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Circular Dichroism Spectra of Amino Acid Complexes. Carboxylatopentaamminecobalt(III) Compounds

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The circular dichroism spectra of a series of optically active (α-aminocarboxylate)pentaamminecobalt(III) complexes have been measured in aqueous solution under different pH conditions and in the presence of salts of polarizable anions. The observed spectra in the visible region have been analyzed to determine the signs of the Cotton effects of the three components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ cobalt(III) transition. For L-amino acids, the transition with $A_{2g}(D_{4h})$ parentage is negative, and the two transitions with $E_g(D_{4h})$ parentage have opposite signs. The acid dissociation constants of the amine groups of the coordinated amino acids have been determined and found to be between 1.3 and 2.3 logarithmic units less than for the uncoordinated compounds.

As part of general study of the factors that govern the circular dichroism (CD) of amino acid complexes, some pentaamminecobalt(III) compounds of optically active α-aminocarboxylates coordinated as unidentates through the carboxylate group have been prepared, and their CD spectra measured and analyzed.[1] By varying the environment in which these complexes were studied, it has been possible to determine the signs of the Cotton effects of the three components of the lowest energy spin-allowed ligand-field transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) for amino acids with the D and L configurations. In these complexes, the central metal ion d–d transitions acquire rotational strength through the vicinal effect of the asymmetric grouping in the amino acid.

The CD spectra of some of these complexes have been reported previously by Shimura and his coworkers.[2] However, they were unable to separate the contributions to the observed CD from the three components. Without this information it is not possible to use this type of system to determine objectively the absolute configuration of an amino acid. Further, this information is vital if we are to determine the factors that govern the rotational strengths of metal complex d–d transitions.

The acid dissociation constants of the amine groups of the coordinated α-aminocarboxylates have also been determined in order to rationalize the observed variation of the CD with the pH of the solutions.

Experimental Section

Preparation of Complexes.—The complexes were prepared from aquapentaamminecobalt(III) by modifications of the methods described by Shimura and his coworkers.[2] For most of the complexes, isolation of analytically pure samples proved to be very difficult. Many variations to the procedures were attempted, and it was found necessary to use different methods for each amino acid.[3] For all of the complexes, the reactions were carried out in acidic conditions with the amino acid in excess, and the progress of the reactions was followed spectrophotometrically. The amino acids were BDH Biochemical grade except for D-phenylglycine, which was obtained from Aldrich Chemical Corp. Analyses were performed by the University of Queensland and the Australian Microanalytical Services.

$[Co(NH_3)_5(L\text{-}alaH)](ClO_4)_3 \cdot H_2O$.—This was prepared by warming the reaction solution at 60–65° for 3.5 hr and purified by recrystallization from a sodium perchlorate solution. *Anal.* Calcd for $[CoC_3H_{22}N_5O_2](ClO_4)_3 \cdot H_2O$: C, 6.6; H, 4.4; N, 15.3. Found: C, 6.6; H, 4.6; N, 15.3.

$[Co(NH_3)_5(L\text{-}leuH)]Cl_3 \cdot 2H_2O$.—The reaction solution was heated first at 75–80° for 3.5 hr and then at 90–100° for 0.5 hr. Unreacted starting material was removed on cooling, and the perchlorate salt of the complex was isolated by evaporating the solution to low volume. Purification of the perchlorate and the sulfate (obtained by an ion-exchange conversion) salts was not achieved. The chloride was prepared from the sulfate by a metathetic reaction with barium chloride and was purified by recrystallization from an alcohol–ether solution. *Anal.* Calcd for $[CoC_6H_{28}N_5O_2]Cl_3 \cdot 2H_2O$: C, 17.3; H, 7.7; N, 20.1. Found: C, 17.2; H, 7.6; N, 20.3.

$[Co(NH_3)_5(L\text{-}pheH)](ClO_4)_3$.—The reaction was carried out at 60–65° for 7.25 hr and at 80–85° for a further 0.5 hr. The product, which precipitated on cooling, was recrystallized from an acidified solution of sodium perchlorate. *Anal.* Calcd for $[CoC_9H_{26}N_5O_2](ClO_4)_3$: C, 17.8; H, 4.3; N, 13.8; Co, 9.7. Found: C, 17.7; H, 4.7; N, 13.9; Co, 9.8.

$[Co(NH_3)_5(L\text{-}metH)](ClO_4)_3 \cdot H_2O$.—The reaction was allowed to proceed at 60–65° for 6.75 hr, after which a large volume of acetone was added to precipitate impurities. The filtrate was evaporated to yield an oil, which solidified on treatment with perchloric acid. The compound was recrystallized from dilute perchloric acid. *Anal.* Calcd for $[CoC_5H_{26}N_5O_2S](ClO_4)_3 \cdot H_2O$: C, 9.9; H, 4.6; N, 13.8; Co, 9.7. Found: C, 9.9; H, 4.4; N, 13.7; Co, 9.7.

$[Co(NH_3)_5(L\text{-}proH)]I_3 \cdot 3H_2O$.—The solution of the reactants (large excess of L-proline) was evaporated at 50–55° almost to dryness. Water was added to dissolve any solid, and a concentrated solution of potassium iodide was added. Precipitated potassium perchlorate was filtered off, and, on cooling the filtrate in ice, the complex iodide separated out and was recrystallized from a small volume of warm water. *Anal.* Calcd for $[CoC_5H_{24}N_5O_2]I_3 \cdot 3H_2O$: C, 8.7; H, 4.4; N, 12.1. Found: C, 8.7; H, 4.5; N, 12.0.

$[Co(NH_3)_5(L\text{-}tryH)](ClO_4)_3$.—A solution of the reactants in boiled out dilute perchloric acid was heated at 75–85° under a nitrogen atmosphere for 6.5 hr. Aqueous ammonia was added with stirring to precipitate the excess ligand, care being taken to keep the pH below 7. The complex, which was obtained from the concentrated filtrate on cooling, was recrystallized from a sodium perchlorate solution. *Anal.* Calcd for $[CoC_9H_{26}N_5O_3](ClO_4)_3$: C, 17.3; H, 4.2; N, 13.5. Found: C, 17.6; H, 4.6; N, 13.8.

(1) For a preliminary report of this work see C. J. Hawkins and P. J. Lawson, *Chem. Commun.*, 177 (1968).

(2) J. Fujita, T. Yasui, and Y. Shimura, *Bull. Chem. Soc. Japan*, **38**, 654 (1965); T. Yasui, J. Hidaka, and Y. Shimura, *ibid.*, **39**, 2417 (1966).

(3) The following abbreviations are used: alanine, alaH; leucine, leuH; phenylalanine, pheH; phenylglycine, phgH; methionine, metH; tyrosine, tyrH; asparagine, asnH; proline, proH; tryptophan, trpH; histidine, hisH.

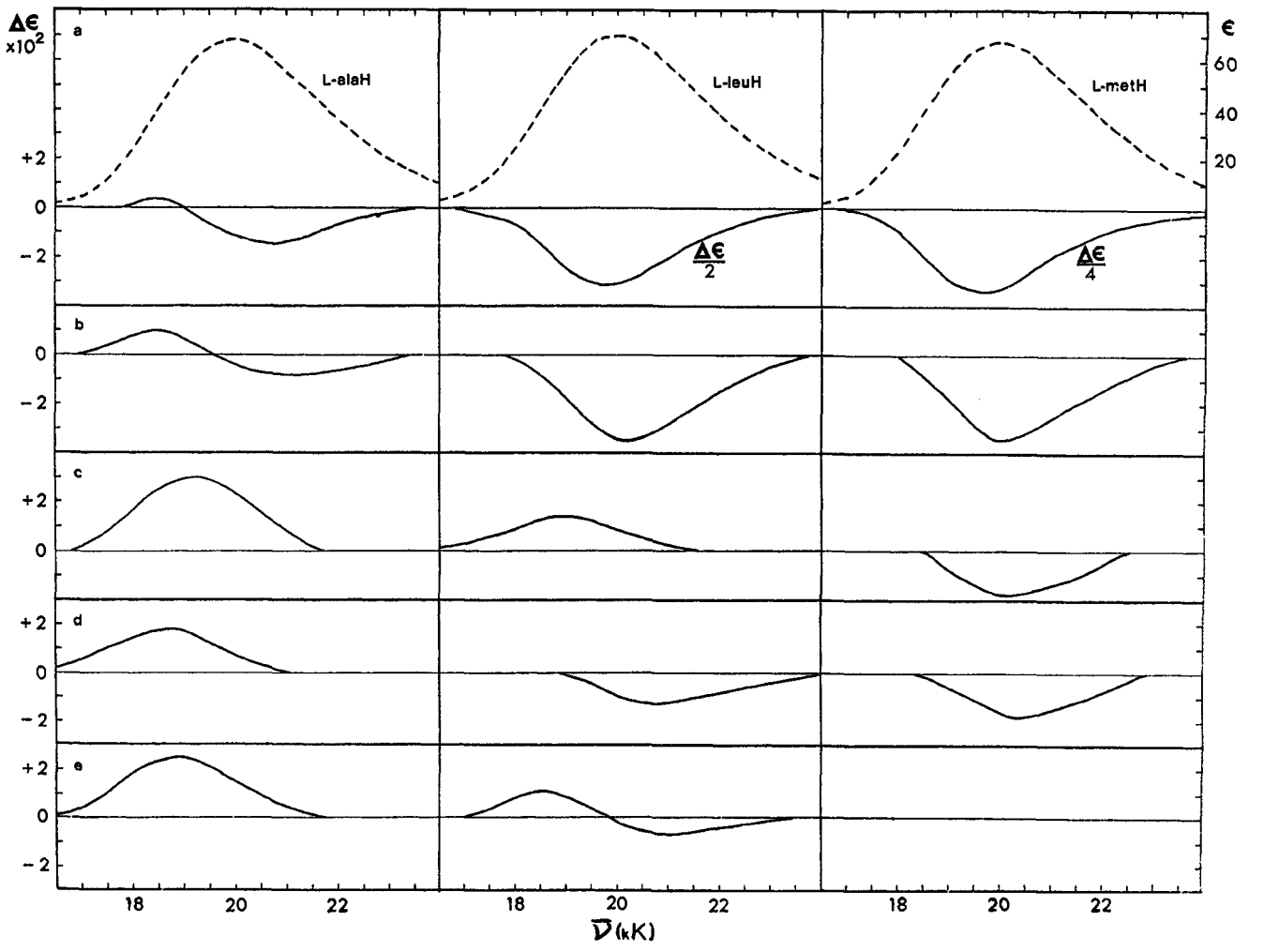

Figure 1.—Absorption (- - -) and circular dichroism (——) spectra of $Co(NH_3)_5$(L-amH)$^{3+}$ in (a) water, (b) 1 *M* aqueous ammonia, (c) 0.05 *M* sodium sulfate, (d) 0.05 *M* sodium phosphate, and (e) 0.05 *M* potassium selenite.

[Co(NH$_3$)$_5$(L-trpH)](ClO$_4$)$_3$·2H$_2$O.—[Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ and L-tryptophan were dissolved in boiled out dilute perchloric acid solution, and the reaction mixture was heated at 80–90° under a nitrogen atmosphere for 3.5 hr. The solution was cooled and evaporated to low volume. Precipitated impurities were filtered off, and the filtrate was passed down a perchlorate anion exchange column. The eluate was acidified with perchloric acid and cooled in ice to precipitate the product, which was recrystallized a number of times from a sodium perchlorate solution and finally from warm water. *Anal.* Calcd for [Co-$C_{11}H_{27}N_7O_2$](ClO$_4$)$_3$·2H$_2$O: C, 19.4; H, 4.6; N, 14.4. Found: C, 19.3; H, 4.7; N, 14.3.

[Co(NH$_3$)$_5$(L-hisH)](ClO$_4$)$_3$·2.5H$_2$O—L-Histidine hydrochloride was treated with a solution of silver perchlorate to remove the chloride ion. [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ and a few drops of perchloric acid were added to the solution, and the temperature was raised to 80–90° for 4 hr. The product crystallized on cooling and was recrystallized from a sodium perchlorate solution. *Anal.* Calcd for [$CoC_6H_{23}N_8O_2$](ClO$_4$)$_3$·2.5H$_2$O: C, 11.2; H, 4.4; Co, 9.2. Found: C, 11.2; H, 4.3; Co, 9.1.

[Co(NH$_3$)$_5$(L-asnH)](ClO$_4$)$_3$·H$_2$O.—The reaction was carried out at 60–65° for 8 hr. The resulting solution was evaporated to small volume, treated with a few drops of perchloric acid, and cooled in ice. Three fractions were isolated; the first which showed no optical activity was discarded and the remainder was combined and recrystallized by dissolution in warm 30% perchloric acid, followed by filtration and precipitation with alcohol. *Anal.* Calcd for [$CoC_4H_{23}N_7O_3$](ClO$_4$)·H$_2$O: C, 8.1; H, 4.3; N, 16.6. Found: C, 8.0; H, 4.2; N, 16.7.

[Co(NH$_3$)$_5$(D-phgH)](ClO$_4$)$_3$.—The reaction with phenylglycine was carried out at 85–90° for 2.5 hr. After cooling, some impurities were filtered off, and the filtrate was treated with sodium iodide to precipitate fractionally iodide salts. The first two fractions showed no optical activity and were discarded. The remainder, which were found to be optically active, were combined and treated with a silver perchlorate solution to remove the iodide. The resulting filtrate was treated with methanol and ether. The first precipitate was discarded. After the addition of a large volume of ether, the desired complex precipitated and was recrystallized from an aqueous methanol solution by the addition of ether. *Anal.* Calcd for [CoC_8-$H_{24}N_6O_2$](ClO$_4$)$_3$: C, 16.2; H, 4.1; N, 14.2. Found: C, 16.2; H, 4.4; N, 14.0.

Absorption and Circular Dichroism Spectra.—Absorption spectra were measured with a Cary 14 spectrophotometer, and the CD spectra were measured with a Roussel Jouan Model B Dichrograph with a maximum sensitivity of 1.5×10^{-5}. The complexes were studied at 1×10^{-2} *M* concentrations. The data for the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption band are recorded in Figures 1–3 and in Table I.

The T_{1g} absorption band of $Co(NH_3)_5$(L-alaH)$^{3+}$ in water was subjected to a Gaussian analysis to determine the tetragonal splitting of this band and the positions of the two components. A computer program developed by Mr. C. L. Wong of this department was utilized, and the results obtained were as follows: $\bar{\nu}_1$ = 19.70 kK, δ_1 = 1.45 kK, ϵ_1 = 60.0; $\bar{\nu}_2$ = 21.85 kK, δ_2 = 1.60 kK, ϵ_2 = 26.0.

Acid Dissociation Constants.—These were determined by

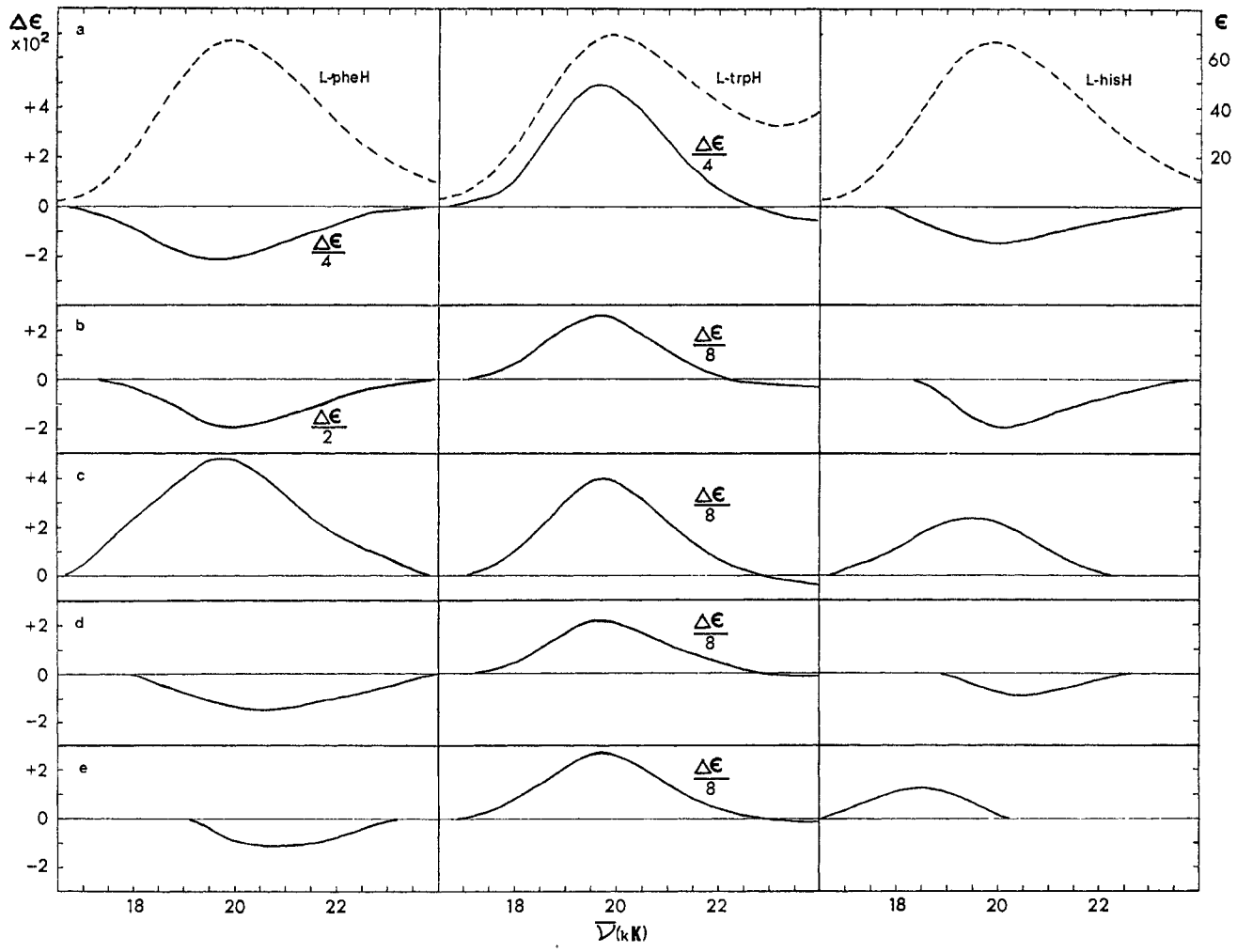

Figure 2.—Absorption (- - -) and circular dichroism (——) spectra of $Co(NH_3)_5(L\text{-amH})^{3+}$ in (a) water, (b) 1 *M* aqueous ammonia, (c) 0.05 *M* sodium sulfate, (d) 0.05 *M* sodium phosphate, and (e) 0.05 *M* potassium selenite.

TABLE I

ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF $[Co(NH_3)_5(amH)](ClO_4)_3$[a]

Amino acid	In H_2O				In 1 *M* NH_3			
	Absorption		CD		Absorption		CD	
	$\bar{\nu}$, kK	ε	$\bar{\nu}$, kK	$\Delta\varepsilon$	$\bar{\nu}$, kK	ε	$\bar{\nu}$, kK	$\Delta\varepsilon$
L-alaH	19.96	68.4	18.45	+0.003	19.92	74.6	18.52	+0.011
	28.57	53.9	20.70	−0.015			21.14	−0.008
L-leuH	19.94	69.9	19.70	−0.063	19.90	74.8	20.12	−0.035
	28.53	56.7						
L-pheH	19.94	67.5	19.70	−0.086	19.92	72.2	20.00	−0.040
	28.65	55.4						
L-metH	20.00	68.0	19.70	−0.137	19.90	75.1	20.12	−0.035
	28.57	54.2						
L-proH	19.94	67.4	19.05	+0.026	19.90	76.0	19.49	+0.041
	28.57	55.7						
L-tyrH	19.96	70.9	19.70	−0.70	20.83[b]	50.6	19.61	−0.064
L-trpH	19.96	69.8	19.70	+0.196	19.96	72.8	19.61	+0.209
L-hisH	19.96	66.9	20.00	−0.015	19.92	73.1	20.20	−0.019
	28.57	53.8						
L-asnH	19.98	69.2	19.80	−0.120	19.90	77.3	19.70	−0.091
	28.57	55.9						
D-phgH	20.00	70.1	20.12	+0.074	19.92	74.7	18.78	−0.042
	28.90[b]	66.3						

[a] If isolated as the halide, the complex was converted quantitatively to the perchlorate with silver perchlorate. [b] Shoulder.

titrating the complexes under nitrogen with 0.2 *M* carbonate-free sodium hydroxide at 20.0° using a Radiometer pH meter, Model 4. The pK_a values are "thermodynamic" constants; the activity coefficients of the complexes were calculated from the Güntelberg modified Debye–Hückel relationship[4]

$$-\log f_i = Az_i^2 I^{1/2}/(1 + I^{1/2})$$

(4) E. Güntelberg, *Z. Physik. Chem.*, **123**, 199 (1926).

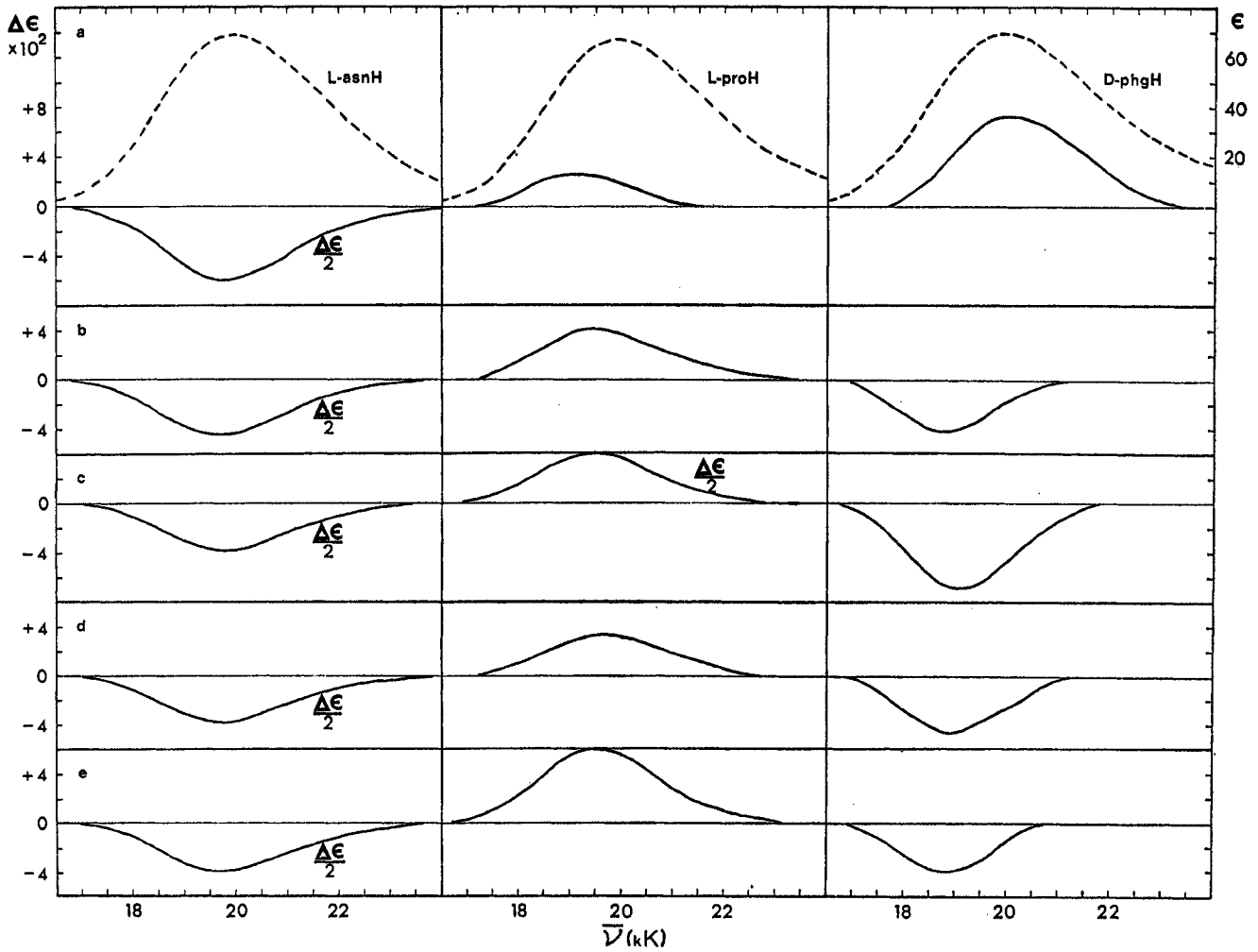

Figure 3.—Absorption (- - -) and circular dichroism (——) spectra of $Co(NH_3)_5(L\text{-amH})^{3+}$ in (a) water, (b) 1 *M* aqueous ammonia, (c) 0.05 *M* sodium sulfate, (d) 0.05 *M* sodium phosphate, and (e) 0.05 *M* potassium selenite.

where z_i is the charge on the species i, and I is the ionic strength. The results are tabulated in Table II along with published pK_{a2} values of the free amino acids.

TABLE II

ACID DISSOCIATION CONSTANTS (WITH STANDARD DEVIATION) OF $Co(NH_3)_5(amH)^{3+}$ IN WATER AT 20°

	Constants	
Ligand	Complex	Amino acid[a]
L-alaH	8.424 ± 0.004	10.006
L-leuH	8.136 ± 0.002	9.744[b]
L-pheH	7.645 ± 0.006	9.34
L-metH	7.056 ± 0.010	9.20
L-proH	9.032 ± 0.005	10.71
L-tyrH	7.594	9.21
	9.105	10.47
L-trpH	7.795 ± 0.009	9.57
L-hisH	4.653 ± 0.003	6.04
	7.900 ± 0.010	9.24
L-asnH	7.347 ± 0.004	8.88
D-phgH	7.356 ± 0.011	9.028[c]

[a] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co. Ltd., London, 1965. [b] Determined at 25°. [c] C. J. Hawkins and C. L. Wong, unpublished data.

Discussion

In carboxylatopentaamminecobalt(III) complexes, the cobalt chromophore has a holohedrized tetragonal symmetry, under which the cubic $^1T_{1g}$ absorption band is split to give a doubly degenerate E_g band at low energy and an A_{2g} transition at higher energy. According to various models,[5] this splitting is approximately given by

$$\Delta E_{tet} = {}^1/_4(\Delta_{NH_3} - \Delta_{COO^-})$$

where Δ_{NH_3} and Δ_{COO^-} are the ligand field splitting parameters for the octahedral ammine and carboxylato complexes. The value of 1.38 calculated for ΔE_{tet} from literature Δ values[6] is considerably less than the value of 2.1 kk determined from the Gaussian analysis of the alanine complex. The latter figure is thought to be more correct because the computed absorption curve for the Gaussian analysis corresponded very closely to the experimental curve (the standard deviation in ϵ over the whole band was 0.7) and because the value of 2.15 kK is similar to the expected value of approximately half the splitting observed[2] for *trans*-bis(alaninato)bis(ethylenediamine)cobalt(III). The discrepancy between the two values probably arises from inaccuracies in the published values of Δ and from the configura-

(5) See, for example, C. E. Schaffer and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **34** (13), 1 (1965).

(6) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 244.

tional interaction between the $E_g(T_{1g})$ and $E_g(T_{2g})$ energy levels.

Although the tetragonal symmetry can adequately account for the features of the absorption spectra, the low symmetry of the molecules would remove the degeneracy of the E_g band to give two nondegenerate transitions, Γ_a and Γ_b. The size of the splitting of the E_g band is unknown; however, from the CD spectra, it would seem to be very small, but, nevertheless, real.

The addition of polarizable oxyanions such as sulfate, phosphate, and selenite are known for some systems to have a dramatic effect on the CD spectra of metal complexes.[7] For example, in tris(diamine) complexes, the addition of these anions makes the $A_2(D_3)$ component of the T_{1g} band increase in size relative to the $E(D_3)$. Because most of the complexes under investigation showed only one Cotton effect under the T_{1g} band when studied in water, it was decided to add various salts in an attempt to alter the relative rotational strengths of the three components. This proved to be most successful. Although the effects on the CD spectra were quite marked, the addition of sulfate, phosphate, and selenite salts had a negligible effect on the energy of the T_{1g} band. The extinction coefficients were also little affected by sulfate, but phosphate and selenite resulted in an increase (about 10%) in the extinction coefficients for the T_{1g} bands, and the T_{2g} bands became masked by large charge-transfer bands.

Most of the complexes in water had a negative Cotton effect at about 19.7 kK, the estimated position of the E_g band.[8] However, the negative bands for phenylglycine and histidine were at slightly higher energy, and positive Cotton effects were observed for alanine, proline, and tryptophan. For the alanine complex, the positive band occurred at 18.45 kK and was followed by a negative band at 20.70 kK. For proline and tryptophan only one band was observed at 19.05 and 19.70 kK, respectively. In the light of the following discussion, these results can be rationalized in the following way. The two E_g components have opposite signs with the positive Cotton effect (Γ_a) at lower energy, and, although the $A_{2g}(D_{4h})$ transition is not explicitly observed, it would appear to have a negative Cotton effect. For the leucine, asparagine, methionine, phenylalanine, and tyrosine complexes, the Γ_b transition is dominant. The Γ_a component is completely cancelled, and the A_{2g} transition simply contributes to the high-energy tail of the band. In histidine and phenylglycine the rotational strength of Γ_a becomes slightly larger relative to Γ_b, and the additional cancellation of Γ_b moves it to higher energy. In the alanine complex, the two E_g components are almost equivalent. The cancellation leads to a small positive band appearing at low energy and a sm all negative band appearing at high energy. For proline and tryptophan, the Γ_a transition dominates the CD. The dominance is complete for tryptophan as its maximum occurs at the energy of the E_g band.

When the CD spectra are measured in 0.05 *M* sodium sulfate, the rotational strength of the Γ_a transition increases relative to Γ_b. Positive Cotton effects are observed for all of the complexes except those of asparagine and methionine. However, for these two complexes, the observed negative CD bands have been reduced in size, and, for methionine, the negative has moved to higher energy. The change in the spectra on adding sodium sulfate is most marked for phenylalanine and tyrosine. Whereas in water a negative Cotton effect is observed at 19.7 kK, in the sodium sulfate solution a positive band occurs at the same energy. For tryptophan, the observed positive CD band simply increases in size without moving its position, showing the complete dominance of the Γ_a component. The positions of the Cotton effects for the various amino acids support the postulate that Γ_a is at lower energy than Γ_b.

When aqueous ammonia is added to solutions of the amino acid complexes, the $-NH_3^+$ groups are neutralized. This has the effect of decreasing the size of the measured Cotton effects and, in some cases, shifting their energy. These changes can be rationalized by an increase in the rotational strength of Γ_a relative to Γ_b. No decomposition took place in the ammonia solution as the protonated complex could be regenerated quantitatively even after 24 hr.

The addition of phosphate and selenite has two distinctly different effects. First, the two anions are bases with pK_a values of about 12 and 8, respectively. From the acid dissociation constants of the amino acid complexes given in Table II it is obvious that these anions must neutralize the NH_3^+ groups. Second, the two anions interact with the neutralized complexes and further alter the observed CD spectra. Again the Γ_a transition is found to be increased relative to Γ_b. A variety of peak patterns are observed. For the complexes with phenylalanine, methionine, histidine, and leucine with phosphate, it would appear that Γ_a and Γ_b are almost completely cancelled, and the observed negative band at about 20.5 kK derives mainly from the A_{2g} component.

The interactions of ammonia and phosphate with the tyrosine complex not only remove the $-NH_3^+$ proton but also deprotonate the phenolic group. The consequent delocalization of electrons causes a strong absorption band to overlap the T_{1g} region making the T_{1g} band appear as little more than a shoulder. The positions and relative sizes of the CD bands are strongly affected by the Cotton effects under the charge-transfer bands.

Because the measurement of CD of complexes in KBr disks has proven useful for the interpretation of the CD of some related complexes,[9] a number of the above complexes were studied in this isotropic medium. All showed a large positive Cotton effect under the T_{1g} band. Al-

(7) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966); S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 339 (1964); *Chem. Commun.*, 73 (1965); J. R. Gollogly and C. J. Hawkins, *ibid.*, 689 (1968).

(8) For the sake of simplicity, the results for D-phenylglycine will be inverted so that in the following discussion the CD of only L-amino acids will be considered.

(9) C. J. Hawkins and C. L. Wong, to be submitted for publication.

though the spectra sharpened on cooling to −190°, only one Cotton effect was still observed, probably due to the relatively small energy differences between the three components.

From the above discussion it is apparent that the observed CD spectra can be rationalized in terms of a vicinal effect from the L-amino acids imposing Cotton effects of opposite sign onto the two components of the E_g band, with the positive Cotton effect at lower energy. Unfortunately, the tetragonal splitting of the first cubic absorption band is not sufficiently large to enable the sign of the Cotton effect of the $A_{1g} \rightarrow A_{2g}$ (D_{4h}) transition to be assigned unambiguously. Nevertheless, the general shape of the observed CD bands and, for some spectra, the position of the high-energy negative Cotton effect suggest that this transition has a negative Cotton effect. This is supported by a study[2] of complexes of the type *trans*-$Co(en)_2(L\text{-}amH)_2^{3+}$, which also have a tetragonal chromophore with the E_g transition at the lower energy. For these complexes, the tetragonal splitting is twice that for the monocarboxylato complexes, and the E_g and A_{2g} components are visibly separated in the absorption spectra. For L-alanine and L-proline, two negative bands are clearly observable under the T_{1g} band, with one directly under the A_{2g} absorption band.

In theory, the signs of the Cotton effects of the d–d transitions of these pentaamminecobalt(III) complexes could be used to assign an absolute configuration to a new α-amino acid. However, in practice, this method is handicapped by the large variation in the observed Cotton effects. This type of system has previously been proposed for the determination of the absolute configuration of α-substituted carboxylates.[10] However, Dunlop and Gillard's proposal that the sign of the dominant Cotton effect for the T_{1g} band is indicative of the absolute configuration would seem to have no foundation.

Acknowledgment.—The authors gratefully acknowledge financial support from the Australian Research Grants Committee and record their appreciation for the assistance given by Mr. C. L. Wong.

(10) J. H. Dunlop and R. D. Gillard, *Tetrahedron*, **28**, 349 (1967).

CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, A.C.T. 2600, AUSTRALIA

Cobalt(III)-Promoted Hydrolysis of Glycine Ethyl Ester. Hg^{2+}-Induced Acid Hydrolysis and Base Hydrolysis of the β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ Ion

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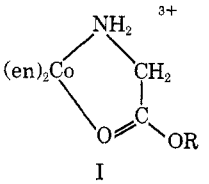
Hg^{2+}-induced acid hydrolysis of β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ follows the rate law $k_{obsd} = k[Hg^{2+}]$, with $k = 1.0 \times 10^{-2}\ M^{-1}$ sec^{-1} at 25°, $\mu = 1.0$. Full retention of configuration is observed, and ^{18}O-tracer studies enable the two positions for oxygen in the β_2-$Co(trien)gly^{2+}$ product to be distinguished. Base hydrolysis of β_2-$Co(trien)Cl(glyOC_2H_5)^{2+}$ follows the rate law $k_{obsd} = k[OH^-]$, with $k = 2.2 \times 10^5\ M^{-1}\,sec^{-1}$ at 25°, $\mu = 1.0$. Full retention of configuration about the metal is observed. Base hydrolysis in ^{18}O-labeled solvent shows that 84% of the β_2-$Co(trien)gly^{2+}$ product arises from coordination of the ester carbonyl oxygen, while the remainder is produced by intervention of a solvent oxygen atom in the bridging position. The latter path is interpreted as an internal nucleophilic displacement of the ester moiety by bound OH^- ion. Visible, CD, and ORD spectra are presented for $D(+)_{589}$-(*SS*)-β_2-$[Co(trien)Cl(glyOC_2H_5)](ClO_4)_2 \cdot 0.5H_2O$.

Introduction

In a recent publication it was demonstrated that the Hg^{2+}- and HOCl-induced removal of bromide from $Co(en)_2Br(glyOR)^{2+}$ (R = CH_3, $CH(CH_3)_2$) leads to the formation of the chelated ester intermediate $Co(en)_2(glyOR)^{3+}$ (I) in which the oxygen atom bound



I

to cobalt is derived from the carbonyl oxygen atom of the monodentate ester. Tracer experiments were used to distinguish between the two oxygen atoms of the chelated glycinate anion of $Co(en)_2gly^{2+}$ formed on acid hydrolysis of I, and the results demonstrated that ester hydrolysis proceeded without opening of the chelate ring.[1]

In a separate investigation it was proposed that $Co(en)_2gly^{2+}$ formed by base hydrolysis of $Co(en)_2Br(glyOCH(CH_3)_2)^{2+}$ arose from two paths. About half was produced by incorpation of the ester carbonyl oxygen to form the intermediate given by structure I, while the second path was attributed to coordination of hydroxide ion to form $Co(en)_2OH(glyOCH(CH_3)_2)^{2+}$, followed by internal attack by the bound hydroxide at the carbonyl center.[2]

(1) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6032 (1968).

(2) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **91**, 4102 (1969).