of 0.75 and the four generated by a $\pi/4$ rotation about the axis, 0.25. Subsequent refinement of the occupancies showed these assignments to be essentially correct. Three cycles of refinement resulted in isotropic convergence at $R_1 = 0.105$ and $R_2 = 0.136$.

In order to test whether the proposed model represented the correct absolute configuration of the molecule, the signs of $\Delta f''$ in the anomalous scattering factor tables of the iron and phosphorus were changed. Three cycles of rerefinement resulted in $R_2 = 0.141$. By applying Hamilton's R test[19] to R_2 it was ascertained that the difference in R values was significant to the 5% level of probability. Hence the original structure was shown to be correct in chirality.

The subsequent difference Fourier showed the presence of regions of relatively high electron density (~0.7 e/Å) which could be attributed to hydrogen atoms. The C–H and N–H distances were adjusted to ~1.0 Å. The three final cycles of refinement in which the temperature factors of all of the atoms except the hydrogens were varied anisotropically and all of the hydrogens except for methyl hydrogens were included as fixed atoms resulted in convergence at $R_1 = 0.065$ and $R_2 = 0.080$. The final difference Fourier showed the presence of no peaks above 0.5 e/Å. Final positional and thermal parameters and structure factor tables are given in Table III.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Registry No. $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$, 56689-50-0.

Supplementary Material Available: A listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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An Electron Diffraction Investigation of the Molecular Structure of Monochlorodiborane, B_2H_5Cl

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The molecular structure of chlorodiborane, B_2H_5Cl, has been investigated at room temperature by gaseous electron diffraction. The results are consistent with a molecule of C_s symmetry having, except for the chlorine atom, the symmetry of diborane itself. Because the B–B and B–Cl distances are very similar, it was possible to measure accurately only their average value. However, an assumption based on results from other molecules allowed the deduction of reasonably accurate values for each. The more important distances (r_a), bond angles, and root-mean-square amplitudes of vibration (l) have the following values with parenthesized uncertainties estimated at 2σ: $r(\text{B–Cl,B})_{\text{av}} = 1.775\ (2)$ Å, $r(\text{B–Cl}) = 1.775\ (5)$ Å, $r(\text{B–B}) = 1.775\ (15)$ Å, $r(\text{B–H})_{\text{av}} = 1.277\ (2)$ Å, $r(\text{B–H}_t) = 1.205\ (13)$ Å, $r(\text{B–H}_b) = 1.331\ (15)$ Å, $\angle\text{BBCl} = 120.9\ (3)^\circ$, $\angle\text{H}_t\text{BH}_t = 125.0\ (60)^\circ$, $l(\text{B–Cl}) = 0.057\ (3)$ Å, $l(\text{B–B}) = 0.060\ (3)$ Å, $l(\text{B–H}_t) = 0.090\ (13)$ Å, $l(\text{B–H}_b) = 0.107\ (13)$ Å, and $l(\text{B}\cdots\text{Cl}) = 0.084\ (5)$ Å. Amplitudes of vibration calculated from an approximate force field fitted to the frequency spectrum are in good agreement with observed values.

It is well-known that the boron hydrides have unusual structures characterized by two different types of bonds between boron and hydrogen atoms, commonly called "bridge" and "terminal" bonds. Simple derivatives of the boron hydrides may be obtained by substitution at either bridge or terminal positions, but bridge substitution is perhaps less common and appears to perturb the structure of the rest of the molecule rather more than the other type. Thus, in the bridge-substituted compounds amino-[1,2] and dimethylaminodiborane[2] the B–B distance is about 0.14 Å longer than in diborane[3-5] itself, whereas in the terminal-substituted compounds monobromo-[6] and *cis*- and *trans*-1,2-dimethyl-[7] and 1,1,2,2-tetramethyldiborane[8] the increase in this distance is less than half this amount.

The differences between the structures of the boron hydride molecules and their derivatives remain an interesting and incompletely understood matter. We report here the results of an electron diffraction investigation of monochlorodiborane, another molecule with the substituent at the terminal position (Figure 1). During the course of the analysis we had occasion to calculate amplitudes of vibration from an approximate vibrational force field for the molecule; those results are also presented.

Experimental Section

The sample of essentially pure B_2H_5Cl was prepared for us by Professor David M. Ritter and kept at liquid nitrogen temperature until use.

The diffraction experiments were made in the OSU apparatus with the nozzle tip at room temperature. Other experimental conditions were an r^3 sector, 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1, 0.3–0.4-μA beam currents, 45–150-s exposure times, 0.05690–0.05696-Å

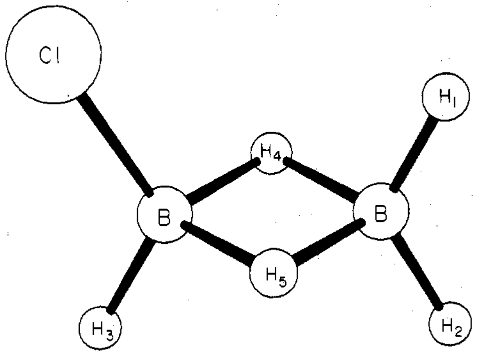

Figure 1. Atom numbering in model.

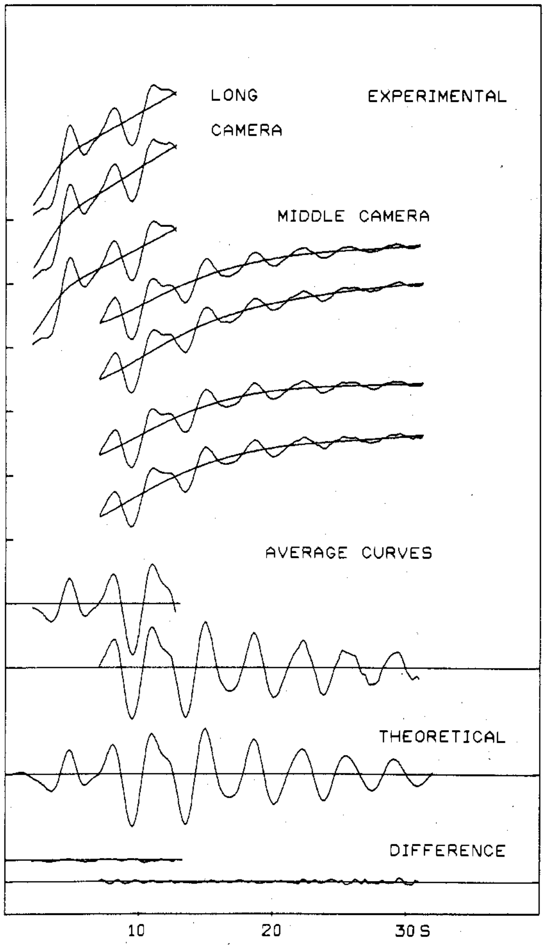

Figure 2. Intensity curves. The experimental curves are s^4I_T superposed on their backgrounds and the averages of the differences. The theoretical curve is from the model of Table II. The difference curves are experimental minus theoretical.

electron wavelength (calibrated in separate experiments against CO_2 (r_a(C–O) = 1.1646 Å, r_a(O···O) = 2.3244 Å), and 74.996- and 30.026-cm nozzle-to-plate distances. Three plates at the longer and four at the shorter distance were selected and scattered intensity data obtained from them in the usual way.[9-11] The useful data from each distance spanned the ranges $2.00 \leq s \leq 13.00$ Å^{-1} and $7.00 \leq s \leq 31.00$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin \theta$). The elastic and inelastic scattering amplitudes, which when multiplied by s^2, are used in parts of the background fitting as well as in the structure analysis, were obtained from tables.[12,13] Curves of the leveled total intensity (s^4I_T), the final backgrounds, and the averaged experimental molecular intensities (sI_m) are shown in Figure 2; the data are available as supplementary material.

Structure Analysis

Radial Distribution Curves and Specification of Model Types. Radial distribution curves were calculated from intensity curves with essentially constant coefficients obtained by multiplying the sI_m curves, the form used in our refinements, by $Z_BZ_{Cl}s^{-4}F_B^{-1}F_{Cl}^{-1}$. The final experimental RD curve was calculated from a composite of the average curves shown in Figure 2 using data from the theoretical curve for the unobserved or uncertain region $s < 2.00$ Å^{-1}. This curve superposed on the distance spectrum from the final model is shown in Figure 3.

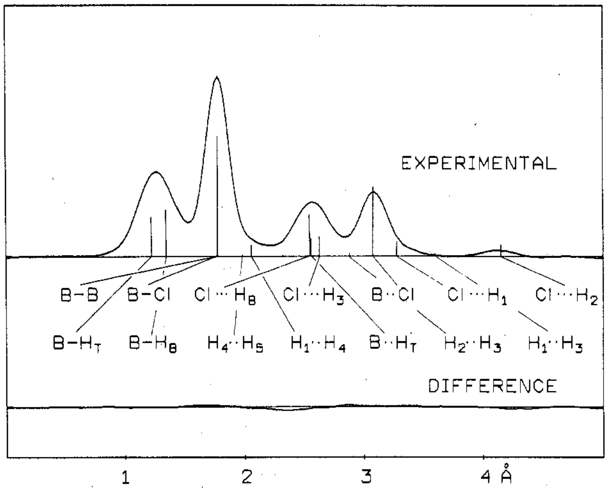

Figure 3. Radial distribution curve calculated from the composite of average curves of Figure 1 with data from the theoretical curve of the final model used for the region $0 \leq s \leq 2.00$ Å^{-1} ($B = 0.0025$ Å^2). Vertical lines show positions of interatomic distances; their lengths are proportional to weights of terms.

The most general model of B_2H_5Cl with assumed C_s symmetry requires 12 geometrical parameters for its specification. These may be reduced to six with the additional reasonable assumption that except for the chlorine atom the molecule has the symmetry of diborane itself; i.e., the four-member ring is planar and all B–H$_t$, B–H$_b$, and ∠BBH$_t$ are equal within each group. The six geometrical parameters were chosen to be B–H$_{av}$ (the weighted average B–H bond length equal to (4B–H$_b$ + 3B–H$_t$)/7), $\Delta_{b,t}$ (the distance difference B–H$_b$ – B–H$_t$), (B–Cl,B)$_{av}$ (the simple average of the B–Cl and B–B bond lengths), $\Delta_{Cl,B}$ (the distance difference B–Cl – B–B), and the two bond angles ∠H$_t$BH$_t$ and ∠BBCl. Corresponding to this choice of geometrical parameters there are 15 different vibrational amplitude parameters, l_{ij}. This unmanageable number may be reduced to about 7 group-amplitude parameters by specifying differences between certain amplitudes as invariant. The groupings were chosen from among distances of roughly similar type or magnitude; the differences were assigned from experience or from consideration of amplitude values calculated from vibrational force fields. The final amplitude parameters may be seen in Table II.

Refinements. The refinements were carried out by the method of least squares[14] fitting a single theoretical intensity curve to the two average curves of Figure 2. As the analysis progressed it became clear that the amplitude parameters l(B···H$_t$) and l(H$_1$···H$_3$) = l(H$_2$···H$_3$) + δ could not be refined. These amplitude parameters are associated with relatively weak terms in the scattered intensity and accordingly they could be assigned values without fear of biasing the refinement results. The B···H$_t$ value was taken from diborane[5] and the H···H ones estimated from experience. Also, as expected, the parameter $\Delta_{Cl,B}$ was found to be highly correlated with l(B–B) and l(B–Cl). In such cases some information about the parameter may often be obtained by using a stepping technique. In this technique a best value for the parameter in question is inferred from comparisons of the quality of agreement, as measured by the well-known R factor, obtained from otherwise identical refinements as the parameter is stepped through a range of assigned values. Unfortunately, when it was applied to $\Delta_{Cl,B}$, the technique was only marginally successful. However, as is described later, the results of the calculations together with data from other sources permitted conclusions about the value of $\Delta_{Cl,B}$ to be drawn with some confidence.

Monochlorodiborane is a somewhat unstable compound with boron trichloride one of the principal products of its decomposition. Since BCl_3 has distances very similar to the B–B, B–Cl, and B···Cl distances in B_2H_5Cl, appreciable amounts of it in the sample (possibly formed as the vapor passed through the nozzle of the diffraction apparatus)

Table I. Dependence of B–B and B–Cl Distances and Amplitudes on the Parameter $\Delta_{\mathrm{Cl,B}}$[a]

$\Delta_{\mathrm{Cl,B}}$/Å	r(B–Cl)/Å	r(B–B)/Å	l(B–Cl)/Å	l(B–B)/Å	R[b]
0.06	1.790	1.730	0.051	0.049	0.055 85
0.04	1.785	1.745	0.055	0.056	0.055 26
0.02	1.780	1.760	0.056	0.059	0.054 99
0.00	1.775	1.775	0.057[c]	0.060[c]	0.054 69
−0.02	1.770	1.790	0.056	0.059	0.054 67
−0.04	1.765	1.805	0.054	0.055	0.054 69
−0.06	1.760	1.820	0.051	0.049	0.055 20

[a] $\Delta_{\mathrm{Cl,B}} = r(\mathrm{B{-}Cl}) - r(\mathrm{B{-}B})$. [b] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i (sI_{\mathrm{m}}(\mathrm{obsd}))^2]^{1/2}$ where $\Delta_i = sI_{\mathrm{m}}(\mathrm{obsd}) - sI_{\mathrm{m}}(\mathrm{calcd})$. [c] At $\Delta_{\mathrm{Cl,B}} = 0.00$ Å the strong correlation between the l values required that they be refined as a pair; $l(\mathrm{B{-}B}) = l(\mathrm{B{-}Cl}) + 0.03$ Å was assumed.

Table II. Final Results for Structure of Chlorodiborane[a]

	r_{a}/Å;[b] θ/deg[c]	l/Å[d]	l_{calcd}/Å[d,e]
$(\mathrm{B{-}Cl,B})_{\mathrm{av}}$[f]	1.775 (2)		
$\Delta_{\mathrm{Cl,B}}$[g]	[0.00 ± 0.02]		
$(\mathrm{B{-}H})_{\mathrm{av}}$[h]	1.277 (6)		
$\Delta_{\mathrm{b,t}}$[i]	0.126 (26)		
∠BBCl	120.9 (3)		
$\angle \mathrm{H_tBH_t}$	125.3 (60)		
B–Cl	1.775 (5)[j]	0.057 } (3)	0.056
B–B	1.775 (15)[j]	0.060	0.057
$\mathrm{B{-}H_t}$	1.205 (13)	0.090 } (13)	0.085
$\mathrm{B{-}H_b}$	1.331 (15)	0.107	0.100
B· · ·Cl	3.088 (5)	0.084 (5)	0.101
$\mathrm{B\cdots H_t}$	2.56 (4)	[0.129]	0.126
$\mathrm{Cl\cdots H_1}$	3.27 (6)	0.195 } (13)	0.234
$\mathrm{Cl\cdots H_2}$	4.15 (3)	0.125	0.115
$\mathrm{Cl\cdots H_3}$	2.62 (4)	0.125	0.104
$\mathrm{Cl\cdots H_b}$	2.557 (9)	0.125	0.126
$\mathrm{H_1\cdots H_2}$	2.14 (7)	0.132 } (38)	0.132
$\mathrm{H_4\cdots H_5}$	1.98 (4)	0.132	0.137
$\mathrm{H_1\cdots H_4}$	2.05 (3)	0.132	0.150
$\mathrm{H_2\cdots H_3}$	2.88 (12)	[0.300]	0.225
$\mathrm{H_1\cdots H_3}$	3.59 (6)	[0.200]	0.137

[a] Quantities in parentheses are 2σ including estimates of correlation and systematic error, those in brackets were assumed, and those in braces were refined as groups. [b] Distance. [c] Angle. [d] Rms amplitude. [e] See text for description of force field. [f] [(B–Cl) + (B–B)]/2. [g] B–B − B–Cl. [h] $(4\mathrm{B{-}H_b} + 3\mathrm{B{-}H_t})/7$. [i] $\mathrm{B{-}H_b} - \mathrm{B{-}H_t}$. [j] Uncertainties estimated from assumption concerning $\Delta_{\mathrm{Cl,B}}$. See text.

could significantly affect the B_2H_5Cl results if its presence were unrecognized or ignored. Accordingly, we refined models comprising a mixture of these molecules in which the known structure of BCl_3[15] was introduced and in which the composition was treated as a parameter. The results indicated no significant BCl_3 contamination and the final refinements were carried out assuming it to be absent.

Structural Results. The refinements outlined above led to well-defined values for all parameters except $\Delta_{\mathrm{Cl,B}}$ and the amplitudes l(B–Cl) and l(B–B) to which it was strongly correlated. Although $\Delta_{\mathrm{Cl,B}}$ was carefully studied by the stepping procedure mentioned above over the range -0.06 Å $\leq \Delta_{\mathrm{Cl,B}} \leq +0.06$ Å, the quality of the agreement did not permit rejection of any models even at the 50% confidence level based on Hamilton's test[16] (Table I). However, by using the results of these refinements together with a plausible assumption based on the structures of diborane and bromodiborane we have been able to deduce reasonable values for the B–Cl and B–B bond distances and amplitudes of vibration. The assumption is that the B–B bond length in B_2H_5Cl is the same as that in B_2H_6 ($r_{\mathrm{g}} = 1.775_0 \pm 0.003_5$ Å, equivalent to $r_{\mathrm{a}} = 1.773$ Å) to within ±0.015 Å; it is consistent with the observation that this distance, vibrationally averaged, in B_2H_5Br at 1.773 ± 0.015 Å[6] is insignificantly different from that in B_2H_6. Accordingly, it is seen from the values of Table I that a B–B distance in B_2H_5Cl of 1.775 ± 0.015 Å corresponds to B–Cl = 1.775 ± 0.005 Å and thus to $\Delta_{\mathrm{Cl,B}} \simeq 0.00 \pm 0.02$ Å. Comparison of the values of the other parameters obtained in refinements over the range indicated for $\Delta_{\mathrm{Cl,B}}$ shows them to be insensitive to $\Delta_{\mathrm{Cl,B}}$. We take the results of the refinement corresponding to $\Delta_{\mathrm{Cl,B}} = 0.00$ Å as representative of the final model; these are given in Table II except for a few of the uncertainties which have been broadened to reflect the assumption about $\Delta_{\mathrm{Cl,B}}$. Table III is the correlation matrix for this model.

Calculation of Amplitudes of Vibration. Our structure analysis required the assignment of some vibrational amplitude values which could not be determined from the diffraction data. Such values may be estimated from calculations based on suitable vibrational force fields. Because such a force field has not been determined for B_2H_5Cl, we used an approximate one based on that found for B_2H_6[17] modified to give agreement with the observed B_2H_5Cl spectrum.[18] The calculated amplitudes obtained from this force field[19] are given in Table II. The important ones are in good agreement with those observed except for l(B···Cl). It is likely that the difference in this case is due to errors in the force field: the spectroscopic data do not include measurements of the low-frequency region and thus direct information about the bending modes most strongly affecting the B···Cl distance was not available. However, further work on the force field did not seem justified.

Discussion

In diborane the effect on the rest of the structure of replacing terminal hydrogen atoms with halogen atoms or methyl groups seems to depend more on steric interaction than on the chemical nature of the entering group. Thus, in 1,1,2,2-tetramethyldiborane[8] the B–B bond is 0.065 Å longer than in B_2H_6[3-5] itself, and although effects such as hybridization or hyperconjugation could play a part, the arguments[8] for the dominant role of nonbonded repulsions are plausible and convincing. In contrast to $(CH_3)_4B_2H_2$, our geometry for B_2H_5Cl and that found earlier for B_2H_5Br are very similar to the geometry of B_2H_6 in respect to those features that can be directly compared. We infer that the halogen atoms interact with the B_2H_5 moiety in a manner very much like the hydrogen atoms they replace, i.e., with the formation of a similar type of bond and with nonbonded interactions of similar, presumably small, magnitude. The lengths of the B–Cl and B–Br

Table III. Correlation Matrix (×10²) for Parameters of the Final Model[a]

	$(\mathrm{B{-}Cl,B})_{\mathrm{av}}$	$(\mathrm{B{-}H})_{\mathrm{av}}$	$\Delta_{\mathrm{b,t}}$	∠BBCl	$\angle \mathrm{H_tBH_t}$	B–Cl	$\mathrm{B{-}H_t}$	$\mathrm{B{-}H_b}$	B· · ·Cl	l(B–Cl)	$l(\mathrm{B{-}H_t})$	l(B· · ·Cl)
σ[b]	0.0004	0.0021	0.0092	0.1048	2.2309	0.0004	0.0045	0.0053	0.0015	0.0006	0.0042	0.0013
	100	−40	0	−37	−9	100	−2	−2	12	2	5	−1
		100	51	−1	7	−4	−14	75	−3	28	−35	15
			100	3	−20	0	−92	94	3	7	−87	3
				100	11	−37	−4	2	92	−5	−6	−6
					100	−9	26	−12	8	−15	15	−15
						100	−2	−2	1	−1	5	−1
							100	−75	−5	17	−1	−10
								100	1	16	−78	8
									100	−4	−5	−7
										100	18	11
											100	11
												100

[a] Distances and amplitudes in angstroms; angles in degrees. [b] Standard deviations from least squares.

bonds (1.775 and 1.930 Å) and $B-H_t$ bond in B_2H_6 (1.196 Å) are consistent with this picture: they are each greater than the covalent radius sums corrected for electronegativity difference (1.71, 1.88, and 1.09 Å)[20] by approximately the same amount.

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Registry No. B_2H_5Cl, 12007-15-7.

Supplementary Material Available: Tables of the experimental intensity data and those for the final backgrounds (7 pages). Ordering information is given on any current masthead page.

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Structures, Chemistry, and Relative Energies of the $[Co(trien)(glyO)]^{2+}$ Ions. 3. α-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ and α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$ Ions

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The synthesis, resolution of enantiomers, spectral properties, and rates of H exchange of Λ,Δ-α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$ and of Λ,Δ-α-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$[1] are described. The structural assignments are confirmed by an x-ray study of Λ,Δ-α-(*RR*,*SS*)-$[Co(trien)(glyO)]I_2\cdot 3H_2O$. Strain energy minimization calculations of four conformational isomers of the α-$[Co(trien)(glyO)]^{2+}$ ion are reported and the minimized structures are compared with the crystal cation. The rates, rate laws, and products for both the Hg^{2+}-catalyzed aquation and base hydrolysis of α-$[Co(trien)(glyOEt)Cl]^{2+}$ are described.

Introduction

Two previous papers dealing with the $[Co(trien)(glyO)]^{2+}$ ion[1] reported crystal structures, structures of minimum energy, and some properties and reactions of the β_1-(*RR*,*SS*), β_1-(*RS*,*SR*)[2] and β_2-(*RR*,*SS*), β_2-(*RS*,*SR*)[3] isomers. In this paper we present similar results for the remaining α-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ complexes.

All ten configurational and optical isomers of the $[Co(trien)(glyO)]^{2+}$ ion, Figure 1, have been isolated,[4] and in the case of β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]Cl_2\cdot H_2O$ two conformational forms have been characterized.[3] This wealth of stereochemical information, together with the observed small energy differences between the ions,[3] provides an exacting test of the value of calculated structures of minimum energy.[5-8]

Despite several attempts,[9-11] the α-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ ion has not previously been prepared. Direct treatment of α-$[Co(trien)X_2]^{+,2+,3+}$ ($X = Cl^-, Br^-, OH^-, H_2O$) with glycine or its methyl or ethyl esters in neutral or alkaline aqueous solution results in the quantitative isomerization to the β-triethylenetetramine configuration. We have only been able to make the α complex via the monodentate glycine ester complex α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]Cl_2$. The preparation, properties, and chemistry of this latter complex are thus relevant to this report and are also described below.

Experimental Section

Visible spectra and spectrophotometric rate data were recorded on a Cary Model 14 or a Varian-Techtron 118C spectrophotometer. Rotatory dispersion (RD) curves were obtained using a Perkin-Elmer P22 spectropolarimeter (±0.002°) and 1-dm cells. H exchange data and ^1H NMR spectra were recorded on JEOL Minimar 100-MHz and Varian HA100 (Me_4Si external lock) spectrometers respectively, at 25 °C. Bio-Rad analytical Dowex 50W×2 (200–400 mesh) ion-exchange resin was used for chromatographic separations. Cobalt concentrations were calculated from known extinction coefficients or measured directly using a Techtron AA4 atomic absorption spectrometer. Circular dichroism measurements were recorded on a Cary 61 instrument.

Analar reagents were used for kinetic measurements without further purification and glycine ethyl ester hydrochloride was made as described previously[12] using ethanol in place of methanol.

Glycine buffers (0.1 M) were made up to unit ionic strength with $NaClO_4$; D_2O–acetic acid buffers (0.1 M) were made using acetic anhydride and sodium acetate. For measurements in D_2O the pD was calculated using the empirical expression $pD = pH + 0.4$.[13] The pH was measured using Radiometer TTT1 plus A630T equipment and a salt bridge containing NH_4NO_3 (1.6 M) and $NaNO_3$ (0.2 M).

Kinetic Measurements. Samples of complex (ca. 10 mg) were dissolved in 1 M $NaClO_4$ at 25 °C and mixed with an equal volume of $Hg(NO_3)_2$ or buffer solution in 1 M $NaClO_4$. Reactions were followed in 1-cm thermostated cells at 25 ± 0.05 °C. For H exchange, about 50 mg of the chloride salt of the complex was dissolved in 0.5 mL of DOAC buffer and the solution filtered into the ^1H NMR tube. The requisite peaks were scanned at appropriate time intervals and kinetic data obtained from peak heights or areas (planimeter). The chloride salts, α-$[Co(trien)(glyO)]Cl_2$ and α-$[Co(trien)(glyOEt)Cl]Cl_2$, were prepared from the iodide- and chloride–perchlorate salts, respectively, using Bio-Rad Dowex 1-X anion-exchange resin (200–400 mesh) in the chloride form.

Product Analysis. Following treatment with Hg^{2+} the solutions were diluted, sorbed on the resin, and eluted with 1 or 2 M HCl. The