the ligand on the energy of the σ^* level. The latter condition may hold for the SO_4^{2-} ligand but certainly does not for the isoelectronic and structurally similar $NHSO_3^-$ ligand.

The measured pK_1 value gives some indirect support to the SN1CB mechanism for the alkaline hydrolysis of cobalt(III)–ammine complexes. The reaction

$$(NH_3)_5CoNH_2SO_3^{2+} \rightleftharpoons (NH_3)_5CoNHSO_3^+ + H^+ \qquad K_1$$

is similar to the formation of the conjugate base proposed in the SN1CB mechanism

$$(NH_3)_4CoNH_3X \rightleftharpoons (NH_3)_4CoNH_2X + H^+ \qquad K_a$$

The same type of back π bonding can occur with NH_2^- as described above for $NHSO_3^{2-}$; therefore, it should be possible to estimate K_a from K_1.

From measured pK values[16] it is known that sulfamic acid is about 10^9 times a stronger acid than NH_4^+. It may then be assumed that the second dissociation constants of these ions also differ by 10^9 and further that the dissociation constants of the coordinated ions differ by 10^9. Then using the measured value of 10^{-6} for K_1, K_a is calculated as 10^{-15}. This value is quite consistent with the inability to measure the value of K_a in aqueous solution and with previous estimates from deuterium exchange and kinetic studies.[1,18]

(18) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

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Circular Dichroism of Some Optically Active Rhodium–Amino Acid Complexes[1]

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Circular dichroism (CD) and electronic absorption spectra are reported for some rhodium(III) complexes of optically active amino acids of the general formula $[Rh(en)_2aa]^{2+}$ (where aa is an amino acid anion). All the (−)D isomers of $[Rh(en)_2aa]^{2+}$ were assigned the Λ configuration which is related to the absolute configuration of the (+)D-$[Co(en)_3]^{3+}$ ion.

Complexes of the type $[Co(en)_2aa]^{2+}$ (where aa is an amino acid anion) have been prepared and resolved, and the absorption spectra, ORD, and CD curves have been reported.[2] Some rhodium(III) complexes of the type $[Rh(en)_2aa]^{2+}$ have been prepared by Waller, Hu, and Bryant.[3] In the present work, some of these complexes were successfully resolved and their electronic absorption and circular dichroism (CD) spectra were measured.

Experimental Section

Reagents.—All optically active amino acids were purchased from Nutritional Biochemical Corp., Cleveland, Ohio, and used as received. The reported specific rotations at the sodium D line were: (*S*)-alanine, +14.25° in 6 *N* HCl; (*S*)-leucine, +15° in 6 *N* HCl; (*S*)-methionine, +23.5° in 5 *N* HCl; (*S*)-serine, +14.3° in 9 *N* HCl; (2*S*,3*R*)-threonine, −28.3° in water; (*S*)-valine, +27.3° in 6 *N* HCl. (*S*) refers to the absolute configuration of the amino acids, commonly designated as L.

Measurements.—The CD spectra were taken in aqueous solutions in 1- or 2-cm cells using a Roussel-Jouan Dichrograph. The concentrations of the solutions were 0.004–0.006 *M*. Measurements of optical rotations were made on the same solutions in a 1-dm cell 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 rhodium complexes of optically active amino acids are summarized in Table I.

Preparation and Resolution of Glycinatobis(ethylenediamine)-rhodium(III) Iodide.—This compound was prepared by the method of Waller, Hu, and Bryant.[3] A slurry of 3.56 g of *trans*-dichlorobis(ethylenediamine)rhodium(III) nitrate[4] and 0.75 g of glycine in a mixture of 10 ml of 1 *N* NaOH, 15 ml of water, and 5 ml of 95% ethanol was warmed gently on the steam bath until a clear solution resulted. The warm solution was filtered, cooled, and treated with 5 g of solid NaI. It was left in a refrigerator overnight to precipitate. The resulting creamy colored precipitate was filtered, washed with absolute ethanol, acetone, and ether, and air dried. The compound was recrystallized from a minimum amount of hot water.

The racemic complex dissolved in a minimum amount of water at room temperature was resolved using freshly prepared silver antimonyl tartrate. The resolutions were carried out using 0.5–1 g of complex and a slight excess of resolving agent. Silver iodide was removed by filtration after shaking the mixture vigorously for 10–15 min away from direct light. Ethanol (*ca.* 15 ml) was slowly and carefully added while the solution (*ca.* 20 ml) was mechanically stirred to precipitate the less soluble diastereoisomer. When the first cloudiness appeared, the solution was gently warmed on a steam bath to clear the cloudiness. On cooling and standing overnight, the less soluble diastereoisomer precipitated. This was filtered, washed with ethanol, acetone, and ether, and air dried. The more soluble diastereoisomer was obtained by first concentrating the filtrate under a stream of compressed air and by further addition of ethanol.

The diastereoisomer dissolved in water was treated with $AgNO_3$ to precipitate the resolving agent, which was removed by filtration, followed by the addition of excess NaI to precipitate the complex in the iodide form.

Preparation and Resolution of Complexes of Optically Active Amino Acids.—These compounds were prepared and resolved by methods similar to that described for the glycine complex. The specific rotations and analytical results are given in Table I.

(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, U. S. Public Health Service.

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

(3) J. F. Waller, Jr., J. Hu, and B. E. Bryant, *J. Inorg. Nucl. Chem.*, **27**, 2371 (1965).

(4) S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 217 (1966).

TABLE I

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

Complex		Elemental anal, % C	H	N	Absorption $\bar{\nu}$, cm^{-1}	ϵ_{max}	Circular dichroism: Complex from less soluble diastereoisomer $[\alpha]_D$, deg	$\bar{\nu}$, cm^{-1}	$(\Delta\epsilon)_{max}$	Complex from more soluble diastereoisomer $[\alpha]_D$, deg	$\bar{\nu}$, cm^{-1}	$(\Delta\epsilon)_{max}$
$[Rh(en)_2gly]I_2$	Calcd	13.09	3.67	12.70	31,650	250	+39	29,850	−2.31	−39	29,850	+2.31
$RhC_6H_{20}N_5O_2I_2$	Found	12.92	3.63	12.64	37,310	286		38,460	−0.38		38,460	+0.38
$[Rh(en)_2((S)\text{-ala})]I_2$	Calcd	14.88	3.93	12.39	31,650	330	+37	29,850	−2.31	−42	29,850	+2.42
$RhC_7H_{22}N_5O_2I_2$	Found	15.07	4.02	12.61	37,040	335		37,740	−0.59		38,460	+0.26
$[Rh(en)_2((S)\text{-val})]I_2$	Calcd	18.23	4.42	11.80	31,650	298	+36	29,850	−2.34	−45	29,850	+2.43
$RhC_9H_{26}N_5O_2I_2$	Found	18.03	4.24	12.06	37,310	350		37,740	−0.61		38,460	+0.23
$[Rh(en)_2((S)\text{-leu})]I_2$	Calcd	19.79	4.65	11.53	31,650	286	+35	29,850	−2.35	−48	29,850	+2.43
$RhC_{10}H_{28}N_5O_2I_2$	Found	19.86	4.89	11.70	37,740	363		37,740	−0.62		38,460	+0.21
$[Rh(en)_2((S)\text{-ser})]I_2$	Calcd	14.48	3.82	12.05	31,650	335	+37	29,850	−2.36	−47	29,850	+2.48
$RhC_7H_{22}N_5O_3I_2$	Found	14.56	3.79	12.13	37,590	350		37,740	−0.51		38,460	+0.54
$[Rh(en)_2((2S,3R)\text{-thr})]I_2$	Calcd	16.15	4.07	11.76	31,650	320	+36	29,850	−2.37	−48	29,850	+2.49
$RhC_8H_{24}N_5O_3I_2$	Found	15.98	4.13	11.84	37,590	355		37,740	−0.49		38,460	+0.53
$[Rh(en)_2((S)\text{-met})]I_2$	Calcd	17.29	4.19	11.20	31,550	285	+27	29,240	−1.64	−52	29,760	+2.53
$RhC_9H_{26}N_5O_2SI_2$	Found	17.01	4.26	11.16				34,130	−0.16			
					37,740	430		38,460	−0.09		38,460	+0.24

Discussion

It is generally assumed that two related dissymmetric molecules have the same absolute configuration if they give a Cotton effect of the same sign in the absorption region. This principle, together with stereoselectivity and solubility, has been used to assign absolute configurations to a wide variety of dissymmetric metal complexes. McCaffery, Mason, and Ballard[5] used the CD spectra, in solution and in the solid state, to assign the same configurations to (+)-$[Co(en)_3]^{3+}$ and (−)-$[Rh(en)_3]^{3+}$, (+) and (−) referring to the sign of rotation at the sodium D line. They are both conventionally termed Λ from the left-handed chirality of the complex along the C_3 axis. The ORD curves of these two complex ions have the same sign of the Cotton effect in their absorption regions but the "tail" of the ORD curve for the rhodium complex ion acquires a negative value at the sodium D line.

From comparison of the signs of the dominant CD peaks of the $[Rh(en)_2aa]^{2+}$ and the $[Co(en)_2aa]^{2+}$ complexes in the region of the first absorption bands, it is reasonable to assume (−)D-$[Rh(en)_2aa]^{2+}$ has the same configuration as that of (+)D-$[Co(en)_2aa]^{2+}$. Since the Λ(C_3) configuration has been assigned to all of the (+)D-$[Co(en)_2aa]^{2+}$ complexes,[6] it is assumed that the (−)D-$[Rh(en)_2aa]^{2+}$ complexes also have the Λ configuration and that the (+)D-$[Rh(en)_2aa]^{2+}$ complexes have the Δ configuration.

Compounds of the type $[RhN_5O]$ possess a tetragonal crystal field. However, when the effects of the chelate rings for complexes of the type $[Rh(en)_2aa]^{2+}$ are considered, the symmetry is C_1. The absorption curves for all of the complexes of this type show an intense peak for the first ligand-field band while the second ligand-field band only appears as a barely visible shoulder of the charge-transfer band (Figures 1–3). Each triply degenerate ligand-field band should split into three nondegenerate levels for C_1 symmetry. The CD curves are of the same form for all of the optically active amino acid complexes except for methionine. The curve for alanine (Figure 2) can be considered to be typical of the others. In the first ligand-field band region, only one dominant band is observed both for the (+) and the (−) isomers. However, Gaussian analysis of the CD band for the (−) isomers reveals a possible negative component. Presumably this component is obscured except for the (+) isomer of the methionine complex where it appears as a shoulder.

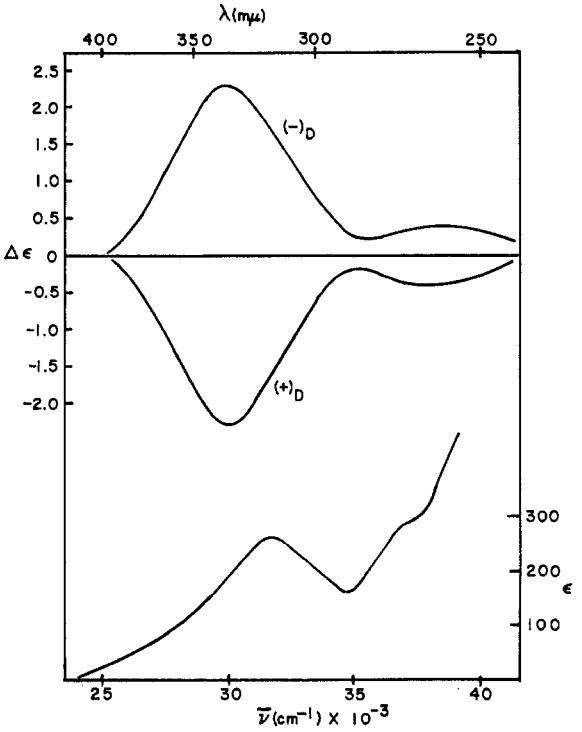

Figure 1.—Absorption and circular dichroism curves for (+)D- and (−)D-$[Rh(en)_2gly]I_2$.

It is assumed that methionine is coordinated through N and O since there are no great differences in the CD curves. The shoulder which appears only for the (+) isomer of the methionine complex has low intensity

(5) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

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

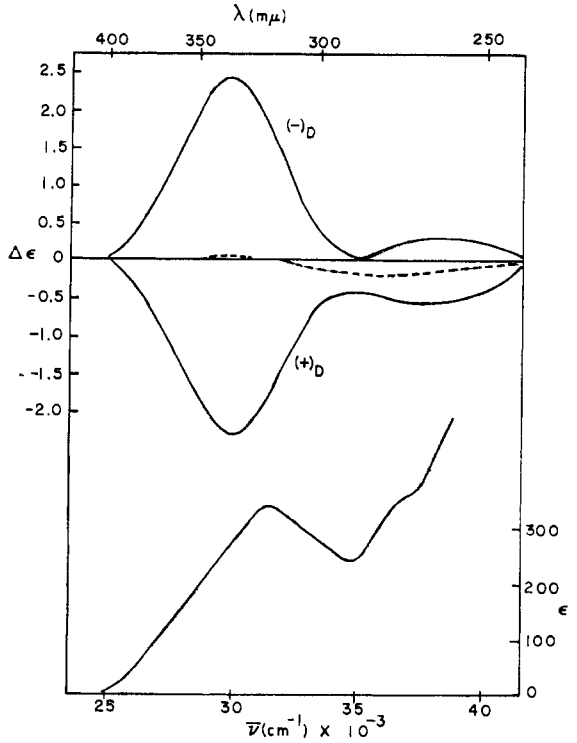

Figure 2.—Absorption and circular dichroism curves for (+)D- and (−)D-[Rh(en)$_2$((*S*)-ala)]I$_2$.

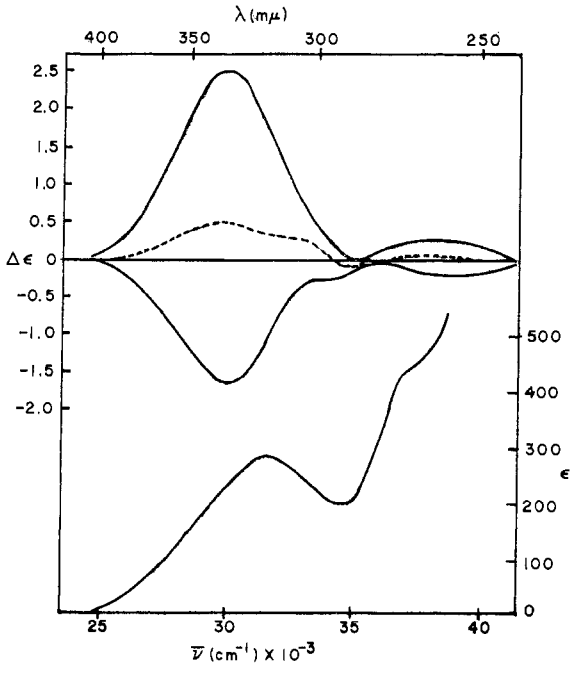

Figure 3.—Absorption and circular dichroism curves for (+)D- and (−)D-[Rh(en)$_2$((*S*)-met)]I$_2$.

and could be obscured or cancelled by small shifts in peak positions. Much greater intensities of the absorption and CD peaks would be expected for coordination through S.[7,8]

(7) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1724 (1964).
(8) G. R. Brubaker and B. E. Douglas, *ibid.*, **6**, 1562 (1967).

The tetragonal component appears to be small but the trigonal component should be no smaller than for [Rh(en)$_3$]$^{3+}$, where it is significant.[9] Consequently, it seems that assignments of the transitions are best made using D_3 symmetry. The low-frequency band around 29,850 cm^{-1} is thus assigned to the $^1A_1 \rightarrow {}^1E^a$ transition since the E^a peak is generally dominant in the first band region.[9,10] Only for the methionine complex (Figure 3) is there any clear indication of the presence of another peak in this region (34,130 cm^{-1}, assigned to A_2). For all of the other optically active amino acids (see Figure 2) there is a significant negative contribution apparent for the (+) isomer in the region expected for the A_2 component. The high-frequency band around 38,000 cm^{-1} is assigned to the $^1A_1 \rightarrow {}^1E^b$ transition.

There is an essentially constant contribution to the CD for each (*S*)-amino acid (Figure 2), except for (*S*)-methionine (*vide infra*). This effect is small and only causes an appreciable difference in the shapes of the CD curves for the two isomers in the region of the A_2 component (*ca.* 34,000 cm^{-1}). Here the contribution is negative for the (*S*)-amino acid, resulting in broadening of the E^a peak for the (+) isomer and sharpening of this peak for the (−) isomer. Subtraction of the contribution for the active amino acid from the CD curves for the two isomers gives curves the same as those for the glycine complex, within experimental error. The curves for the two isomers deviate more from mirror images for the (*S*)-methionine complex (Figure 3), indicating a greater effect for this ligand, presumed to be the result from a greater ring conformational effect than for the other amino acids. The greater contribution to the CD from the active ligand ((*S*)-methionine) containing a polar substituent[11] can account for the difference in the CD curves for the (*S*)-methionine complex and those of the complexes of other amino acids without assuming coordination through sulfur.

The chiral effect of the three chelate rings (the "configurational" effect[2]) and the ring conformational effect (the "vicinal" effect[2]) appear to be reasonably additive for the rhodium complexes studied. The smaller contribution of the optically active ligand for the rhodium complexes, compared to the corresponding cobalt(III) complexes,[2] suggests a more nearly planar conformation of the amino acid chelate ring. The conformational contributions of methionine in the corresponding cobalt(III) complex will be considered in another publication.

(9) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).
(10) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 661 (1966).
(11) J. H. Dunlop, R. D. Gillard, and N. C. Payne, *J. Chem. Soc., Sect. A*, 1469 (1967).