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Kinetic Study of the Transfer of Methyl Groups to Mercury(II) from a Series of Methylcobalt(III)-Chelate Complexes[1]

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Kinetics studies of the electrophilic cleavage of the Co–C σ bond in a series of six $CH_3Co(chelate)H_2O$ complexes by Hg^{2+} were carried out. The kinetic data support an electrophilic ($\mathrm{S_E2}$) mechanism, in that changes in electron density at the cobalt center which accompany the variation in chelate structure are transmitted to the transition state for the heterolytic cleavage of the Co–CH_3 bond. The values of k/M^{-1} sec^{-1} at 25.0° and μ 1.0 M in aqueous solution are as folows: saloph, $(3.3 \pm 0.3) \times 10^4$; salen, $(2.6 \pm 0.4) \times 10^4$; Me_2salen, $(2.1 \pm 0.1) \times 10^4$; $(dmgH)_2$, 65 ± 2; dpnH, 1.77 ± 0.03; tim (at μ 1.60 M), $(4.5 \pm 0.5) \times 10^{-4}$. For the first four members, the reaction rate is lowered by $[H^+]$, attributed to the protonation of the cobalt complex to an unreactive form; the equilibrium constants for these interactions were also evaluated.

Introduction

Mercury(II) ion acts as an effective electrophile toward cleavage of the metal–carbon σ bond in alkyl–transition metal complexes. Complexes studied in this respect include methylpentacyanocobaltate(III),[2] alkylcobalamins,[3] and alkylcobaloximes,[4-10] as well as alkylchromium complexes.[11-13] The most thoroughly studied reaction to date is that between the alkylcobaloximes and Hg(II)

$$RCo(dmgH)_2H_2O + Hg^{2+} = RHg^+ + (H_2O)_2Co(dmgH)_2^+ \qquad (1)$$

for which both kinetic[5-8] and stereochemical[9,10] determinations have been carried out.

There appears to be concensus among the workers directly involved in these efforts as well as by others commenting upon these results[14,15] that the reaction is properly described as proceeding by the $\mathrm{S_E2}$ mechanism;[16] the surprising result[9,10] that inversion occurs at the α carbon atom requires an "open" transition state.

We report here on further studies of the $\mathrm{S_E2}$ cleavage of cobalt alkyls with mercuric ion, as in the reaction

$$CH_3Co(chel)H_2O^n + Hg^{2+} = CH_3Hg^+ + (H_2O)Co(chel)^{n+1} \qquad (2)$$

utilizing the different macrocyclic (and pseudomacrocyclic) chelates of Figure 1. These chelates serve the function of changing the electron density at cobalt to a significant extent, a change which we felt would alter the rate of cleavage of the Co–CH_3 bond in a very significant fashion in this electrophilic reaction. Since the completion of this work two different studies of two of the same reactions have appeared,[17] and it is of interest to compare these results with ours.

Experimental Section

The following compounds (refer to Figure 1) were prepared and purified by standard techniques:[18-20] $[CH_3Co(salen)H_2O]$,[19] $[CH_3Co(Me_2salen)H_2O]$,[19] $[CH_3Co(saloph)H_2O]$,[19] $[CH_3Co(dpnH)H_2O](ClO_4)$,[20] and $[CH_3Co(tim)CH_3CN](BPh_4)_2\cdot CH_3CN$.[20] Stock solutions of mercury(II) perchlorate were prepared by dissolving reagent grade mercury(II) oxide in a slight excess of perchloric acid. Solutions were analyzed by the Volhard method. Lithium and barium perchlorates were recrystallized twice before use.

The faster reactions were studied using a Durrum stopped-flow spectrophotometer with a 2-cm optical path, and the slower reactions, using Cary Models 12 and 14 spectrophotometers. The kinetic data were determined at appropriate wavelengths in the visible and ultraviolet region, as follows: $CH_3Co(dpnH)H_2O^+$, 458 nm; $CH_3Co(tim)H_2O^{2+}$, 485 nm; $CH_3Co(salen)H_2O$, 250, 340, and 380 nm; $CH_3Co(Me_2salen)H_2O$, 255–275 nm; $CH_3Co(saloph)H_2O$, 240–255 nm.

The reactions were studied at 25° in solutions of ionic strength 1.0 M, maintained with lithium perchlorate, except for $[CH_3Co(tim)H_2O]^{2+}$, where the very slow reaction necessitated the use of high concentrations of Hg^{2+}. In that instance, therefore, in addition to the 1.00 M ionic strength provided by $HClO_4 + LiClO_4$, the solutions of $Hg(ClO_4)_2$ added appreciably to the ionic strength, up to 0.6 M additional. Two series of measurements were performed in this case, one with the ionic strength consequently varying between 1.0 and 1.6 M and another in which the ionic strength was maintained at 1.6 M by adding, in addition to 1.00 M of 1:1 electrolyte $HClO_4$–$LiClO_4$, the inert electrolyte $Ba(ClO_4)_2$, such that $[Ba^{2+}] + [Hg^{2+}] = 0.200$ M.

Results

The 1:1 stoichiometry and the formation of $HgCH_3^+$ have been confirmed in the earlier work[5-9] and were studied for this group of methylcobalt–chelate complexes only cursorily; Figure 2 depicts the spectrophotometric titration of $CH_3Co(salen)H_2O$ with Hg^{2+} at λ 340 nm, supportive of eq 2.

The kinetics experiments were performed with at least a tenfold excess of Hg^{2+}, and each experiment conformed quite closely to a pseudo-first-order rate law. Apparent second-order rate constants were computed as the quotient of the pseudo-first-order rate constant and the concentration of Hg^{2+} at the midpoint of the kinetic run. Plots of k_{obsd} *vs.* $[Hg^{2+}]$ at 1.00 M H^+ are shown in Figure 3 for four of the reactions. The values of k/M^{-1} sec^{-1} are 1.77 ± 0.03 for $CH_3Co(dpnH)H_2O^+$ [21] and $(4.5 \pm 0.5) \times 10^{-4}$ for $CH_3Co(tim)H_2O^{2+}$,[22] independent of $[H^+]$.

The rate dependence upon $[H^+]$ for the remaining compounds, on the other hand, takes the same form as reported previously[5,8] for $CH_3Co(dmgH)_2H_2O$, plots of $1/k_2$ *vs.* $[H^+]$ being linear as depicted in Figure 4. In the reactions of the bis(dimethylglyoximato) complexes this behavior was ascribed[5] to protonation of the chelate ring at the O···H···O position, an assignment which was confirmed later.[23] The kinetic data are consistent with a mechanism in which a similar rapid protonation equilibrium occurs (the site of protonation will be considered later), the rate-determining step being the reaction of Hg^{2+} with the unprotonated form of the methylcobalt complex, as shown in eq 3 and 4. According to this mechanism

$$CH_3Co(chelate)H_2O + H^+ \overset{K_B}{\rightleftharpoons} [CH_3Co(chelate\ H)H_2O]^+ \qquad (3)$$

$$CH_3Co(chelate)H_2O + Hg^{2+} \xrightarrow{k} (H_2O)_2Co(chelate)^+ + HgCH_3^+ \qquad (4)$$

in which the protonation equilibrium is maintained throughout, the apparent second-order rate constant k_2 is given as

$$k_2 = \frac{k}{1 + K_B[H^+]} \qquad (5)$$

Least-squares fits of the kinetic data to this expression gave the parameters summarized in Table I.

In support of the suggested mechanism, ionic strength variation in the case of $CH_3Co(salen)H_2O + Hg^{2+}$ was carried out at $[H^+] = 5 \times 10^{-3}$ M. Values of $10^{-4}k_2/M^{-1}$ sec^{-1} are 2.3, 2.4, 2.2, and 2.6 at μ/M 0.0065, 0.0175, 0.0215, and 1.00.

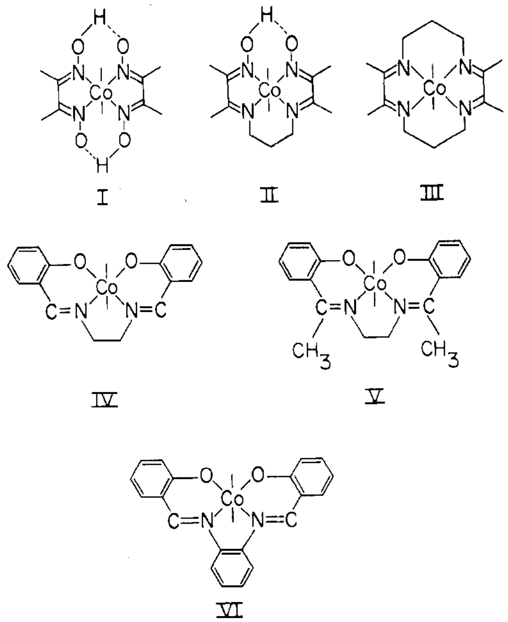

Figure 1. Structures of the cobalt chelates studied; the formulas of the methylaquo derivatives of chelates I-VI are abbreviated[27] as $[CH_3Co(dmgH)_2H_2O]$, $[CH_3Co(dpnH)H_2O]^+$, $[CH_3Co(tim)H_2O]^{2+}$, $[CH_3Co(salen)H_2O]$, $[CH_3Co(Me_2salen)H_2O]$, and $[CH_3Co(saloph)H_2O]$, respectively.

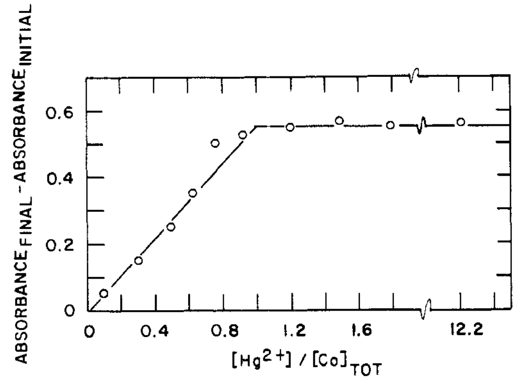

Figure 2. Spectrophotometric titration of $CH_3Co(salen)H_2O$ with Hg^{2+}.

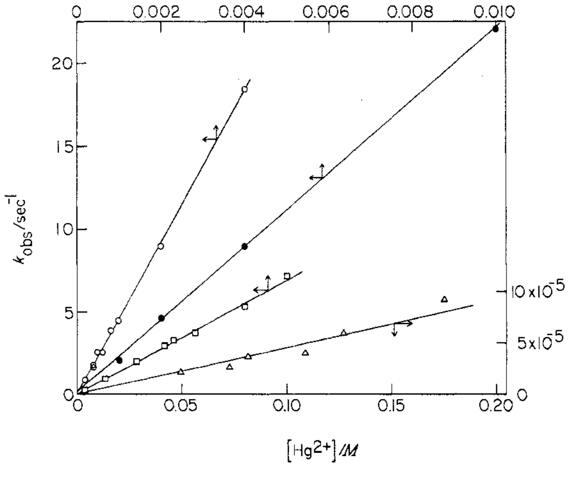

Figure 3. Plot of k_{obsd} against $[Hg^{2+}]$ at 1.0 M H^+ for $CH_3Co(chelate)H_2O$ reactions; data for chelates dpnH, salen, Me_2salen, and saloph are shown by triangles, squares, filled circles, and open circles, respectively.

The invariance of rate constant with ionic strength is reasonable seeing that in this instance the cobalt complex carries no ionic charge.

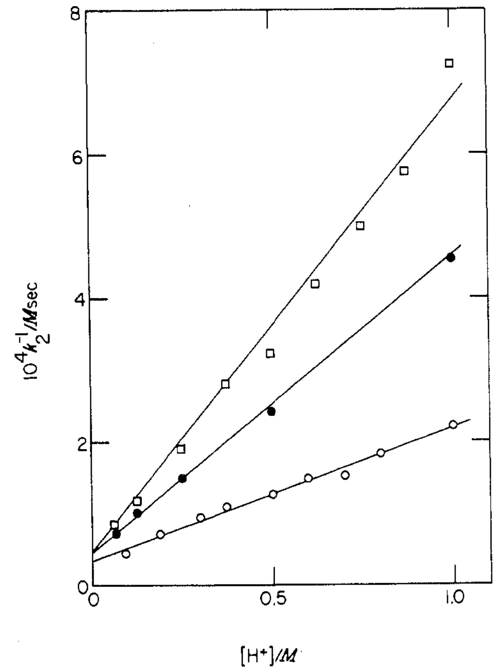

Figure 4. Plot of k_2^{-1} against $[H^+]$ for $CH_3Co(chelate)H_2O$ reactions with Hg^{2+}; symbols are as in Figure 3.

Table I. Rate and Equilibrium Parameters for the Reactions of $CH_3Co(chelate)H_2O$ Complexes with Hg^{2+} [a]

Complex	k/M^{-1} sec^{-1}	K_B/M^{-1}
$[CH_3Co(dmgH)_2H_2O]$[b]	65 ± 2	3.5 ± 0.2
$[CH_3Co(dpnH)H_2O]^+$	1.77 ± 0.03	c
$[CH_3Co(tim)H_2O]^{2+}$	$(4.5 \pm 0.5) \times 10^{-4}$	c
$[CH_3Co(salen)H_2O]$	$(2.6 \pm 0.4) \times 10^4$	17.4 ± 2.8
$[CH_3Co(salen)H_2O]$	$(3.15 \pm 0.37) \times 10^4$ [d]	20.6 ± 2.3[d]
$[CH_3Co(Me_2salen)H_2O]$	$(2.1 \pm 0.1) \times 10^4$	8.6 ± 0.5
$[CH_3Co(saloph)H_2O]$	$(3.3 \pm 0.3) \times 10^4$	6.4 ± 0.8

[a] At 25.0° and $\mu = 1.00$ M, except for $CH_3Co(tim)H_2O^{2+}$ for which $\mu = 1.60$ M was used (see text). [b] Data from ref 5. [c] Estimated $K_B < 0.01\ M^{-1}$. [d] Data from ref 17b.

Discussion

The rate effects reported herein reflect the influence of the macrocyclic chelate system upon cleavage of the Co–CH_3 bond by reaction with Hg^{2+}. The mechanism of the cleavage reaction is generally agreed to be bimolecular electrophilic substitution (SE2 mechanism), and stereochemical results on two different alkylcobaloximes have defined the reaction as proceeding with stereochemical inversion at carbon. The large rate effects accompanying these changes in chelate structure are consistent with this mechanism, in that by several measures, discussed subsequently, it is known that these changes affect the electron density at the cobalt. The electronic effects are undoubtedly transmitted to the axial ligands (both to CH_3 and to the trans base, H_2O in the case at hand); the influences in the present reaction should be particularly pronounced since a (formal) carbanion-transfer process is expected to show particular sensitivity to changes in the polarity of the Co–CH_3 bond.

The various chelates considered here do, in fact, change electron density at the cobalt center in ways perceived other than by the kinetic data on electrophilic Co–CH_3 bond cleavage. This can be established by considering measures such as the following: (a) the $E_{1/2}$ values for one-electron reduction of the family of alkylcobalt–chelate complexes;[24] (b) the pK_a's of axial water molecules in the diaquocobalt–chelate complexes;[24a,25] (c) the chemical shifts of the methyl proton resonances in the methylcobalt derivatives;[26,27] (d) the formation constants for converting a five-coordinate alkylcobalt–chelate complex (or the six-coordinate dimer) to the six-coordinate, "base-on" form;[24a,28,29] (e) the rate of base dissociation from the position trans to the alkyl substituent.[29,30] (Other parameters appearing less sensitive to changes in chelate structure include bond lengths, stretching frequencies, and energies of d–d absorption bands, although correlations of the last parameter with chelate structure do not appear to have been made in a systematic fashion.)

The complexes $[CH_3Co(chelate)H_2O]$ for chelates salen, Me_2salen, and saloph react with Hg^{2+} as a group much more rapidly than do the others and among themselves show relatively small rate effects. This group comprises the same three having the most negative $E_{1/2}$'s (salen, −1.57; Me_2salen, −1.65; saloph, −1.30 V *vs.* SCE in DMF solution, compared to −0.86 V for the more slowly reacting $MeCo(dpnH)H_2O^+$ [24]), the most acidic axial water molecules in $(H_2O)_2Co(chelate)^+$ complexes (pK_a's are 6.86 for salen, 7.06 for Me_2salen, and 6.73 for saloph, compared to 5.14 for $(H_2O)_2Co(dmgH)_2^+$), the most accessible five-coordinate derivatives compared to the other three chelates, and the least affinity for axial bases.[24,28-30] These effects all appear to be manifestations of the same influences, the consequence of changing the extent of electron donation from the chelate to the cobalt.[31]

Within the group of three slower reacting methylcobalt complexes of chelates the rate effects are quite pronounced, $(dmgH)_2$ > dpnH > tim relative rates (10^5:4 × 10^3:1), which appears to be in accord with the effects of the various measures of electron donation. The rates of dissociation of axial bases[27,28] may provide the most quantitative assessment. For the complexes $CH_3Co(dmgH)_2H_2O$, $CH_3Co(dpnH)H_2O^+$, and $CH_3Co(tim)H_2O^{2+}$ the rate constants for dissociation of, for example, acetonitrile coordinated in the axial position trans to the $Co–CH_3$ group, at 10° are 52, 7.0, and 2.5 sec^{-1}, respectively.[29] This effect is in the same order as the rate of $Co–CH_3$ cleavage by mercuric ion, indicating not surprisingly that the more electron density placed at the cobalt atom by the chelate, the more facile the heterolytic scission of a bond between cobalt and an axial ligand. The extreme of the rate effects in the cleavage with Hg^{2+} amounts to a factor of 10^5, compared to $10^{1.5}$ for the substitution rates. We suggest two factors which may account for the greater sensitivity of Hg^{2+} cleavage than substitution to the changes in chelate structure. First, the $Co–CH_3$ bond distances are "normal", whereas the ground-state influence of the alkyl ligand is so great as considerably to lengthen and weaken the bond between cobalt and the trans base ($NCCH_3$ in the comparison offered here). Consequently, changes in electron density at cobalt should be transmitted comparatively less effectively in base dissociation reactions than in heterolytic $Co–CH_3$ bond scission. Second, the electrostatic factor toward reaction with the Hg^{2+} cation would favor the reactivity sequence $[CH_3Co(dmgH)_2H_2O]$ > $[CH_3Co(dpnH)H_2O]^+$ > $[CH_3Co(tim)H_2O]^{2+}$ (although we are inclined to discount pronounced electrostatic influences on ionic reactions in polar solvents at high ionic strength).

As far as the effects of H^+ go, we note that in every instance only the base form of the alkylcobalt complex is reactive toward Hg^{2+}, which is consistent with the S_E2 mechanism, in that protonation of the chelate would serve to render heterolytic cleavage of $Co–CH_3$ much less favorable. The complex $[CH_3Co(dpnH)H_2O]^+$ is not protonated at O···H···O in the fashion established for methylcobaloxime,[5,23] which is easily understood as a reflection of the basicity of the monoanion $dpnH^-$ compared to the dianion $(dmgH)_2^{2-}$. The chelate tim, of course, lacks a suitable site for protonation. The protonation of the salen-type chelates is surprising, however, as their structures are different from the $(dmgH)_2$ structure. It may be that one of the donor oxygen atoms is the site of protonation, possibly with decoordination of the chelate at this one site. Whether that is really the case, however, and whether such a coordination vacancy would be filled by a water molecule from the solvent, cannot be inferred from these results.

Registry No. $[CH_3Co(dmgH)_2H_2O]$, 25360-55-8; $[CH_3Co(dpnH)H_2O]^+$, 26334-78-1; $[CH_3Co(tim)H_2O]^{2+}$, 50600-07-2; $[CH_3Co(salen)H_2O]$, 27073-12-7; $[CH_3Co(Me_2salen)H_2O]$, 43043-84-1; $[CH_3Co(saloph)H_2O]$, 32105-86-5; Hg^{2+}, 14302-87-5.

Supplementary Material Available. A table of kinetic data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40677+.

References and Notes

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(21) After completion of this work, two independent determinations of the rate of reaction of $[CH_3Co(dpnH)H_2O^+]$ with Hg^{2+} were published.[17] The reported rate constants at 25.0° are 1.56 ± 0.01 M^{-1} sec^{-1} (ionic strength 1.0 *M*)[17b] and 5.9 M^{-1} sec^{-1} (ionic strength 2.2 *M*).[17a] The former agrees reasonably well with our data, and the latter represents the salt effect expected for a reaction of two cations. Tauzher et al.[17b] conducted studies at much high $[Hg^{2+}]$, up to 0.3 *M*, and noted for the dpnH and salen complexes a mass law retardation at the higher concentrations, consistent with formation of a 1:1 complex, which may or may not be an intermediate lying along the reaction path.

(22) The data given for $CH_3Co(tim)H_2O^{2+}$ refer to measurements extending to 0.175 *M* Hg^{2+} in which $Ba(ClO_4)_2$ was added in an effort to maintain as constant an ionic environment as possible. The constant value of *k* so obtained is an indication that this was a useful procedure. In contrast, in a series of experiments in 1.00 *F* $HClO_4$, in which $Hg(ClO_4)_2$ was added with no compensating adjustment in the medium, the apparent rate constant was not constant with Hg^{2+} variation, which was present in these runs at fairly high concentration. Values for $10^4k_2/M^{-1}$ sec^{-1}:

1.8, at 0.035 *M* Hg^{2+}; 1.4, at 0.073 *M*; 2.7, at 0.145 *M*. The irregular variation probably arises from nonuniform changes in activity coefficients in this region of high ionic strength.
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(31) One anomaly should be noted: within this group of chelates IV–VI, rate variations, while minor, lie in the order saloph > salen > Me_2salen (relative rates 1.6:1.2:1.0), whereas by both of the criteria referred to a trend in exactly the reverse order would have been expected. The differences in any of the parameters is so small, that we regard small changes within the group IV–VI as not particularly significant.

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Reaction of Acetaldehyde with Some Optically Active Cobalt(III) Complexes Containing Coordinated Glycine

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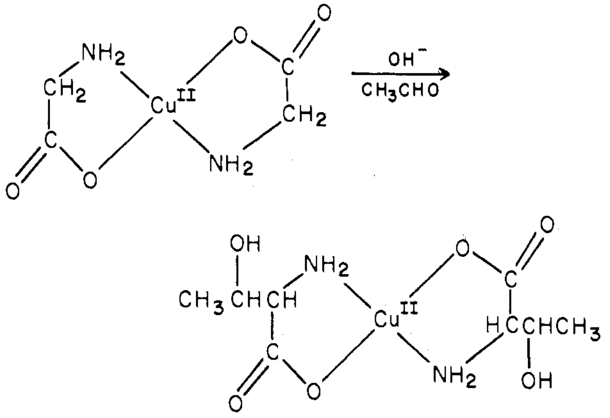
The resolution and assignment of absolute configuration of the isomers of $[Co(en)(gly)_2]^+$ is reported. The optically active cations (+)-$[Co(en)_2(gly)]^{2+}$, (+)-*trans*(*O*)-, (+)-*β-cis*(*O*)-, and (+)-*α-cis*(*O*)-$[Co(en)(gly)_2]^+$ react with acetaldehyde in an aldol-type condensation reaction to give optically active threonine and allothreonine. Using kinetically controlled conditions, the reaction yields products with relatively high optical purities (16–35%). The isolated threonine and allothreonine contain an excess of the *S* isomer indicating that the aldehyde prefers to attack the *S* "side" of the coordinated glycine in these cations. However, analysis of the amino acid distribution suggests that the diversity of geometric environments exhibited by the cations has little effect on the stereochemical course of the reaction. Finally, the product distribution found reinforces the assignment of the absolute configuration of the cations based on circular dichroism arguments.

Introduction

The chemical reactivity of the amino acid glycine coordinated to a transition metal ion has been recognized for some time. Akabori and coworkers[1] demonstrated that the glycine molecules in bis(glycinato)copper(II), $Cu(gly)_2$, react with acetaldehyde in an aldol-type condensation reaction to give threonine and allothreonine (eq 1). The structures of the *S* forms of threonine and allothreonine are shown in Figure 1.



(1)

Acetaldehyde has also been shown to react with the geometric isomers[2] of $[Co(gly)_3]$ as well as the *N*-salicylideneglycinatoaquocopper(II) complex.[3] Various other reactants such as formaldehyde, benzaldehyde, and pyruvic acid[4] have been used in this reaction to produce serine, β-phenylserine, and β-hydroxy-β-methylaspartic acid, respectively.

Recognizing the stereochemical possibilities of this reaction, Murakami and Takahashi[5] examined the condensation products obtained from the reaction of acetaldehyde with two optically active Co(III) complexes. They found that the reaction of the optically active cation (−)-$[Co(en)_2(gly)]^{2+}$ with acetaldehyde yields product amino acids with low optical activity (8% asymmetric synthesis). We have reexamined the stereospecificity of this reaction with the enantiomer of (−)-$[Co(en)_2(gly)]^{2+}$ as well as the optically pure geometric isomers of $[Co(en)(gly)_2]^+$ (Figure 2). This series of complexes provides an opportunity to study the product distribution obtained from the reaction as a function of changes in complex geometry.

Experimental Section

Reagents and Equipment. All chemicals were reagent grade unless otherwise noted. The amino acids glycine and (*S*)-threonine were purchased from Nutritional Biochemicals Corp., Cleveland, Ohio. Reagent grade acetaldehyde was purified just prior to use by distillation (under N_2) of 10 ml of aldehyde acidified with 2 drops of H_3PO_4. All uv–visible spectra were obtained using a Cary 14 spectrophotometer. The optical rotatory dispersion (ORD) spectra were obtained with a Beckman DU spectrophotometer, fitted with a Keston polarimeter attachment. Circular dichroism (CD) spectra were obtained using a Cary 60 spectrophotometer. A Sargent pH-Stat fitted with a Sargent miniature combination electrode was used for the reactions. The pH-Stat was standardized at pH's of 7.00 and 10.00 with standard buffers prior to each run.

The proton magnetic resonance (pmr) spectra were recorded using a Varian A-60 spectrometer with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as a reference. The pmr samples were prepared by dissolving 80–100 mg of the complex in 0.5 ml of D_2O. Exchange of the NH_2 protons was accomplished by addition of 1.0 *N* NaOD until the solution turned basic (pH 10) followed immediately by the addition of 1 drop of 6 *N* DCl.

An F & M (Hewlett-Packard, Stokie, Ill.) Model 402 gas–liquid chromatograph (glc) with dual column flame ionization detectors was used for the amino acid analyses. The elemental analyses of the complexes were done by Galbraith Laboratories, Knoxville, Tenn.

Syntheses. ***trans*(*O*)-$[Co(en)(gly)_2]Cl\cdot 2H_2O$ and *β-cis*(O)-$[Co(en)(gly)_2]Cl\cdot H_2O$.** The synthesis and characterization of these