likely to occur because as mentioned above ffars is reluctant to form chelate type complexes.

In contrast the reaction of $CF_3CCo_3(CO)_9$ and ffars in refluxing hexane produces a small amount of some air-stable black crystals which have an elemental analysis corresponding to the formula $Co_4(CO)_8(ffars)_2$. The fate of the CF_3C group is unknown. The mass spectrum of the solid is consistent with the formula. The structure of the solid as determined by X-ray studies[19] is shown in Figure 6. It consists of a tetrahedron of cobalt atoms bridged by two ligands. Because of the absence of bridging carbonyl groups, the structure is related to that of $Ir_4(CO)_{12}$, (T_d symmetry)[20] rather than the carbonyl-bridged (C_{3v}) structures of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$.[21-23] The infrared spectrum of $Co_4(CO)_8(ffars)_2$ has five sharp bands in the terminal carbonyl region and two in the bridging carbonyl region. Thus the structure in solution is probably different. Although there has been some debate[24-26] about the possibility that in solution $Co_4(CO)_{12}$ has a structure (or structures) different from that of the solid state, including a nonbridged structure of T_d symmetry, the ^{59}Co nmr results[27,28] indicate that this is not so.

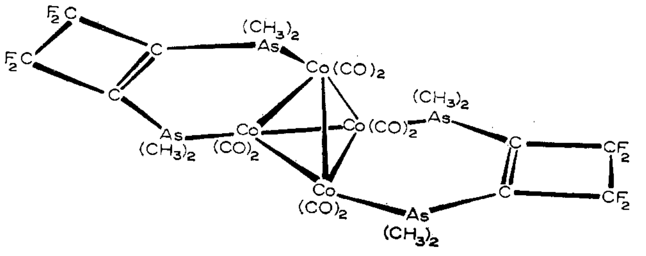

Figure 6.—X-Ray diffraction structure of $(ffars)_2Co_4(CO)_8$ (**13**).

Very few other tertiary phosphine, arsine, or stibine derivatives of $Co_4(CO)_{12}$ have been isolated[29] and only a little more is known about the derivatives of $Ir_4(CO)_{12}$ and $Rh_4(CO)_{12}$.[30,31] It is worth noting that both $Ir_4(CO)_{10}(P(C_6H_5)_3)_2$ and $Ir_4(CO)_9(P(C_6H_5)_3)_3$ have bridging carbonyl groups.

In view of the ease with which $Co_2(CO)_8$ is converted into $Co_4(CO)_{12}$ on warming, we thought that strong heating of $ffarsCo_2(CO)_6$ might yield $(ffars)_2Co_4(CO)_8$ (as mentioned above, Scheme I, mild heating gives ffars $Co_2(CO)_5$). This does not happen.

Acknowledgments.—We wish to thank Mr. B. H. Hoffert for preparing the mixed ligand 1-diphenylphosphino-2-dimethylarsinohexafluorocyclopentene and the National Research Council for financial assistance. Figures were drawn by Beatrix Krizsan.

(19) F. W. B. Einstein and R. Jones, to be submitted for publication.

(20) G. R. Wilkes and L. F. Dahl quoted in C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(21) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).

(22) P. Corradini, *Ric. Sci.*, **36**, 188 (1966).

(23) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 4792 (1967).

(24) F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1882 (1960).

(25) D. L. Smith, *J. Chem. Phys.*, **42**, 1460 (1965).

(26) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(27) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

(28) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(29) S. Cetini, O. Gambino, R. Rossetti, and P. L. Stangellini, *Inorg. Chem.*, **7**, 609 (1968).

(30) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967).

(31) R. Whyman, *ibid.*, 230 (1970).

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Mixed-Ligand Complexes of Cobalt(III). Chelated (Amino acid)(tetramine)cobalt(III) Complexes

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The syntheses, resolution, and properties of some cobalt(III) complexes with 1,3-diaminopropane (tn) and with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine, alanine, valine, and sarcosine are reported. The tetramine ligands exhibit marked topological specificity; α-Co(3,2,3-tet)aa^{2+} and β_2-Co(2,3,2-tet)aa^{2+} appear to be formed exclusively under the conditions of these syntheses.

Introduction

We have described the synthesis and properties of some *trans*-bis(amino acid)(tetramine)cobalt(III) complexes.[1] The *trans*-bis(amino acid)(tetramine) complexes react in warm alkaline solution to produce chelated amino acid complexes as the ultimate product. We have prepared and characterized some mixed-ligand complexes with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine, alanine, valine, and sarcosine. These chelated amino acid complexes clearly define the products of the rearrangement

$$trans\text{-Co(tet)(aa)}_2^{+} \longrightarrow cis\text{-Co(tet)(aa)}^{2+} + \text{aa}^{-}$$

The details of the steric course of these reactions are now under study.

Experimental Section

Syntheses.—The preparations of the tetramine ligands 3,7-diaza-1,9-nonanediamine and 4,7-diaza-1,10-decanediamine and of the complexes *trans*-dichloro(3,7-diaza-1,9-nonanediamine)-

(1) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, **10**, 811 (1971).

cobalt(III) chloride and *trans*-dichloro(4,7-diaza-1,10-decanediamine)cobalt(III) chloride have been described previously.[1]

Preparation of α-Glycinato(4,7-diaza-1,10-decanediamine)cobalt(III) Iodide, α-[Co(3,2,3-tet)gly]I_2.—Equimolar amounts of *trans*-[Co(3,2,3-tet)Cl_2]Cl and glycine were dissolved in water and the solution was adjusted to pH 5.5 with 5 *M* NaOH. The solution was then heated on a steam bath for 1 hr with checks to make sure the pH remained about 5.5. The pH was then adjusted to 8.5 and heating continued for an additional 3 hr. On adding NaI and evaporating the solution in an air stream, α-[Co(3,2,3-tet)gly]I_2 crystallized, was removed by filtration, washed with methanol, and recrystallized once from hot water. *Anal.* Calcd for $CoC_{10}H_{26}N_5O_2I_2$: C, 21.39; H, 4.63; N, 12.48. Found: C, 21.56; H, 4.77; N, 12.65.

Preparation of (β_2-Chelated amino acid)(3,7-diaza-1,9-nonanediamine)cobalt(III) Iodide, β_2-[Co(2,3,2-tet)aa]I_2.—The preparation of the glycinato, alaninato, valinato, and sarcosinato complexes was similar to that of α-[Co(3,2,3-tet)gly]I_2 using *trans*-[Co(2,3,2-tet)Cl_2]Cl in place of *trans*-[Co(3,2,3-tet)Cl_2]Cl.

Anal. Calcd for the glycinato complex, β_2-[Co(2,3,2-tet)gly]I_2, $CoC_9H_{24}N_5O_2I_2$: C, 19.74; H, 4.39; N, 12.79. Found: C, 19.77; H, 4.41; N, 12.78. Calcd for the valinato complex, β_2-[Co(2,3,2-tet)((*S*)-val)]$_2$, $CoC_{12}H_{30}N_5O_2{-}_2$: C, 24.45; H, 5.09; N, 11.88. Found: C, 24.22; H, 5.29; N, 11.93. Calcd for the alaninato complex, β_2-[Co(2,3,2-tet)((*S*)-ala)]I_2, $CoC_{10}H_{26}N_5O_2I_2$: C, 21.39; H, 4.63; N, 12.48. Found: C, 21.50; H, 4.72; N, 12.68. Calcd for the sarcosinato complex, β_2-[Co(2,3,2-tet)sar]I_2, $CoC_{10}H_{26}N_5O_2I_2$: C, 21.39; H, 4.63; N, 12.48. Found: C, 21.41; H, 4.75; N, 12.71.

Preparation of Glycinatobis(trimethylenediamine)cobalt(III) Iodide, [Co(tn)$_2$gly]I_2.—*trans*-[Co(tn)$_2Cl_2$]Cl (9.4 g, 0.03 mol) and silver oxide (3.5 g, 0.015 mol) were stirred in 50 ml of water for 1 hr and filtered. Then 2.2 g of glycine was added and the solution was heated on a steam bath 2 hr. On adding excess NaI and cooling, red crystals formed which were filtered, washed with a little cold methanol, and recrystallized from hot water. *Anal.* Calcd for $CoC_8H_{24}N_5O_2I_2$: C, 17.94; H, 4.49; N, 13.08. Found: C, 18.26; H, 4.56; N, 12.85.

Preparation of Potassium Hydrogen *d*-Tartrate Dibenzoate.—Dibenzoyl-*d*-tartaric acid monohydrate [Aldrich Chemical Co., Milwaukee, Wis.] (18.8 g, 0.05 mol) was added slowly to a warm solution of 3.35 g (0.025 mol) of K_2CO_3 in about 500 ml of water. Additional water was added as needed to produce a saturated solution of the acid salt at 45°. The solution was cooled in a refrigerator overnight, producing a nearly quantitative yield of colorless crystals (needles), which were used without further purification.

Resolution of Mixed-Ligand Amino Acid–Tetraminecobalt(III) Complexes.—The following general procedure was used to resolve the complexes α-[Co(3,2,3-tet)gly]I_2, [Co(tn)$_2$gly]I_2, β_2-[Co(2,3,2-tet)aa]I_2 (aa = gly, ala, val, sar), β_2-[Co(trien)gly]I_2, and β_2-[Co(trien)sar]I_2. The complex (0.01 mol) was dissolved in 800 ml of hot water. To this was added 2 g (0.005 mol) of potassium hydrogen *d*-tartrate dibenzoate in 100 ml of hot water. After standing overnight at room temperature or in some cases after evaporation under an air stream at room temperature, the diastereoisomer crystallized. It was then removed by filtration, washed with water, and recrystallized by dissolving it in a large volume of hot water and evaporating the solution under an air stream at room temperature.

The diastereoisomer was converted to the perchlorate salt by dissolving it in a mixture of 5 ml of water and 1.5 ml of $HClO_4$ and filtering to remove *d*-tartaric acid dibenzoate. To the filtrate was then added ethanol and ether and on cooling the resolved complex was obtained as the perchlorate salt. The molar extinction coefficients of the perchlorate salts, which detonate on heating, are identical with those of the iodide salts within experimental error. The rotations observed for the ions obtained from the least soluble diastereoisomers were as follows: $(-)_{546}$-α-[Co(3,2,3-tet)gly]$(ClO_4)_2$, $[M]_{546}$ −1837°; (−)-[Co(tn)$_2$gly]$(ClO_4)_2$, $[M]_{546}$ −1200°; (−)-β_2-[Co(2,3,2-tet)gly]$(ClO_4)_2$, $[M]_{546}$ −1590°; (−)-β_2-[Co(2,3,2-tet)((*S*)-ala)]$(ClO_4)_2$, $[M]_{546}$ −1680°; (−)-β_2-[Co(2,3,2-tet)((*S*)-val)]$(ClO_4)_2$, $[M]_{546}$ −2094°; (+)-β_2-[Co(2,3,2-tet)sar]$(ClO_4)_2$, $[M]_{589}$ +340°; (−)-β_2-[Co(trien)gly]$(ClO_4)_2$, $[M]_{546}$ −2608°. The isomer of β_2-Co(trien)sar^{2+} obtained as the least soluble diastereoisomer was (+)-β_2-Co(trien)sar^{2+}.

The filtrate from the formation of the diastereoisomer was evaporated to about 100 ml and filtered, discarding any more diastereoisomer that had formed. The filtrate was then evaporated to near dryness collecting the more soluble antipode as the iodide salt in fractions and recrystallizing them to constant rotation. The molar rotations observed for these isomers were, within experimental limits, equal to but of opposite sign from those observed for their optical antipodes except for (+)-β_2-[Co(2,3,2-tet((*S*)-val)]I_2 for which $[M]_{546}$ is 1071°.

$(+)_{546}$-α-[Co(3,2,3-tet)gly]$(ClO_4)_2$ → (−)*trans*-(*RR*)-[Co(3,2,3-tet)Cl_2]ClO_4.—$(+)_{546}$-α-[Co(3,2,3-tet)gly]$(ClO_4)_2$ was heated on a steam bath in concentrated HCl containing a little concentrated $HClO_4$. The green crystals of (−)-*trans*-(*RR*)-[Co(3,2,3-tet)Cl_2]ClO_4 were removed by filtration and air-dried; $[M]_{614}$ −540°.

(+)-β_2-[Co(2,3,2-tet)aa]$(ClO_4)_2$ → (+)-*trans*-(*RR*)-[Co(2,3,2-tet)Cl_2]ClO_4.—(+)-β_2-[Co(2,3,2-tet)aa]$(ClO_4)_2$ (aa = gly or ala) was heated on a steam bath in concentrated HCl containing a little $HClO_4$. The green crystals which formed were removed by filtration; $[M]_{613}$ 1600°.

Physical Measurements. Electronic and Circular Dichroism Spectra and Optical Rotatory Dispersion Curves.—Electronic absorption spectra were measured on a Beckman Model DBG spectrophotometer equipped with a Beckman Model 1005 10-in. potentiometric recorder using matched 1-cm silica cells. ORD curves were recorded with a Cary Model 60 spectropolarimeter equipped with a Cary Model 6002 circular dichroism accessory. For both the CD and ORD spectra, the solutions were approximately 10^{-3} *M*, and the cell path length was 1, 2, 5, or 10 cm as dictated by the optical density and the rotation. A solvent blank was used to determine the base lines for these spectra; the solvent was water unless otherwise noted. Optical isomers are denoted by (+) or (−), the sign of the rotation at the Na D line, or, if another wavelength was used, the wavelength appears as a subscript.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer at about 35°, the internal temperature of the probe. Solutions were prepared by dissolving as much sample as necessary to get a good spectrum in about 1 ml of 99.9% D_2O or in D_2O acidified with DCl. Increasing the concentration of the acid was found to shift the HDO peak downfield so that all the peaks due to the complex could be observed. Chemical shifts were measured from the methyl resonance of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) which served as an internal reference.

Chromatography.—The ion-exchange column was prepared by pouring a slurry of 10 g (6.8 mequiv) of Bio-Rad Cellex CM cation-exchange cellulose in the sodium form into a column (ϕ = 2.2 cm, *h* = 50 cm), followed by impaction with a constant flow of 0.5 *M* $NaNO_3$ (0.4 ml min^{-1}) for 12 hr. A sample of the reaction mixture from the preparation of β_2-Co(2,3,2-tet)((*S*)-val^{2+} estimated to contain 0.5 mequiv of cobalt (about 2 ml) was introduced onto the column. The complexes eluted with 0.5 *M* $NaNO_3$ acidified to pH 3 with HNO_3 were identified as *trans*-Co(2,3,2-tet)((*S*)-valH_2)$^{3+}$ and β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ by means of the electronic and pmr spectra.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and by Micro-Tech Laboratories, Skokie, Ill.

Results and Discussion

Synthesis.—The chelated amino acid–2,3,2-tet and –3,2,3-tet complexes were prepared by treating the *trans*-Co(2,3,2-tet)Cl_2^+ and *trans*-Co(3,2,3-tet)Cl_2^+ complexes with the appropriate amino acid at a pH of approximately 5.5 and at 60° for about 1 hr, followed by adjusting the pH to 8.5 and continuing heating for an additional 2 hr. The complexes α-[Co(3,2,3-tet)aa]I_2 and β_2-[Co(2,3,2-tet)aa]I_2 were isolated on the addition of sodium iodide. Fractional crystallization failed to reveal the presence of more than one geometrical isomer for any of the [Co(2,3,2-tet)aa]I_2 or [Co(3,2,3-tet)aa]I_2 complexes.

The valinato complex, β_2-[Co(2,3,2-tet)((*S*)-val)]Cl_2, provides a simple, positive means for determining the number of geometrical isomers in the product. The pmr spectrum of the racemic complex is shown in Figure 1. The asymmetric C–H(A) proton of coordi-

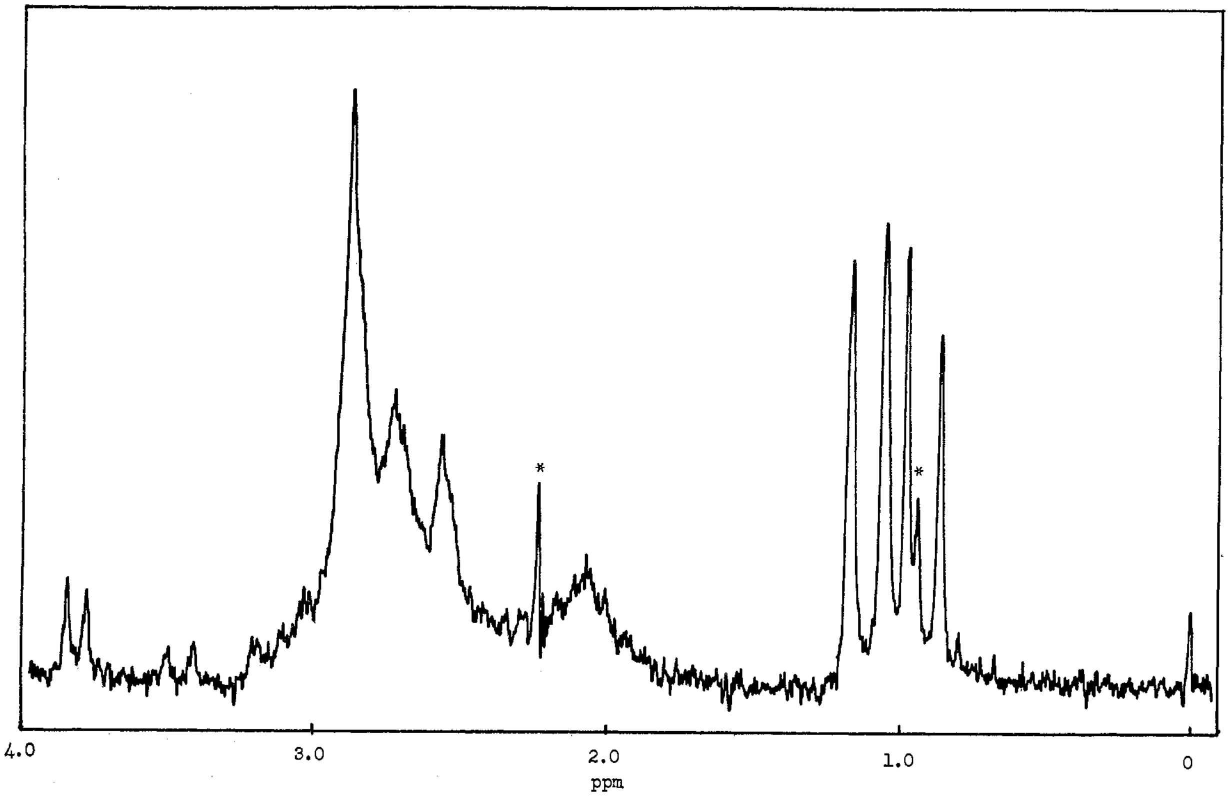


Figure 1.—Pmr spectrum of (±)-[Co(2,3,2-tet)((*S*)-val)]Cl_2 relative to DSS as an internal standard. (Asterisks designate signals arising from DSS methylene proton.)

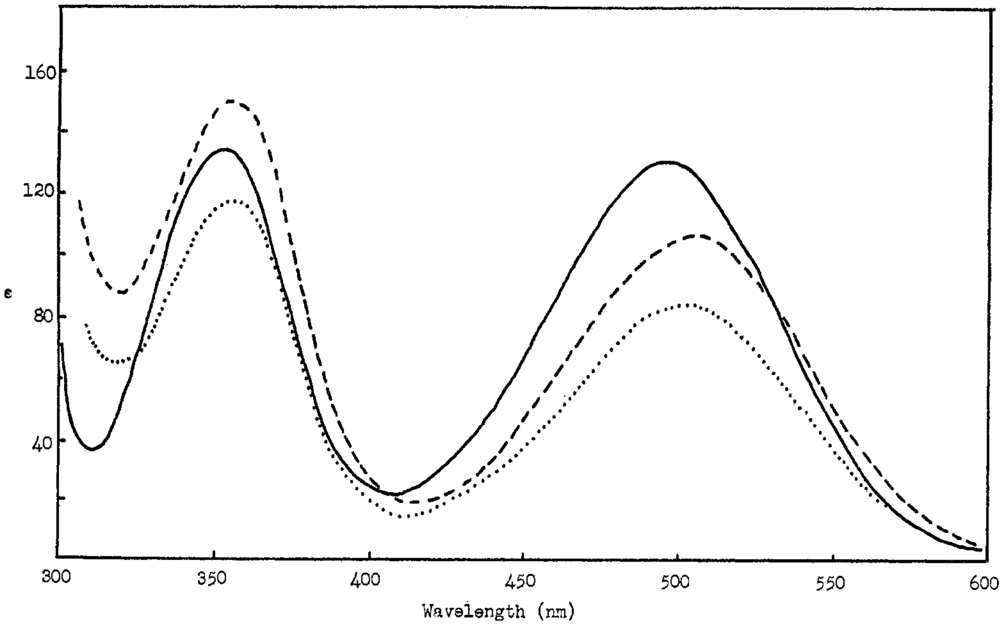
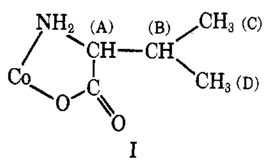


Figure 2.—Electronic spectra: β_2-[Co(2,3,2-tet)gly]I_2, ——; α-[Co(3,2,3-tet)gly]I_2, - - - - -; [Co(tn)$_2$gly]I_2, ······· .



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nated valine produces two sets of doublets at 3.34 and 3.88 ppm. These signals may be assigned to the diastereomeric isomers (+)-β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ and (−)-β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$, respectively, in correspondence with (+)$_{546}$-Co(en)$_2$((*S*)-val)$^{2+}$ and (−)$_{546}$-Co(en)$_2$((*S*)-val)$^{2+}$ which show doublets at 3.57 and 3.78 ppm, respectively.[2,3] The splitting arises from coupling with the -CH(B) proton. No splitting arises from the amine protons which are deuterated in neutral D_2O solution. If the Co(2,3,2-tet)((*S*)-val)$^{2+}$ complex under consideration consisted of any mixture of α, β_1,

[2] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 5133 (1967).

[3] D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).

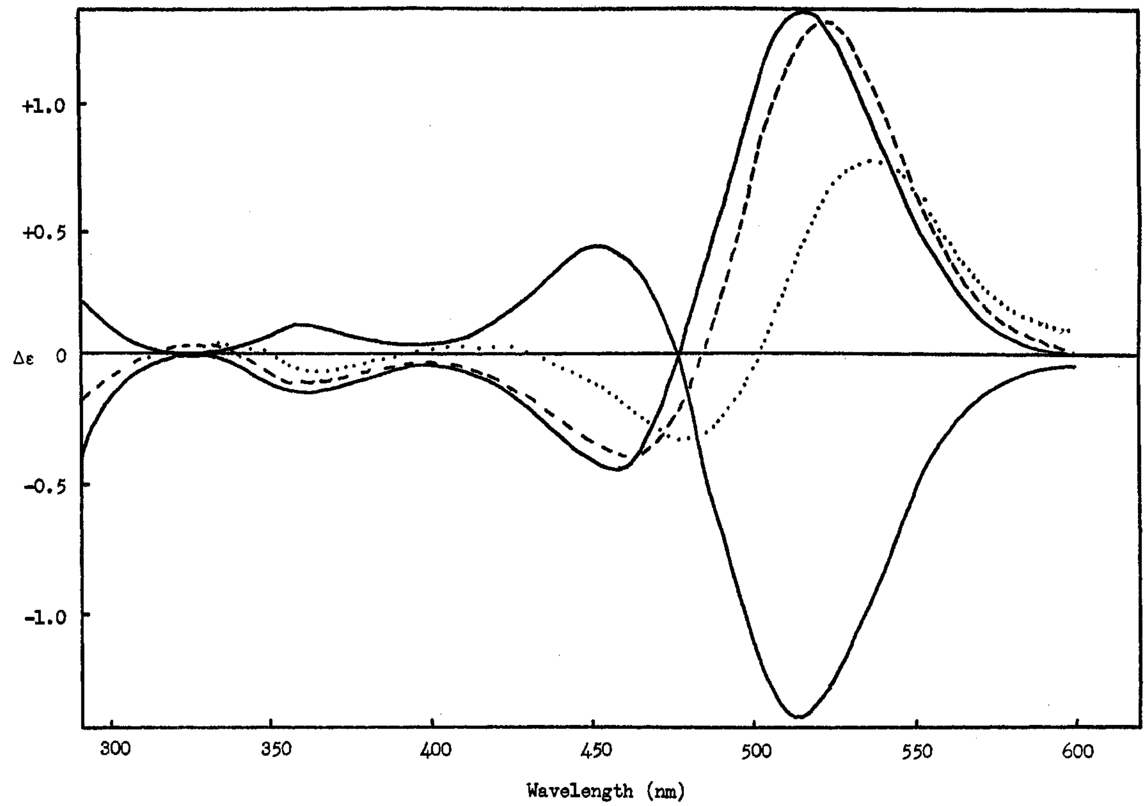

Figure 3.—Circular dichroism spectra: (+)- and (−)-β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$, ——; (+)-β_2-Co(2,3,2-tet)gly^{2+}, - - - - - -; (+)-β_2-Co(2,3,2-tet)sar^{2+}, · · · .

and β_2 isomers, a more complex spectrum should appear. The complex pattern at about 1.0 ppm for the racemic complex corresponds to two sets of doublet pairs arising from the coupling of the nonequivalent methyl groups (C) and (D) with the –CH(B) proton.

Electronic Spectra.—The electronic spectra of the β_2-[Co(2,3,2-tet)aa]I$_2$ compounds (aa = gly, ala, sar, val) are tabulated in Table I and that of β_2-Co(2,3,2-tet)gly^{2+} is shown in Figure 2. All are very similar in shape and intensity and qualitatively support the contention that all represent the same geometric isomer as would be inferred from the similar preparative conditions. A shift in λ_{max} for the low-energy band would be expected between β_1 and β_2 isomers based on previous work for β_1- and β_2-[Co(trien)aa]I$_2$ complexes.[4] Moreover, both bands are shifted by approximately 5 nm to higher wavelength in the sarcosinato complex indicating a slightly reduced ligand field for sarcosine compared to glycine. This is also observed for the Co(en)$_2$gly^{2+} and Co(en)$_2$sar^{2+} ions as well as for the β_2-Co(trien)gly^{2+} and β_2-Co(trien)sar^{2+} ions.[5] Since the pmr spectrum indicates that the β_2-Co(2,3,2-tet)(L-val)$^{2+}$ complex is isomerically pure, the similarity in the absorption curves suggests that the other [Co(2,3,2-tet)aa]I$_2$ complexes are also isomerically pure.

TABLE I

ELECTRONIC ABSORPTION SPECTRA FOR SOME CoN$_4$aa^{2+} COMPLEXES

	λ_{max}, nm (ϵ)	
Compound	Band I	Band II
[Co(en)$_2$gly]I$_2$	487 (98)	346 (107)
β_1-[Co(trien)gly]I$_2$	490 (161)	346 (125)
β_2-[Co(trien)gly]I$_2$	478 (134)	346 (145)
β_2-[Co(trien)sar]I$_2$	484 (144)	350 (156)
[Co(tn)$_2$gly]I$_2$	499 (83)	354 (115)
α-[Co(3,2,3-tet)gly]I$_2$	503 (105)	355 (150)
β_2-[Co(2,3,2-tet)gly]I$_2$	494 (128)	353 (132)
β_2-[Co(2,3,2-tet)sar]I$_2$	502 (142)	356 (145)
β_2-[Co(2,3,2-tet)((*S*)-val)]I$_2$	495 (136)	353 (144)
β_2-[Co(2,3,2-tet)((*S*)-ala)]I$_2$	494 (128)	353 (131)

The visible spectra of [Co(tn)$_2$gly]I$_2$ and α-[Co(3,2,3-tet)gly]I$_2$ (Figure 2) are similar in shape and intensity. However, without the β-Co(3,2,3-tet)gly^{2+} complex for comparison, we can reach no definite conclusion about the stereochemistry of α-[Co(3,2,3-tet)gly]I$_2$ on this basis alone. There is no apparent splitting in any of the electronic spectra.

Optical Activity and Absolute Configuration.—The circular dichroism spectra (Figures 3–5, Table II) of all the β_2-Co(2,3,2-tet)aa^{2+} ions, the α-Co(3,2,3-tet)gly^{2+} ion, and the Co(tn)$_2$gly^{2+} ion show two transitions in the vicinity of the $^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) electronic transition. This is in contrast to the β_1- and β_2-Co(trien)gly^{2+} and Co(en)$_2$gly^{2+} complexes which show only one CD band in this region.[5] The X-ray determination of the absolute configuration of Δ-(−)-β_2-[Co(trien)((*S*)-pro)]I$_2$,[6] coupled with extensive circular dichroism studies,[4] clearly establish that the Δ-β_2 ion has a dominant negative CD band in the region of the low-energy octahedral electronic transition. It is likely that Mason's formalism for Co(en)$_2$L$_2$$^{2+}$—the transition derived from the ^1E_a state dominates the sign of the first ligand field CD band—may be applied to these Co(tn)$_2$aa^{2+} and Co(N$_4$)aa^{2+} complexes. Therefore, those ions with dominant positive CD bands in the $^1T_{1g}$ (O_h) region,

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[4] C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, **4**, 3 (1970).

[5] L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1942 (1967).

[6] H. C. Freeman and I. E. Maxwell, *ibid.*, **9**, 649 (1970).

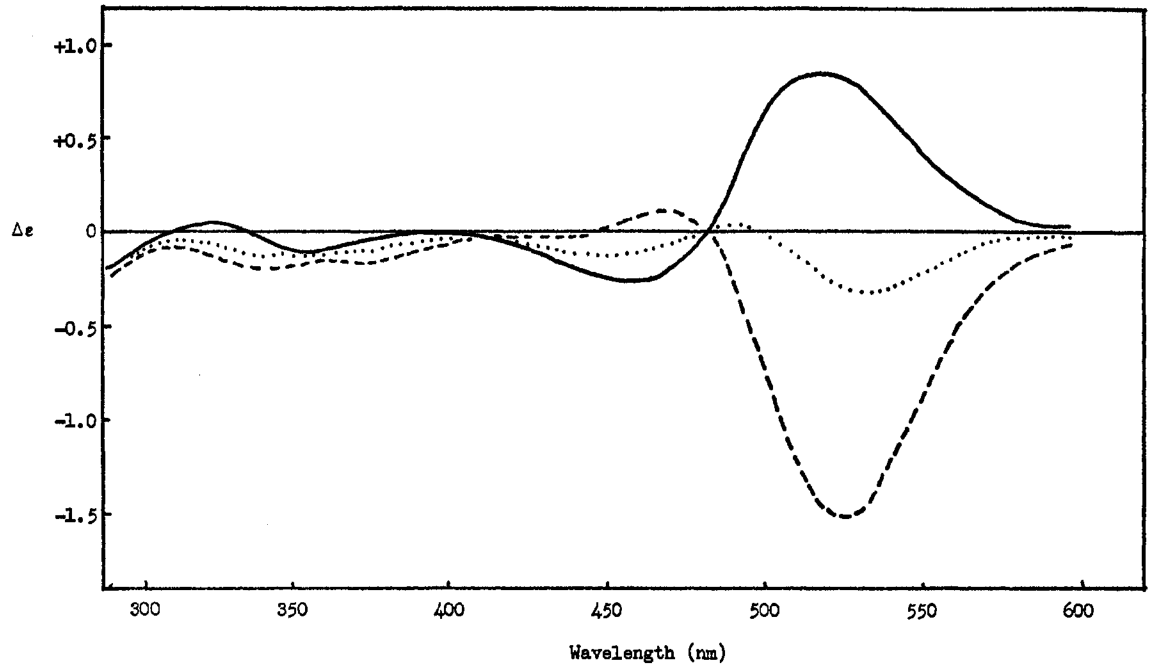

Figure 4.—Circular dichrosim spectra of β_2-[Co(2,3,2-tet)((*S*)-val)$^{2+}$: (+), ———; (−), - - - - -; unresolved, ······· .

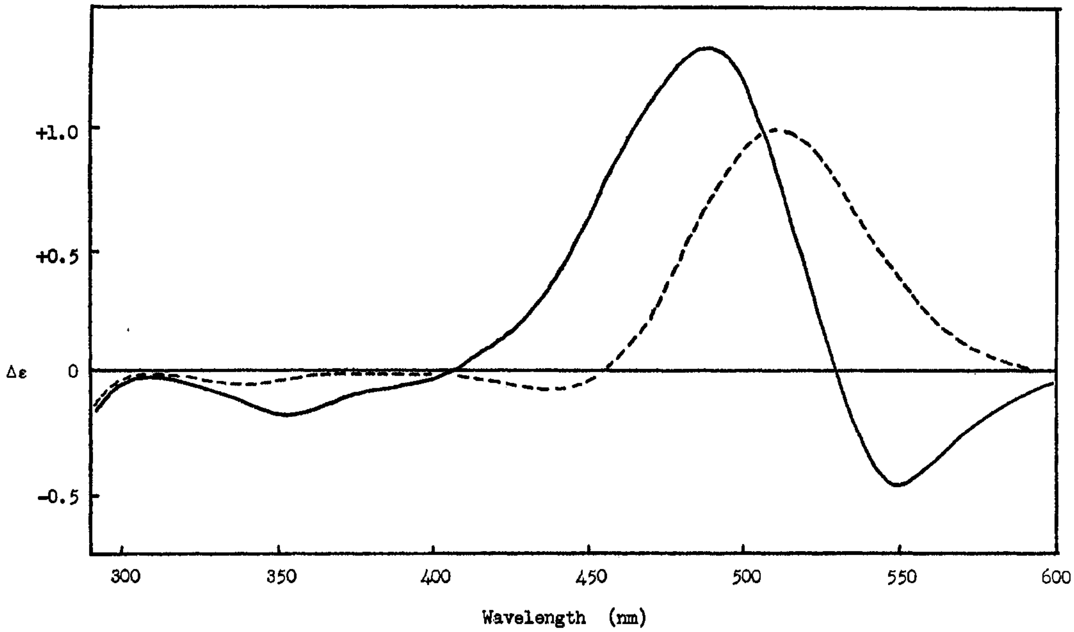

Figure 5.—Circular dichroism spectra: (+)$_{546}$-α-Co(3,2,3-tet)gly^{2+}, ———; (+)-Co(tn)$_2$gly^{2+}, - - - - -.

(+)-β_2-Co(2,3,2-tet)gly^{2+}, (+)-β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$, (+)-β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$, (+)-β_2-Co-(2,3,2-tet)sar^{2+}, (+)$_{546}$-α-Co(3,2,3-tet)gly^{2+}, and (+)-Co(tn)$_2$gly^{2+} are assigned Λ absolute configuration.

Support for the assumption that the dominant band in all these complexes is of ^1E_a parentage comes from a study of the effect of electrolytes on the CD curves.[7-9]

The effect of the addition of phosphate anion on the circular dichroism spectra of (+)$_{546}$-α-[Co(3,2,3-tet)gly](ClO$_4$)$_2$, (+)-β_2-[Co(2,3,2-tet)gly](ClO$_4$)$_2$, and (+)-[Co(tn)$_2$gly](ClO$_4$)$_2$ is shown in Figure 6. For (+)-β_2-[Co(2,3,2-tet)gly](ClO$_4$)$_2$ and (+)-[Co(tn)$_2$-gly](ClO$_4$)$_2$ the dominant band decreases in intensity and the smaller band increases in intensity. The effect is at its maximum with phosphate concentration of 0.5 *M* and remains constant with increasing concentration thereafter. Addition of small amounts of phosphate to (+)$_{546}$-α-[Co(3,2,3-tet)gly](ClO$_4$)$_2$ causes the dominant band at 488 nm significantly to decrease in intensity. The low-energy band at 550 nm increases in intensity slightly. With phosphate concentration of about 0.01 *M*, the major band has almost disappeared, and, finally, when the phosphate concentration is 0.5 *M*, a small band of opposite sign appears at about 475 nm. These results are in agreement with previous predictions. The transition occurring at about 470 nm, the absorption maximum for Co(NH$_3$)$_6$$^{3+}$, for all the complexes has its CD intensity enhanced by addition of phosphate and can therefore be assigned as $^1A_1 \rightarrow {}^1A_2$.

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(7) S. F. Mason and B. J. Norman, *Proc. Chem. Soc., London*, 339 (1964).
(8) S. F. Mason and B. J. Norman, *Chem. Commun.*, 74 (1965).
(9) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).

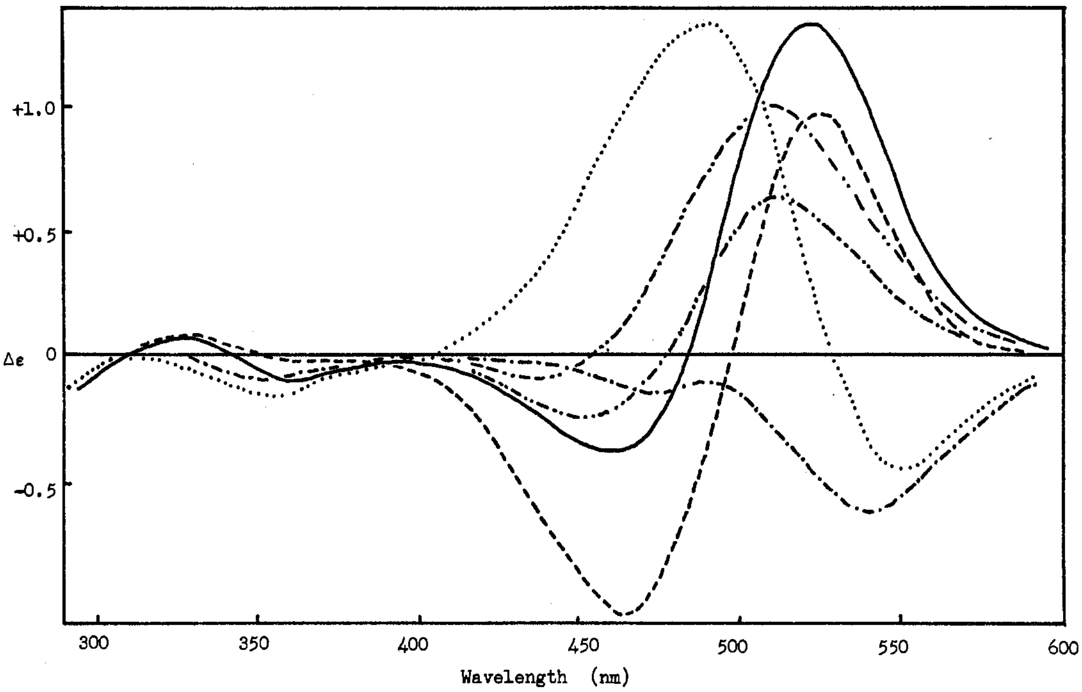

Figure 6.—Circular dichroism spectra: (+)$_{546}$-α-Co(3,2,3-tet)gly^{2+} in H$_2$O, ········; in 0.5 *M* K$_3$PO$_4$, -·-·-·-·; (+)-β_2-Co(2,3,2-tet)gly^{2+} in H$_2$O, ——; in 0.5 *M* K$_3$PO$_4$, ----; (+)-Co(tn)$_2$gly^{2+} in H$_2$O, —·—·—; in 0.5 *M* K$_3$PO$_4$, -··-··-··.

TABLE II

CIRCULAR DICHROISM DATA FOR SAME AMINO ACID–TETRAMINE COMPLEXES OF COBALT(III)

Compound	λ_{max}, nm	$\Delta\epsilon_{max}$
(+)-[Co(en)$_2$gly](ClO$_4$)$_2$	505	2.10
	370	0.088
	328	0.128
(+)-[Co(tn)$_2$gly](ClO$_4$)$_2$	510	1.00
	436	−0.06
	340	−0.05
(+)-β_2-[Co(trien)gly](ClO$_4$)$_2$	487	2.22
	344	−0.18
(+)-β_2-[Co(2,3,2-tet)gly](ClO$_4$)$_2$	522	1.32
	460	−0.40
	361	−0.10
	328	0.04
(+)-β_2-[Co(2,3,2-tet)((*S*)-ala)](ClO$_4$)$_2$	515	1.35
	455	−0.43
	360	−0.14
(+)-β_2-[Co(2,3,2-tet)((*S*)-val)](ClO$_4$)$_2$	517	0.86
	458	−0.27
	356	−0.07
	325	0.04
(+)-β_2-[Co(2,3,2-tet)((*S*)-val)](ClO$_4$)$_2$	523	−1.53
	470	0.12
	373	−0.16
	340	−0.18
(±)-β_2-[Co(2,3,2-tet)((*S*)-val)](ClO$_4$)$_2$	530	−0.31
	490	0.03
	450	−0.13
	350	−0.11
(+)-β_2-[Co(2,3,2-tet)sar](ClO$_4$)$_2$	535	0.77
	477	−0.33
	414	0.03
	361	−0.06
	340	0.04
(+)$_{546}$-α-[Co(3,2,3-tet)gly](ClO$_4$)$_2$	550	−0.45
	490	1.32
	350	−0.16

At lower energy are the components of the $^1A_1 \rightarrow {}^1E_a$ transition. The two components are observable only for (+)-α-Co(3,2,3-tet)gly^{2+} and appear as transitions of opposite sign. Assignment of absolute configuration is based on the sign of the dominant band which has now been established as being of ^1E_a parentage.

With one exception, the assignment of absolute configurations is consistent with solubility criteria. All the chelated amino acid–3,2,3-tet and –2,3,2-tet complexes were resolved with potassium hydrogen *d*-tartrate dibenzoate (dbdt) as the resolving agent. The least soluble diastereoisomers obtained with this resolving agent were (−)$_{546}$-α-Co(3,2,3-tet)gly^{2+}, (−)-Co(tn)$_2$gly^{2+}, and (−)-β_2-Co(2,3,2-tet)aa^{2+} (where aa = gly, ala, val). The sarcosinato complex formed the least soluble diastereoisomer as (+)-β_2-[Co(2,3,2-tet)sar](dbdt)$_2$. To show that this was an exception, the β_2-Co(trien)gly^{2+} and β_2-Co(trien)sar^{2+} ions were resolved using dbdt. These ions have previously been resolved using the antimonyl-*d*-tartrate and *d*-bromocamphor-π-sulfonate anions, respectively, and absolute configurations have been assigned. The ions obtained as the least soluble diastereoisomers with the hydrogen *d*-tartrate dibenzoate anion were (−)-β_2-Co(trien)gly^{2+} and (+)-β_2-Co(trien)sar^{2+}.

Note, in Figure 4, that the optical isomers of β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ having opposite signs for the major components of the low-energy CD bands have circular dichroism curves which are not strictly mirror images. In the alkaline medium employed for the synthesis of these complexes, it is expected that only the most stable chelate ring conformations will be obtained (Δ-*SS* and Λ-*RR* for both 2,3,2-tet and 3,2,3-tet complexes) and that this effect arises solely from the vicinal contribution to the overall optical activity of the complexes.[4,10–13]

Addition of the CD curves of (+)-β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ and (−)-β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ gives

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(10) Y. Shimura, *Bull. Chem. Soc. Jap.*, **31**, 315 (1958).
(11) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).
(12) B. E. Douglas, *ibid.*, **4**, 1813 (1965).
(13) S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).

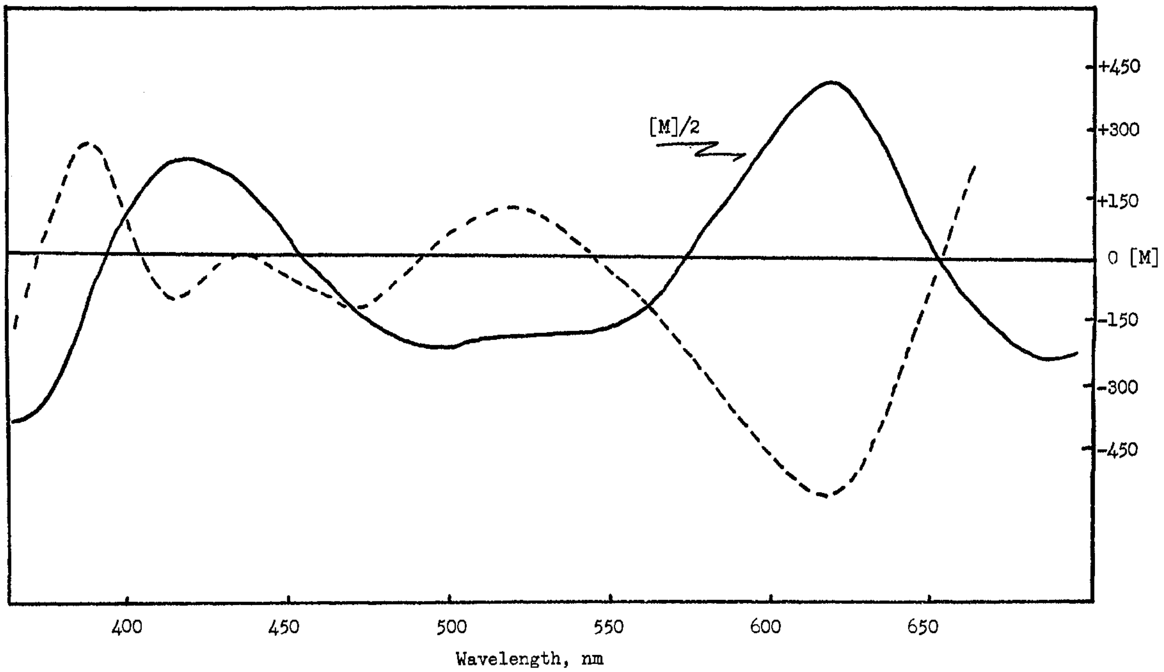

Figure 7.—Optical rotatory dispersion: (−)-*trans*-(*RR*)-[Co(3,2,3-tet)Cl_2]ClO_4, - - -; (+)-*trans*-(*RR*)-[Co(2,3,2-tet)Cl_2]ClO_4, ——.

essentially the same curve as that obtained from a sample of the unresolved complex or from the solution before any solid product is isolated. When half of the vicinal curve is subtracted from either total curve, one obtains a CD spectrum essentially the same as that of the optical isomers of β_2-Co(2,3,2-tet)gly^{2+}. This gives confidence to the belief that complete resolution of the isomers has been attained and also to the contention that only one geometric isomer is involved since the vicinal effect is expected to be dependent on the configuration of the tetradentate ligand. It also shows that the isomers assigned as β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ and β_2-Co(2,3,2-tet)gly^{2+} do, in fact, correspond to the same geometric isomers. The CD curve for the unresolved β_2-Co(2,3,2-tet)((*S*)-val)$^{2+}$ shows three peaks in the region of the first absorption band in the order −, +, −. This is typical for amino acid–tetramine complexes, Co(NH_3)$_4$aa^{2+}, bis-ethylenediamine complexes, Co(en)$_2$aa^{2+}, and triethylenetetramine complexes, Co(trien)aa^{2+}, although it does not necessarily apply for all amino acids.[4,14]

The case of the β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$ ion is somewhat puzzling. The vicinal effect for this complex was too small to be measured accurately; the curves for the resolved complexes are nearly mirror images. The similarity of the CD curves for β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$ and β_2-Co(2,3,2-tet)gly^{2+} indicates, however, that both have the same geometric configuration of the tetradentate ligand; that is, both are β_2 isomers as assigned.

Transformation Reactions and Geometrical Configuration.—The chelated amino acid can be removed from the 3,2,3-tet- and 2,3,2-tet–Co^{III} complexes by heating the complexes in concentrated HCl or in methanol saturated with anhydrous HCl. This is in contrast to the Co(en)$_2$aa^{2+} system and results from the strong preference for the trans configuration by the 3,2,3-tet and 2,3,2-tet ligands. It has been reported that in [Co(en)$_2$gly]Cl_2 the glycinato chelate ring can be opened by refluxing the complex in ethanolic HCl.[15] The product of this reaction is the glycine ester complex *cis*-[Co(en)$_2$Cl($NH_2CH_2CO_2C_2H_5$)]Cl_2. When this reaction is carried out on the α-[Co(3,2,2-tet)gly](ClO_4)$_2$ and β_2-[Co(2,3,2-tet)gly](ClO_4)$_2$ complexes, the products are *trans*-[Co(3,2,3-tet)Cl_2]ClO_4 and *trans*-[Co(2,3,2-tet)Cl_2]ClO_4, respectively.

When (+)$_{546}$-α-[Co(3,2,3-tet)gly](ClO_4)$_2$ and (+)-β_2-[Co(2,3,2-tet)gly](ClO_4)$_2$ are treated with concentrated HCl, optically active trans dichloro products result which are of opposite configurations based on the shapes of their ORD curves (Figure 7). Moreover, these trans dichloro products can be assigned as (−)-*trans*-(*RR*)-[Co(3,2,3-tet)Cl_2]ClO_4 and (+)-*trans*-(*RR*)-[Co(2,3,2-tet)Cl_2]ClO_4.[16] This series of reactions may be summarized as

$$\Lambda\text{-}(+)_{546}\text{-}\alpha\text{-[Co(3,2,3-tet)gly](ClO}_4)_2 \xrightarrow{\text{HCl}} (-)\text{-}trans\text{-}(RR)\text{-[Co(3,2,3-tet)Cl}_2]\text{ClO}_4$$

$$\Lambda\text{-}(+)\text{-}\beta_2\text{-[Co(2,3,2-tet)gly](ClO}_4)_2 \xrightarrow{\text{HCl}} (+)\text{-}trans\text{-}(RR)\text{-[Co(2,3,2-tet)Cl}_2]\text{ClO}_4$$

The (+)-β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$ ion can also be converted to (+)-*trans*-(*RR*)-[Co(2,3,2-tet)Cl_2]ClO_4 by reaction with hot concentrated HCl confirming the β configuration for that complex. The chelated valinato and sarcosinato ligands in β_2-[Co(2,3,2-tet)((*S*)-val)](ClO_4)$_2$ and β_2-[Co(2,3,2-tet)sar](ClO_4)$_2$ could not be removed by heating for several days in concentrated HCl. However, the similarity of their ORD, CD, and visible absorption spectra to those of β_2-Co(2,3,2-tet)gly^{2+} and β_2-Co(2,3,2-tet)((*S*)-ala)$^{2+}$ strongly suggests that these complexes have the same configuration.

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

[15] M. D. Alexander and D. H. Busch, *ibid.*, **5**, 1590 (1966).

[16] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).