CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Circular Dichroism of Some Complexes of the Type $Co(en)_2aa^{2+}$ Containing Optically Active α-Amino Acids[1]

BY STEPHEN K. HALL AND BODIE E. DOUGLAS

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The circular dichroism (CD) and electronic absorption spectra are reported for some cobalt(III) complexes of optically active α-amino acids of the general formula $Co(en)_2aa^{2+}$ (where aa is an amino acid anion). The amino acids studied were (*S*)-serine, (2*S*,3*R*)-threonine, (*S*)-proline, and (*S*)-methionine. The (+)D isomers of the $Co(en)_2aa^{2+}$ ions were assigned the Λ configuration, corresponding to that of the (+)D $Co(en)_3^{3+}$ ion. The effect of conformation of coordinated chelates on the CD curve in the first ligand field band region is discussed.

Lifschitz[2] prepared several compounds of the type $[Co(en)_2aa]Cl_2$ (where aaH = glycine, alanine, or leucine) and observed that no dissymmetric synthesis had occurred with the optically active amino acids; *i.e.*, the proportions of the optical isomers were equal within experimental error. Liu and Douglas,[3] using (*R*)- and (*S*)-alanine, (*R*)- and (*S*)-leucine, and (*S*)-phenylalanine prepared compounds of the same type and reported the absorption spectra, circular dichroism (CD), and optical rotatory dispersion (ORD) curves over an extended range. They showed that these unresolved complexes are optically active because of the effect from the optically active ligand. For the resolved complexes the contributions from the chirality of the chelate rings and from the optically active ligand are essentially additive. No dissymmetric synthesis was observed. In the present work, however, when (*S*)-serine, (2*S*,3*R*)-threonine, and (*S*)-proline were used, the first products isolated were found to contain more of one of the optical isomers, and repeated recrystallization gave one optically pure isomer. The separation of the optical isomers without a resolving agent is possible, in principle, for any of these complexes which are diastereomeric, rather than enantiomorphic, because of the optically active ligands.

Experimental Section

Reagents.—All optically active amino acids were used as received from Nutritional Biochemical Corp., Cleveland, Ohio. The reported specific rotations at the sodium D line were: (*S*)-methionine, +23.5° in 5 *N* HCl; (*S*)-proline, −51.8° in 0.5 *N* HCl; (*S*)-serine, +14.3° in 9 *N* HCl; and (2*S*,3*R*)-threonine, −28.3° in water. (*S*) refers to the absolute configuration of the amino acids, commonly designated as L.[4]

Measurements.—The CD spectra were taken in aqueous solutions (0.004–0.006 *M*) in 1- or 2-cm cells using a Roussel-Jouan Dichrograph. Measurements of optical rotations were made in aqueous solution in a 1-dm tube at the sodium D line, at room temperature. Absorption spectra were recorded on a Cary Model 14 spectrophotometer using 1-cm cells. Results of measurements on the complexes are summarized in Table I.

Preparation and Resolution of Complexes.—The complex ions of the type $Co(en)_2aa^{2+}$ were prepared as described by Liu and Douglas.[1] The (*S*)-methionine, (*S*)-serine, and (2*S*,3*R*)-threonine complexes were resolved using freshly precipitated silver antimonyl tartrate as the resolving agent.[3] The (+)D isomers of the (*S*)-serine and (2*S*,3*R*)-threonine complexes as the iodide salts were also obtained optically pure by repeated recrystallization from water, without using a resolving agent. The (−)D isomers were obtained optically pure only by using the resolving agent. The only product for the (*S*)-proline complex was found to be the optically pure (−)D isomer.

Results and Discussion

The CD spectra for both isomers of $[Co(en)_2$-(*S*)-met$]I_2$ are shown in Figure 1. The absorption spectrum for $[Co(en)_2$-(*S*)-thr$]I_2$ in Figure 2 differs only slightly in peak intensities (Table I) from the spectra of the corresponding methionine and serine complexes. The CD spectrum of the serine complex (Table I) is almost identical with that of the threonine complex (Figure 2). The spectra for the one isomer of $[Co(en)_2$-(*S*)-pro$]I_2$ (Figure 3) differ significantly from the others.

X-Ray studies have shown that the copper(II)–glycinato chelate ring[5] and the cobalt(III)–sarcosinato ring[6] are slightly puckered, but not as much as 1,2-diamine chelate rings. Any stereoselectivity that occurs in complexes with α-amino acid ligands might be expected to be smaller than that in complexes of 1,2-diamines.

The absolute configuration of (*S*)-amino acids is known. From the generalized treatment of Corey and Bailar,[7] C substituents are expected to prefer the more stable equatorial positions. Thus, the coordinating (*S*)-amino acid anions would probably adopt the more stable δ conformation.[8] For complexes of the type

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[1] Taken from the Ph.D. Dissertation of S. K. Hall, the University of Pittsburgh, 1967. This work was supported by a research grant (GM10829-09) from the Division of General Medical Studies, Public Health Service.

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[5] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Cryst.*, **17**, 1463 (1964).

[6] J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 324 (1967).

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

[8] The absolute configurations of the complexes are designated as Δ or Λ relative to the pseudo C_3 axis. A chelate ring conformation is designated as δ if the C–C bond defines a right spiral about the edge of the octahedron spanned by that ring and λ if a left spiral is so defined. This notation is consistent with a forthcoming IUPAC tentative rule.

TABLE I

ANALYSES, SPECIFIC ROTATIONS, ELECTRONIC ABSORPTION, AND CIRCULAR DICHROISM OF SOME COBALT–AMINO ACID COMPLEXES

Complex		Elemental anal, %				Absorption		Complex from less soluble diastereoisomer			Complex from more soluble diastereoisomer		
		C	H	N	S	$\tilde{\nu}$, cm^{-1}	ϵ_{max}	$[\alpha]_D$, deg	$\tilde{\nu}$, cm^{-1}	$\Delta\epsilon_{max}$	$[\alpha]_D$, deg	$\tilde{\nu}$, cm^{-1}	$\Delta\epsilon_{max}$
$[Co(en)_2$-(*S*)-met$]I_2$	Calcd	18.60	4.51	12.05	5.52	20,500	105	−440	19,500	−2.24	+275	19,900	+2.33
$CoC_9H_{26}N_5O_2SI_2$	Found	18.88	4.99	11.92	5.59	29,000	135		27,400	−0.22		23,200	−0.13
									30,300	−0.23		26,800	+0.05
												28,800	−0.05
												30,500	+0.08
$[Co(en)_2$-(*S*)-ser$]I_2$	Calcd	15.66	4.13	13.04		20,500	118	−455	19,900	−2.26	+297	19,600	+2.34
$CoC_7H_{22}N_5O_3I_2$	Found	15.82	3.98	12.93		29,000	135		27,000	−0.11		23,000	−0.08
									30,300	−0.13		26,900	+0.11
												30,500	+0.18
$[Co(en)_2$-(2*S*,3*R*)-thr$]I_2$	Calcd	17.44	4.39	12.70		20,500	116	−458	19,900	−2.28	+295	19,600	+2.35
$CoC_8H_{24}N_5O_3I_2$	Found	17.32	4.41	12.65		29,000	140		27,000	−0.12		23,000	−0.09
									30,300	−0.14		27,000	+0.10
												30,500	+0.18
$[Co(en)_2$-(*S*)-pro$]I_2$[a]	Calcd	19.76	4.42	12.80		20,400	100	−425	19,200	−1.86			
$CoC_9H_{24}N_5O_2I_2$	Found	19.42	4.54	12.60		28,700	132		22,200	−0.26			
									26,800	−0.19			
									29,600	−0.26			

[a] Only one optical isomer was isolated, without a resolving agent.

$Co(en)_2aa^{2+}$ the Λ configuration with δδδ conformations might be expected to be favored,[7] although the ethylenediamine rings in (−)D-$[Co(en)_2sar]I_2 \cdot 2H_2O$ have opposite conformations[6] in the solid state. Since greater proportions of (+)D isomers of $Co(en)_2$-(*S*)-ser^{2+} and $Co(en)_2$-(2*S*,3*R*)-thr^{2+} were found in the initial products and the (+)D isomers could be crystallized from the mixture optically pure, the stereoselectivity of (*S*)-serine and (2*S*,3*R*)-threonine is presumed to be greater than that of (*S*)-alanine, (*S*)-leucine, (*S*)-methionine, (*S*)-phenylalanine, and (*S*)-valine.[3] Recently, stereoselectivity of (*S*)-glutamic acid was reported in the preparation of $[Co(en)_2$-(*S*)-glu$]ClO_4$.[9] The (+)D isomer was found to be the major product and could also be obtained optically pure by repeated recrystallization from water. Since serine and threonine are hydroxyamino acids, hydrogen bonding might play a role in the stereoselectivity, as suggested for glutamic acid.[9]

The $\Delta(C_3)$ configuration has been assigned to the (−)D-$Co(en)_2aa^{2+}$ complex ions[6] for which the dominant CD band is negative. The absolute configuration of the (−)D isomers in the present study should be assigned accordingly. The signs of optical rotation are the same at 546 and 589 mμ, so the earlier assignments of absolute configuration made for a series of $(-)_{546}$-$[Co(en)_2aa]I_2$ complexes is in error.[3] The dominant CD peak for these complexes must be related to the E_a transition for $Co(en)_3^{3+}$, not the A_2 transition (Figures 1–3).

The product isolated from the preparation of the (*S*)-proline complex was the pure (−)D isomer. Framework molecular models indicate strong steric interaction involving the proline ring of the (+)D isomer which has a Λ configuration. This steric interaction is absent in the (−)D isomer (Δ configuration) owing to the arrangement of the two ethylenediamine chelate rings. This basis of assigning the Δ configuration to (−)D-$Co(en)_2$-(*S*)-pro^{2+} is consistent with the assignment from the CD curves above. In their preparation of tris(amino acidato)cobalt(III) complexes, Denning and

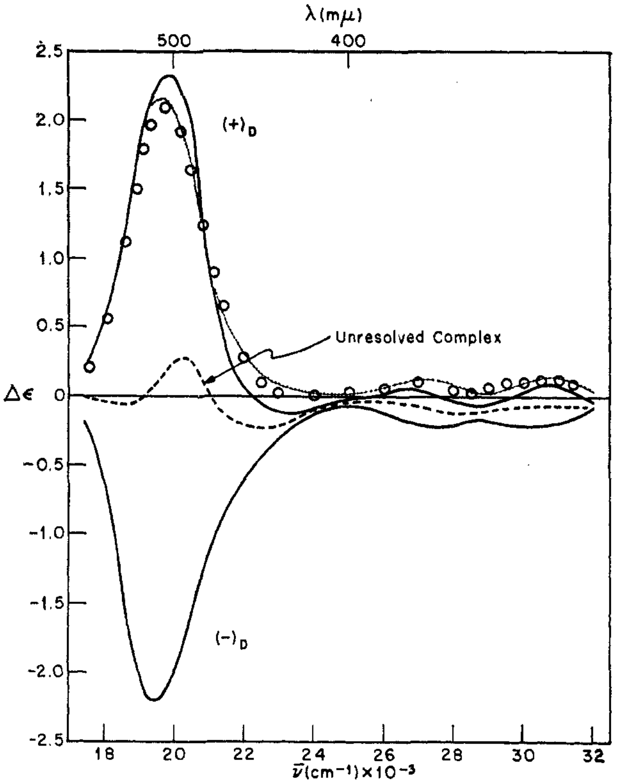

Figure 1.—Circular dichroism curves for (+)D, (−)D, and unresolved $[Co(en)_2$-(*S*)-met$]I_2$. The difference curve for the (+)D isomer and the unresolved complex is shown (- - -) with the experimental points for the CD curve of (+)D-$[Co(en)_2gly]I_2$.

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(9) J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).

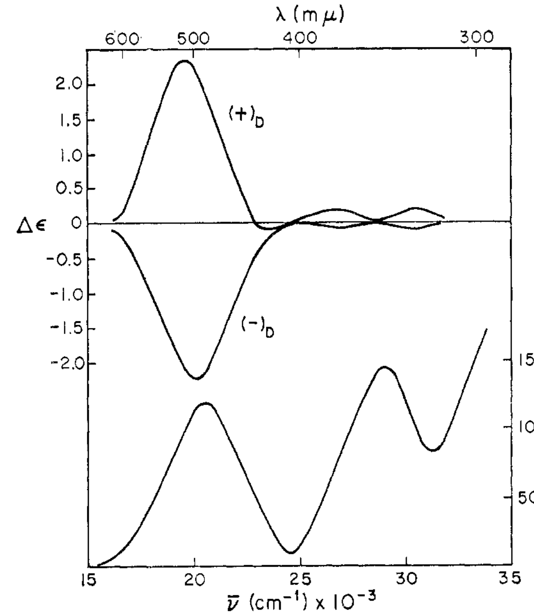

Figure 2.—Circular dichroism and absorption curves for the optical isomers of $[Co(en)_2\text{-}(2S,3R)\text{-thr}]I_2$.

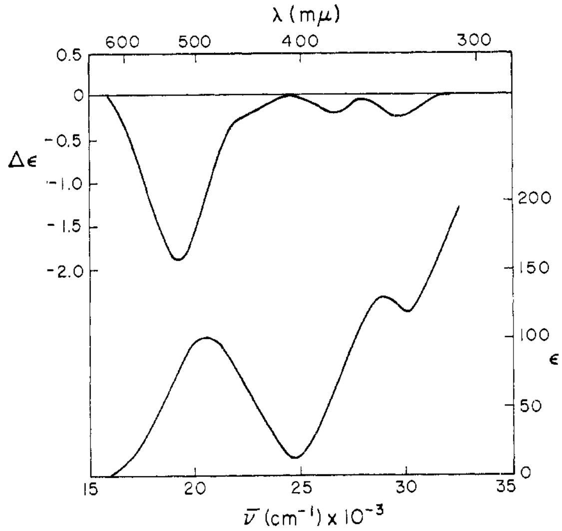

Figure 3.—Circular dichroism and absorption curves for (−)D-$[Co(en)_2\text{-}(S)\text{-pro}]I_2$.

Piper[10] only succeeded in obtaining three of the possible four isomers of tris((*S*)-prolinato)cobalt(III). The fourth isomer was not expected because of absolute stereospecificity of (*S*)-proline in this case. Only one isomer was isolated in another study.[11]

The CD curves for both isomers of $[Co(en)_2gly]I_2$ (gly = glycinate ion) reveal a single intense peak in the first ligand field band region. In the presence of electrolytes, a second CD peak of opposite sign appears in this region.[12] This second peak is apparent for the (+)D isomers of the corresponding complexes of optically active amino acids[3] (Table I and Figures 1 and 2). Only one broader peak is observed in this region for the (−)D isomers[3] (Figures 1 and 2). These results indicate that the T_1 (O_h) level is split into (at least) two components for complexes of the type $Co(en)_2aa^{2+}$. The weaker component A_2 (D_3) is masked in the glycinato complex in the absence of other electrolytes.

The unresolved $[Co(en)_2\text{-}(S)\text{-met}]I_2$ first isolated gave a CD curve (Figure 1) similar to those of other optically active amino acids.[3] Also, as before, the CD curve for the unresolved complex is the same as the average of the CD curves for the resolved Δ and Λ isomers, so the unresolved complex contained equal proportions of the Δ and Λ isomers. The curve obtained by subtracting the CD curve for the unresolved complex from that for (+)D-$[Co(en)_2\text{-}(S)\text{-met}]I_2$ agrees very well with that for (+)D-$[Co(en)_2gly]I_2$[3] (Figure 1), demonstrating the additivity of the contributions from the chiral arrangements of the chelate rings and that from the coordination of (*S*)-methionine. This additivity has been observed by Liu and Douglas[3] and by Sargeson, *et al.*,[13] for other amino acids. The CD curve for the unresolved $[Co(en)_2\text{-}(S)\text{-met}]I_2$ (or the curve obtained by subtracting the CD curve for (+)D-$[Co(en)_2gly]I_2$ from that for (+)D-$[Co(en)_2\text{-}(S)\text{-met}]I_2$) shows three peaks (−, +, −) in the first absorption band region. The CD curves are similar for "typical" amino acid, *e.g.*, (*S*)-alanine, (*S*)-leucine, and (*S*)-phenylalanine, complex ions of the types $Co(NH_3)_4aa^{2+}$ [3,14] and $Co(trien)aa^{2+}$ [15] (trien = triethylenetetramine). Thus, this is the CD pattern for a complex of the type $Co(N)_4\text{-}(S)\text{-}aa^{2+}$, where (*S*)-aa is the anion of (*S*)-alanine, (*S*)-leucine, (*S*)-phenylalanine, (*S*)-methionine, (*S*)-serine, or (2*S*,3*R*)-threonine, whether the N ligands are NH_3, en, or trien, but without any net chirality resulting from the spiral arrangements of chelate rings in the case of polyamines. Complexes of some other amino acids, such as proline, give curves of different types.

There is no ring substituent to impose a preferred conformation of the glycinato chelate ring. The substituents for the optically active amino acids are expected to occupy equatorial positions, favoring one ring conformation. Since one obtains similar CD curves in the first band region for $Co(N)_4\text{-}(S)\text{-}aa^{2+}$ complex ions if the contributions of chelate rings of polyamines are absent or subtracted out, the amino acid chelate ring must have little effect on the conformations of the en rings in $Co(en)_2\text{-}(S)\text{-}aa^{2+}$. The optical activity presumably arises from a fixed conformation of the amino acid chelate ring and/or the dissymmetry of the entire complex conferred by the presence of the amino acid ring substituent. The conformational contribution of the amino acid chelate ring is not expected to be great because of its near planarity. Similar CD effects have

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been observed for nonchelated amino acid complexes.[14] Shimura[16] used the term *vicinal effect* for the optical activity observed for $[Co(NH_3)_4$-(*S*)-leu$](ClO_4)_2$. Although the term vicinal effect implies that the optical activity arises from the presence of the asymmetric center in the ligand, it has not been used in such a limited sense, but to include all contributions other than that from the spiral arrangement of the chelate rings.

The appearance of two CD peaks for the resolved complexes in the first ligand field band region would be consistent with effective D_3 symmetry. The effective symmetry must be lower, however, since, in the second band region, E (T_{2g}) is allowed, but A_1 (T_{2g}) is not for D_3 symmetry.[17] Two CD peaks are observed in this region except for (+)D-$[Co(en)_2$-(*S*)-met$]I_2$, for which three weak peaks are apparent (Figure 1). The CD spectrum was checked on a Jasco instrument. Three CD peaks in this region have been observed also for some of the corresponding complexes of other amino acids.[3] Three CD peaks in the T_{2g} region, three peaks in the first-band region for $[Co(NH_3)_4$-(*S*)-palan$]I_2$[3] and similar complexes,[14] and three peaks in the first-band region for the unresolved complex strongly suggest that the effective symmetry is low enough and the splitting is great enough for the complete removal of degeneracy. Except in these favorable cases, some peaks are masked by more intense neighboring peaks of opposite sign. It does not appear reasonable to expect that three apparent peaks result from the overlap of two peaks of greatly different band widths. Since the same effective symmetry must pertain to Δ- or Λ-$[Co(en)_2$-(*S*)-aa$]I_2$, the same splittings would result. The differences among the resulting CD curves should arise from varying intensity contributions for each of the transitions from the sources cited for an optically active ligand and from the chiral pattern of the chelate rings in the resolved isomers. The CD spectrum is dominated by the contributions from the ring chirality for the resolved complexes. Apparently the conformational contributions for en rings is negligible in these cases.

The dengeneracy of the T levels is removed in C_{2v}, C_2, or C_1 symmetry. The molecular symmetry is C_1 for these complexes, but assignments have no significance for C_1 symmetry since the only representation is A. The X-ray determination of the absolute configuration[6] makes it clear that the sign of the dominant CD peak in the first-band region is derived from E_a (D_3) parentage.

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CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE INORGANICA (II SEZIONE),
UNIVERSITA DI PADOVA, PADUA, ITALY

Thermodynamic Studies of the Relative Stabilities of Bis- and Tris-Phosphine Complexes of Nickel(II) Cyanide in Solution

BY P. RIGO, G. GUASTALLA, AND A. TURCO

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Thermodynamic data are reported for the four-coordinate–five-coordinate equilibria $Ni(PR_3)_2(CN)_2 + PR_3 \rightleftarrows Ni(PR_3)_3(CN)_2$ (where $PR_3 = P(C_2H_5)_3$, $P(C_3H_7)_3$, $P(C_4H_9)_3$, $P(C_2H_5)_2C_6H_5$, $PC_2H_5(C_6H_5)_2$) in ethanol, *n*-hexane, and dichloroethane. The stability order for the complexes $Ni(PR_3)_3(CN)_2$, measured by the equilibrium constants at 20° in ethanol, is $P(C_3H_7)_3 \sim P(C_4H_9)_3 < P(C_2H_5)_3 < PC_2H_5(C_6H_5)_2 \ll P(C_2H_5)_2C_6H_5$. It is shown that the values of the enthalpy changes $\Delta H°$, determined spectrophotometrically by measuring the equilibrium constants at different temperatures, provide a fairly good measure of the growing covalency of the bonds on formation of the five-coordinate complexes.

Complexes with various coordination numbers are formed by nickel(II) and cobalt(II) in their compounds with trisubstituted phosphines and anionic ligands. When the anionic partners X are weak-field ligands, tertiary phosphines give only the four-coordinate complexes $M(P)_2X_2$[1,2] (where P is the phosphorus atom of a tertiary phosphine). With ditertiary phosphines, in addition, the cationic five-coordinate compounds $M(P)_4X^+$ can be obtained in which four phosphorus atoms are bound to the metal ion. The possibility to give the neutral five-coordinate complexes $M(P)_3X_2$ with both tertiary and ditertiary phosphines appears to be restricted to compounds containing "strong" anions such as CN^- or also NCS^- in the case of cobalt(II).[3,4] As a part of the investigations carried on in order to elucidate the factors which

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