Studies on the Cobalt(III) Complexes Containing Only One Chelate Ring. III[1]. Rotatory Dispersion of Tetrammine-l-leucinato-cobalt(III) Perchlorate, $[Co(NH_3)_4(l\text{-}leuc)](ClO_4)_2$[2]

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It is well known that optically active complexes of cobalt(III) or chromium(III) exhibit very marked anomalous rotatory dispersion in the vicinity of their first absorption bands. In some cases, the curve of the anomalous rotatory dispersion is typical and has a point-symmetrical shape. In the present paper, such a point-symmetrical dispersion will be named as "inversive dispersion". In other cases, the rotatory dispersion is intricate and "anomalous" in the literal sense of the word. This "anomalous" rotatory dispersion, however, may be analyzed into two or more typical inversive dispersions as will be shown below.

The above results have been obtained mainly from the studies on the complexes of the $[M(AA)_3]$-[3] or $[M(AA)_2BC]$-type[4], in which the asymmetry is around the central metallic ion. As to the complexes, in which the asymmetric center is at the atom in the co-ordinated ligand, the studies of Lifschitz[5] and Pfeiffer et al.[6] have been reported. These authors stated that no anomalous rotatory dispersion occurred in the complexes having the asymmetric center far apart from the central metallic ion and that the anomalous rotatory dispersion might be produced by the so-called "vicinal effect" provided that the asymmetric center and the central metallic ion were so close to interact each other. The experimental evidences for the above claim, however, have scarcely ever been obtained.

In the present paper the rotatory dispersion of $[Co^{III}(NH_3)_4(l\text{-leuc})]^{2+}$* will be studied in the vicinity of its first and second absorption band. In this uni-chelate complex the asymmetric center is only on a carbon atom of the ligand leucinate ion. As a result of the measurements and the analyses of the rotatory dispersion curves, the existence of the "vicinal effect" between the central cobalt atom and the asymmetric carbon atom will be clarified.

Experimental

Tetrammine-*l*-leucinato-cobalt(III) Perchlorate, $[Co(NH_3)_4(l\text{-leuc})](ClO_4)_2$—This new compound was prepared by a modification of the method which was described in the part I of the present series for the syntheeses of the corresponding glycinato or alaninato complexes[7]. One gram of anhydrous sodium carbonate and 3.5 g. of *l*-leucine were dissolved in 60 ml. of hot water. To this solution were added 7.4 g. of $[Co(NH_3)_4(OH_2)Cl]SO_4$[8], 2 g. of decolorizing charcoal and 5 ml. of aqueous ammonia (30%). The resulting mixture was evaporated on a water bath almost to dryness. The residue was treated with about 50 ml. of warm water and insoluble materials** were filtered off by suction. After cooling, a large amount of 95% ethanol was fractionally added to the filtrate. First, about 2 g. of $[Co(NH_3)_6]SO_4\cdot Cl\cdot 3H_2O$, and then the impure sulfate of the desired complex were precipitated. For purification the impure sulfate was converted into the perchlorate as follows. The impure sulfate was dissolved in a small quantity of water and was treated with an equivalent amount of barium chloride solution and the resulting barium sulfate was filtered off. To the filtrate, sodium perchlorate and ethanol were added and the solution was evaporated in vacuo over sulfuric acid. The desired perchlorate was separated as light red crystals. This was recrystallized from water-ethanol mixture by evaporation over sulfuric acid. The yield was very small (not exceed one g.).

Anal. Found: C, 15.90; H, 5.35; Cl, 15.40%. Calcd. for $C_6H_{24}O_{10}N_5Cl_2Co$: C, 15.80; H, 5.30; Cl, 15.55%.

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[1] Part II of This series: Y. Shimura, This Bulletin, **31**, 311 (1958).

[2] Presented at the Symposium on Co-ordination Compounds, Nagoya, November 16, 1957.

[3] J.-P. Mathieu, *J. chim. phys.*, **33**, 78 (1936).

[4] J.-P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936).

[5] I. Lifschitz, *Z. physik. Chem.*, **105**, 27 (1923); **114**, 485 (1925).

[6] P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzner and H. Thielert, *J. prakt. Chem.*, **150**, 261 (1938).

* The following abbreviations are used: gly, $NH_2CH_2CO_2^-$; alan, $NH_2CH(CH_3)CO_2^-$; leuc, $NH_2CH(CO_2^-)CH_2CH(CH_3)_2$.

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

[8] S. M. Jörgensen, *J. prakt. Chem.*, **42**, 211 (1890).

** This is a mixture of decolorizing charcoal and two geometrical isomers (pink and reddish violet) of $[Co^{III}(l\text{-leuc})_3]$.

TABLE

SUMMARY OF

Complexes	Inversive rotatory dispersion		
	Center of inversion[a)]	Sign of Cotton effect	Degree of rotation[b)]
$[Co(NH_3)_4(l\text{-leuc})]^{2+}$	Ia: 59.6	+	320°
	Ib: 65.6	−	650°
d-$[Co\ en_2\ (NH_3)Cl]^{2+}$	Ia: 54.6	+	580°
	Ib: 63.4	+	390°
d-$[Co\ en_2\ (l\text{-leuc})]^{2+}$	59.5	+	ca. 5000°
d-$[Co\ en_3]^{3+}$	61.2	+	ca. 4000°

a) These values are given by the unit of 10^{13}/sec.

d-$[Co\ en_2\ (l\text{-leuc})]Cl_2$—This was prepared and resolved by the method of Lifschitz[9)] with reference to Mathieu's report[10)].

d-$[Co\ en_2\ (NH_3)Cl]Br_2$—This was prepared and resolved by Werner and King's method[11)].

d-$[Co\ en_3]Br_3\cdot 2H_2O$—For the resolution Werner's method[12,13)] was followed.

Measurements of Rotatory Dispersion and Absorption Spectra.—The rotatory dispersion measurements were made in aqueous solutions by a Rudolph photoelectric spectropolarimeter, Model 200S—80. The concentration of the solution was 1.0×10^{-3} gram complex-ion per liter. The absorption measurements were made by a Beckman DU spectrophotometer. All the measurements were made at room temperature.

Results and Discussion

The rotatory dispersion curve and the absorption curve of $[Co(NH_3)_4(l\text{-leuc})](ClO_4)_2$ are shown in Fig. 1. For comparison, similar measurements were also made for d-$[Co\ en_2\ (l\text{-leuc})]Cl_2$, d-$[Co\ en_2\ (NH_3)Cl]Br_2$ and d-$[Co\ en_3]Br_3\cdot 2H_2O$ (Figs. 2—4). The numerical data for these measurements are summarized in Table I.

From the Figs. 1—4, it is seen that all the four complexes studied exhibit the remarkable change of rotation in the region of the first absorption bands. On the other hand, there have been found few indications of such anomalous rotatory dispersion in the region of their second absorption bands. This fact coincides with the observations reported heretofore by Mathieu[3)], Kuhn and Bein[15)], Tsuchida[16)] and Kobayashi[17)] for many cobalt(III) or chromium(III) complexes.

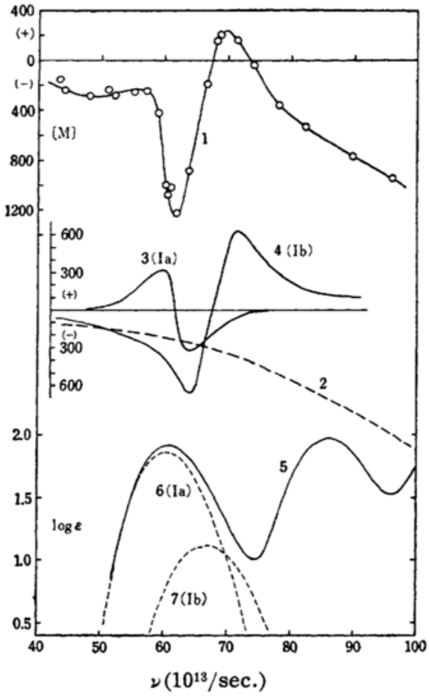

Fig. 1. Rotatory dispersion and absorption of $[Co(NH_3)_4(l\text{-leuc})](ClO_4)_2$: 1, rotatory dispersion curve; 2~4, curve analyses of the rotatory dispersion curve; 5, absorption curve; 6~7, curve analyses of the first absorption band.

The shape of the rotatory dispersion curve of $[Co(NH_3)_4(l\text{-leuc})]^{2+}$ in its first absorption band suggests that an overlapping of two inversive dispersions occurred. As a result of a tentative curve analysis, it was shown that the experimental dispersion curve (1) was well reproduced by

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9) I. Lifschitz, *Rec. trav. chim.*, **58**, 785 (1939).

10) J.-P. Mathieu, *Bull. soc. chim. France*, [5] **6**, 873 (1939).

11) A. Werner and V. L. King, *Ber.*, **44**, 1887 (1911).

12) A. Werner, *Ber.*, **45**, 121 (1912).

13) D. H. Busch, *J. Am. Chem. Soc.*, **77**, 2747 (1955).

14) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

15) W. Kuhn and K. Bein, *Z. anorg. Chem.*, **216**, 321 (1934).

16) R. Tsuchida, *J. Chem. Soc. Japan* (*Nippon Kagaku Zassi*), **58**, 621 (1937).

17) M. Kobayashi, ibid., **64**, 648 (1934).

18) J.-P. Mathieu, *Bull. soc. chim. France*, [5] **5**, 105 (1938).

I

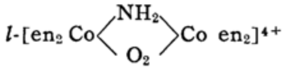
MEASUREMENTS

First absorption band				Second absorption band			
ν_{max}[a]	$\log \varepsilon_{max}$	Half-value width[a]	Inclination parameter[14, a]	ν_{max}[a]	$\log \varepsilon_{max}$	Half-value width[a]	Inclination parameter[14, a]
60.8	1.90	11.3	0.55	86.1	1.97	12.5	0.35
Ia: 57.0	1.85	10.2	0.5	82.7	1.90	12.4	0.3
Ib: 65.6	1.38	11.8	0.5				
61.5	2.02	11.3	0.65	86.1	2.06	12.4	0.5
63.9	1.94	10.4	0.55	88.4	1.90	12.0	0.4

b) The difference between the maximum and the minimum value of the partial inversive rotatory dispersion was halved.

TABLE II

ABSORPTION MAXIMUM AND THE CENTER OF INVERSIVE ROTATORY DISPERSION

Complex ion	ν_{rot}	ν_{abs}	$\nu_{abs}-\nu_{rot}$	Ref.
$d\text{-}[\mathrm{Co\,en_3}]^{3+}$	61.2	63.9	+2.7	*
$l\text{-}[\mathrm{Co\,ox_3^{**}}]^{3-}$	48.8	50.2	+1.4	15
$d\text{-}[\mathrm{Co\,en_2\,ox}]^{+}$	57.7	60.0	+2.3	4
$d\text{-}[\mathrm{Co\,en_2\,CO_3}]^{+}$	57.0	59.0	+2.0	4
$d\text{-}[\mathrm{Co\,en_2\,(NH_3)_2}^{(1)}_{(2)}]^{3+}$	60.4	64.4	+4.0	4
$l\text{-}[\mathrm{Co\,en_2\,gly}]^{2+}$	58.8	61.4	+2.6	10
$d\text{-}[\mathrm{Co\,en_2}\,(d\text{-alan})]^{2+}$	59.2	61.9	+2.7	10
$l\text{-}[\mathrm{Co\,en_2}\,(l\text{-phenylalan})]^{2+}$	59.0	61.7	+2.7	10
$d\text{-}[\mathrm{Co\,en_2}\,(d\text{-val}^{***})]^{2+}$	59.3	61.8	+2.5	10
$d\text{-}[\mathrm{Co\,en_2}\,(l\text{-leuc})]^{2+}$	59.5	61.5	+2.0	*
$d\text{-}[\mathrm{Co\,en_2\,(NO_2)(OH_2)}^{(1)}_{(2)}]^{2+}$	59.0	65.1	+6.1	4
 $l\text{-}[\mathrm{en_2\,Co}\langle{}^{\mathrm{NH_2}}_{\mathrm{O_2}}\rangle\mathrm{Co\,en_2}]^{4+}$	60.9	64.3	+3.4	18
$d\text{-}[\mathrm{Co\,en_2\,(NH_3)Cl}^{(1)}_{(2)}]^{2+}$	Ia: 54.6 Ib: 63.4	57.0 65.6	+2.4 +2.2	* *
$d\text{-}[\mathrm{Cr\,en_3}]^{3+}$	64.9	65.5	+0.6	3
$d\text{-}[\mathrm{Cr\,ox_3}]^{3-}$	54.3	52.6	−1.7	3
$d\text{-}[\mathrm{Cr\,en_2\,ox}]^{+}$	62.5	63.0	+0.5	4

ν_{rot}: Center of inversive rotatory dispersion (10^{13}/sec.).
ν_{abs}: Absorption maximum (10^{13}/sec.).
* New measurement by the present author. ** ox stands for oxalate ion.
*** val stands for valinate ion.

the overlap of the curves (2), (3) and (4). Thus it was concluded that the first absorption band of this complex showed two inversive dispersions, the one of which had positive Cotton effect and the other negative Cotton effect.

Since the complex ion, $[\mathrm{Co(NH_3)_4}\,(l\text{-leuc})]^{2+}$, belongs to the type of $[\mathrm{CoN_5O}]$, it is expected that its first absorption band splits into two components, Ia and Ib. Therefore, the two inversive dispersions above obtained probably correspond to the two components of the first absorption band.

A survey of the data for the cobalt(III) or chromium(III) complexes, which are found in literature as well as in the present author's measurements, revealed that the center of inversion of the rotatory dispersion was almost always in the longer wave-length region as compared with the position of the absorption maximum (Table II). Taking this fact into consideration, a tentative curve analysis was made to separate the two components of the first absorption band of $[\mathrm{Co(NH_3)_4}\,(l\text{-leuc})]^{2+}$. In the analyses of the absorption curves, the experimental equation was used, which was recently developed by the present author[14]. The results are shown in Fig. 1. The similar curve analyses of the rotatory dispersion curve and the absorption curve were performed for $d\text{-}[\mathrm{Co\,en_2\,(NH_3)Cl}^{(1)}_{(2)}]^{2+}$ (Fig. 2). In this case the two inversive dispersions

Ia and Ib have equally the positive sign of the Cotton effect. This coincides very well with the results of direct measurement of the Cotton effect (circular dichroism) by Mathieu⁴⁾.

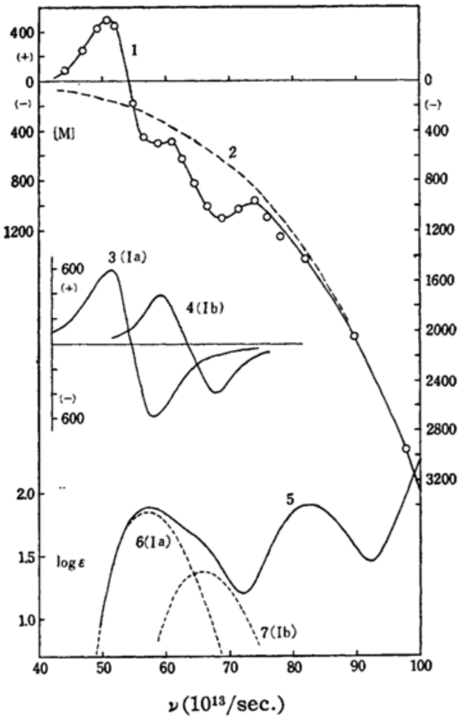
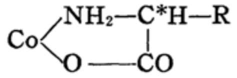


Fig. 2. Rotatory dispersion and absorption of d-[Co en$_2$ (NH$_3$)Cl]Br$_2$: 1, rotatory dispersion curve: 2∼4, curve analyses of the rotatory dispersion curve; 5, absorption curve; 6∼7, curve analyses of the first absorption band.

On the basis of the facts above discussed it is concluded that, so far as the first absorption band is concerned, the so-called "vicinal effect" exists between the cobalt atom and the asymmetric carbon atom C* in the structure of



$$\mathrm{Co}\langle\begin{array}{l}\mathrm{NH_2{-}C^*H{-}R}\\ \quad\ \ |\\ \mathrm{O{-}{-}CO}\end{array}$$

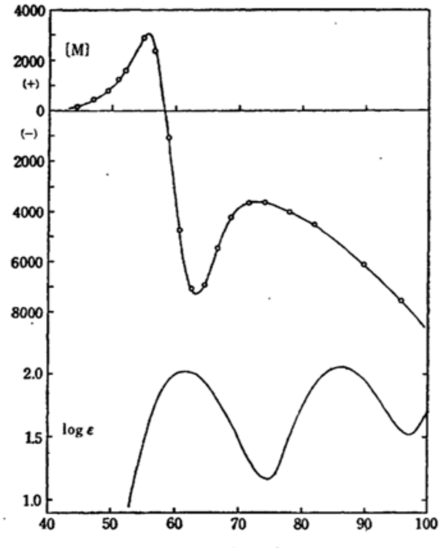


Fig. 3. Rotatory dispersion and absorption of d-[Co en$_2$ (l-leuc)]Cl$_2$.

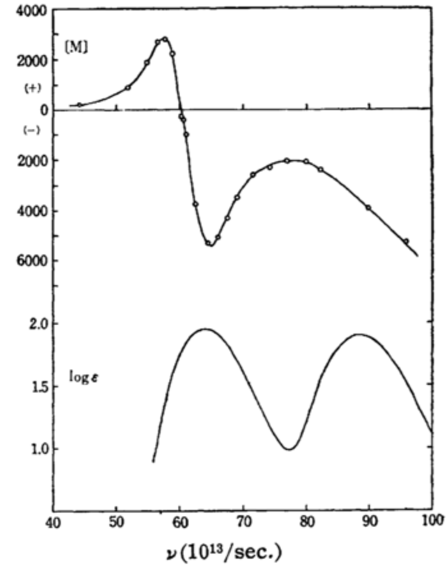


Fig. 4. Rotatory dispersion and absorption of d-[Co en$_3$]Br$_3\cdot$2H$_2$O.

In contrast with [Co(NH$_3$)$_4$ (l-leuc)]$^{2+}$, no evidence was obtained for the overlap of two or more inversive dispersions in d-[Co en$_2$ (l-leuc)]Cl$_2$ (Fig. 3). The rotatory dispersion of the latter compound, as well as that of d-[Co en$_3$]$^{3+}$ (Fig. 4), has a typical shape of a single inversive dispersion. The reason for this difference between the *bis*-ethylenediamine complex and the tetrammine complex is unknown. It should be added, however, that the degree of rotation is extraordinarily greater in the *bis*-ethylenediamine complex than in the tetrammine complex. It is probable that the asymmetry around the central cobalt atom contributes more profoundly to the rotatory power of the region of the first absorption band than the asymmetric carbon atom in the co-ordinated ligand.

Summary

A new complex compound, $[Co^{III}(NH_3)_4(l\text{-leuc})](ClO_4)_2$, has been prepared, in which the asymmetric center is only on a carbon atom of the ligand leucinate ion. From the measurements of the visible and the ultraviolet rotatory dispersion of this compound, it has been concluded that the so-called "vicinal effect" exists between the cobalt atom and the asymmetric carbon atom.

The rotatory dispersion measurements have also been made for d-$[Co\,en_2(l\text{-leuc})]Cl_2$, d-$[Co\,en_2(NH_3)Cl^{\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right\}}]Br_2$ and d-$[Co\,en_3]Br_3 \cdot 2H_2O$. On the basis of these data the relation of the splitting of the first absorption band with the so-called anomalous rotatory dispersion has been discussed. Thus it has been shown that the anomalous rotatory dispersion of $[Co(NH_3)_4(l\text{-leuc})]^{2+}$ or of $[Co\,en_2(NH_3)Cl]^{2+}$ is explicable by assuming the overlap of the two inversive dispersions, Ia and Ib, which correspond to the component bands, Ia and Ib, of the split first absorption band.

In agreement with the observations by several previous authors, it has been shown that all the complexes studied scarecely show the anomalous rotatory dispersion in the vicinity of their second absorption bands.

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