philic with respect to $C_5H_5Co(CO)P(C_6H_5)_3$.[17] The tricyclohexylphosphine complex, however, shows that the steric effect is important, since $P(C_6H_{11})_3$ is one of the most basic but also one of the bulkiest phosphines.[7] As expected, the CO stretching band in $C_5H_5Co(CO)P(C_6H_{11})_3$ is appreciably lower in frequency than those of the other complexes used (Table I). We were unable to isolate any acyl product, but the rate of disappearance of $C_5H_5Co(CO)P(C_6H_{11})_3$ with CH_3I was one-fifth as large as that of $C_5H_5Co(CO)P(C_6H_5)_3$, so that in this case at least the steric effect predominates.

The rate difference between CH_3I and C_2H_5I is surprisingly large. Hine stated that "in SN2 reactions methyl halides are usually found to be 4–150 times as reactive as the corresponding ethyl halides."[18] The absolute values of our rate constants, however, are not unlike those reported for well-known systems.[13,14] The complexes under investigation behave therefore as nucleophiles of moderate reactivity but unusual steric selectivity.

Effect of Metal.—The initial nucleophilic attack on methyl and ethyl iodides seems to be an essentially similar process for the three metals Co, Rh, and Ir in the compounds $C_5H_5M(CO)P(C_6H_5)_3$. The kinetic patterns and activation parameters (for CH_3I) are all of the same kind. The failure of the iridium reaction to undergo the second stage is interesting; a related case has been discussed.[3]

The relative rates of reaction of the complexes with different metals are as follows: CH_3I: Co, 1.0; Rh, 1.4; Ir, *ca.* 8; C_2H_5I: Co, 2; Rh, 1; Ir, 6. Thus the expected[9] increase in nucleophilicity on descending the group is apparent in the reaction with methyl iodide but is outweighed in the ethyl iodide case by the alternating effect so common in this triad.[7] $C_5H_5Rh(CO)P(C_6H_5)_3$ has a higher CO stretching frequency than either the Co or the Ir analogs, which suggests that the electron density at the metal atom is relatively low and may be related to its low nucleophilicity. Similar trends in reactivity have been noted for metal carbonyl anions.[19]

In order to gain further insight into these systems we have studied the reactions of $C_5H_5Rh(CO)P(C_6H_5)_3$ with benzyl and allyl halides. These results will be reported in a subsequent paper.

Acknowledgment.—We thank the National Research Council of Canada for financial support.

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Preparation, Stereochemistry, and Conformational Analysis of Cobalt(III)–Triethylenetetramine-*N*-methyl-(*S*)-alaninato Complexes

BY D. A. BUCKINGHAM, I. E. MAXWELL, AND A. M. SARGESON*

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The preparations and structural assignments of some β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ions are described; the $\Lambda(+)_{589}$-β_2-(*SSR*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, $\Delta(-)_{589}$-β_2-(*RSS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, and $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ diastereoisomers have been separated by fractional crystallization and resolution methods or observed following mutarotation at pH 7 or 12. Under equilibrium conditions, pH 6.5 (25°), the Δ-*RRS*(*S*) and Δ-*RSS*(*S*) isomers exist in approximately equal amounts; at pH 12 (25°) the equilibrated solution contains Δ-*RRS*(*R*) (~60%), Δ-*RRS*(*S*) (~20%), and Δ-*RSS*(*S*) (~20%). Strain energy minimization calculations support the structural assignments and predict that significant angular deformations will occur in the molecular ions to relieve steric crowding.

Introduction

Previous experiments have shown that the reaction of β-Co(trien)(OH)(H_2O)$^{2+}$ (trien = triethylenetetramine) with (*S*)-proline is kinetically controlled and that equal amounts of the diastereoisomers Δ-β_2-(*RRS*)-Co(trien)((*S*)-pro)$^{2+}$ and Λ-β_2-(*SSS*)-Co(trien)((*S*)-pro)$^{2+}$ are formed.[1,2] However, it was not possible to measure the relative stabilities of the Δ-β_2-(*RRS*)-Co(trien)((*S*)-pro)$^{2+}$ and Δ-β_2-(*RRR*)-Co(trien)((*R*)-pro)$^{2+}$ ions, since base-catalyzed dissociation of the amino acid moiety preceded mutarotation. The slow rate of mutarotation compared to other chelated amino acids[3] was attributed to the requirement that protons

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[2] Nomenclature: *R* and *S* designate the asymmetry about the "angular" and "planar" asymmetric N atoms of triethylenetetramine and the secondary N atom of the amino acid in that order and follow the rules suggested by C. K. Ingold, V. Prelog, and R. S. Cahn, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966), and accepted by the IUPAC. For consistency we have also used this nomenclature to specify the configuration of the α-C atom of the amino acid (*e.g.*, (*S*)-proline = L-proline). The use of β, β_1, and β_2 follows that used by L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967). The absolute configuration about the cobalt center is indicated by the prefix Δ or Λ: *ibid.*, **9**, 1 (1970).

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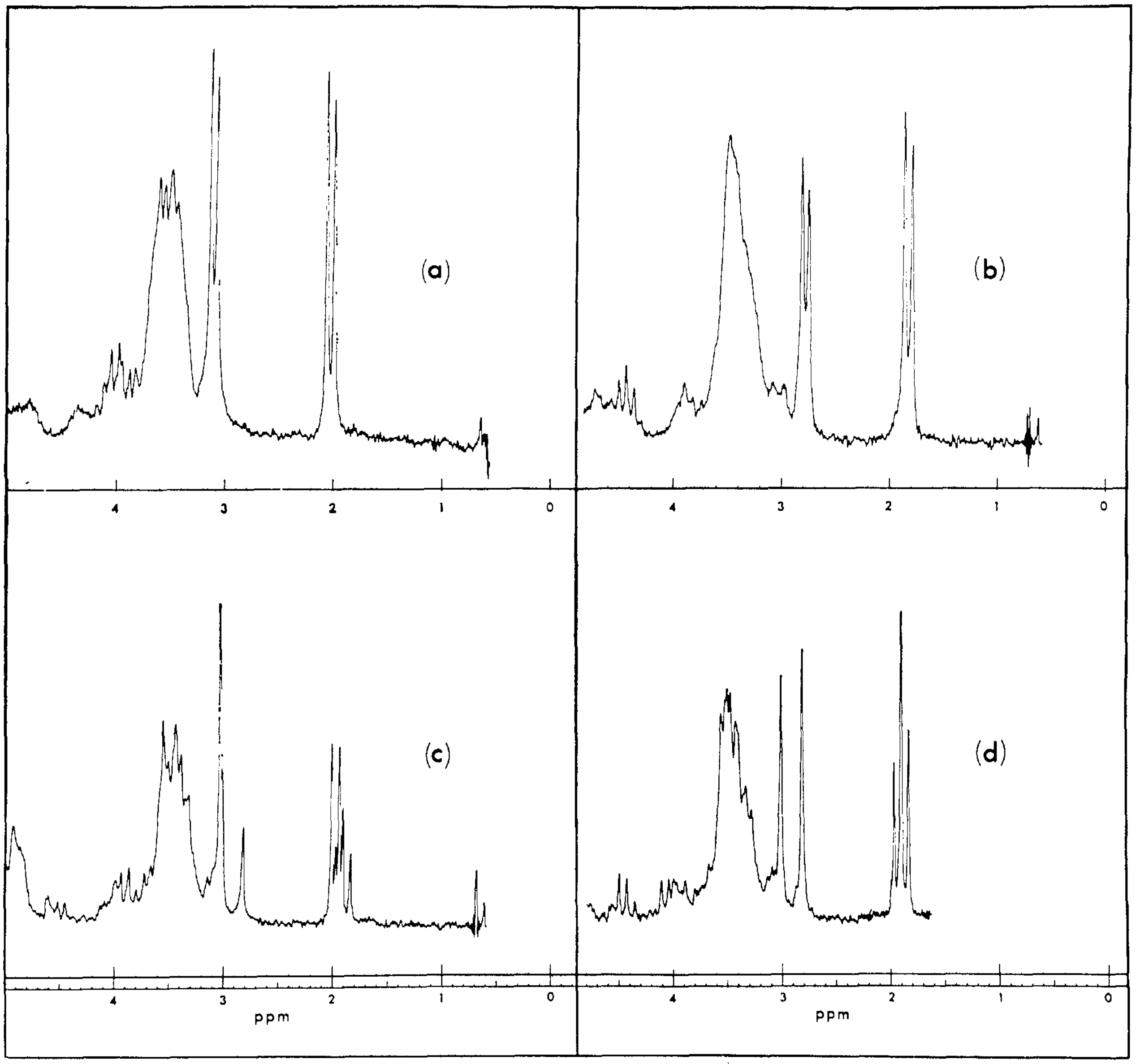

Figure 1.—The 100-MHz ^{1}H nmr spectra of β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers (external reference ($(CH_3)_4Si$): (a) $(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br_2 in DCl (0.01 *N*); (b) $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl_2 in DCl (0.01 *N*); (c) $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl_2 isomers in neutral D_2O after equilibration of $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]I_2 at pH 12; (d) $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl_2 isomers in 0.01 *N* DCl after equilibration of $(-)_{589}$-β_2-[Co(trien)(*N*-Me(*S*)-ala)]I_2 in H_2O at pH 7.

on both the asymmetric nitrogen and carbon centers of the pyrrolidine ring be simultaneously ionized before ring inversion could occur. Since the pK_a for both centers is likely to be >14, the concentration of the doubly deprotonated intermediate will be exceedingly small at pH <12, and a marked retardation in the rate of inversion relative to other amino acid systems requiring only deprotonation at carbon results.

However, in the analogous *N*-methyl-(*S*)-alanine complexes the possibility of observing mutarotation is enhanced, since inversion at the asymmetric nitrogen and carbon centers can now occur independently. For this reason it was decided to prepare some β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ complex ions and measure the relative stabilities of a set of diastereoisomers containing adjacent asymmetric Co, N, and C centers.

In addition, the strain energy minimization calculations which predicted the molecular geometries and relative stabilities for the Δ-β_2-(*RRS*)- and Λ-β_2-(*SSS*)-Co(trien)((*S*)-pro)$^{2+}$ complexes[4] have now been applied to the corresponding *N*-methylalaninato complexes. This paper describes the preparation, structural assignments, and relative stabilities and predicts the detailed structures of some of the β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers.

Experimental Section

Optically pure *N*-methyl-(*S*)-alanine was synthesized by the method of Quitt, Hellerbach, and Vogler.[5] The preparation of β-[Co(trien)CO_3]Cl·1.5H_2O follows a method previously described.[6] Rotatory dispersion (RD) spectra were measured in

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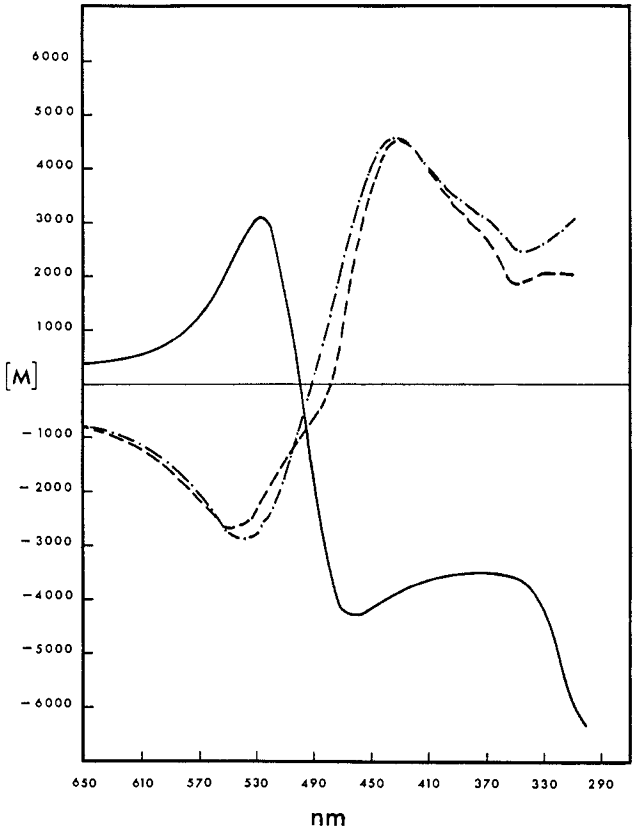

Figure 2.—RD spectra of β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers: ——, $(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br$_2$ in HClO$_4$ (0.1 *N*); ------, $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]I$_2$ in HClO$_4$ (0.1 *N*); -·-·-·, $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl$_2$ isomers in H$_2$O after equilibration at pH 7.

1-dm cells with a Perkin-Elmer P22 spectropolarimeter. Circular dichroism (CD) curves were obtained using a Cary 60 spectropolarimeter with CD attachment. A Varian 100-MHz spectrometer was used to measure proton magnetic resonance (pmr) spectra using tetramethylsilane as an external standard. Visible spectra were obtained with a Cary 14 spectrophotometer.

β_2-[Co(trien)(*N*-Me-(*S*)-ala)](ClO$_4$)$_2$ (Isomeric Mixture).—β-Co(trien)(H$_2$O)$_2{}^{3+}$ was prepared *in situ* by adding HClO$_4$ (14 ml, 5.8 *N*) to β-[Co(trien)CO$_3$]Cl·1.5H$_2$O (12.7 g) at 25°. After the reaction was complete (10 min), the solution was made basic (pH 9) by addition of NaOH (2 *N*), and *N*-methyl-(*S*)-alanine (4 g) was added. The reaction mixture was left to stand for 20 hr at 35°. Addition of LiClO$_4$ to the cooled solution gave orange crystals of β_2-[Co(trien)(*N*-Me-(*S*)-ala)](ClO$_4$)$_2$ which were collected and washed with acetone. Pmr spectra of this product indicated that it was a mixture of at least three isomeric species. Fractional crystallization, however, did not yield any significant isomer separation.

$(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]((+)BCS)$_2$.—β_2-[Co(trien)-(*N*-Me(*S*)-ala)](ClO$_4$)$_2$ (12.0 g) was dissolved in a minimum volume of water and converted to the chloride salt using an anion-exchange column (Bio-Rad AG1-X8, 200-400 mesh) in the chloride form. The eluent was evaporated to dryness and the product was redissolved in the minimum volume of warm water. Silver (+)-bromocamphor-π-sulfonate monohydrate (Ag(+)BCS) (12.0 g) was then shaken with the warm solution and precipitated AgCl was removed. When the filtrate volume was reduced on a rotary evaporator, the diastereoisomer crystallized. By removing fractions and further evaporation, four fractions were obtained with specific rotations $[\alpha]_{546}$ of −162, −140, +194, and +194°, respectively. The most soluble fractions with positive rotations were recombined and fractionated to constant specific rotation $[\alpha]_{546}$ +305° and $[\alpha]_{436}$ −259° (0.1% solutions in H$_2$O (pH 4)). Attempts to purify the $(-)_{589}$ diastereoisomer fractions by this method were unsuccessful. Pmr spectra showed that the levo fractions contained at least two other isomers.

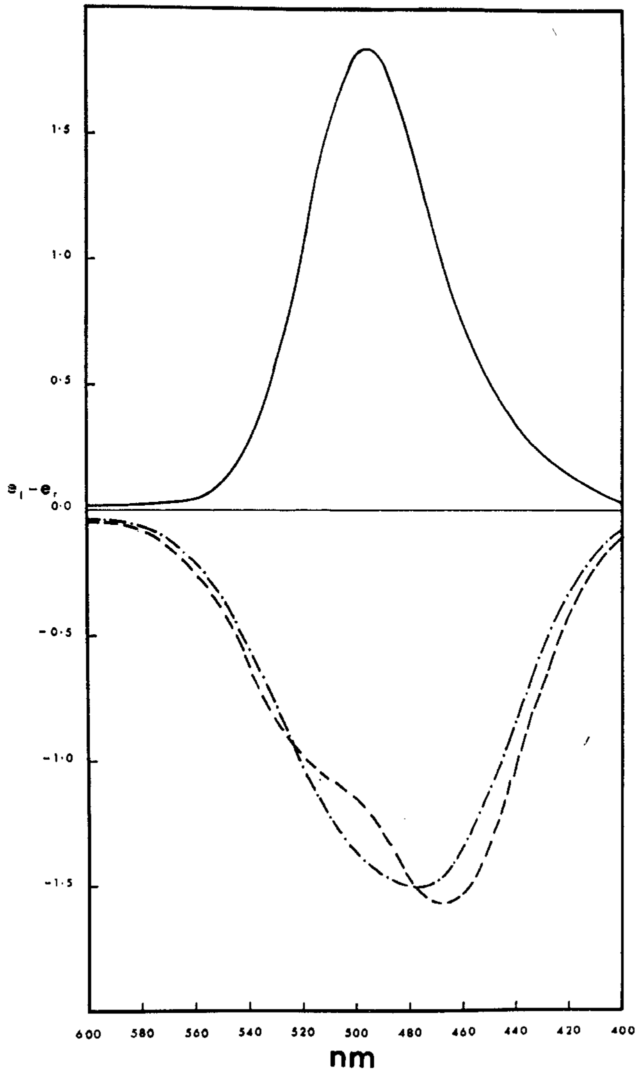

Figure 3.—CD spectra of β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ions: ——, $(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br$_2$ isomers in HClO$_4$ (0.1 *N*); ------, $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala]I$_2$ in HClO$_4$ (0.1 *N*); -·-·-·, $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl$_2$ isomers in H$_2$O after equilibration at pH 7.

$(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br$_2$·H$_2$O.—The optically pure diastereoisomer $(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]((+)-BCS)$_2$ was converted to the bromide salt by grinding with excess NaBr and water (10 ml). The active bromide salt was washed with an acetone–water mixture and finally with pure acetone and dried under vacuum. The specific rotations were $[\alpha]_{546}$ +484° and $[\alpha]_{436}$ −852° (0.1% solutions in H$_2$O (pH 4)). *Anal.* Calcd for $\mathrm{Co[(C_3N_2H_9)_2(C_4H_8NO_2)]Br_2\cdot H_2O}$: C, 24.75; H, 5.83; N, 14.44. Found: C, 24.90; H, 5.74; N, 14.07.

$(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]I$_2$·2H$_2$O.—The preparative isomeric mixture β_2-[Co(trien)(*N*-Me-(*S*)-ala)](ClO$_4$)$_2$ (25.1 g) was converted to the iodide salt by grinding with excess NaI and water (20 ml). This was fractionated in acidified water (pH 3), fractions of similar rotation were recombined, and the least soluble was purified to constant rotation, $[\alpha]_{546}$ −462°, $[\alpha]_{436}$ +751° (0.1% solutions in H$_2$O (pH 4)). The $(+)_{589}$ isomer was contained in the most soluble fractions and no attempt was made to purify it by this route. *Anal.* Calcd for $\mathrm{Co[(C_3N_2H_9)_2(C_4H_8NO_2)]I_2\cdot 2H_2O}$: C, 20.11; H, 5.07; N, 11.73. Found: C, 20.09; H, 4.65; N, 11.39.

Pmr Spectra of Pure Isomers.—$(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]I$_2$·2H$_2$O (0.1 g) was dissolved in a minimum amount of water acidified with acetic acid. Excess AgCl was added and the

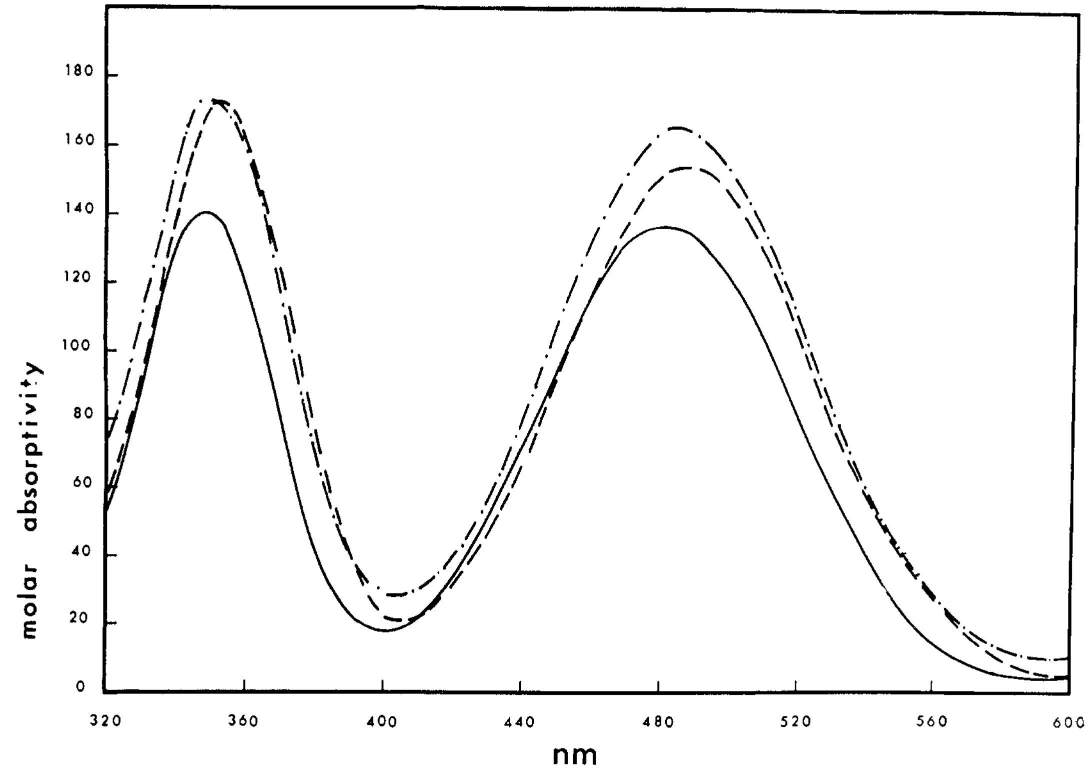

Figure 4.—Absorption spectra of β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers: ——, $(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br_2 in $HClO_4$ (0.1 *N*); -----, $(-)_{589}$-β_2-[Co(trien)(*N*-Me(*S*)-ala)]I_2 in $HClO_4$ (0.1 *N*); -·-·-·, $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Cl_2 isomers in H_2O after equilibration at pH 7.

precipitated AgI removed by filtration. The filtrate was evaporated to dryness and taken up in DCl (0.5 ml, 0.01 *N*), and the pmr spectrum was measured (Figure 1(b)).

$(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]$Br_2 \cdot H_2O$ (0.1 g) was sufficiently soluble in DCl (0.5 ml, 0.01 *N*) for measurement of the pmr spectrum (Figure 1(a)).

Pmr Spectra of Equilibrated Isomers. (a) **Equilibration at pH 7.**—$(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]$I_2 \cdot 2H_2O$ (0.1 g) was dissolved in water at pH 7. The solution was left at 25° for 35 min ($\sim 6t_{1/2}$) and then acidified with acetic acid. Excess AgCl was added and the precipitated AgI removed. The filtrate was evaporated to dryness and then dissolved in DCl (0.5 ml, 0.01 *N*) for measurement of the pmr spectrum (Figure 1(d)).

(b) **Equilibration at pH 12.**—$(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]$I_2 \cdot 2H_2O$ (0.1 g) was dissolved in 0.01 *N* NaOH. The solution was left for 25 min at 25° ($\sim 6t_{1/2}$) and then acidified with acetic acid (pH 3). The complex was adsorbed on a cation-exchange column (Bio-Rad AG 50W-X4, 200–400 mesh) and washed with water to remove small amounts of hydrolysis products. Finally, the amino acid complex was eluted with HCl (2 *N*), evaporated to dryness, and dissolved in D_2O (0.5 ml), and the pmr spectrum was measured (Figure 1(c)).

Polarimetric Kinetic Studies.—The rates of mutarotation at pH 6.5 and 12 were followed polarimetrically. Weighed samples (0.05 g) of $(-)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]$I_2 \cdot 2H_2O$ were dissolved in buffer (10 ml) or NaOH solution (10 ml) and quickly transferred to a thermostated cell. The rate of equilibration in pyridine buffer (0.05 *M*) at pH 6.5, 27°, $\mu = 1.0$ ($NaClO_4$), was followed at 480 nm. Equilibration at pH 12 (NaOH, 0.01 *N*) was followed at 490 nm, 27°, $\mu = 1.0$ ($NaClO_4$). In both experiments the change in rotation was $\sim 0.1°$.

Results and Discussion

The pmr spectrum of the reaction mixture contains absorptions for at least three β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers. This spectrum is analogous to that obtained when the $(-)_{589}$-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion was equilibrated at pH 12 (Figure 1(c)). The three peaks at 3.04, 3.02, and 2.83 ppm are attributed to three different *N*-methyl singlets; under the experimental conditions all N protons have been replaced by deuterium. In the 2-ppm region of the spectrum there are three superimposed doublets arising from three different *C*-methyl groups split by the proton on the α-carbon atom of the coordinated amino acid.

Two of the diastereoisomers have been isolated in a pure state by fractional crystallization, and their pmr, RD, CD, and visible absorption spectra are shown in Figures 1–4, respectively. In the pmr spectra (Figure 1(a) and (b)), the *N*-methyl signals appear as doublets since this center remains protonated in 0.01 *M* DCl. It is evident from the RD and CD spectra (Figures 2 and 3) that these two complexes are enantiomeric with respect to the configuration about each cobalt center. Unfortunately, several attempts at purifying the remaining isomer using fractional crystallization, ion-exchange, paper chromatography, and resolution techniques were unsuccessful. Despite the impurity, most of the properties of this isomer were obtained and are discussed below.

Isomerism in these complexes may arise from a variety of sources, namely, the configuration about the metal ion, the configuration of the coordinated amino acid, and the configurations at the *N*-methyl and "planar" secondary N centers (the "planar" secondary N atom of β-trien is that which links the two ethylenediamine rings sharing a common coordination plane;

the "angular" secondary N atom joins the two ethylenediamine residues not in the same plane). The assignments given below are based on a correlation of the spectral properties with closely related compounds of known structure and with the results of the equilibration experiments.

There is a close correspondence between the visible spectra of the isolated isomers (Figure 4) and the complexes $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(sar)$^{2+}$,[7] $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)((*S*)-pro)$^{2+}$,[8] and $\Lambda(+)_{589}$-β_2-(*SSS*)-Co(trien)((*S*)-pro)$^{2+}$.[8] It is concluded therefore that the *N*-methyl-(*S*)-alanine complexes have the β_2 configuration (*N*-methyl group trans to the trien "planar" secondary N atom). This conclusion is supported by an examination of Dreiding models which indicate that for the β_1-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers there could be large steric interactions between the *N*-methyl groups and the trien ligand.

The absolute configurations of the trien moieties about cobalt, except for the configuration at the "planar" N center, were assigned by comparing the RD and CD spectra with those for the β_2-Co(trien)((*S*)-pro)$^{2+}$ isomers[1,8] as $\Lambda(+)_{589}$-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ and $\Delta(-)_{589}$-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ (Figures 2 and 3).

As anticipated in the Introduction all three isomers are interconvertible for the same configuration about cobalt, and the positions of the equilibria and rates of mutarotation have been measured. Two distinct equilibria occurred in different pH ranges; at pH 6.5 (27°) the $\Delta(-)_{589}$-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion undergoes a mutarotation reaction with a rate constant $k = 6.4 \times 10^{-4}$ sec^{-1} and with retention of configuration about the cobalt center. The pmr, RD, CD, and visible absorption spectra of the equilibrated solution are shown in Figures 1(d) and 2–4 and clearly differ from those of the reactant. At this pH the *N*-methyl protons have exchanged with solvent D_2O and the pmr signals have collapsed to singlets (Figure 1(d)). The apparent triplet signal in the *C*-methyl region ($\sim$2 ppm) corresponds to the overlap of two doublets. The peaks at 3.00 (*N*-methyl) and at 1.96 and 1.89 ppm (*C*-methyl) correspond to the formation in equal abundance of the isomer which could not be purified by fractional crystallization. In this pH region the rate constant corresponds to that expected for mutarotation at an asymmetric N center.[9,10] At pH 12 a second mutarotation reaction was observed, also with retention of configuration about the cobalt center and with a rate constant $k = 3.1 \times 10^{-3}$ sec^{-1} (27°). The pmr spectrum for the final equilibrated solution is shown in Figure 1(c). The RD spectra (at 5 half-lives) showed some evidence of slow base hydrolysis of the amino acid moiety, but this did not interfere with the study of the equilibration reaction. In this pH region proton exchange at the α-carbon atoms of coordinated amino acids has been found to be quite fast[3] and pmr spectra in 0.01 *M* NaOD showed that deuteration at the *C*-methyl center had occurred during this mutarotation reaction. Further, the new pmr signals in the spectrum of the equilibrated solution (Figure 1(c)) correspond with those for the isolated $\Lambda(+)_{589}$-β_2-[Co(trien)(*N*-Me-(*S*)-ala)]Br_2 complex (Figure 1(a)). Therefore it is proposed that the second mutarotation reaction corresponds to inversion at the amino acid asymmetric C center leading to $\Delta(-)_{589}$-β_2-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$, the enantiomer of the isolated $\Lambda(+)_{589}$-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomer.

Two possibilities exist for mutarotation at the N center (pH 6.5–7.0); inversion occurs either at the *N*-methyl group or at the "planar" secondary N center of β-trien. In the complexes Co(en)$_2$(sar)$^{2+}$,[11,12] β_2-Co(trien)(sar)$^{2+}$,[7] and Co(en)$_2$(*N*-Me-(*S*)-ala)$^{2+}$,[13] mutarotation at the *N*-methyl center was excluded. The exclusion was attributed to unfavorable steric interactions between the methyl group and the adjacent en or trien chelate ring for the less stable form. It is concluded therefore that in the Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ complexes the mutarotation at pH 6.5 is associated with N inversion and synchronous conformational interchange in the trien ligand (Figure 5, I, III) and that the *N*-methyl group is stereospecifically oriented under all conditions.

The most stable configuration for the β-trien topology is that shown in Figure 5, I, for the $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion. This conclusion has been reached from a study of a number of β-trien complexes[7,9] and is supported by several crystal structure analyses.[14-17] However, the equilibrium results (Figure 1(c) and (d)) demonstrate that the $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ and $\Delta(-)_{589}$-β_2-(*RSS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers have similar stabilities in solution at pH 7 and 12. Therefore it is difficult to make individual structural assignments for the two isomers, although the structural relationship between the isomers is clear. One other example has been found where the *RRS* and *RSS* isomers have similar thermodynamic stabilities in aqueous solution. This is for the $\Delta(-)_{589}$-β_1-(*RRS*)-Co(trien)glyI_2 and $\Delta(-)_{589}$-β_1-(*RSS*)-Co(trien)glyI_2 compounds for which crystal structures have been completed.[17] The reason for these minor departures from the general stability relationship found for the β-trien diastereoisomers is not understood but it may be derived from an entropy rather than an enthalpy factor. A structural analysis is in progress to solve the structural problem, and measurements of ΔH and ΔS for this type of equilibrium are also in progress.

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[17] R. Dellaca, V. Janson, and W. T. Robinson, to be submitted for publication.

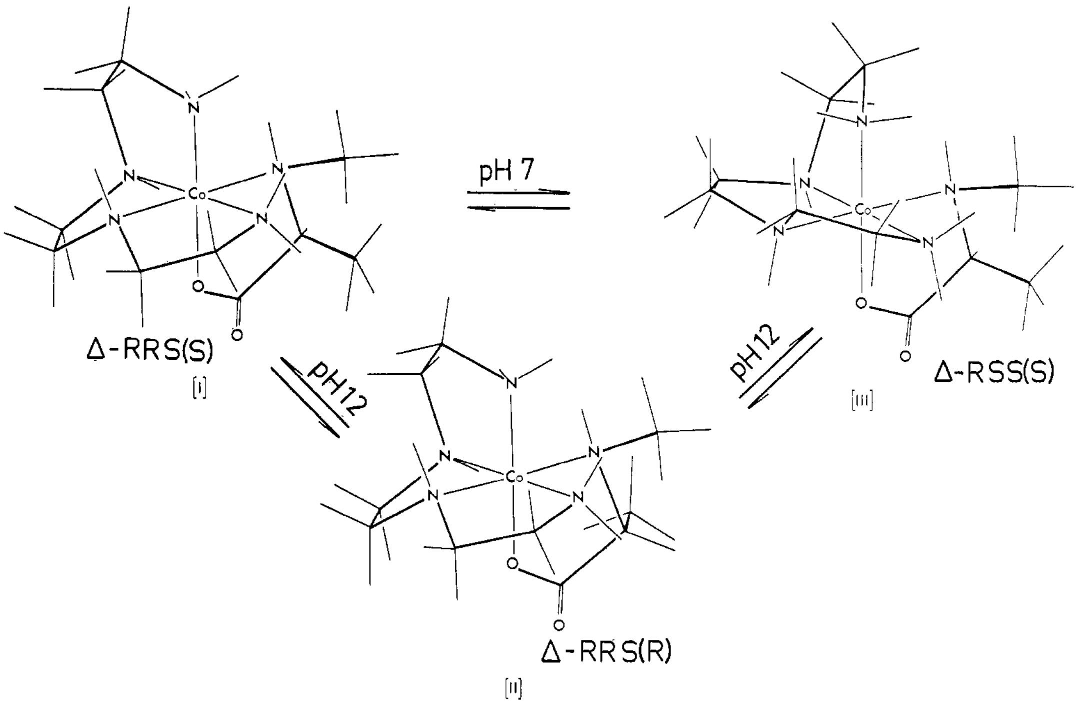

Figure 5.—Equilibrium and structural relationships between Δ-β_2-Co(trien)(*N*-Me-ala)$^{2+}$ ions: (I) Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ cation; (II) Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ cation; (III) Δ-β_2-(*RSS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ cation.

The most stable configuration for the chelated *N*-methyl-(*S*)-alanine moiety should be that in which the two adjacent methyl groups are trans to each other; in the cis configuration the *N*-methyl and *C*-methyl groups are in a sterically less favorable, eclipsed configuration. This analysis requires the $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ ion (Figure 5, II) to be more stable than the $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion where the methyl groups are now cis to each other (Figure 5, I). The equilibrium results support this conclusion and the pmr spectrum (Figure 1(c)) indicates that the $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ ion is approximately three times more stable than the Δ-*RRS*(*S*) and Δ-*RSS*(*S*) isomers. In the related ethylenediamine complexes the Λ-(*R*)-Co(en)$_2$(*N*-Me-(*S*)-ala)$^{2+}$ ion, which has trans methyl groups, is formed stereospecifically.[13] In alkaline conditions, when the proton on the α-carbon atom exchanges rapidly with solvent D_2O, it was shown that mutarotation at this center was excluded. It was deduced therefore that stereospecificity in the formation reaction was likely to be of thermodynamic origin. The difference between the trien and en systems may be associated with differences in the nonbonded interactions.

Strain Energy Minimization Calculations.—The strain energy minimization procedure has been described in some detail in a previous publication.[4] In summary, the total molecular strain energy is expressed as a sum of four terms

$$U = \sum_{ij} U(r_{ij})_{\mathrm{NB}} + \sum_{ijk} U(\theta_{ijk}) + \sum_{ijkl} U(\phi_{ijkl}) + \sum_{ij} U(r_{ij})_{\mathrm{B}}$$

where $U(r_{ij})_{\mathrm{NB}}$ is the nonbonded potential energy between two atoms i and j, $U(\theta_{ijk})$ is the potential energy for valence angle deformation between bonded atoms i, j, and k, $U(\phi_{ijkl})$ is the potential energy for torsional strain about the bond jk as defined by bonded atoms i, j, k, and l, and $U(r_{ij})_{\mathrm{B}}$ is the potential energy for bond deformation between bonded atoms i and j.

The terms used in the force field are analagous to those used for minimization calculations on the β_2-Co(trien)((*S*)-pro)$^{2+}$ complexes.[4] Minimization of the total molecular strain energy was achieved by a modified Newton–Raphson method of optimization due to Boyd.[18] The advantage of this method is that all the independent molecular coordinates are allowed to vary simultaneously.

Minimization calculations have been carried out on four β_2-Co(trien)(*N*-Me-ala)$^{2+}$ isomers whose trial coordinates were derived from the related β_2-Co(trien)(gly)$^{2+}$ isomers.[19] The methyl substituents on the amino N atom and α-carbon atom were initially placed at calculated positions assuming a tetrahedral geometry and standard bond lengths. The calculations were carried out on the Δ-*RRS*(*R*), Δ-*RRS*(*S*), Δ-*RSS*(*R*), and Δ-*RSS*(*S*) isomers (the last letter in the abbreviated nomenclature denotes the absolute configurations at the α carbon of the amino acid) using 297, 303, 308, and 308 energy terms, respectively. For each isomer a total of 126 independent coordinates were varied during the minimization procedure and no new nonbonded interactions of any significance were produced during refinement. Perspective views of the complex ions drawn under computer control from the

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(18) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

(19) D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, to be submitted for publication.

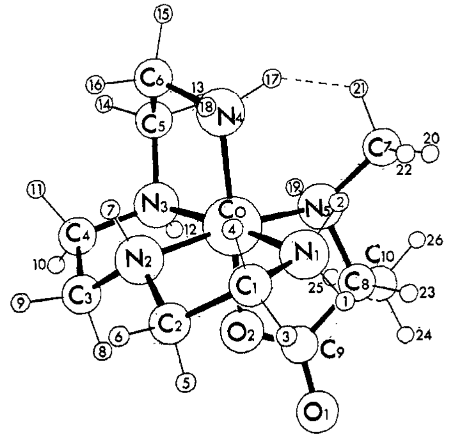

Figure 6.—Perspective view of Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ ion drawn from minimized coordinates. The dashed line indicates a major nonbonded interaction (>0.5 kcal/mol).

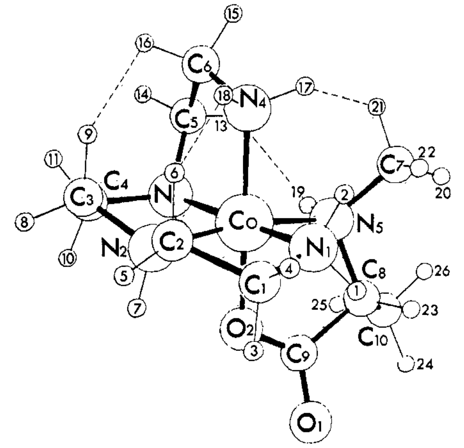

Figure 8.—Perspective view of Δ-β_2-(*RSS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ ion drawn from minimized coordinates. The dashed lines indicate the major nonbonded interactions (>0.5 kcal/mol).

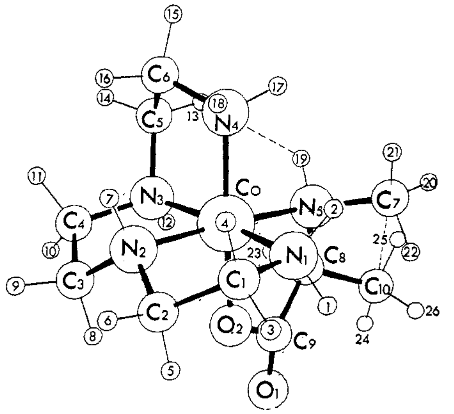

Figure 7.—Perspective view of Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion drawn from minimized coordinates. The dashed lines indicate the major nonbonded interactions (>0.5 kcal/mol).

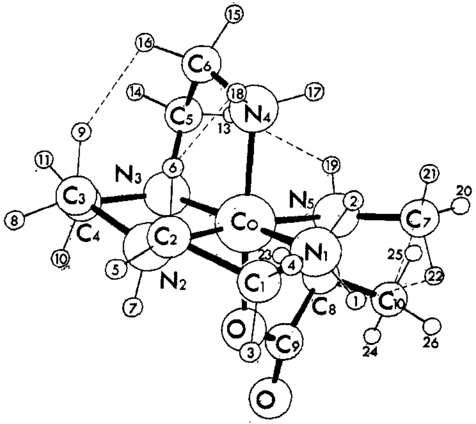

Figure 9.—Perspective view of Δ-β_2-(*RSS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion drawn from minimized coordinates. The dashed lines indicate the major nonbonded interactions (>0.5 kcal/mol).

minimized coordinates[20] are shown in Figures 6–9, respectively. In these diagrams nonbonded interactions greater than 0.5 kcal/mol are shown as dashed lines.

For the Δ-*RRS*(*R*) isomer there is only one major nonbonded interaction (H(17)···H(21), 2.07 Å, 0.8 kcal/mol) which is reduced by expansion of the Co–N(5)–C(7) bond angle (118.4°, 0.7 kcal/mol) and stretching the Co–N(2) bond (1.992 Å, 0.6 kcal/mol). No interaction occurs between the *N*-methyl and *C*-methyl groups of the amino acid which are in the favorable trans configuration.

However, in the Δ-*RRS*(*S*) isomer, which has the inverted configuration at the α-carbon atom, unfavorable steric interactions occur between the *N*-methyl and *C*-methyl groups which are in a less favorable cis configuration. Important nonbonded interactions are as follows: H(13)···H(19), 2.16 Å, 0.5 kcal/mol; C(7)···C(10), 2.80 Å, 0.7 kcal/mol. The methyl groups are oriented to minimize H···H nonbonded interactions between them, and the major interaction occurs between the carbon atoms. Angular distortions at the N(5)–C(8)–C(10) (114.6°, 0.6 kcal/mol) and C(7)–N(5)–C(8) (113.4°, 0.3 kcal/mol) bond angles relieve this interaction. Some bond angle bending also occurs at the Co–N(5)–C(7) bond angle (115.2°, 0.3 kcal/mol) and stretching of the Co–N(5) bond is also observed (1.990 Å, 0.5 kcal/mol).

Inversion at the trien "planar" secondary N atom, N(2), is unfavorable for the Δ-*RSS*(*R*) isomer. Major nonbonded interactions are as follows: H(6)···H(18), 2.08 Å, 0.7 kcal/mol; H(9)···H(16), 2.16 Å, 0.5 kcal/mol; H(13)···H(19), 2.10 Å, 0.7 kcal/mol; H(17)···H(21), 2.11 Å, 0.6 kcal/mol. Angular deformations occur at the expected angles, namely, N(2)–Co–N(4), 96.0°, 0.5 kcal/mol, and Co–N(5)–C(7), 117.4°, 0.5 kcal/mol. As previously observed, steric interactions associated with the bulky *N*-methyl group are accompanied by bond stretching at the Co–N(5) bond (1.990 Å, 0.5 kcal/mol).

The configuration at N(2) and cis methyl groups in the Δ-*RSS*(*S*) isomer also produces considerable steric interaction. Important nonbonded interactions are as follows: C(7)···C(10), 2.81 Å, 0.7 kcal/mol; H(1)···H(22), 2.13 Å, 0.6 kcal/mol; H(6)···H(18), 2.11 Å, 0.6 kcal/mol; H(9)···H(16) 2.12 Å, 0.6 kcal/mol; H(13)···H(19), 2.09 Å, 0.7 kcal/mol. These interactions are reduced by angular deformations in both the trien and amino acid ligands (C(7)–N(5)–C(8), 113.0°, 0.3 kcal/mol; N(5)–C(8)–C(10), 114.4°, 0.5 kcal/mol;

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[20] Minimized coordinates are available on request from the authors.

N(2)–Co–N(4), 97.2°, 0.8 kcal/mol). Bond stretching at the *N*-methyl center is once again observed (Co–N(5), 1.993 Å, 0.6 kcal/mol).

TABLE I

FINAL ENERGY TERMS FOR β_2-Co(trien)(*N*-Me-ala)$^{2+}$ ISOMERS (KCAL/MOL)

	Δ-β_2-(*RRS*)-Co(trien)-(*N*-Me-(*R*)-ala)$^{2+}$	Δ-β_2-(*RRS*)-Co(trien)-(*N*-Me-(*S*)-ala)$^{2+}$	Δ-β_2-(*RSS*)-Co(trien)-(*N*-Me-(*R*)-ala)$^{2+}$	Δ-β_2-(*RSS*)-Co(trien)-(*N*-Me-(*S*)-ala)$^{2+}$
Bond length deformations, $\Sigma U(r_{ij})_B$	1.4	1.5	1.5	1.7
Nonbonded interactions, $\Sigma U(r_{ij})_{NB}$	6.0	6.2	6.0	6.7
Valence angle deformations, $\Sigma U(\theta_{ijk})$	5.0	5.6	6.9	7.4
Torsional strain, $\Sigma U(\phi_{ijkl})$	5.5	5.1	6.1	5.8
Total conformational energy, U	17.9	18.4	20.5	21.6
Energy differences (relative to Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ isomer)	0	0.5	2.6	3.7

Final energy terms for the four isomers are listed in Table I. The calculated energy difference between the Δ-*RRS*(*R*) and Δ-*RRS*(*S*) isomers (which differ only in the configuration at the asymmetric α-carbon atom) is 0.5 kcal/mol in favor of the Δ-*RRS*(*R*) isomer. This result is in good agreement with the equilibration studies, where $\Delta G_{25°}$ was found to be 0.7 kcal/mol in favor of the Δ-*RRS*(*R*) isomer. The result was unexpected in view of the considerable steric interaction evident from Dreiding models between the cis *N*-methyl and *C*-methyl groups for the Δ-*RRS*(*S*) isomer. However, it appears that angular deformations can relieve these interactions with the expenditure of only a relatively small amount of bond angle strain energy. The Δ-*RSS*(*R*) isomer was calculated to be 2.6 kcal/mol less stable than the Δ-*RRS*(*R*) isomer, these two complexes being related by inversion at the trien "planar" secondary N atom, N(2). This result is in accord with experiment which showed that the Δ-*RSS*(*R*) isomer is not formed in solution in detectable amounts (<2%) under equilibrium conditions. This places a lower limit of 2.3 kcal/mol on the free energy difference between these isomers.

In the case of the Δ-*RSS*(*S*) isomer, with the unstable *S* configuration at atom N(2) and unfavorable cis methyl groups for the amino acid moiety, the minimization calculations predict this isomer to be less stable than the *RRS*(*S*) isomer by 3.2 kcal/mol; a similar qualitative result is obtained from an examination of Dreiding models. However the equilibration studies show that the Δ-*RSS*(*S*) and Δ-*RRS*(*S*) isomers have approximately equal stabilities. If the calculations correctly predict the relative enthalpy differences between the isomers, it would seem that an entropy term is an important factor in determining the free energy difference. Experiments designed to check this possibility are now in progress.

It can be seen that the strain energy minimization calculations on the β_2-Co(trien)(*N*-Me-ala)$^{2+}$ isomers predict some interesting geometrical distortions. A structural analysis is in progress on one of the isomers with cis methyl groups to establish the validity or otherwise of these predictions and also to determine the configuration about the "planar" N atom of trien.

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Insertion Reactions into the Methylplatinum Bond.
I. Thermal Reactions

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Insertion reactions of tetrafluoroethylene, hexafluorobut-2-yne, and carbon monoxide into the Pt–C bond of methylplatinum complexes of types *trans*-PtXCH$_3$L$_2$ and *cis*-Pt(CH$_3$)$_2$L$_2$ (X = halogen, L = tertiary phosphine or arsine) are described. Insertion into either one or both Pt–C bonds of *cis*-Pt(CH$_3$)$_2$L$_2$ can occur. The reactions are believed to proceed by rearrangement of intermediate π complexes, the stability of which governs the rate of insertion.

Introduction

Insertion reactions of unsaturated compounds into the metal–hydrogen or metal–carbon bond represent an important stage in the catalytic process of hydrogenation or polymerization, respectively.[1] Insertion reactions of fluoroolefins and -acetylenes, which give stable fluoroalkyl- or fluorovinylmetal compounds, have proved particularly useful since the product of a single

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(1) M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 312.