CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA

Circular Dichroism of Coordination Compounds. III. Cobalt(III) Complexes of Optically Active Amino Acids[1]

BY CHONG TAN LIU AND BODIE E. DOUGLAS

Received May 14, 1964

For complexes of optically active amino acids of the type $[Co(en)_2aa]I_2$ (where aa = the anion of D- or L-alanine, D- or L-leucine, and L-phenylalanine) there are contributions to the optical activity (optical rotatory dispersion and circular dichroism) from the configuration of the complex and from the vicinal effect of the optically active ligand. The contributions from the two effects are essentially additive. The study of the CD data for the resolved and racemic complexes containing the optically active ligands along with the corresponding complexes of glycine and picolinic acid and the compound $[Co(NH_3)_4$L-palan$]I_2$ reveals three components within each absorption band. The $(-)_{546}$-$[Co(en)_2aa]I_2$ complexes are assigned the Λ configuration based on the CD data.

Introduction

Most optically active coordination compounds which have been studied are octahedral complexes of the type $[M(AA)_3]^{n+}$ or *cis*-$[M(AA)_2X_2]^{m+}$ where the optical activity arises because of the spiral arrangement of the chelate rings formed by the ligand AA. Pfeiffer[2] demonstrated that transition metals coordinated with optically active ligands exhibit the Cotton effect in the visible region. The optically active ligands caused an induced asymmetry at the site of the metal ion. Shimura[3] showed that for $[Co(NH_3)_4$L-leuc$](ClO_4)_2$ [leuc = $NH_2CH(CO_2^-)C_2H_3(CH_3)_2$] the presence of the optically active ligand caused two Cotton effects in the region of the first (low-frequency) absorption band of Co(III). This complex could not exhibit the Cotton effect in this region except through induced asymmetry. Shimura referred to this as a "vicinal effect."

There are obviously contributions to the optical activity of a complex containing two or more chelated ligands and one or more optically active ligands from the dissymmetric spiral configuration and from the vicinal effect of the optically active ligand. It is difficult to separate these effects using optical rotatory dispersion (ORD) data because of the serious overlap of the individual components.[4] It has been shown[5] that circular dichroism (CD) curves are much more easily resolved and reveal more splitting of bands than can be seen from absorption curves or ORD curves. This paper reports the study of both configurational and vicinal contributions to the CD of some complexes of the type $[Co(en)_2aa]^{2+}$ (aa = amino acid anion). Some compounds of this type were reported by Lifschitz[6] and Meisenheimer.[7] Mathieu[8] reported the absorption spectra, ORD, and CD curves for some of the compounds using L-alanine, L-valine, L-leucine, and L-phenylalanine. His ORD data did not agree well with the later results of Shimura,[3] his CD data were not adequate for a detailed analysis of the curves, and only a narrow wave length range was covered.

Experimental

Reagents.—All optically active amino acids were purchased from Nutritional Biochemical Corp., Cleveland, Ohio. The reported specific rotations at the D-line were: L-alanine, +14.2°; D-alanine, −14.3°; L-leucine, +15.2°; D-leucine, −15.2°; L-phenylalanine, −35.1°; and D-phenylalanine, +35.0° (D and L refer to the absolute configurations). The solvents for the measurements were hydrochloric acid for alanine and leucine and water for phenylalanine.

Measurements.—Absorption spectra were recorded on a Cary Model 14 spectrophotometer. ORD curves were obtained with a Rudolph 80Q6 polarimeter with quartz optics and a photoelectric attachment using a 100-watt zirconium arc lamp in the visible region and a xenon arc lamp below 400 mμ. CD curves were recorded with a Roussel-Jouan Dichrograph. All measurements were made in aqueous solution in an air-conditioned room. The solutions for CD measurements were 0.006–0.02 M for the unresolved complexes and 0.004–0.008 M for the resolved complexes. These same solutions were diluted for both ORD and absorption measurements to 0.002–0.005 and 0.002–0.006 M, respectively. The cells used for the measurements were 5 cm. for ORD, 1 cm. for absorption, and 1 or 2 cm. for CD.

Preparations.—All of the complexes of optically active ligands were prepared using active, rather than racemic, ligands followed by the resolution of the two configurational isomers. In this way all four isomers, in a high state of purity, could be isolated for each amino acid except that the resolution of the configurational isomers of D-phenylalanine was unsuccessful.

$[Co(en_2)_2aa]I_2$.—Meisenheimer's method[7] was modified for the preparation of the complexes of glycine (gly), L- and D-alanine (alan), L- and D-leucine (leuc), and L- and D-phenylalanine (palan). The amino acid was dissolved in warm water containing an equimolar amount of NaOH. Solid *trans*-$[Co(en)_2Cl_2]Cl$ (equimolar amount) was added to the solution at about 40°. The mixture was heated on a steam bath for about 5 min. with stirring. The solution was stored at 3° overnight and then the resulting precipitate ($[Co(aa)_3]$ and other impurities) was removed by filtration. A large excess of NaI was added to the filtrate followed by a large excess (several times the volume of the filtrate) of 95% ethanol with stirring. The precipitate of the unresolved $[Co(en)_2aa]I_2$ was recrystallized by dissolving in the minimum amount of hot water followed by cooling in an ice bath. The unresolved samples used for ORD and CD studies were recrystallized at least three times. The complexes were obtained as orange-red crystals

---

[1] This work was supported by a research grant (AMO2219-06S1) from the Division of General Medical Studies, Public Health Service. Paper II in the series: *Inorg. Chem.*, **3**, 1180 (1964).

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

[3] Y. Shimura, *Bull. Chem. Soc. Japan*, **31**, 315 (1958).

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

[5] B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

[6] I. Lifschitz, *Rec. trav. chim.*, **58**, 785 (1939).

[7] J. Meisenheimer, *Ann.*, **438**, 217 (1924).

[8] J.-P. Mathieu, *Bull. Soc. Chim. France*, **6**, 873 (1939).

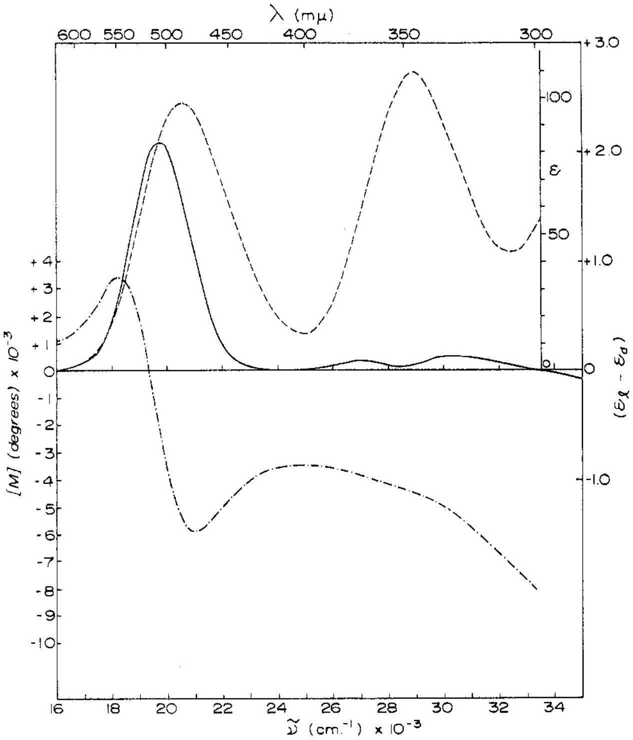

Fig. 1.—Molar absorptivity (---------), ORD (—·—·), and CD (———) for $(+)_{546}$-$[Co(en)_2gly]I_2$.

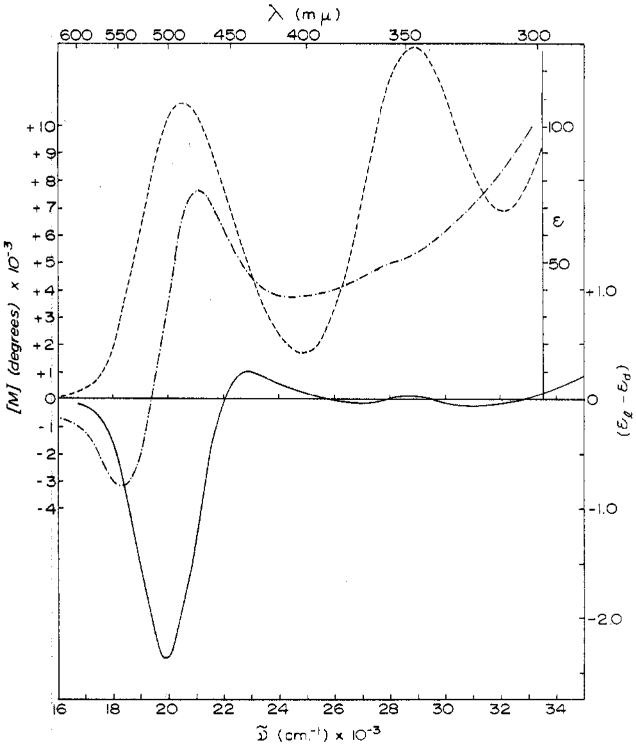

Fig 2.—Molar absorptivity (– – – –), ORD (—·—·), and CD (———) for $(-)_{546}$-$[Co(en)_2\text{D-leuc}]I_2$.

which were dried in a vacuum oven at 55° and 10 mm. pressure for 5 hr. *Anal.* Calcd. for $CoC_{13}H_{26}N_5O_2I_2$, $(+)_{546}$-L-palan complex: C, 26.23; H, 4.38; Co, 9.86; N, 11.72. Found: C, 26.79; H, 4.31; Co, 10.09; N, 11.79. Calcd. for $CoC_{10}H_{28}N_5O_2I_2$, $(+)_{546}$-L-leuc complex: C, 21.33; H, 5.01; Co, 10.48; N, 12.44. Found: C, 21.49; H, 5.50; Co, 10.49; N, 12.44. Calcd. for $CoC_6H_{20}N_5O_2I_2$: $(-)_{546}$-gly complex: C, 14.21; H, 3.98; Co, 11.62; N, 13.82. Found: C, 14.17; H, 3.90; Co, 11.80; N, 14.06.

Racemic-$[Co(en)_2pic](ClO_4)_2$ (pic = picolinate ion).—The same procedure as that for the amino acid complexes was used for this new compound. A solution of the sparingly soluble iodide salt was treated with silver perchlorate to precipitate AgI, followed by crystallization of the perchlorate salt.

Anal. Calcd. for $CoC_{10}H_{20}N_5O_{10}Cl_2$: $(+)_{546}$-pic complex: C, 24.01; H, 4.03; N, 14.01. Found: C, 23.91; H, 3.94; N, 13.88.

$[Co(NH_3)_4palan]I_2$.—Shimura's method for the preparation of $[Co(NH_3)_4\text{L-leuc}](ClO_4)_2$ was used for the preparation of $[Co(NH_3)_4palan]SO_4$ except that an equivalent amount of NaOH was used to neutralize the amino acid instead of using Na_2CO_3. The complex was isolated as the iodide after precipitation of $BaSO_4$ by the addition of BaI_2 to the solution. This improved the yield and gave a compound (orange-red needles) which was easier to crystallize than the perchlorate salt. Samples were dried at 40° for 5 hr. at 15 mm. pressure. *Anal.* Calcd. for $CoC_9H_{22}N_5O_2I_2$ (L-palan complex): C, 19.83; H, 4.07; Co, 10.81; N, 12.85. Found: C, 20.11; H, 4.47; Co, 10.88; N, 13.06. Calcd. for $CoC_9H_{22}N_5O_2I_2\cdot H_2O$ (D-palan complex): C, 19.20; H, 4.30; Co, 10.47; N, 12.44. Found: C, 19.07; H, 4.33; Co, 10.68; N, 12.34.

Resolutions. **$[Co(en)_2gly]I_2$.**—A very slight excess of silver antimonyl *d*-tartrate (2 moles of resolving agent per mole of complex) was added to a solution of the complex as the iodide salt. The AgI was removed by filtration after stirring the mixture on a steam bath for 10 min. away from direct light. The filtrate from the removal of AgI was diluted with water and warmed on a steam bath. Ethanol was added slowly until the first turbidity remained after complete mixing. Just enough water was added to clear the solution. On slow cooling the complex crystallized. After crystallization seemed complete the crystals were removed and recrystallized many times until the optical rotation became constant, $[M]_{546}$ −2230°. The more soluble diastereoisomer was obtained by further addition of ethanol in the same way, followed by repeated recrystallizations, $[M]_{546}$ +4240°.

The diastereoisomers dissolved in water were treated with $AgNO_3$ to precipitate the resolving agent which was removed by filtration, followed by the addition of excess NaI to crystallize the iodide salt. $[M]_{546}$ for the iodides, ±3450°; values previously reported, −3100°[6] and −2750°.[8]

$[Co(en)_2\text{L-alan}]I_2$.—The solution of the diastereoisomer was prepared as above using silver *d*-bromocamphor-π-sulfonate (AgBcs) as the resolving agent. The crystallization of the diastereoisomer was accomplished by adding acetone (it is appreciably soluble in ethanol) to a cold aqueous solution followed by slow warming of the solution since its solubility decreased with increasing temperature, $[M]_{546}$ +5480°.

The resolving agent was removed by adding an excess of NaI in ethanol to a concentrated solution of the diastereoisomer in ethanol to precipitate the complex as the iodide. It was then recrystallized from water. $[M]_{546}$ +3370° for $[Co(en)_2\text{L-alan}]I_2$; reported values, +3000° as the bromide[8] salt and +2400 as the nitrate[6] salt.

The more soluble diastereoisomer could not be crystallized, so it was necessary to obtain this isomer, $(-)_{546}$, using $AgSbO(d\text{-}C_4H_4O_6)$ as for the glycine complex, using methanol instead of ethanol. Here the $(-)_{546}$ isomer formed the less soluble diastereoisomer, $[M]_{546}$ −2660°. $AgSbOC_4H_4O_6$ was precipitated and the complex crystallized as the iodide as before (see glycine complex), $[M]_{546}$ −3700° for the iodide; no value previously reported.

$[Co(en)_2\text{D-alan}]I_2$.—The resolution was accomplished as described for the glycine complex using $AgSbO(d\text{-}C_4H_4O_6)$ and methanol instead of ethanol. $[M]_{546}$ for the less soluble diastereoisomer, +4690°; for the corresponding iodide, +3700°; no value previously reported. $[M]_{546}$ for the more soluble diastereoisomer, −2300°; for the corresponding iodide, −3370°; no value previously reported.

$[Co(en)_2\text{L-leuc}]I_2$.—The resolution was carried out as described

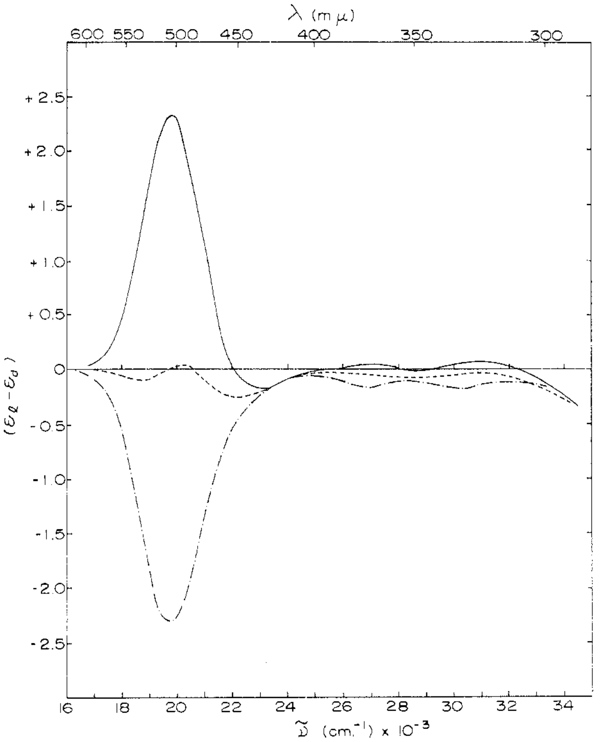

Fig. 3.—CD curves for [Co(en)$_2$L-palan]I$_2$: (+)$_{546}$ (———), (−)$_{546}$ (—·—·), and unresolved (- - - -).

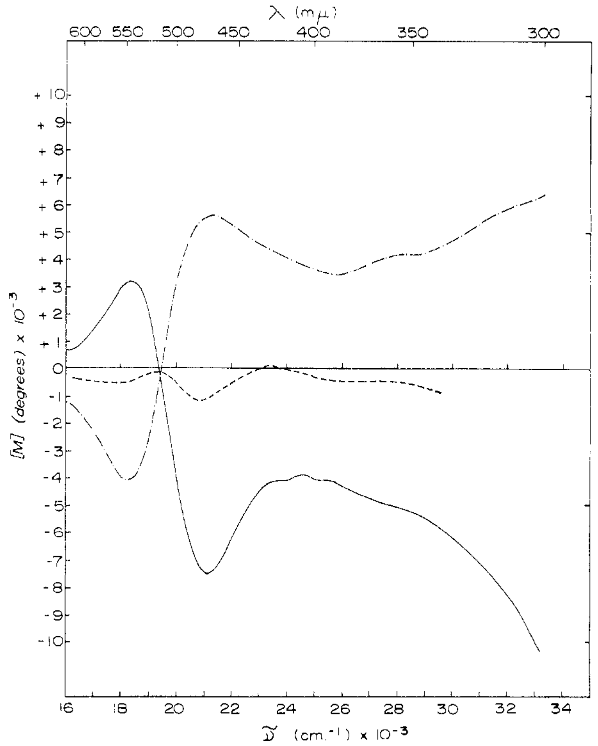

Fig. 4.—ORD curves for [CO(en)$_2$L-palan]I$_2$: (+)$_{546}$ (———) (−)$_{546}$ (—·—·), and unresolved (- - - -).

for the glycine complex except that silver *d*-tartrate was the resolving agent. The diastereoisomer was converted to the iodide as described for the glycine complex. [M]$_{546}$ for the less soluble diastereoisomer, +3100°; for the corresponding iodide, +3200°; values previously reported, +4000° for the bromide,[8] +3150°[6] and +2950°[3] for the chloride. [M]$_{546}$ for the more soluble diastereoisomer, −3660°; for the corresponding iodide, −4390°; previously reported value for the diastereoisomer,[6] −4100°.

[Co(en)$_2$D-leuc]I$_2$.—The diastereoisomer formed, using AgBcs as the resolving agent, was crystallized from water by slow evaporation. The diastereoisomer is appreciably soluble in the alcohols and acetone. The complex was isolated as the iodide as described for the L-alanine complex. [M]$_{546}$ for the less soluble diastereoisomer, −2540°; for the corresponding iodide, −3200°; no value previously reported. [M]$_{546}$ for the more soluble diastereoisomer, +4430°; for the corresponding iodide, +4390°; no value previously reported. The (+)$_{546}$ isomer was also obtained as described previously using AgSbO(d-C$_4$H$_4$O$_6$) as the resolving agent and methanol to crystallize the diastereoisomer. Only the less soluble diastereoisomer was isolated, [M]$_{546}$ +5130°; for the corresponding iodide, [M]$_{546}$ +4390°; the same value was obtained using AgBcs.

[Co(en)$_2$L-palan]I$_2$.—The diastereoisomers were crystallized from water as for the D-leucine complex using AgBcs as the resolving agent. [M]$_{546}$ for the less soluble diastereoisomer, +4110°; for the corresponding iodide, +3220°; previously reported value for the corresponding bromide,[8] −4000°. This resolution was repeated with the same result (opposite sign to Mathieu's value, using the same resolving agent) and the more soluble diastereoisomer was also isolated here, but not by Mathieu. [M]$_{546}$ for the more soluble diastereoisomer, −3720°; for the corresponding iodide, −4100°.

The attempted resolution of [Co(en)$_2$D-palan]$^{2+}$ was unsuccessful even though crystals of the salts containing optically active anions were obtained.

[Co(en)$_2$pic]I$_2$.—The resolution was accomplished by the crystallization of the diastereoisomers from water as described above, using AgBcs as the resolving agent. [M]$_{546}$ for the less soluble diastereoisomer, −2760°; for the corresponding iodide, −3770°; for the other isomer as the iodide, +3770°; this compound has not been reported previously.

All preparations and resolutions were duplicated at least once, The completeness of the resolutions was checked by recrystallization until rotations were constant, by agreement between the rotations of enantiomers, and by comparison to values from the literature, where available. In most cases the literature values were obtained only from published ORD curves for a variety of salts. The optical rotations and heights of the CD peaks were reproduced within ±1.5% for different samples.

Discussion

Comparison of the CD and ORD curves of (+)$_{546}$-[Co(en)$_2$gly]I$_2$ (Fig. 1) shows that the transition associated with the positive CD peak within the low-frequency absorption band dominates the ORD curve. The absorption, CD, and ORD curves of (+)$_{546}$-[Co(en)$_2$D-leuc]I$_2$ are very similar to those of the glycine complex except for small differences in the peak intensities (Table I). The CD and ORD curves of (+)$_{546}$-[Co(en)$_2$D-leuc]I$_2$ are mirror images of the corresponding curves for its enantiomorph, (−)$_{546}$-[Co(en)$_2$L-leuc]I$_2$. The absorption curve of (−)$_{546}$-[Co(en)$_2$D-leuc]I$_2$ (Fig. 2) is identical with that of (+)$_{546}$-[Co(en)$_2$D-leuc]I$_2$ but the ORD curves are not mirror images. The CD curve of the (−)$_{546}$ complex (Fig. 2) shows three weak peaks in the high-frequency region and a second one in the low-frequency region. The patterns for the other complexes of optically active amino acids are similar to those for the corresponding complexes of leucine. Only the phenylalanine complex was selected for the detailed comparisons to be made later while CD and absorption data are given in Table I for all of the complexes.

When the complexes of the type [Co(en)$_2$D- or L-aa]$^{2+}$ are prepared, they are optically active because

TABLE I

ABSORPTION AND CIRCULAR DICHROISM DATA

Complex[a]	Absorption peaks cm.$^{-1}$	ϵ	Circular dichroism peaks cm.$^{-1}$	$(\epsilon_l - \epsilon_d)$
$(-)$-[Co(en)$_2$gly]I$_2$[b]	20,530	98.5	19,800	−2.10
	28,880	109.4	27,000 30,500	−0.088 −0.128
Unresolved [Co(en)$_2$L-alan]I$_2$[b]	20,520	110.2[c]	18,670 20,350 22,470	−0.074 +0.144 −0.303
	28,820	118.0	29,400	−0.070
$(+)$-[Co(en)$_2$L-alan]I$_2$	20,520	110.2	19,900 22,900	+2.38 −0.226
	28,820	118.0	27,250 28,700 31,500	+0.048 (0.000) +0.081
$(-)$-[Co(en)$_2$L-alan]I$_2$[b]	20,520	110.2	19,700	−2.19
	28,820	118.0	27,030 30,200	−0.135 −0.173
Unresolved [Co(en)$_2$L-leuc]I$_2$[b]	20,530	108.8[c]	18,740 20,240 22,420	−0.097 +0.121 −0.288
	28,860	129.2	29,400	−0.089
$(+)$-[Co(en)$_2$L-leuc]I$_2$[b]	20,530	108.8	19,920 22,880	+2.38 −0.242
	28,860	129.2	26,850 28,740 31,150	+0.044 −0.024 +0.064
$(-)$-[Co(en)$_2$L-leuc]I$_2$	20,530	108.8	19,720	−2.24
	28,860	129.2	27,170 30,120	−0.172 −0.177
Unresolved [Co(en)$_2$L-palan]I$_2$[b]	20,500	104.4[c]	18,870 20,360 22,220	−0.093 +0.028 −0.255
	28,820	118.0	29,500	−0.071
$(+)$-[Co(en)$_2$L-palan]-I$_2$	20,500	104.4	19,840 22,960	+2.33 −0.173
	28,820	118.0	27,030 28,820 30,860	+0.030 −0.017 +0.053
$(-)$-[Co(en)$_2$L-palan]-I$_2$	20,500	104.4	19,720	−2.32
	28,820	118.0	27,200 30,120	−0.165 −0.174
$(+)$-[Co(en)$_2$pic]-(ClO$_4$)$_2$[b]	20,870	102.5	19,920	+2.53
	29,850 (sh)	143.3	26,800 28,650 31,000	+0.145 −0.012 +0.164
[Co(NH$_3$)$_4$L-palan]I$_2$	20,280	79.3[c]	18,280 19,600 21,800	−0.026 +0.003 −0.114
	28,940	107.7	29,300	−0.032
[Co(NH$_3$)$_4$D-palan]-I$_2$·H$_2$O	20,280	79.3	18,250 19,600 21,800	+0.032 −0.027 +0.191
	28,940	107.7	29,000	+0.069

[a] The signs refer to the rotation at 546 mμ. [b] Only one of two enantiomers is listed The CD values of their enantiomers not listed here were found to agree within ±1.5% (*i.e.*, the CD of $(+)$-[Co(en)$_2$L-alan]I$_2$ is equal but of opposite sign to $(-)$-[Co(en)$_2$D-alan]I$_2$, and the CD of unresolved-[Co(en)$_2$L-leuc]I$_2$ is equal but of opposite sign to unresolved-[Co(en)$_2$D-leuc]I$_2$. [c] Best average value for D- and L-amino acid and resolved and unresolved complexes. The individual values all agreed within 0.5%.

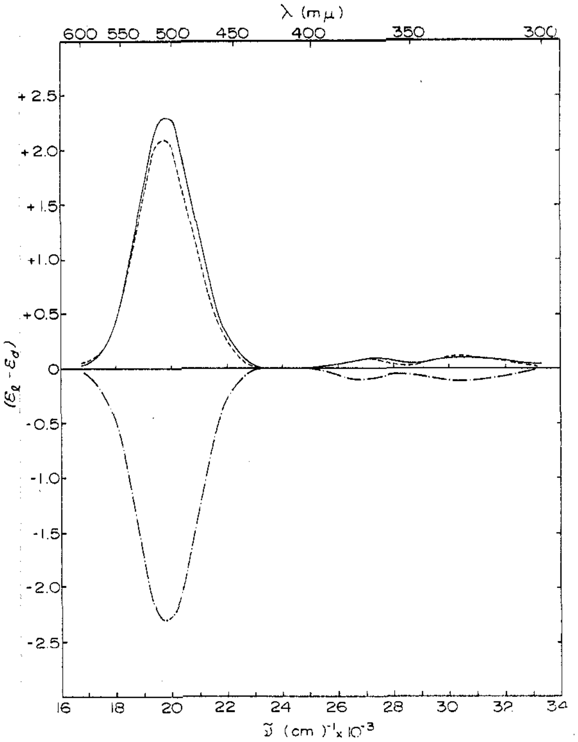

Fig. 5.—Resultant CD curves from Fig. 3: $(+)_{546}$-[Co(en)$_2$L-palan]I$_2$ minus unresolved complex (———), $(-)_{546}$-[Co(en)$_2$L-palan]I$_2$ minus unresolved complex (—·—·), CD for $(+)_{546}$-[Co(en)$_2$gly]I$_2$ (– – – –).

of the induced asymmetry caused by the active ligand. The complexes exhibit the Cotton effect in the visible region, indicating that the d–d electronic transitions have become optically active. The CD curve for unresolved [Co(en)$_2$L-palan]I$_2$ is shown in Fig. 3 along with the curves for both resolved complexes. The corresponding ORD curves are shown in Fig. 4.

Corey and Bailar[9] provided an explanation of stereospecific effects in complexes which has been shown to be consistent with experimental results.[10] For cobalt(III) complexes of optically active propylenediamine the complexes as prepared are not 50–50 mixtures.[10] However, the deviation from a 50–50 mixture of the Δ and Λ complexes is attributed to the conformation of the substituted ethylenediamine ring. Such conformational preferences are expected to be much smaller for a ligand such as an amino acid which gives a nearly planar chelate ring.

The CD curve for the unresolved [Co(en)$_2$L-palan]I$_2$ was subtracted from the corresponding curves for the two resolved complexes. The resultant curves (Fig. 5) are mirror images within experimental error. This result demonstrates the additivity of the configurational contribution (curves in Fig. 5) and the vicinal contribution (the curve for the unresolved complex in Fig. 3) and the fact that the complex as prepared is a 50–50 mixture. Similar results were obtained with the other complexes of optically active amino acids. The CD curve for the glycine complex is also shown

---

[9] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[10] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

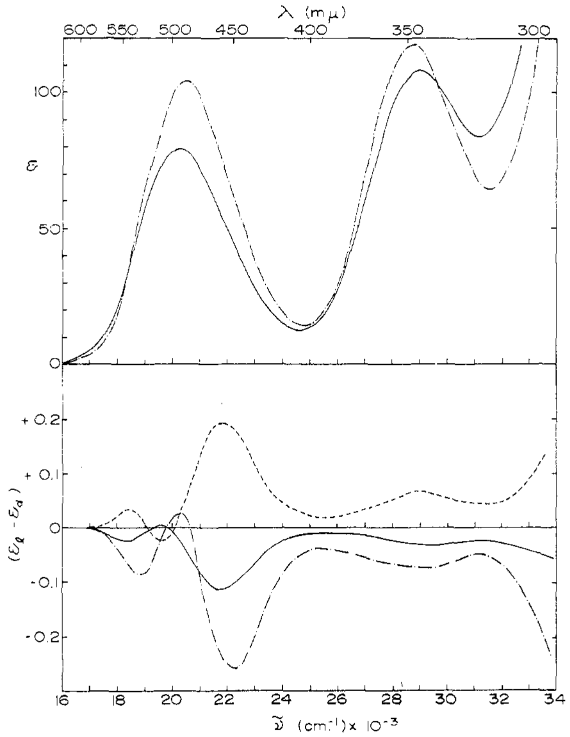

Fig. 6.—Upper: Molar absorptivities for [Co(NH$_3$)$_4$L-palan]I$_2$ (———) and [Co(en)$_2$L-palan]I$_2$ (—·—·). Lower: CD curves for [Co(NH$_3$)$_4$L-palan]I$_2$ (———), [Co(NH$_3$)$_4$D-palan]I$_2$·H$_2$O (— — — —), and unresolved [Co(en)$_2$L-palan]I$_2$ (—·—·).

in Fig. 5 for comparison. Here there is no vicinal contribution and the CD curve is as similar to the resultant curve for (+)$_{546}$-[Co(en)$_2$L-palan]I$_2$ as one should expect from the differences in the spectra (Table I). All of these facts together make it most improbable that the vicinal contribution just compensates for deviations from 50–50 proportions in the unresolved complex. The ORD curves were treated similarly with reasonable results.

The compounds [Co(NH$_3$)$_4$L-palan]I$_2$ and [Co(NH$_3$)$_4$D-palan]I$_2$·H$_2$O were prepared to clarify the vicinal effects. These compounds have no configurational contribution and no resolution is required. The CD curves for these complexes shown in Fig. 6 differ only in sign and intensity. The CD curve of unresolved [Co(en)$_2$L-palan]I$_2$ is very similar to that of the corresponding ammonia complex except for intensities and slight frequency shifts to be expected from the differences in the positions of the absorption peaks.

The absorption curves of all of the complexes of the type [Co(en)$_2$aa]I$_2$ and [Co(NH$_3$)$_4$aa]I$_2$ show two symmetrical peaks which would lead one to assume that the symmetry could be approximated as O$_h$, *i.e.*, no splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ bands. The CD curve of [Co(en)$_2$gly]I$_2$ (Fig. 1) reveals only one component in the low-frequency band region and two in the high-frequency band region. The presence of two components indicates a lowering of the symmetry as one might expect for a tetragonal compound of the type [CoN$_5$O], neglecting the effects of the chelate rings.

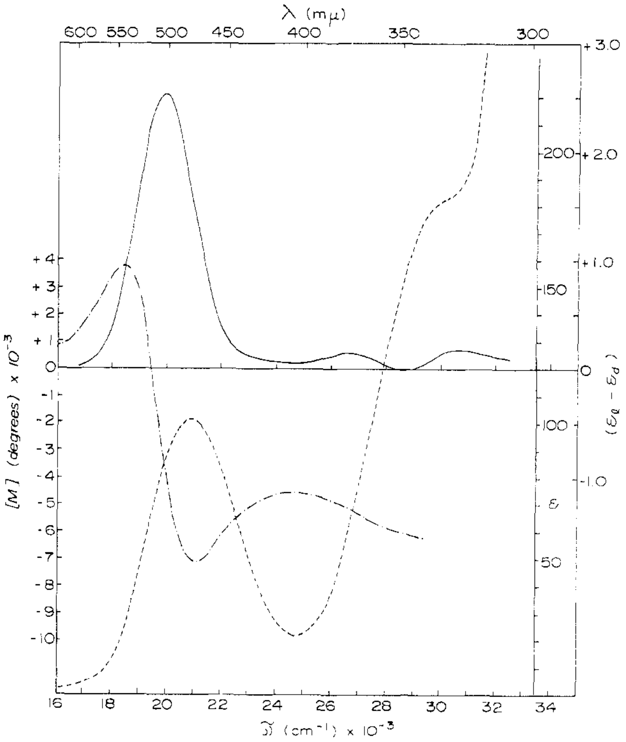

Fig. 7.—(+)$_{546}$-[Co(en)$_2$pic](ClO$_4$)$_2$: molar absorptivity (– – – –), CD (———), ORD (—·—·).

The CD curve for (−)$_{546}$-[Co(en)$_2$L-palan]I$_2$ (Fig. 3) shows the same splitting pattern as the glycine complex, but the (+)$_{546}$ isomer reveals two components in the low-frequency region and three weak peaks (+, −, +) in the high-frequency region. The CD curve for the unresolved complex reveals three components (−, +, −) in the low-frequency region. For the resolved complexes the presence of the negative peak at about 23,000 cm.$^{-1}$ is not apparent when the dominant peak at about 19,800 cm.$^{-1}$ has the same sign, which is the case for the (−)$_{546}$ isomer. The presence of a third component is not apparent for either resolved complex because one component is very intense, but the three components can be seen clearly for the unresolved complex. The three components in the low-frequency region are also clear from the CD curve for [Co(NH$_3$)$_4$L- or D-palan]I$_2$ (Fig. 6). Taking all of the CD data into account, there are obviously three components within the region of each absorption band, indicating that the effective symmetry is the true molecular symmetry, C$_1$. The approximate positions for the six components are: 18,800, 20,300, 22,200, 27,000, 28,700, and 31,100 cm.$^{-1}$.

Support for the assumption that [Co(en)$_2$gly]I$_2$ should have the same splitting pattern as the complexes of the optically active amino acids has been obtained from the effects of electrolytes on the CD curve. On addition of 0.5 *M* Na$_3$PO$_4$ the presence of a second CD peak (negative) at about 446 mμ was revealed for (+)$_{546}$-[Co(en)$_2$gly]I$_2$. It has been observed[11] that the addition of electrolytes generally increases the intensities of CD peaks, but some peaks are in-

---

[11] H. L. Smith and B. E. Douglas, *J. Am. Chem. Soc.*, **86**, 3885 (1964).

creased much more than others. This provides a means of detecting the presence of poorly resolved components in favorable cases.

The CD curve of $(+)_{546}$-$[Co(en)_2pic](ClO_4)_2$ (Fig. 7) shows three peaks (+, −, +) in the region of the high-frequency absorption band. This further supports the assumption that the same splitting pattern applies to complexes of this general type, even if no optically active ligand is present. The CD curve in the low-frequency region is strikingly similar to that of the $(+)_{546}$ glycine complex (Fig. 1).

The spiral pattern of the chelate rings in the complexes reported here is similar to that for $[Co(en)_3]^{3+}$. If one considers the symmetry to be lowered from $[Co(NH_3)_6]^{3+}$ (O_h) to $[Co(en)_3]^{3+}$ (D_3), the T_{1g} (O_h) level is split into the ^1E and $^1A_2$ (D_3) levels. Further lowering of the symmetry to C_1 by replacing one nitrogen by an oxygen in $[Co(en)_2aa]^{2+}$ removes the degeneracy to give three A levels. Polarized absorption spectra[12] and CD studies[13] of $[Co(en)_3]^{3+}$ showed that the A_2 peak is very close to the E peak. Mason's data for $(+)_{546}$-$[(Co(en)_3]^{3+}$ in solution and in the solid have shown that the positive CD peak is $^1A_1 \rightarrow {}^1E$ and the negative peak is $^1A_1 \rightarrow {}^1A_2$. It is expected that for $[Co(en)_2aa]^{2+}$ the two components split out of the E level should have the same sign,[14] which should be opposite to that of the third component. Since the $^1A_2$ and ^1E components for D_3 symmetry are close together, it is reasonable to expect that lowering of the symmetry would give one of the components from the E level at higher energy and one at lower energy compared to the component related to $^1A_2$. Therefore, the center component of the low-frequency band, which is opposite in sign to the other two, is related to the $^1A_2$ component for D_3 symmetry.

The $(+)_{546}$-$[Co(en)_3]^{3+}$ ion has been shown to have a left spiral (Λ) configuration.[15] For this isomer the $^1A_2$ CD peak is negative and hence the Λ configuration is assigned to all of the $(-)_{546}$-$[Co(en)_2aa]I_2$ complexes reported here since their corresponding CD peaks are also negative. The solubilities of the diastereoisomers of $[Co(en)_3]^{3+}$, $[Co(en)_2gly]^{2+}$, and $[Co(en)_2pic]^{2+}$ are consistent with this assignment of configurations.

---

(12) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960).

(13) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

(14) A. D. Liehr, private communication.

(15) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Green Band of Crystalline Nickel Dimethylglyoxime. I. Mixed Crystals with Palladium, Platinum, and Copper and the Questions of Nonlocalized or d-p Transitions[1]

BY G. BASU, GLENN M. COOK,[2] AND R. LINN BELFORD[3]

Received June 2, 1964

Quantitative spectra of single crystals of Ni, Pt, and Pd dimethylglyoximates in polarized light show extinction coefficients much smaller than earlier values, which were obtained from polycrystalline specimens. This evidence, plus arguments based on band polarizations, cast serious doubt on a previous assignment of the visible band to a highly-allowed p ← d transition. Preparation and visible salt pellet spectra of true binary mixed crystals of Ni, Pt, Pd, and Cu dimethylglyoximates are reported. The spectrum of a binary mixed crystal can be interpreted as containing bands belonging to each component. This interpretation is consistent with the solid-unique visible absorption's being caused by molecular transitions rather than by completely delocalized whole-crystal transitions. A new band is reported in the near-infrared spectrum of a single crystal of nickel dimethylglyoximate; it is probably a nickel d-like transition.

Introduction

Solid nickel bis(dimethylglyoxime) $[Ni(DMG)_2]$ has a strong green absorption[4−8] that is not reported for the solutions. This absorption was seen in single crystals by Yamada and Tsuchida[5] and Banks and Barnum[9] as a rather featureless absorption edge. However, it was reported by Sone,[6] Belford,[7] and Banks and Barnum[8,9] as a sharp, well-defined peak in the absorption spectra of powders, mulls, and suspensions. Zahner and Drickamer[4] found that this sharp band, and the presumably analogous bands of the isomorphic

---

(1) Partly abstracted from the Ph.D. thesis of G. M. Cook. This work was supported partly by National Science Foundation and U. S. Public Health Service (Division of General Medical Sciences) research grants.

(2) National Science Foundation Fellow, summer 1960; supported by Illinois Drug and Chemical Industries Scholarship Award.

(3) Alfred P. Sloan Research Fellow.

(4) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960); also J. C. Zahner, Ph.D. Thesis, University of Illinois, 1961.

(5) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **27**, 156 (1954); *J. Am. Chem. Soc.*, **75**, 6351 (1953); S. Yamada, *ibid.*, **73**, 1579 (1951).

(6) K. Sone, *ibid.*, **75**, 5207 (1953).

(7) R. L. Belford, University of California Radiation Laboratory Report UCRL 3051 (June, 1955).

(8) D. W. Barnum, Doctoral Dissertation, Iowa State College, 1957.

(9) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958); C. V. Banks and D. W. Barnum, *ibid.*, **80**, 3579 (1958); C. V. Banks and S. Anderson, *ibid.*, **84**, 1486 (1962). Also see numerous other references cited in these works.