The extent to which the empty p_z orbital can be utilized for higher coordination depends upon a number of factors, most of which are controlled by the effective nuclear charge.[17]

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Some (L-Aminoacido)triethylenetetraminecobalt(III) Iodides[1]

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The preparation of seven stable crystalline complex compounds of the type $[Co(trien)(L\text{-aminoacido})]I_2 \cdot H_2O$ is reported. The cations of these complexes are assumed to be α forms, although conclusive evidence is lacking. Existence of diastereoisomers is demonstrated and separation of some pairs of isomers is achieved simply by successive fractionations. The equilibration of optical isomers with activated charcoal and the effect of coordination on the optical activity of the L-amino acid are discussed. Infrared and electronic spectra are also presented.

Inorganic complexes of the quadridentate ligand triethylenetetramine have recently been prepared and their geometrical isomers identified.[4-7] The present paper reports the preparation and properties of seven complexes of the type $[Co(trien)(L\text{-AA})]I_2 \cdot H_2O$, in which L-AA refers to an L-amino acid anion.

Experimental Section

Reagents.—*cis*-Dichlorotriethylenetetraminecobalt(III) chloride was prepared by the methods of Basolo[4] and Bailar.[5] Both methods yielded products with identical infrared and visible–ultraviolet spectra. The amino acids were purchased from Nutritional Biochemicals Corp., Cleveland, Ohio, and used as received.

Preparation of Complexes.—L-Amino acid (0.03 mole) was dissolved in 50 ml of water containing NaOH (0.03 mole) at 60° by magnetic stirring, after which solid *cis*-α-$[Co(trien)Cl_2]Cl$ (0.03 mole) was added. The solution was filtered while warm, and an excess of solid sodium iodide (0.1 mole) was added. The solution was cooled in an ice bath for a few minutes after which crystallization was induced by scratching with a glass rod, and the beaker was stored in a refrigerator for several hours. The crystals were collected and washed with ethanol and acetone. Purification of the product was accomplished by recrystallization from aqueous sodium iodide solutions. The purified compound was dried in a heated vacuum desiccator at 40° overnight.

In the preparation of L-methioninato, L-tyrosinato, and L-phenylalaninato complexes, slight modifications of the procedure were made. In preparing the L-methioninato complex, after treatment with sodium iodide, the resulting solution crystallized slowly on standing at room temperature for 4 hr. Chilling was avoided because this led to the formation of a rubberlike precipitate. In the case of the other two complexes, a saturated solution of sodium iodide was added slowly with stirring to effect precipitation. Addition of solid sodium iodide in this case led to the formation of a rubberlike precipitate.

Fractionation of the Complexes.—The procedure was essentially the same as described in the preparation of the complexes, except in the manner in which the sodium iodide was added. The first precipitate was obtained by adding 0.02 mole of solid sodium iodide and allowing the solution to stand overnight. To the first filtrate was then added 0.02 mole of sodium iodide to obtain a second precipitate. The third precipitate likewise was obtained from the second filtrate. All isolated fractions were recrystallized and washed with ethanol and acetone and dried in a heated vacuum desiccator before measurement of optical rotation.

Equilibration of the Diastereoisomers.—A 0.1% aqueous solution (400 ml) was prepared from each of the fractionated products. Each solution was divided into four equal portions. Activated charcoal (0.05 g) was added to two portions, one of which was shaken at room temperature. A charcoal-free portion was also shaken at room temperature. Likewise, two portions, one containing charcoal, were loosely stoppered and warmed on steam baths. Optical rotations were measured after 20, 60 min, etc.

Optical Rotations.—Optical activities of the complexes were measured on aqueous solutions in a 1-dm tube with a Rudolph 80 precision polarimeter equipped with a mercury-vapor lamp and green filter. Each rotation reported was based on an average of ten readings. A determination of water blank was made before each measurement.

Infrared Spectra.—Spectra for the range 2.5–16 μ were obtained using a Perkin-Elmer Model 237 grating infrared spectrophotometer. Both Nujol-mull and KBr-disk tenchniques were used. Nujol mull spectra for the range 15–35 μ were obtained using a Perkin-Elmer Model 21 recording spectrophotometer with cesium bromide optics.

Electronic Spectra.—Visible and ultraviolet spectra were recorded by Beckman DK-1 and Hitachi Perkin-Elmer Model 139 spectrophotometers. Samples were prepared as aqueous solutions.

Results and Discussion

Preparation of the Complexes.—Analytical data of the (L-aminoacido)triethylenetetraminecobalt(III) iodides are summarized in Table I. The yields ranged from 25 to 60%. The crystalline complexes had characteristic colors of orange-red to brick-red similar to

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[1] The letters D and L refer to the configuration of the amino acid, whereas *d*, *l*, +, and − refer to the optical rotation. Trien refers to triethylenetetramine; en refers to ethylenediamine.

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[7] D. A. Buckingham and D. Jones, *ibid.*, **4**, 1387 (1965).

Table I

(L-Aminoacido)triethylenetetraminecobalt(III) Iodides

Complex	% I Calcd	% I Found	% C Calcd	% C Found	% N Calcd	% N Found	% H Calcd	% H Found
$[Co(C_6H_{18}N_4)(C_5H_{10}NO_2)]I_2 \cdot H_2O$	42.8	42.8	22.3	22.1	11.8	11.2	5.1	5.1
(L-valinato)		42.8		22.1		10.9		5.2
$[Co(C_6H_{18}N_4)(C_6H_{12}NO_2)]I_2 \cdot H_2O$	41.8	41.4	23.7	23.7	11.5	11.8	5.3	5.4
(L-leucinato)		41.5		23.6		11.1		5.4
$[Co(C_6H_{18}N_4)(C_3H_6NO_2)]I_2 \cdot H_2O$	45.0	44.1	19.2	19.3	12.4	11.3	4.6	5.4
(L-alaninato)		43.9		19.1		11.2		5.3
$[Co(C_6H_{18}N_4)(C_9H_{10}NO_2)]I_2 \cdot H_2O$	39.6	38.3	28.1	28.1	10.9	10.5	4.7	5.1
(L-phenylalaninato)		38.0		27.9		10.1		5.2
$[Co(C_6H_{18}N_4)(C_9H_{10}NO_3)]I_2 \cdot H_2O$	38.7	38.1	27.4	27.4	10.7	10.4	4.6	4.8
(L-tyrosinato)		38.1		27.7		10.3		5.0
$[Co(C_6H_{18}N_4)(C_5H_8NO_2)]I_2 \cdot H_2O$	43.0	42.5	22.4	22.6	11.8	11.9	4.7	4.8
(L-prolinato)		42.4		23.0		11.6		4.8
$[Co(C_6H_{18}N_4)(C_5H_{10}NO_2S)]I_2 \cdot H_2O$	40.6	40.5	21.2	21.1	11.2	11.1	4.8	4.9
(L-methioninato)		39.3		21.1		11.0		5.0

complexes of the type [Co(en)$_2$(L-aminoacido)]I$_2$. Though the crude products were contaminated with impurities, one recrystallization was enough to give fairly pure products. The compounds were quite stable in aqueous solutions even upon heating for hours on a steam bath.

Fractionation of the Complexes.—The appreciable difference in solubility of optical isomers containing a single optically active bidentate ligand has seldom been reported. Jonassen, Bailar, and Huffman[8] reported that partial separation of the isomers of [Co(en)$_2$(*d*-tart)]$^+$ could be obtained by fractionation as bromides. The seven amino acids used in the preparation of the complexes reported here are themselves optically active, and their corresponding complexes are expected to exist as pairs of "internal" diastereoisomers. Some pairs of these optical isomers show remarkable differences in solubility which have made possible the separation of isomers by fractionation. The results are shown in Table II.

Table II

Specific Rotations[a] of the Fractionated Complexes [Co(trien)(L-AA)]I$_2$

L-AA	Fraction no. 1	2	3
L-Proline	−460	−453	−451
L-Methionine	−510	−81	+330
L-Phenylalanine	−446	−179	−49

[a] Measured at 546 mμ.

H. J. H. has previously separated the isomers of [Co(en)$_2$(L-prolinato)]I$_2$·H$_2$O by fractionation and found that the separation was excellent.[9] The optical rotation of the fractionated levorotatory product agreed exactly with that of the resolved product obtained by using potassium antimonyl-*d*-tartrate as the resolving agent.[9] The isolated fractions of [Co(trien)(L-prolinato)]I$_2$·H$_2$O were highly levorotatory and had no significant difference in values of rotations. The filtrate that remained was found to be dextrorotatory. All attempts to isolate the *d* isomer failed. The fact that there were no intermediate fractions with rotations indicative of blending of *d* and *l* isomers as in the case of the L-phenylalaninato complex led us to assume that a nearly perfect separation of the isomers had been obtained.

The results for [Co(trien)(L-methioninato)]I$_2$·H$_2$O can be interpreted by assuming that the solubility difference between diastereoisomers was smaller than in the case of the L-prolinato complex. The first fraction isolated was highly levorotatory and the value for rotation was reproduced after recrystallization. The second and the third fractions were found to be more dextrorotatory; the fraction with the highest dextrorotatory power had a specific rotation of +330°. The first fraction and this most dextrorotatory fraction were assumed to be nearly pure *l* and *d* isomers as rationalized in the following section.

Diastereoisomers of some complexes, such as L-valinato and L-alaninato complexes, did not have appreciable differences in solubility and the separation of isomers by means of fractionation was not satisfactory.

Equilibration of the Diastereoisomers.—Douglas[10] has used activated charcoal to catalyze the racemization of *d*-[Co(en)$_3$]$^{3+}$. In the investigation reported here, the amount of activated charcoal used as catalyst was kept at a minimum to avoid significant adsorption of complexes. This was assured by no detectable loss in absorbance at the wavelength of maximum absorption. Results for *d*- and *l*-[Co(trien)(L-methioninato)]I$_2$·H$_2$O are shown in Figure 1. From Figure 1 it is apparent that an equilibrium state is established after heating for 3 hr at the steam bath temperature with activated charcoal. Additional data for other complexes followed the same pattern.

A question of greater interest, however, is the composition of the equilibrium mixture. The equilibrium mixtures are always levorotatory with specific rotations of −90 ± 2° if one equilibrates solutions of either the fraction with rotation of +330° or the fraction with rotation of −510°. The most plausible explanation assumes that the fraction with specific rotation of +330° and the fraction with specific rotation of −510° are nearly pure *d* isomer and nearly pure *l* isomer, respectively, and that the levorotatory equilibrium

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[8] H. B. Jonassen, J. C. Bailar, Jr., and E. H. Huffman, *J. Am. Chem. Soc.*, **70**, 756 (1948).

[9] H. J. Hu, M.S. Thesis, North Texas State University, Jan 1966.

[10] B. E. Douglas, *J. Am. Chem. Soc.*, **76**, 1020 (1954).

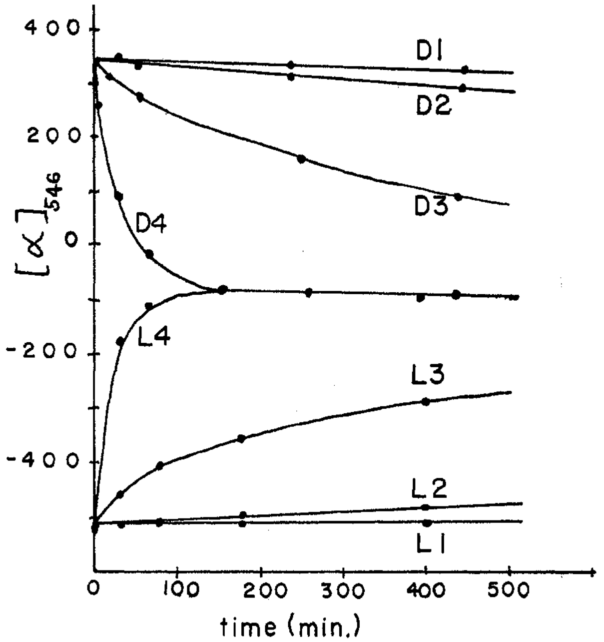

Figure 1.—Equilibrations of *l*- and *d*-[Co(trien)(L-methioninato)]$I_2 \cdot H_2O$: D, *d* isomer, $[\alpha]_{546}$ +330°; L, *l* isomer, $[\alpha]_{546}$ −510°; 1, without charcoal, room temperature; 2, without charcoal, steam bath temperature; 3, with charcoal, room temperature; 4, with charcoal, steam bath temperature.

mixtures are equimolar in these isomers. According to the following calculation, the equilibrium solution should have a rotation of −90°

$$(0.5)(-510°) + (0.5)(+330°) = -90°$$

If there were no asymmetric center in L-methionine, the specific rotations of the *d* and *l* isomers of [Co(trien)(L-methioninato)]$I_2 \cdot H_2O$ should have the same absolute magnitude. The L-methionine in the coordination sphere, therefore, is calculated to have magnified specific rotation of −90°, which is about 10 times greater than the specific rotation of free L-methionine (−8.1° at 546 mμ).

The conclusions stated in the preceding paragraphs agree with the work of Douglas and Liu, who have resolved some analogous bis(ethylenediamine) complexes.[11] The resolved optical isomers also show surprising differences in their optical activities, which indicates that the asymmetric center of the amino acid has magnified optical activity due to coordination.

Electronic Spectra.—The visible and ultraviolet absorption frequencies of the complexes show two symmetrical bands at 482–484 mμ (ε 135–136) and 345–347 mμ (ε 150–230). The positions of these bands do not vary appreciably throughout the series of complexes. The positions, intensities, and shapes of these two bands are similar to those of many octahedral complexes, especially those of the type $[Co(en)_2(L\text{-}AA)]^{2+}$ reported by Liu and Douglas[11] and other triethylenetetramine complexes prepared by Sargeson and Searle.[6]

Circular dichroism measurements by these two groups have shown that the symmetry of the ethylenediamine and triethylenetetramine complexes probably is distorted from the D_3 symmetry of $[Co(en)_3]^{3+}$, although the absorption spectra show no signs of field splitting. In the absence of CD measurements on the complexes reported here, a detailed interpretation of the electronic spectra seems unjustified.

Infrared Spectra and Configurations of the Complexes.—The cation $[Co(trien)(L\text{-aminoacido})]^{2+}$ may exist as the α or β isomer corresponding to the *cis*-α and *cis*-β isomers of the cation $[Co(trien)Cl_2]^+$.[5,6] The complexes reported here were expected to be *cis*-α forms for several reasons. The starting material $[Co(trien)Cl_2]Cl$, prepared by the method of Basolo, is the α form.[12] An alternate method of preparation described by Bailar yielded an identical product.[5] Furthermore, the cation *cis*-α-$[Co(trien)Cl_2]^+$ has been shown to undergo substitution reactions with retention of configuration.[6]

Buckingham and Jones have indicated that the infrared spectra of cobalt(III) trien complexes may be used to distinguish *cis*-α and *cis*-β forms.[7] Three regions were proposed in which the isomers differ in absorption: (1) the N–H stretching region (3300–3100 cm^{-1}), (2) the NH_2 bending region (1560–1590 cm^{-1}), and (3) the 990–1090-cm^{-1} region. An examination of the spectra of triethylenetetramineaminoacido complexes of cobalt(III) indicates that resolution in region 1 is insufficient to distinguish whether three or four bands occur and that no conclusions may be drawn from that region. Region 2 is also unhelpful to us since the strong carboxylate absorption at 1635 cm^{-1} masks the region in most complexes. It does appear that two of the complexes, L-valinato and L-methionato, have sufficiently resolved spectra to indicate only a single absorption in this region. If this is the case, the complexes would be similar in behavior to the *cis*-α form of $[Co(trien)Cl_2]Cl$.

The complexes investigated by Buckingham and Jones were reported to differ in region 3, the 990–1090-cm^{-1} region, with the *cis*-α form showing *two* strong absorptions while the *cis*-β form shows *four.* The amino acid complexes prepared in this work show *two* medium absorptions at 1085 and 1056 cm^{-1} whose shapes and positions are somewhat reminiscent of two similar bands which one observes for *cis*-α-$[Co(trien)Cl_2]Cl$ in this region. However, the amino acid complexes show an absorption at 990–1000 cm^{-1} which is stronger by comparison than the band found in the dichloride complex at 983 cm^{-1}.

In summary, the spectra of the triethylenetetramine–aminoacido complexes of cobalt(III) prepared by direct substitution of *cis*-α-$[Co(trien)Cl_2]^+$ seem to indicate retention of configuration of the tetramine moiety, although it must be admitted that more conclusive physical evidence is needed.

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