]^{2+}$ ions, in which L-am is a bidentate ligand, show a variety of behavior; they are discussed from a stereochemical point of view. An intense CD band of the $[Co(L\text{-}prol)(NH_3)_4]^{2+}$ ion at about 510 m$\mu$ can be attributed to the vicinal effect of an asymmetric nitrogen atom of the coordinated L-prolinate ion. For the *trans*-$[Co\ en_2(L\text{-}amH)_2]X_3$ complexes, the rotatory parameters and rotatory strengths were calculated by means of analyses of the experimental CD and RD curves.

Circular dichroism (CD) spectra have been proved to give useful information on the splittings of d→d absorption bands of metal complexes with a rather low symmetry. On the other hand, such splittings are not always observed in ordinary absorption curves.

It is well known that a metal complex containing an optically-active ligand (for example, optically-active amino acid,[2-7] tartaric acid, [8,9] or propylenediamine),[10] shows some weak CD bands in the region of its d→d absorption band as a result of the vicinal effect of the optically-active center in the ligand on the central metal ion. Of these ligands, the optically-active amino acids* behave in

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[1] Part II of this series: T. Yasui and Y. Shimura, This Bulletin, **39**, 604 (1966).

[2] Y. Shimura, ibid., **31**, 315 (1958).

[3] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[4] J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, **1964**, 2822.

[5] J. Fujita, T. Yasui and Y. Shimura, This Bulletin, **38**, 654 (1965).

[6] T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).

[7] T. Yasui, This Bulletin, **38**, 1746 (1965).

[8] D. C. Bhatnagar and S. Kirshner, *Inorg. Chem.*, **3**, 1256 (1964).

[9] K. M. Jones and E. Larsen, *Acta Chem. Scand.*, **19**, 1210 (1965).

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

* The following abbreviations will be used: L-alaH$=CH_3CH(NH_3^+)COO^-$; L-ala$=CH_3CH(NH_2)$-$COO^-$; L-serH$=CH_2(OH)CH(NH_3^+)COO^-$; L-ser$=CH_2(OH)CH(NH_2)COO^-$; L-valH$=(CH_3)_2CHCH$-$(NH_3^+)COO^-$; L-val$=(CH_3)_2CHCH(NH_2)COO^-$; L-thrH$=CH_3CH(OH)CH(NH_3^+)COO^-$; L-thr$=CH_3$-$CH(OH)CH(NH_2)COO^-$; L-leuH$=(CH_3)_2CHCH_2$-$CH(NH_3^+)COO^-$; L-leu$=(CH_3)_2CHCH_2CH(NH_2)$-$COO^-$; L-isoleu$=CH_3CH_2CH(CH_3)CH(NH_2)COO^-$; L-phalaH$=CH_2(C_6H_5)CH(NH_3^+)COO^-$; L-phala$=CH_2(C_6H_5)CH(NH_2)COO^-$; L-prolH

$=\underbrace{NH_2^+CH_2CH_2CH_2CH}COO^-$; L-prol

$=\underbrace{NHCH_2CH_2CH_2CH}COO^-$.

an especially interesting way in that they can be coordinated both as unidentate and as bidentate ligands.

In a previous paper,[5] pentammine and tetrammine cobalt(III) complexes containing optically-active amino acids were reported, and it was suggested that the magnitude of the anomalous rotatory dispersion (RD) in the region of the first absorption band depends mainly on the conformational mobility of the optically-active ligand coordinated. In the present paper, the CD spectra of cobalt(III) ammine and ethylenediamine complexes which contain various L-amino acids will be described. The relationship among the ordinary absorption spectra and CD and some RD spectra will be considered precisely on the basis of the vicinal effect. Previously, several workers[2,11–14] made analyses of RD curves, but it was quite difficult to establish the individual inversive dispersions by the RD curve analyses alone. It was, therefore, been desirable to study in more detail the relation among the CD, the RD, and the ordinary absorption curves. In relation to this point, the present paper will discuss some typical d→d absorption bands of the cobalt(III) complexes of a new type, *trans*-$[Co\ en_2(L\text{-}amH)_2]X_3$.

## Experimental

**Preparation.**—By evaporating a mixed aqueous solution of $[Co(OH_2)(NH_3)_5](ClO_4)_3$[15] and an excess of L-amino acid below 60°C, the $[Co(NH_3)_5(L\text{-}amH)]X_3$ complex was obtained in a good yield. In this condition, the L-amino acid coordinates to cobalt(III) as a unidentate ligand[5] by an oxygen atom of the carboxyl group. At temperatures higher than 60°C, it was difficult to obtain the desired complexes because of the decomposition of $[Co(OH_2)(NH_3)_5]^{3+}$. The complexes with L-valine, L-leucine and L-threonine were readily soluble in methanol and were insoluble in ethanol.

The $[Co(am)(NH_3)_4]SO_4$ complexes have already been reported on by one of the present authors,[2,16] who prepared the complexes from $[Co\ Cl(OH_2)(NH_3)_4]SO_4$ and glycine, DL-alanine or L-leucine in ammoniacal alkaline solutions. In the present work, however, all of the $[Co(L\text{-}am)(NH_3)_4]SO_4$ complexes were obtained from the reaction of $[Co(OH_2)(NH_3)_5](ClO_4)_3$ with L-amino acid in the presence of activated charcoal. This method was proved to be superior to that described previously in respect to the yield and the diminution of the by-product. The *trans*-$[Co\ en_2(L\text{-}amH)_2]X_3$ complex was prepared by the evaporation almost to dryness of an aqueous solution containing $[Co(OH_2)_2en_2](ClO_4)_3$[17] and an excess of L-amino acid at a temperature higher than 70°C. The *trans* complexes are very soluble in water. At temperatures lower than 70°C, $[Co(OH_2)en_2(L\text{-}amH)]X_3$ is produced mainly.

The preparation of *trans*-$[Co(NH_3)_4(L\text{-}amH)_2]X_3$ was attempted by similar ways, but all such attempts were unsuccessful.

**$[Co(NH_3)_5(L\text{-}valH)]Cl_3$.**—An aqueous solution containing 5 g. of $[Co(OH_2)(NH_3)_5](ClO_4)_3$[15] and 3 g. of L-valine in 30 ml. of warm water was gradually evaporated almost to dryness on a water bath at about 55°C. To the resulting material there was added a solution containing 5 g. of potassium chloride in a small amount of water, and then 50 ml. of methanol was added. After the potassium perchlorate which settled had been removed, a large amount of an ethanol-ether mixture (2 : 1) was added, drop by drop, to the filtrate. The pinkish powder obtained was washed with ethanol and then with ether. The crude complex was recrystallized from 95% methanol by adding ethanol. The pinkish-orange complex obtained was then dried in a vacuum desiccator.

Found: C, 16.28; H, 7.19; N, 22.16. Calcd. for $CoC_5H_{26}N_6O_2Cl_3$: C, 16.33; H, 7.14; N, 22.86%.

**$[Co(NH_3)_5(L\text{-}leuH)]Cl_3$ and $[Co(NH_3)_5(L\text{-}thrH)]Cl_3$.**—These complexes were prepared by the method described above for the L-valine complex.

Found: C, 18.29; H, 7.23; N, 22.21. Calcd. for $CoC_6H_{28}N_6O_2Cl_3$: C, 18.88; H, 7.41; N, 22.02%.

Found: C, 13.45; H, 6.68; N, 22.67. Calcd. for $CoC_4H_{24}N_6O_3Cl_3$: C, 13.00; H, 6.56; N, 22.74%.

**$[Co(NH_3)_5(L\text{-}serH)]Cl_3$.**—The crude complex was obtained by the same way as was used for the L-valine complex; it was recrystallized from a small amount of water by adding methanol.

Found: C, 9.98; H, 6.25; N, 23.56. Calcd. for $CoC_3H_{22}N_6O_3Cl_3$: C, 10.13; H, 6.25; N, 23.64%.

**$[Co(NH_3)_5(L\text{-}prolH)]I_3\cdot 3H_2O$.**—This was isolated by adding potassium iodide to a reaction mixture prepared by the method mentioned above.

Found: C, 9.00; H, 4.56; N, 11.88; $H_2O$, 8.04. Calcd. for $CoC_5H_{24}N_6O_2I_3\cdot 3H_2O$: C, 8.65; H, 4.37; N, 12.11; $H_2O$, 7.79%.

**$[Co(L\text{-}val)(NH_3)_4]SO_4\cdot H_2O$.**—To an aqueous solution containing 5 g. of $[Co(OH_2)(NH_3)_5](ClO_4)_3$ and 1.5 g. of L-valine in 50 ml. of warm water, about 0.2 g. of activated charcoal was added. The mixture was evaporated on a water bath at 80°C to a volume of about 12 ml. After the resultant solution had been cooled to room temperature, a solution of 2.5 g. of potassium sulfate in 10 ml. of water was added to it. The solution was filtered, and then about 50 ml. of methanol was added, drop by drop, to the filtrate. The crude compound formed was collected, and washed with methanol and then with ether. The pinkish-orange crystals were separated into flakes by adding a small amount of methanol to an aqueous solution of the product.

Found: C, 16.81; H, 6.63; N, 19.20; $H_2O$, 4.93. Calcd. for $CoC_5H_{22}N_5O_6S\cdot H_2O$: C, 16.81; H, 6.78; N, 19.60; $H_2O$, 5.04%.

**$[Co(L\text{-}ser)(NH_3)_4]SO_4$, $[Co(L\text{-}leu)(NH_3)_4]SO_4$ and $[Co(L\text{-}prol)(NH_3)_4]SO_4\cdot 3H_2O$.**—These complexes were

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11) M. Kobayashi, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **64**, 648 (1934).

12) J.-P. Mathieu, *Bull. soc. chim.*, **(5)3**, 476 (1936); ibid., **(5)6**, 873 (1937); *J. chim. phys.*, **33**, 78 (1936).

13) J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **33**, 847 (1960).

14) J. G. Brushmiller, E. L. Amma and B. E. Douglas, *J. Am. Chem. Soc.*, **84**, 3227 (1962).

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

16) Y. Shimura, This Bulletin, **31**, 173 (1958).

17) M. Linhard and G. Stirn, *Z. anorg. Chem.*, **268**, 105 (1952).

obtained in orange crystals by methods similar to that used for the L-valine complex above.

Found: C, 11.21; H, 5.66; N, 21.29. Calcd. for $CoC_3H_{18}N_5O_7S$: C, 11.00; H, 5.56; N, 21.40%.

Found: C, 20.37; H, 6.75; N, 19.58. Calcd. for $CoC_6H_{24}N_5O_6S$: C, 20.39; H, 6.86; N, 19.82%.

Found: C, 15.38; H, 6.89; N, 17.46; $H_2O$: 13.20. Calcd. for $CoC_5H_{20}N_5O_6S{\cdot}3H_2O$: C, 15.34; H, 6.71; N, 17.90; $H_2O$, 13.81%.

**[Co(L-isoleu)$(NH_3)_4$]$SO_4{\cdot}H_2O$, [Co(L-thr)$(NH_3)_4$]$SO_4$ and [Co(L-phala)$(NH_3)_4$]$SO_4{\cdot}H_2O$.**—These complexes were separated by recrystallizing from warm water the crude products which were obtained by procedures similar to that used for the L-valine complex. These complexes were sparingly soluble in water.

Found: C, 18.98; H, 7.07; N, 19.02; $H_2O$, 4.40. Calcd. for $CoC_6H_{24}N_5O_6S{\cdot}H_2O$: C, 19.04; H, 7.07; N, 18.86; $H_2O$, 4.85%.

Found: C, 14.10; H, 5.99; N, 20.56. Calcd. for $CoC_4H_{20}N_5O_7S$: C, 14.08; H, 5.92; N, 20.53%.

Found: C, 26.69; H, 5.99; N, 17.57; $H_2O$, 4.42. Calcd. for $CoC_9H_{22}N_5O_6S{\cdot}H_2O$: C, 26.86; H, 5.98; N, 17.28; $H_2O$, 4.45%.

***trans*-[Co $en_2$(L-alaH)$_2$]$Cl_3$.**—To an aqueous solution containing 5 g. of $[Co(OH_2)_2en_2](ClO_4)_3$[17] in 50 ml. of water, 2.2 g. of L-alanine was added. The mixture was then evaporated almost to dryness on a water bath at about 80°C. After cooling, the crude product obtained was dissolved in 80 ml. of water. To the solution was added 3.5 g. of potassium chloride, and then 10 ml. of methanol. The potassium perchlorate which was deposited was removed from the violetish-red solution by filtration. A few drops of concentrated hydrochloric acid and a small amount of ethanol were added to the filtrate, and the solution was kept in a refrigerator for several hours. The violetish-red crystals obtained were then washed with a water-ethanol mixture (1 : 1), with ethanol, and then with ether. This complex was recrystallized from water by adding a small amount of ethanol.

Found: C, 25.92; H, 6.66; 18.33. Calcd. for $CoC_{10}H_{30}N_6O_4Cl_3$: C, 25.90; H, 6.53; N, 18.13%.

***trans*-[Co $en_2$(L-serH)$_2$]$Cl_3$, *trans*-[Co $en_2$(L-thrH)$_2$]$Cl_3{\cdot}2H_2O$, and *trans*-[Co $en_2$(L-prolH)$_2$]$Br_3$.**—These complexes were prepared by procedures similar to that described above for the L-alanine complex.

Found: C, 24.39; H, 6.22; N, 17.40. Calcd. for $CoC_{10}H_{30}N_6O_6Cl_3$: C, 24.25; H, 6.11; N, 16.96%.

Found: C, 25.98; H, 7.00; N, 15.04; $H_2O$, 6.19. Calcd. for $CoC_{12}H_{34}N_6O_6Cl_3{\cdot}2H_2O$: C, 25.73; H, 6.86; N, 15.01; $H_2O$, 6.43%.

Found: C, 25.96; H, 5.37; N, 13.11. Calcd. for $CoC_{14}H_{34}N_6O_4Br_3$: C, 26.30; H, 5.37; N, 13.15%.

***trans*-[Co $en_2$(L-leuH)$_2$]$Br_3{\cdot}2.5H_2O$.** — The violet needle crystals were separated by adding a large amount of acetone to a solution which was obtained by a method similar to that used for the L-alanine complex.

Found: C, 26.92; H, 6.54; N, 11.35; $H_2O$, 5.99. Calcd. for $CoC_{16}H_{44}N_6O_4Br_3{\cdot}2.5H_2O$: C, 26.38; H, 6.51; N, 11.54; $H_2O$, 6.19%.

**Measurements.**—The visible and ultraviolet absorption spectra were measured by using a Beckman DU spectrophotometer. The CD curves were obtained by a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co., and by a Shimadzu QR-50 spectrophotometer with a CD attachment, while the RD curves were recorded with an ORD/UV-5 spectrophotometer. The concentrations of complexes were 1/20 or 1/30 mole/l. for $[Co(NH_3)_5(\text{L-amH})]X_3$, 1/30 mole/l. for $[Co(\text{L-am})(NH_3)_4]X_2$, and 1/20 or 1/30 mole/l. for *trans*-$[Co\ en_2(\text{L-amH})_2]X_3$. All the measurements were made in aqueous solutions and at room temperature.

## Results and Discussion

**Circular Dichroism.**—The CD and absorption data of $[Co(NH_3)_5(\text{L-amH})]^{3+}$ ions are summarized in Table I, while representative curves are shown, with their RD curves, in Fig. 1. The absorption curve is one typical of a $[Co\ N_5O]$-type complex; this indicates that the L-amino acid is coordinated to the cobalt(III) ion as a unidentate ligand.

Recently, Larsen and Olsen[18] have reported on the $[Co(NH_3)_5(OCOR^*)]^{2+}$ and *trans*-$[Co(NH_3)_4(OCOR^*)_2]^+$ of an optically-active carboxylic acid anion, $OCOR^{*-}$. According to their CD measurements, no CD band was found in the region of the first absorption band. All of the present complexes with L-amino acid as a unidentate ligand, however, exhibit CD bands in the corresponding region. These facts suggest that the

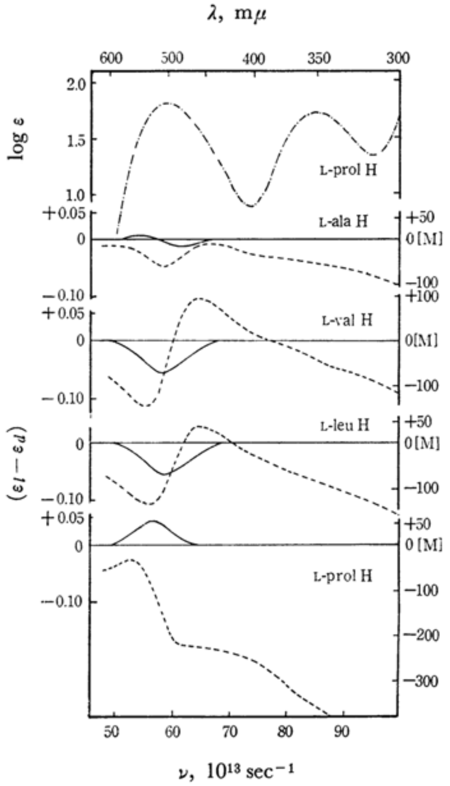

Fig. 1. Absorption (—·—), CD (——) and RD (- - -) curves of $[Co(NH_3)_5(\text{L-amH})]^{3+}$ ions.

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18) E. Larsen and I. Olsen, *Acta Chem. Scand.*, **18**, 1025 (1964).

TABLE I. THE CD AND ABSORPTION DATA OF $[Co(NH_3)_5(L\text{-amH})]^{3+}$, $[Co(L\text{-am})(NH_3)_4]^{2+}$ AND *trans*-$[Co\,en_2(L\text{-amH})_2]^{3+}$ IONS IN AQUEOUS SOLUTIONS

| Complex ion | I Band | | | | II Band | | | |
|---|---|---|---|---|---|---|---|---|
| | $\lambda_{ext}^{CD}$ mμ | $(\varepsilon_l-\varepsilon_d)$ | $\lambda_{max}^{AB}$ mμ | $(\log\varepsilon)$ | $\lambda_{ext}^{CD}$ mμ | $(\varepsilon_l-\varepsilon_d)$ | $\lambda_{max}^{AB}$ mμ | $(\log\varepsilon)$ |
| $[Co(NH_3)_5(L\text{-alaH})]^{3+}$ | 543 | $(+0.00_5)$ | 500 | (1.83) | — | — | 350 | (1.73) |
| | 484 | $(-0.01_5)$ | | | | | | |
| $[Co(NH_3)_5(L\text{-serH})]^{3+}$ | 505 | $(-0.05_5)$ | 500 | (1.83) | — | — | 350 | (1.73) |
| $[Co(NH_3)_5(L\text{-valH})]^{3+}$ | 505 | (−0.05) | 500 | (1.81) | — | — | 350 | (1.71) |
| $[Co(NH_3)_5(L\text{-thrH})]^{3+}$ | 508 | (−0.10) | 500 | (1.82) | — | — | 350 | (1.72) |
| $[Co(NH_3)_5(L\text{-leuH})]^{3+}$ | 505 | (−0.05) | 500 | (1.82) | — | — | 350 | (1.73) |
| $[Co(NH_3)_5(L\text{-phalaH})]^{3+}$ | 505 | $(-0.08_5)$ | 500 | (1.82) | — | — | 348 | (1.72) |
| $[Co(NH_3)_5(L\text{-prolH})]^{3+}$ | 525 | (+0.04) | 500 | (1.85) | — | — | 348 | (1.93) |
| $[Co(L\text{-ala})(NH_3)_4]^{2+}$ | 547 | $(-0.02_5)$ | 493 | (1.89) | 351 | (−0.02) | 348 | (1.95) |
| | 512 | (+0.07) | | | | | | |
| | 495 | (−0.22) | | | | | | |
| $[Co(L\text{-leu})(NH_3)_4]^{2+}$ | 544 | (−0.05) | 492 | (1.90) | 350 | (−0.06) | 349 | (1.97) |
| | 505 | (+0.04) | | | | | | |
| | 458 | (−0.30) | | | | | | |
| $[Co(L\text{-phala})(NH_3)_4]^{2+}$ | 546 | (−0.06) | 495 | (1.91) | 353 | (−0.06) | 348 | (1.99) |
| | 508 | (+0.02) | | | | | | |
| | 458 | (−0.34) | | | | | | |
| $[Co(L\text{-prol})(NH_3)_4]^{2+}$ | 556 | (−0.07) | 495 | (1.89) | 342 | (−0.05) | 348 | (2.00) |
| | 508 | (+0.42) | | | | | | |
| | 450 | (−0.21) | | | | | | |
| $[Co(L\text{-val})(NH_3)_4]^{2+}$ | 540 | (−0.16) | 495 | (1.91) | 353 | (−0.07) | 349 | (1.97) |
| | 462 | (−0.34) | | | | | | |
| $[Co(L\text{-isoleu})(NH_3)_4]^{2+}$ | 540 | $(-0.12_5)$ | 493 | (1.90) | 355 | $(-0.06_5)$ | 348 | (1.96) |
| | 460 | (−0.32) | | | | | | |
| $[Co(L\text{-ser})(NH_3)_4]^{2+}$ | 476 | (−0.32) | 492 | (1.88) | 355 | $(-0.02_5)$ | 347 | (1.95) |
| $[Co(L\text{-thr})(NH_3)_4]^{2+}$ | 469 | (−0.30) | 492 | (1.90) | 355 | (−0.04) | 348 | (1.97) |
| *trans*-$[Co\,en_2(L\text{-alaH})_2]^{3+}$ | 550 | (−0.14) | 542 | (1.72) | 346 | $(+0.03_3)$ | 355 | (1.80) |
| | 445 | $(-0.05_2)$ | 446 | (1.46) | | | | |
| *trans*-$[Co\,en_2(L\text{-serH})_2]^{3+}$ | 548 | $(-0.28_6)$ | 542 | (1.72) | 350 | $(+0.03_3)$ | 355 | (1.79) |
| | 445 | $(-0.01_5)$* | 446 | (1.46) | | | | |
| *trans*-$[Co\,en_2(L\text{-leuH})_2]^{3+}$ | 552 | (−0.33) | 542 | (1.74) | 349 | $(+0.05_5)$ | 355 | (1.82) |
| | 445 | $(-0.04_2)$* | 445 | (1.46) | | | | |
| *trans*-$[Co\,en_2(L\text{-thrH})_2]^{3+}$ | 550 | (−0.34) | 544 | (1.74) | 350 | (+0.03) | 355 | (1.81) |
| | 440 | $(+0.01_1)$* | 446 | (1.47) | | | | |
| *trans*-$[Co\,en_2(L\text{-prolH})_2]^{3+}$ | 540 | (−0.03) | 544 | (1.74) | 345 | (+0.02) | 355 | (1.80) |
| | 445 | (−0.04) | 443 | (1.45) | | | | |

* These values were estimated from the curve analysis.

vicinal effect of the asymmetric carbon atom on the cobalt(III) ion may be more effective in the amino acid complexes than in the carboxylic acid complexes. The $[Co(NH_3)_5(L\text{-amH})]^{3+}$ ion belongs approximately to the $C_{4v}$ symmetry, so two absorption components, ${}^1A_1\rightarrow{}^1A_2$ and ${}^1A_1\rightarrow{}^1E_a$, may be expected in the first absorption band region.[19] As may be seen in Fig. 1 and Table I, the L-alanine complex shows two weak CD bands, with signs opposite to each other. It is reasonable to assign these two CD bands to the transitions of ${}^1A_1\rightarrow{}^1A_2$ and ${}^1A_1\rightarrow{}^1E_a$.

The other L-amino acid complexes show only a negative CD band at about 505 mμ. It may be assumed that each single CD peak of these complexes is a residual one resulting from an overlap or a cancellation of the two CD components. On the other hand, a positive CD peak was observed for the L-proline complex at 525 mμ. The difference in sign between the L-proline complex and the other L-amino acid complexes may be explained from the occlusion of the asymmetric carbon atom of L-proline in a sieged pyrrolidine ring.

The CD and absorption data of the complex ions containing L-amino acid as a bidentate ligand are also summarized in Table I. Some CD and RD curves of these complex ions are shown in

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

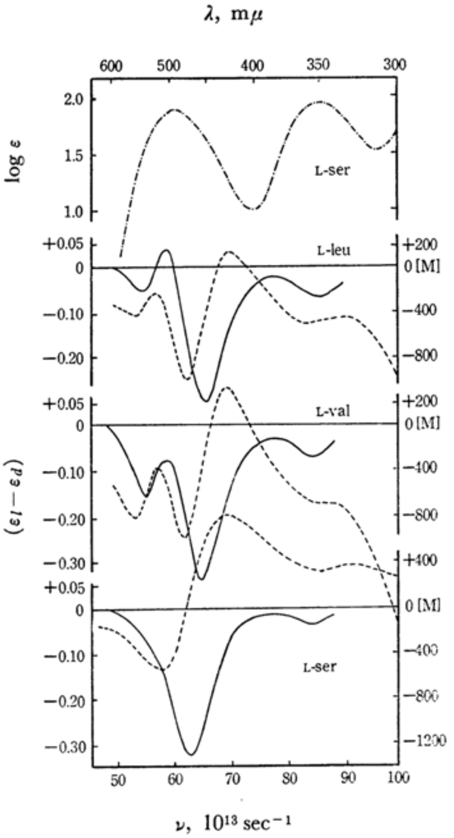


Fig. 2. Absorption (—·—), CD (——) and RD (- - -) curves of $[Co(\text{L-am})(NH_3)_4]^{2+}$ ions.

Fig. 2. The first absorption band does not show any indication of a split on the ordinary absorption curve. Now, the true symmetry of $[Co(\text{L-am})(NH_3)_4]^{2+}$ is $C_1$, so a $T_{1g}$ level under an $O_h$ symmetry should split into three $^1A$ levels, and three $^1A \rightarrow {}^1A$ transitions, which are magnetic-dipole allowed, should be observed in the first absorption band region. As may be seen in Fig. 2, the CD curve of the L-leucinato complex shows three components, at 544, 505 and 458 mμ, in this region. This fact suggests that the first absorption band of a complex of this type can actually split into three components.

Experimentally the L-amino-acidato-tetrammine complexes are divided into the following three groups, according to the behavoir of the CD curves in the region of the first absorption band:

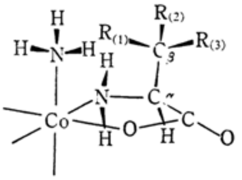
(1) L-am=L-ala, L-leu and L-phala. The complexes of this group exhibit three CD bands in the first absorption band region; their signs are (−), (+) and (−) (from longer to shorter wavelengths).

(2) L-am=L-val and L-isoleu. These complexes exhibit two CD bands, of a negative sign, in the first absorption band region.

(3) L-am=L-ser and L-thr. These complexes exhibit only one CD band, of a negative sign, in the first absorption band region.

The differences among these groups are less explicit in their RD curves than in their CD curves.

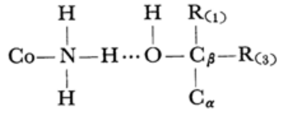
Stereochemically, the differences among these complexes are concentrated in the three substituents, $R_{(1)}$, $R_{(2)}$ and $R_{(3)}$, on the β-carbon atom of the amino acid ligands; in the group 1, $R_{(1)}=R_{(2)}=H$ and $R_{(3)}=H$, $CH(CH_3)_2$ or $C_6H_5$; in group 2, $R_{(1)}=H$, $R_{(2)}=CH_3$ and $R_{(3)}=CH_3$ or $C_2H_5$; in group 3, $R_{(1)}=H$, $R_{(2)}=OH$ and $R_{(3)}=H$ or $CH_3$. By the construction of molecular models, it is shown that some intramolecular interactions exist between a coordinated ammonia molecule and the substituents on the β-carbon atom (Fig. 3).



L-leu: $R_{(1)}=H$, $R_{(2)}=H$, $R_{(3)}=CH(CH_3)_2$
L-val: $R_{(1)}=H$, $R_{(2)}=CH_3$, $R_{(3)}=CH_3$
L-ser: $R_{(1)}=H$, $R_{(2)}=OH$, $R_{(3)}=H$

Fig. 3. The interaction between a coordinated ammonia molecule and substituted groups at the β-carbon atom of the chelated amino acid in $[Co(\text{L-am})(NH_3)_4]^{2+}$ ions.

Of course, internal rotations occur around the $C_\alpha$—$C_\beta$ axis, and it will be pointed out that, for example, the internal rotations are more hindered in the L-valinato complex ($R_{(1)}=H$, $R_{(2)}=R_{(3)}=CH_3$) than in the L-alaninato complex ($R_{(1)}=R_{(2)}=R_{(3)}=H$). In the group 3 complexes, the intramolecular interactions of another kind may also be possible, namely, a hydrogen bond between the coordinated ammonia and the $R_{(2)}=OH$ substituent on the β-carbon atom:



$$\begin{array}{cccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R_{(1)}} & \\ & & | & & | & & | & \\ \mathrm{Co} & - & \mathrm{N} & -\mathrm{H}\cdots & \mathrm{O} & - & \mathrm{C}_\beta & -\mathrm{R_{(3)}} \\ & & | & & & & | & \\ & & \mathrm{H} & & & & \mathrm{C}_\alpha & \end{array}$$

It is difficult, however, at present to relate the behavior of CD curves to the stereochemical differences considered above.

On the whole, the CD curve of $[Co(\text{L-prol})(NH_3)_4]^{2+}$ shows a behavior similar to that of the L-leucinato complex, but the positive CD component at about 508 mμ is more intense than that of the other complexes (Fig. 4 and Table I). As was pointed out in previous papers,[6,7] the asymmetric nitrogen atom of the bidentatically-coordinated L-prolinate has a forced configuration antipodal to that of the similarly-coordinated D-prolinate. In the present complex, one of the reasons why the CD band at 508 mμ predominates is the vicinal effect of such a nitrogen atom of the L-prolinate.

TABLE II. THE ROTATORY PARAMETERS AND ROTATORY

| L-amH | K | CD<br>$\lambda_K^{CD}$ m$\mu$ | $(\varepsilon_l-\varepsilon_d)_{ext}$ | $\Delta_K^{CD}$ (red) m$\mu$ | $\Delta_K^{CD}$ (blue) m$\mu$ | $R_K^{CD}$ $\{\times 10^{42}$(c.g.s.)$\}$ |
|---|---|---|---|---|---|---|
| L-alanine | Ia | 550 | −0.140 | 46.7 | 46.3 | −48.1 |
| | Ib | 445 | −0.052 | 45.0 | 46.0 | −21.6 |
| | II | 346 | +0.033 | 31.8 | 30.2 | +12.0 |
| L-serine | Ia | 548 | −0.286 | 50.7 | 50.5 | −107 |
| | Ib | 445 | −0.015 | 38.3 | 39.5 | −5.32 |
| | II | 350 | +0.033 | 27.3 | 28.0 | +10.6 |
| L-leucine | Ia | 552 | −0.330 | 49.0 | 49.0 | −119 |
| | Ib | 445 | −0.042 | 33.0 | 39.0 | −13.8 |
| | II | 349 | +0.055 | 26.0 | 25.0 | +16.3 |
| L-threonine | Ia | 550 | −0.340 | 49.5 | 51.8 | −127 |
| | Ib | 440 | +0.011 | 30.0 | 29.0 | +2.99 |
| | II | 350 | +0.030 | 30.5 | 29.2 | +10.4 |

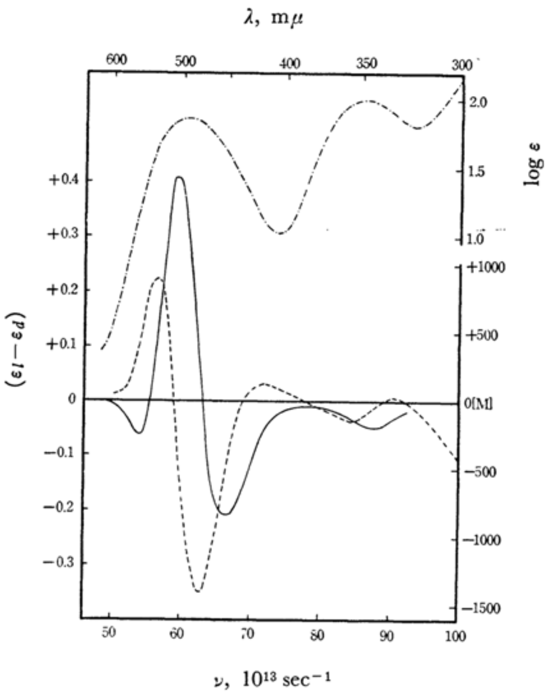


Fig. 4. Absorption (—·—), CD (——) and RD (- - -) curves of $[Co(L\text{-}prol)(NH_3)_4]^{2+}$ ion.

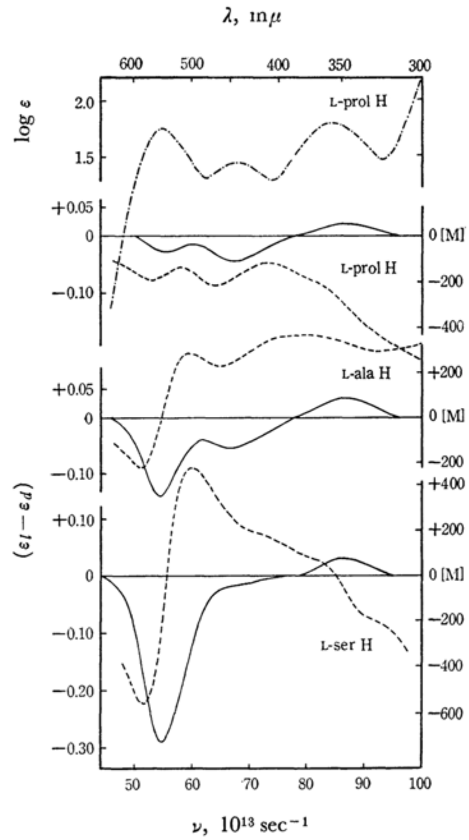


Fig. 5. Absorption (—·—), CD (——) and RD (- - -) curves of *trans*-$[Co\,en_2(L\text{-}amH)_2]^{3+}$ ions.

Single negative CD bands are commonly observed in the second absorption band region of the $[Co(L\text{-}am)(NH_3)_4]^{2+}$ complexes. They are all almost the same in magnitude and are located in the region from 342 to 355 m$\mu$; these CD bands will be useful in the determination of the configurations of amino acids.

The CD and absorption data of *trans*-$[Co\,en_2(L\text{-}amH)_2]^{3+}$ ions are listed in Table I, while their CD and RD curves are shown in Figs. 5 and 6. Their absorption spectra coincide well with those of *trans*-$[Co(OCOR)_2en_2]^+$ and of *trans*-$[Co(OCOR)_2(NH_3)_4]^+$.[20] It is well known that the first absorption band of the *trans*-$[Co\,N_4O_2]$-type complex with the $D_{4h}$ symmetry splits into two components, Ia ($^1A_{1g}\rightarrow{}^1E_g$) and Ib ($^1A_{1g}\rightarrow{}^1A_{2g}$),[20,21] which are magnetic-dipole allowed.

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20) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

21) K. Kuroda and P. S. Gentile, This Bulletin, **38**, 1368 (1965); ibid., **38**, 2159 (1965).

STRENGTHS FOR THE *trans*-[Co $en_2$(L-amH)$_2$]$^{3+}$ COMPLEX ION

| RD | | | | | | | $[M]=\frac{k}{\lambda^2-\lambda_0^2}$ | |
|---|---|---|---|---|---|---|---|---|
| $\lambda_K^{RD}$ mμ | $[M]_{ext}$ (red) | $[M]_{ext}$ (blue) | $\Delta_K^{RD}$ (red) mμ | $\Delta_K^{RD}$ (blue) mμ | $R_K^{RD}$ $\{\times 10^{42}$(c.g.s.)$\}$ | $R_K^{RD}/R_K^{CD}$ | $\lambda_0(\mu)$ | $k$ |
| 547 | −245 | +280 | 40.0 | 48.0 | −46.1 | 0.96 | 0.216 | +16.2 |
| 440 | −85 | +95 | 42.0 | 39.0 | −18.1 | 0.84 | | |
| 341 | +61 | −61 | 29.0 | 29.0 | +11.3 | 0.94 | | |
| 543 | −530 | +555 | 43.0 | 47.0 | −98.2 | 0.92 | 0.265 | −9.1 |
| 442 | −34 | +32 | 34.5 | 32.0 | −5.42 | 1.02 | | |
| 346 | +56 | −56 | 30.0 | 30.0 | +10.7 | 1.00 | | |
| 550 | −615 | +635 | 45.0 | 46.2 | −113 | 0.95 | 0.246 | +7.5 |
| 443 | −89 | −76 | 32.8 | 33.3 | −13.4 | 0.97 | | |
| 351 | +93 | +91 | 24.2 | 25.0 | +14.1 | 0.87 | | |
| 551 | −609 | +650 | 45.0 | 49.0 | −117 | 0.92 | 0.245 | −29.0 |
| 448 | +22 | −20 | 30.0 | 26.0 | +2.87 | 0.96 | | |
| 353 | +66 | −64 | 25.5 | 22.0 | +9.55 | 0.92 | | |

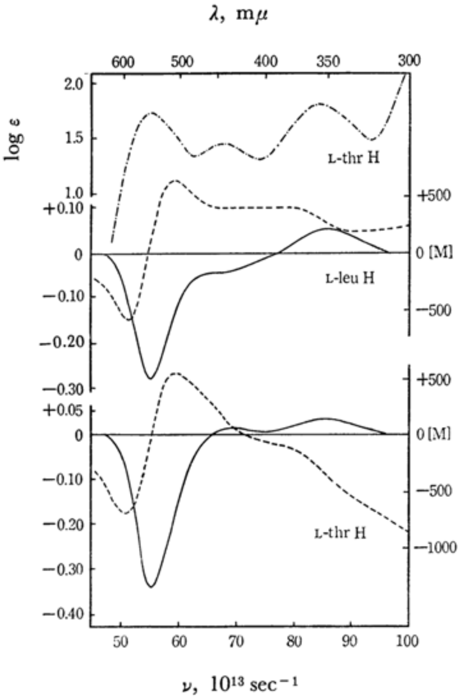

Fig. 6. Absorption (—·—) CD (——) and RD (- - -) curves of *trans*-[Co $en_2$(L-amH)$_2$]$^{3+}$ ions.

The absorption and the CD spectra of *trans*-[Co-$en_2$(L-amH)$_2$]$^{3+}$ exhibit the two first band components; their extremum positions are consistent with each other (Table I).

In the region of the second absorption band, the CD bands of the *trans*-[Co $en_2$(L-amH)$_2$]$^{3+}$-type complexes are situated in a narrow range from 350 to 345 mμ. It is interesting that all of these CD bands have a positive sign, in contrast to those of the [Co(L-am)$(NH_3)_4$]$^{2+}$-complex ions.

**Rotatory Strength.**—In general, it is quite difficult to analyze the observed CD and RD curves into individual component curves, since the first or the second absorption bands are contributed by two or three absorption components which are located very close to each other. When the absorption band splits largely, however, the analysis can be made easily and precisely. In the case of the first absorption band of *trans*-[Co $en_2$(L-amH)$_2$]$^{3+}$, this condition is quite well satisfied, as may be seen in Figs. 5 and 6. The rotatory parameters and rotatory strengths of the individual absorption components were calculated by curve analyses from the observed CD and RD curves of *trans*-[Co $en_2$(L-amH)$_2$]$^{3+}$; the results are summarized in Table II.

The RD curves were analyzed using Moscowitz's Eq. 1:[22]

$$[M_K(\lambda)] = \frac{2[\theta^\circ{}_K]}{\sqrt{\pi}}\left[\exp\left(-\frac{\lambda-\lambda_K^{CD}}{\Delta_K^{CD}}\right)^2 \times \int_0^{\lambda-\lambda_K^{CD}/\Delta_K^{CD}} e^{x^2}dx - \frac{\Delta_K^{CD}}{2(\lambda+\lambda_K^{CD})}\right] \tag{1}$$

where $[\theta^\circ{}_K] \simeq 3300(\varepsilon_l-\varepsilon_d)_{ext}$ is the extremum value of the CD band for the Kth transition, $\lambda_K^{CD}$ is the wavelength of the CD band extremum, and $\Delta_K^{CD}$ is the $1/e$-halfwidth of the CD band.

The curve analyses were made by the following steps. In the first, the CD bands which were assumed to be Gaussian on the wavelength scale of the abscissa were separated from the observed CD curve by using the equation:

$$(\varepsilon_l-\varepsilon_d) = (\varepsilon_l-\varepsilon_d)_{ext}\exp\{-(\lambda-\lambda_K^{CD})^2/(\Delta_K^{CD})^2\} \tag{2}$$

Each inversive RD curve was calculated by substituting the parameters estimated from the Gaussian CD band into Eq. 1, and then the resultant individual RD curves were subtracted from the observed RD curve. From the residual curve, the constants in Drude's equation ($\lambda_0$ and $k$) were

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[22] A. Moscowitz, "Optical Rotatory Dispersion" (C. Djerassi, ed.), McGraw-Hill, New York (1960), p. 150.

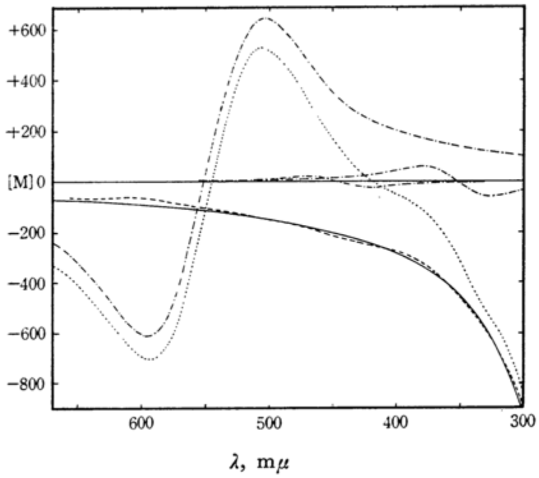

Fig. 7. The analyses of RD curves of *trans*-[Co en$_2$(L-thrH)$_2$]$^{3+}$ ion; (……) observed RD curve, (—·—) individual RD curves of each absorption components, (- - -) observed curve minus the sum of individual RD curves and (——) Drude's curve.

estimated by the method of Lowry[23] (Table II).

In the second step, independent of the CD data mentioned above, the individual RD curve of each absorption component was again determined by subtracting Drude's curve from the observed RD curve, and by analyzing the residual curve into several individual RD curves. These treatments were made separately both on the longer and on the shorter wavelength sides of the inversive center, $\lambda_K^{RD}$. The individual RD components obtained for *trans*-[Co en$_2$(L-thrH)$_2$]$^{3+}$ are shown in Fig. 7 as an example.

It is possible to estimate the rotatory strengths from the data of the CD bands in the first step, and also from the RD data in the second step.

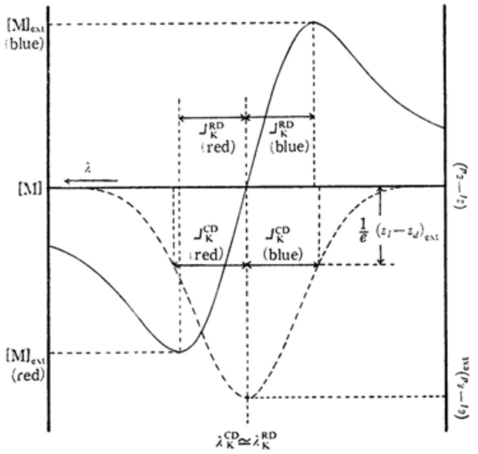

Fig. 8. Parameters for the isolated CD and RD curves.

The rotatory strength from the CD data, $R_K^{CD}$, is given by:

$$R_K^{CD}\simeq 2.03\times 10^{-39}(\varepsilon_l-\varepsilon_d)_{ext}\{\Delta_K^{CD}(\mathrm{red})+\Delta_K^{CD}(\mathrm{blue})\}/(\lambda_K^{CD}) \qquad (3)$$

while the rotatory strength from the RD data, $R_K^{RD}$, is given by:

$$R_K^{RD}\simeq 5.46\times 10^{-43}\{[\mathrm{M}]_{ext}(\mathrm{red})-[\mathrm{M}]_{ext}(\mathrm{blue})\}\times\{\Delta_K^{RD}(\mathrm{red})+\Delta_K^{RD}(\mathrm{blue})\}/(\lambda_K^{RD}) \qquad (4)$$

The parameters which appear in Eqs. 3 and 4 are defined as in Fig. 8, and a relation, $\Delta_K^{RD}\simeq 0.9233\times\Delta_K^{CD}$, exists[24] for the ideal case in which Moscowitz's Eq. 1 holds perfectly.

As may be seen in Table II, the experimental values of $R_K^{CD}$ are approximately equal to those of $R_K^{RD}$; furthermore, the positions of $\lambda_K^{RD}$ coincide well with those of $\lambda_K^{CD}$ within the range of ±5 mμ. These facts prove the adequacy of the equations used and of the curve analyses.

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[23] T. M. Lowry, "Optical Rotatory Power," Longmans, Green and Co., London (1935), p. 419.

[24] F. Woldbye, *Tech. Inorg. Chem.*, **4**, 249 (1965).