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$_2$O) 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 ^{1}H NMR spectra were recorded on JEOL Minimar 100-MHz and Varian HA100 (Me$_4$Si 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$_2$O–acetic acid buffers (0.1 M) were made using acetic anhydride and sodium acetate. For measurements in D$_2$O 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$_4$NO$_3$ (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 ^{1}H 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

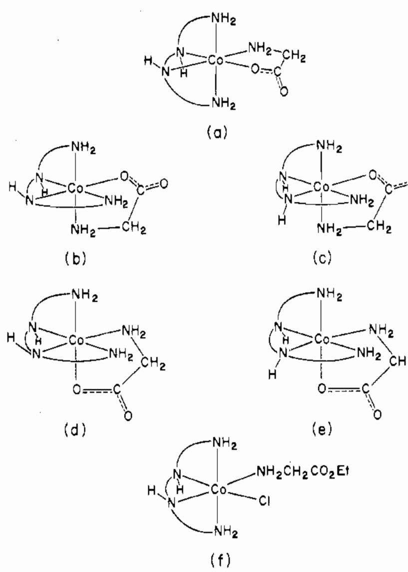


Figure 1. Various configurational isomers of the $[Co(trien)(glyO)]^{2+}$ ion: (a) Λ-(*RR*)-α, (b) Δ-(*RR*)-β_1, (c) Δ-(*RS*)-β_1, (d) Δ-(*RR*)-β_2, (e) Δ-(*RS*)-β_2, (f) Λ-(*RR*)-α-$[Co(trien)(glyOEt)Cl]^{2+}$. Each isomer exists in mirror image forms.

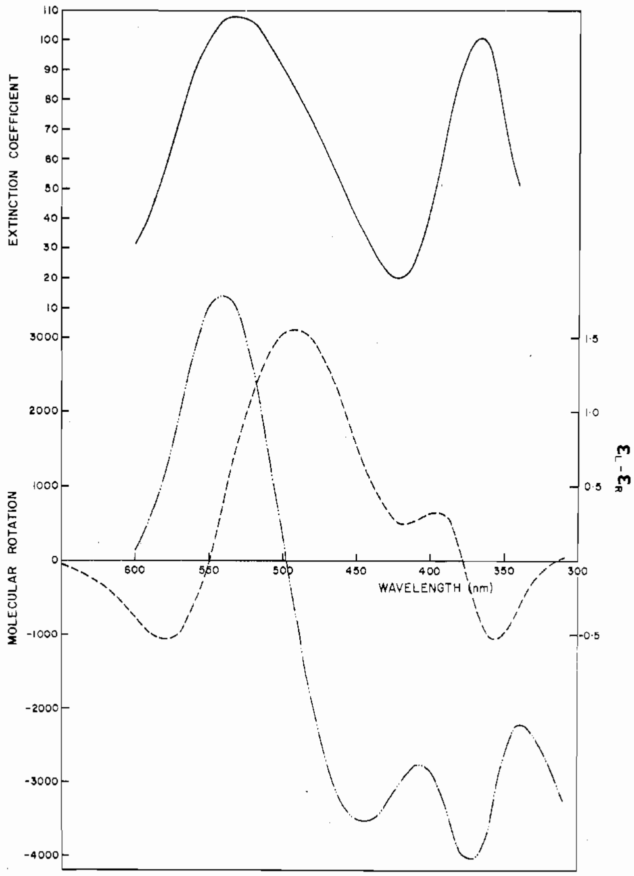


Figure 2. Visible spectrum (—), rotatory dispersion (······), and circular dichroism (---) curves for $(+)_{589}$-α-(*RR*)-[Co(trien)(glyOEt)Cl]$(ClO_4)Cl$ in water at pH ~4 and 25 °C.

products of base hydrolysis were similarly eluted at pH 6.8 using 0.25 M NaH_2PO_4/0.25 M Na_2HPO_4 until the bands were well separated and then removed using 1 M HCl. In a separate experiment it was shown that the phosphate eluent separates the $[Co(trien)(glyO)]^{2+}$ isomers in the order α, β_2, β_1 (Figure 1). Visible spectra and atomic absorption determinations for Co were carried out on the eluted fractions.

Preparation and Resolution of α-[Co(trien)(glyOEt)Cl](ClO_4)Cl·H_2O. To α-$[Co(trien)CO_3]ClO_4$[14] (35.5 g) in a 3-L beaker was added hydrochloric acid (40 mL, 11.6 N) and water (10 mL), and the contents were swirled rapidly until effervescence had almost stopped (~30 s). Ethanol (500 mL) was added with good mixing followed by acetone (2 L), and the coagulated precipitate was allowed to settle. The supernatant liquid was removed by decantation and the crude α-$[Co(trien)(H_2O)Cl]Cl_2$ product collected and dried in an evacuated desiccator (15 min). This material[15] was then added to glycine ethyl ester hydrochloride (30 g) in a mortar and ground with water (20 mL) to a fine paste. $LiClO_4$ (25 g) was added and grinding continued for 3 min, and then diethylamine (12 mL) was added dropwise over 15 min with continuous mixing. On adding a further 2 mL of diethylamine with intimate mixing, the α-[Co(trien)(glyOEt)Cl](ClO_4)Cl slowly crystallized. After standing for 45 min, the product was collected on a glass filter and washed thoroughly with ethanol. The crude material was ground in a mortar containing LiCl (6 g) and $LiClO_4$ (10 g) in water (40 mL), and the product was collected and washed with a small volume of ice cold water and methanol and air-dried (31 g). This material eluted as one band from cation-exchange resin using 1 M $NaClO_4$ as eluent. It was recrystallized as purple needles from hot water (pH 7) by cooling slowly to 0 °C. Anal. Calcd for $[Co(C_6H_{18}N_4)(C_4H_9NO_2)Cl](ClO_4)Cl\cdot H_2O$: C, 24.18; H, 5.89; N, 14.10. Found: C, 24.3; H, 5.6; N, 13.7. For visible spectrum see Figure 2.

Sodium arsenyl-(+)-tartrate (7.1 g)[16] was added to a hot solution of the complex in water (8.6 g in 120 mL, 60–70 °C) over 5 min. On scratching, the diastereoisomer crystallized. The solution was cooled to 50 °C and after 15 min the diastereoisomer $(+)_{589}$-α-[Co(trien)(glyOEt)Cl]$(As_2((+)\text{-tart})_2)$ was collected and washed with water and methanol (4.9 g). Recrystallization from hot water gave fractions with similar rotations, α_{546} 0.485° (0.1% solution). Anal. Calcd for $[Co(C_6H_{18}N_4)(C_4H_9NO_2)Cl](AsC_4H_2O_6)_2\cdot 3H_2O$: C, 25.74; H, 4.20; N, 8.34. Found: C, 25.6; H, 3.9; N, 8.0. The diastereoisomer was dissolved in hot water (100 mL/g, pH 4) and eluted from a Cl^- form AG1×4 anion-exchange resin. Evaporation of the eluate to low volume, addition of excess LiCl and $LiClO_4$, and cooling in ice gave purple crystals of $(+)_{589}$-α-[Co(trien)(glyOEt)Cl](ClO_4)Cl, α_{589} 0.138° (0.1% aqueous solution, pH ~4). Anal. Calcd for $(+)_{589}$-α-[Co(trien)(glyOEt)Cl](ClO_4)Cl: C, 25.09; H, 5.69; N, 14.63. Found: C, 25.1; H, 5.7; N, 14.7 (ORD, CD curves, Figure 2). On cooling the filtrate reserved from the separation of the diastereoisomer two $(-)_{589}$ fractions crystallized (1.65 g). Reducing the solution volume to 25 mL and adding $LiClO_4$ gave further fractions of similar rotations. These were combined and recrystallized from warm water; α_{589} −0.129°, α_{546} −0.825° (0.1% solution). Anal. Found for $(-)_{589}$-α-[Co(trien)(glyOEt)Cl](ClO_4)Cl: C, 25.2; H, 5.9; N, 14.9.

Preparation and Resolution of α-[Co(trien)(glyO)]I_2·$3H_2O$. To α-[Co(trien)(glyOEt)Cl]$(ClO_4)Cl\cdot H_2O$ (1 g) dissolved in water (30 mL) was added $Hg(NO_3)_2\cdot H_2O$ (1 g), and the solution was left to stand for 2 h. Precipitated $HgCl_2$ was removed, the volume increased to 60 mL, and the complex sorbed on Dowex 50W×2 cation-exchange resin (25 × 2.5 cm column). It was washed with water and then eluted with 1 M HCl. The eluate was reduced to dryness on a rotary evaporator, twice dissolved in water, and reduced to dryness to remove residual acid, and NaI was added to the final solution (5 mL, pH ~3). On scratching and cooling in ice, orange crystals of α-[Co(trien)(glyO)]I_2 formed. These were recrystallized from the minimum volume of hot water by cooling, and the collected material was washed with ice-cold aqueous methanol and air-dried. Anal. Calcd for α-[Co(trien)(glyO)]$I_2\cdot 3H_2O$: C, 16.37; H, 4.81; N, 11.93. Found: C, 16.4; H, 4.7; N, 12.0. On occasions crystals analyzing for four water molecules of crystallization were obtained (Found: C, 15.9; H, 5.0; N, 11.7), and crystals obtained from water/methanol solutions, or by salting out with NaI, contained less water of crystallization. For visible spectrum see Figure 3.

The racemic iodide (3 g) was dissolved in ~20 mL of water at 50 °C, silver arsenyl-(+)-tartrate (4.14 g) added, and the mixture vigorously mixed for 5 min. AgI was removed, and the filtrate and washings were evaporated to near dryness. Careful addition of MeOH and scratching induced the $(+)_{589}$-diastereoisomer to crystallize (0.8 g, $[\alpha]_{589}$ 325°). Cooling and standing resulted in the separation of two fractions of the $(-)_{589}$-diastereoisomer (0.55 g, $[\alpha]_{589}$ −235°; 0.25 g, $[\alpha]_{589}$ −250°). In a separate resolution on a 1-g scale, the above order of isolation was reversed. The two diastereoisomers were fractionated separately from aqueous solution by addition of methanol with samples of similar rotation being combined and recrystallized until no further improvement in rotation occurred (seven recrys-

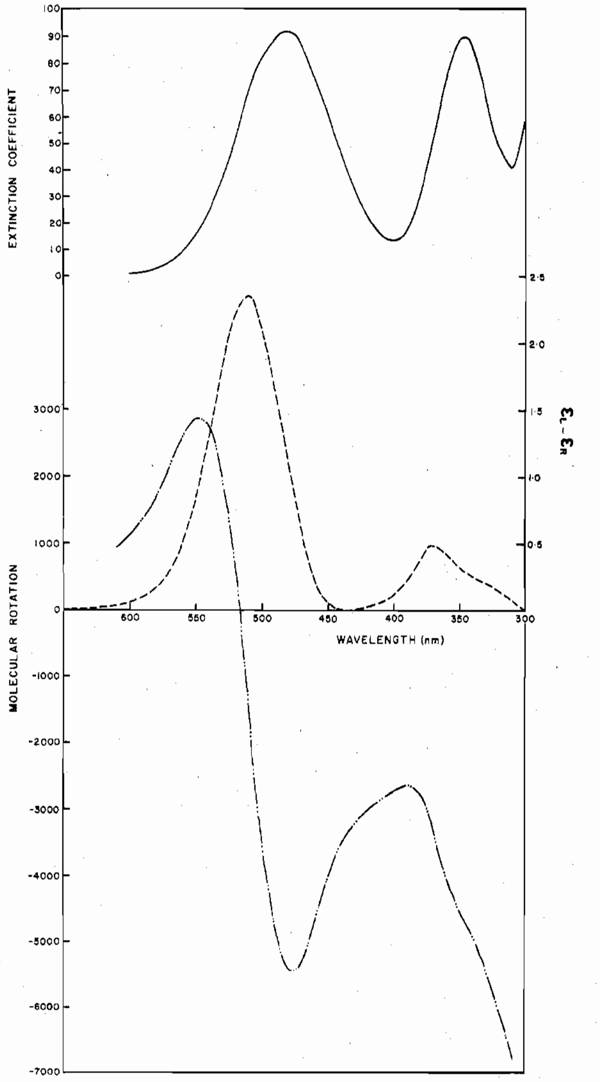


Figure 3. Visible spectrum (—), rotatory dispersion (······), and circular dichroism (- - -) curves for $(+)_{589}$-α-$[Co(trien)(glyO)]I_2{\cdot}H_2O$ in water at 25 °C.

tallizations). Final rotations for the $(+)_{589}$- and $(-)_{589}$-arsenyl-(+)-tartrate salts were 0.385° (589 nm), 0.775° (546 nm), −1.160° (346 nm), and −0.375° (589 nm) and −0.760° (546 nm) and +1.140° (346 nm), respectively, for 0.1% aqueous solutions. The diastereoisomers were converted to the iodide salts by trituration with NaI in a little water and extraction with methanol. The iodides were recrystallized from hot water by cooling and adding NaI. Anal. Calcd for $[Co(trien)(glyO)]I_2{\cdot}H_2O$: C, 17.44; H, 4.39; N, 12.71. Found for $(+)_{589}$ isomer: C, 17.5; H, 4.3; N, 13.0. A 0.1% aqueous solution gave rotations of 0.320 and 0.633° at 589 and 546 nm, respectively; for ORD and CD curves see Figure 3.

Stereochemistry of Products of Base Hydrolysis. $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyOEt)Cl](ClO_4)Cl$ (77.4 mg) was dissolved in 1 M $NaClO_4$ (25 mL) and hydrolyzed at pH 9.17 under pH-stat control (0.1 M NaOH). After 56 min, the solution was adjusted to pH ~4 with acetic acid, diluted to 200 mL, and quantitatively transferred to a column of Dowex 50W×2 cation-exchange resin. Elution with Na_2HPO_4 (0.5 M) (pH ~6.8) separated two bands which were eluted with 1 M HCl. The first band was characterized as optically pure $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyO)]^{2+}$ (315 mL; α_{589} +0.056°, α_{546} +0.108°; [Co] = 3.27×10^{-4} M; A_{481} 0.299 (10-cm cell)) and the second as a mixture of ~90% $(-)_{589}$-β_2-(*RR*)- and ~10% $(-)_{589}$-β_2-(*RS*)-$[Co(trien)(glyO)]^{2+}$ (350 mL; α_{589} −0.020°, α_{546} −0.047°, α_{436} +0.078°; [Co] = 1.630×10^{-4} M; A_{480} 0.215 (10-cm cell)).

Crystallography of Racemic α-(*RR,SS*)-$[Co(trien)(glyO)]I_2{\cdot}3H_2O$. Well-formed orange crystals of α-(*RR,SS*)-$[Co(trien)(glyO)]I_2{\cdot}3H_2O$ were readily obtained by slow, room temperature recrystallization from a saturated aqueous solution. Crystals are triclinic prismatic with maximum extension parallel to the arbitrarily assigned *b* axis. Unit cell dimensions were determined in the usual manner by least-squares analysis of the setting angles, determined on a Picker FACS-1 diffractometer, for 12 carefully centered reflections in the range $50 < 2\theta < 56°$ (crystal monochromated Mo Kα radiation, $\lambda(K\alpha_1)$ 0.709 26 Å). The measured crystal density (d_{measd} = 2.05 ± 0.01 g cm^{-3}; flotation in CH_2Br_2/CCl_4) requires two formula units per cell (d_{calcd} = 2.054 g cm^{-3} for $Z = 2$). Intensity statistics are consistent with the centrosymmetric space group ($P\bar{1}$), and choice of this space group was subsequently confirmed by successful solution and refinement of the structure.

Crystal Data. $CoC_8N_5O_2H_{22}I_2{\cdot}3H_2O$; formula weight 587.1; triclinic with $a = 7.704$ (1), $b = 8.928$ (1), $c = 14.791$ (1) Å; α = 96.863 (6), β = 94.535 (8), γ = 108.690 (9)°; space group $P\bar{1}$; V_{calcd} = 949.33 Å^3; d_{measd} = 2.05 g cm^{-3}; $Z = 2$; d_{calcd} = 2.054 g cm^{-3}; $\mu_{(MoK\alpha)}$ = 42.51 cm^{-1}.

Diffraction data were collected from a well formed but noncentrosymmetric crystal bounded by nine faces and having approximate dimensions 0.020 × 0.033 × 0.012 cm in the a^*, b^*, and c^* directions, respectively. All unique data within the range $3 < 2\theta < 60°$ were recorded at 25 ± 1 °C on a Picker FACS-1 diffractometer using graphite-monochromated Mo Kα radiation (λ (Mo K$\bar{\alpha}$) 0.7107 Å). Data were recorded in the θ–2θ scan mode with a 2θ scan speed of 2° min^{-1} and scan range $\Delta(2\theta) = 2° + \delta(2\theta)$ where $\delta(2\theta)$ is the angular separation of the Kα_1–Kα_2 doublet of the appropriate diffraction maximum. Background intensities were measured for 10 s at each extremity of the scan with both crystal and counter stationary. Intensities of three "standard" reflections (indices 0,0,14, 700, and $\bar{2}8\bar{1}$; 2θ = 37.1–40.1°), which were remeasured after every 100 data, exhibited a time-dependent intensity decrease averaging ca. 10% over the course of the data collection. Data were subsequently corrected for this, assuming the decrease in intensity to be independent of scattering angle.[17] Corrections were also applied for Lorentz, polarization, and specimen absorption effects.[18] Reflections for which background measurements differed by more than 10 times the standard error of the difference (3), or for which the integrated intensity *I* was less than 3 times its standard error (746), were discarded and equivalent reflection forms averaged. The resultant data set contained 4810 unique reflection intensities each with an associated standard error $\sigma(F_o)$ given by $\sigma(F_o) = \{[\sigma(I)/Lp]^2 + (\rho|F_o|^2)^2\}^{1/2}/2|F_o|$ where $\sigma(I)$ is the estimated standard error of the intensity calculated from counting statistics, *Lp* is the appropriate Lorentz and polarization correction, and ρ (0.045) is an instrumental uncertainty constant.

Solution and Refinement of Crystal Structure. Iodine and cobalt atom coordinates were determined in the usual way from a three-dimensional Patterson map, and the remaining nonhydrogen atoms were located in successive Fourier maps. Atom coordinates and anisotropic thermal parameters (except for hydrogens) were refined by full-matrix least-squares analysis. Hydrogen atoms, other than those of the water molecules (vide infra), were included in the scattering model with fixed, calculated coordinates (regular tetrahedral geometry d(C–H) = 0.95 Å, d(N–H) = 0.87 Å) and fixed isotopic thermal papermeters set at 1.1 times the isotropic-equivalent value of the attached nonhydrogen atom. Atomic scattering factors for nonhydrogen atoms were taken from the compilation of Cromer and Waber[19] with $\Delta f'$ and $\Delta f''$ values tabulated by Cromer.[20] For hydrogen atoms the scattering factors of Stewart et al.[21] were employed. Late in the refinement the presence of extinction effects was observed, and in subsequent cycles the secondary extinction parameter Bo in the correction term applied to F_c, $[1.0 + I{\cdot}\beta{\cdot}Bo]^{-1}$, with I = the observed reflection intensity and β = Zachariasen's β factor,[40] was also refined. At convergence the value of Bo was 0.33 (4) × 10^{-5}.

All computations were performed on the UNIVAC 1108 computer at the Australian National University. The programs used were those of the A.N.U. System for Crystal Structure Analysis developed by Drs. P. O. Whimp and D. M. Taylor.

In the final refinement cycle, the parameter shifts were all less than 0.25 times the corresponding parameter estimated standard deviation, while the estimated standard deviation of an observation of unit weight was 1.33. The final values of $R_1 = (\sum||F_o| - |F_o||)/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ were 0.026 and 0.049 for the 4810 unique observed reflections. In the final difference map, the largest peaks (1.5–0.5 e/Å^3) were found in tetrahedral locations at about 0.7 Å from the iodide ions while the next six occurred in the positions expected for hydrogens attached to the water molecules. Contributions from the water hydrogens were at no time included in the scattering

Table I. Fractional Atomic Positional and Thermal Parameters for α-(*RR*,*SS*)-[Co(trien)(glyO)]$I_2 \cdot 3H_2O$[a,b]

ATOM	X/A	Y/B	Z/C	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
I(1)	0.7242(1)	0.8041(1)	0.3362(1)	0.0183(1)	0.0090(1)	0.0052(1)	0.0049(1)	0.0010(1)	0.0009(1)
I(2)	0.1370(1)	0.5053(1)	0.3118(1)	0.0142(1)	0.0105(1)	0.0055(1)	0.0038(1)	0.0004(1)	0.0014(1)
CO	0.5028(1)	0.1916(1)	0.2497(1)	0.0127(1)	0.0065(1)	0.0024(1)	0.0033(1)	0.0010(1)	0.0009(1)
O(1)	0.7836(3)	0.1592(3)	0.0447(2)	0.0261(5)	0.0185(4)	0.0051(1)	0.0055(4)	0.0057(2)	0.0008(2)
O(2)	0.5978(2)	0.1020(2)	0.1509(1)	0.0202(4)	0.0090(2)	0.0037(1)	0.0048(2)	0.0029(1)	0.0011(1)
O(3)	0.3982(4)	0.5717(4)	0.1184(2)	0.0365(7)	0.0255(5)	0.0066(2)	0.0157(5)	0.0025(3)	0.0016(2)
O(4)	0.1101(4)	0.3596(3)	-0.0024(2)	0.0278(6)	0.0245(5)	0.0102(2)	0.0086(5)	0.0069(3)	0.0061(3)
O(5)	0.6519(4)	0.8090(3)	0.0333(2)	0.0337(6)	0.0187(4)	0.0067(1)	0.0129(4)	-0.0019(2)	-0.0017(2)
N(1)	0.7191(3)	0.1967(2)	0.3306(1)	0.0140(3)	0.0082(2)	0.0035(1)	0.0035(2)	0.0004(1)	0.0008(1)
N(2)	0.4198(3)	0.2742(2)	0.3602(1)	0.0182(4)	0.0103(3)	0.0032(1)	0.0071(3)	0.0015(2)	0.0008(1)
N(3)	0.3591(3)	-0.0237(2)	0.2688(1)	0.0133(3)	0.0079(2)	0.0030(1)	0.0028(2)	0.0013(1)	0.0015(1)
N(4)	0.2843(3)	0.1818(2)	0.1682(1)	0.0162(4)	0.0107(3)	0.0035(1)	0.0052(3)	0.0004(2)	0.0019(1)
N(5)	0.6389(3)	0.4001(2)	0.2161(1)	0.0186(4)	0.0076(2)	0.0039(1)	0.0038(3)	0.0015(2)	0.0014(1)
C(1)	0.7046(4)	0.2457(3)	0.4289(2)	0.0202(5)	0.0138(4)	0.0031(1)	0.0058(4)	-0.0010(2)	0.0006(2)
C(2)	0.5815(4)	0.3473(3)	0.4320(2)	0.0238(6)	0.0127(4)	0.0030(1)	0.0063(4)	0.0008(2)	-0.0009(2)
C(3)	0.2652(4)	0.1427(4)	0.3873(2)	0.0177(5)	0.0157(4)	0.0038(1)	0.0063(4)	0.0033(2)	0.0012(2)
C(4)	0.2895(4)	-0.0169(3)	0.3601(2)	0.0189(5)	0.0124(4)	0.0035(1)	0.0027(4)	0.0024(2)	0.0028(2)
C(5)	0.2135(4)	-0.0945(3)	0.1885(2)	0.0171(5)	0.0089(3)	0.0039(1)	0.0011(3)	-0.0003(2)	0.0009(1)
C(6)	0.1305(4)	0.0284(4)	0.1660(2)	0.0150(4)	0.0147(4)	0.0041(1)	0.0041(4)	-0.0006(2)	0.0019(2)
C(7)	0.7156(4)	0.3743(3)	0.1296(2)	0.0186(5)	0.0103(3)	0.0034(1)	0.0015(3)	0.0019(2)	0.0021(1)
C(8)	0.7021(3)	0.2015(3)	0.1053(2)	0.0156(4)	0.0112(3)	0.0030(1)	0.0032(3)	0.0011(2)	0.0011(1)

ATOM	X/A	Y/B	Z/C	B(A**2)	ATOM	X/A	Y/B	Z/C	B(A**2)
H(1)	0.817	0.264	0.315	3.0	H(12)	0.425	-0.086	0.271	2.7
H(2)	0.729	0.102	0.324	3.0	H(13)	0.120	-0.185	0.203	3.6
H(3)	0.823	0.306	0.461	4.0	H(14)	0.267	-0.128	0.137	3.6
H(4)	0.652	0.154	0.457	4.0	H(15)	0.051	0.042	0.210	4.0
H(5)	0.649	0.452	0.421	4.1	H(16)	0.062	-0.004	0.107	4.0
H(6)	0.540	0.354	0.491	4.1	H(17)	0.314	0.190	0.113	3.3
H(7)	0.375	0.349	0.351	3.2	H(18)	0.247	0.261	0.188	3.3
H(8)	0.151	0.142	0.358	4.0	H(19)	0.729	0.453	0.260	3.4
H(9)	0.265	0.161	0.452	4.0	H(20)	0.565	0.455	0.209	3.4
H(10)	0.174	-0.099	0.357	3.8	H(21)	0.842	0.440	0.136	3.7
H(11)	0.376	-0.031	0.405	3.8	H(22)	0.648	0.403	0.082	3.7

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$. [b] Hydrogen atoms located by calculation and not refined.

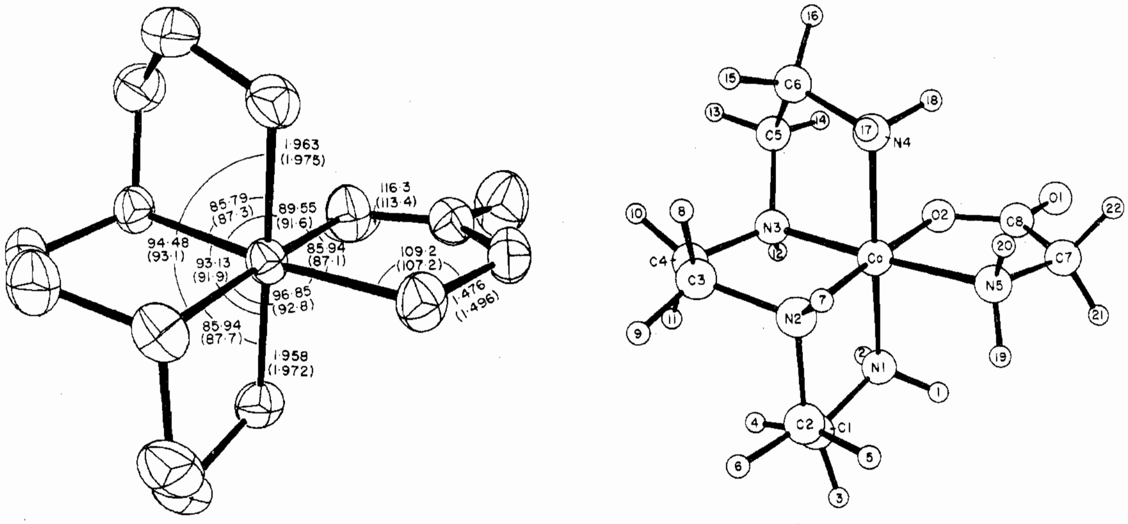


Figure 4. Perspective views of the crystal structure and minimized Λ-α-(*RR*)-[Co(trien)(glyO)]$^{2+}$ cations. The atom numbering scheme used and a comparison of major structural differences are shown (minimized values in parentheses). Thermal ellipsoids are drawn at the 50% probability level.

model. The final atomic positional and vibrational parameters are listed in Table I and the observed and calculated structure factors are given in Table II.[22] The atom nomenclature for the cation is defined in Figure 4.

Strain Energy Minimization Calculations. Both the method and the input parameters used in the calculations have been described in detail in previous publications.[2,3] The calculations were carried out on a UNIVAC 1108 computer.

Results and Discussion

Preparations, Resolutions, and Spectral Properties. α-[Co(trien)(glyOEt)Cl](ClO_4)Cl·H_2O was obtained in good yield by triturating a moist mixture of freshly prepared α-[Co(trien)(H_2O)Cl]Cl_2 and glycine ethyl ester hydrochloride with 2 equiv of diethylamine. The purple complex was readily separated from a small amount of β_2-[Co(trien)(glyOEt)Cl]Cl_2 impurity by recrystallization from warm water at pH ~7.[23] Treatment with sodium arsenyl-(+)-tartrate gave (+)$_{589}$-α-(*RR*)-[Co(trien)(glyOEt)Cl](As_2(+)-$tart_2$)·H_2O as the least soluble diastereoisomer from which (+)-α-(*RR*)-[Co(trien)(glyOEt)Cl](ClO_4)Cl ([α]$_{589}$ 138°) was obtained following ion exchange removal of the resolving agent and addition of LiCl and $LiClO_4$. Almost pure (−)$_{589}$-α-(*SS*)-[Co(trien)(glyOEt)Cl](ClO_4)Cl ([α]$_{589}$ −129°) was recovered from the more soluble fractions. Visible absorption, rotatory

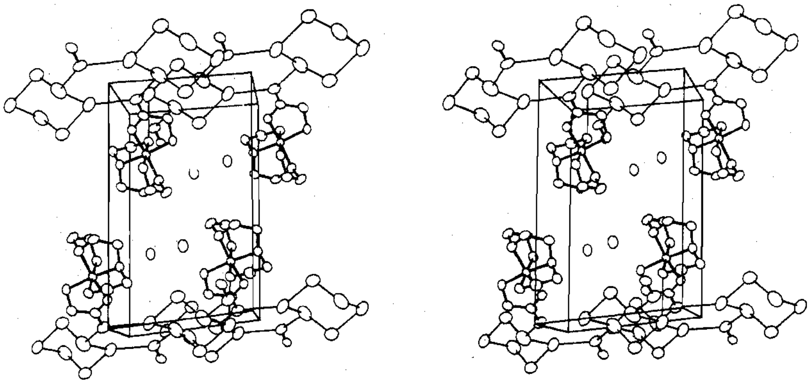


Figure 5. Stereoview of contents of the unit cell showing H bonding between the cations and H_2O molecules (cell origin at top upper left corner, *a* axis into paper, *b* axis horizontal to right, *c* axis vertically downward).

dispersion (RD), and circular dichroism (CD) curves for $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyOEt)Cl](ClO_4)Cl$ are given in Figure 2. If this curve is typical of the pattern observed for other α-(*RR*)-$[Co(trien)X_2]^{+,2+,3+}$ ions,[24] then the dominant positive dichroism associated with the first ligand field band indicates a Λ configuration for the terminal chelate rings. A similar result and argument hold for $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyO)]I_2{\cdot}H_2O$ whose absorption and RD and CD curves are given in Figure 3. In this instance, the case is even stronger since the configurations of all eight β isomers are known along with the configurations of numerous $[Co(en)_2(aminoacido)]^{2+}$ ions. Without exception in these complexes the Λ configuration generates a dominant positive CD band in conjunction with the first ligand field band derived from T_{1g} parentage in $Co(NH_3)_6{}^{3+}$. The chiral α-glycinato isomer was obtained by exhaustive fractional crystallization of the (+)-arsenyltartrate salts and racemic α-$[Co(trien)(glyO)]I_2{\cdot}3H_2O$ was obtained from the chloro ester complex following treatment with Hg^{2+} in acidic solution.

Description of Crystal Structure. The stereochemical arrangement of the complex cation is shown in Figure 4, along with the atom nomenclature, and the crystal packing arrangement is illustrated by the stereopair in Figure 5. Bond lengths and bond angles in the crystal are compared with those derived from strain energy minimization calculations in Table III.

The coordination geometry of the cation is near regular octahedral with the tetradentate trien ligand present in the α configuration. Both of the secondary nitrogen atoms in the trien ligand take the same chirality (*RR* or *SS*) with the five-membered chelate rings adopting $\delta\lambda\delta$ and $\lambda\delta\lambda$ conformations in the *RR* and *SS* enantiomers, respectively.

Inspection of the Co–N distances in the trien–cobalt moiety shows that Co–N4 bond (1.963 (2) Å) to be significantly longer than either of the bonds to the secondary nitrogens (Co–N2 = 1.950 (2) Å, $\Delta/\sigma = 4.6$; Co–N3 = 1.954 (2) Å, $\Delta/\sigma = 3.4$). A similar but smaller lengthening of the Co–N1 bond vis-a-vis Co–N2 and Co–N3 is not consistently significant ($\Delta/\sigma = 1.6$ and 2.9, respectively). We suggest, nevertheless, that these data, together with observation of a similar effect involving the nonplanar secondary nitrogen atoms in the β_1-(*RR*) and β_1-(*RS*) cations,[2] are indicative of a real but small shortening (ca. 0.01 Å) of the secondary nitrogen–cobalt bonds; cf. the terminal nitrogen–cobalt bonds. In contrast, distances to the planar secondary nitrogens in a wide range of β-trien complexes are generally fore-shortened by ca. 0.03 Å.[2,26] The Co–N distance in the glycinate ring (1.965 (2) Å) does not differ significantly from the terminal nitrogen–cobalt distances (1.963 (2), 1.958 (2) Å) in the Co–trien moiety.

Within the trien chelate all internal angles at C and N are close to the regular tetrahedral value except those at the primary terminal nitrogens which are somewhat larger, 111.9 (2)° (N1) and 111.4 (2)° (N4), respectively. However, the external angles at both of the secondary nitrogen atoms (C2–N2–C3 = 114.6 (2)°; C4–N3–C5 = 115.2 (2)°) are substantially strained ($\Delta = 5.4°$ av), a feature also observed in the β_2 complexes.[2] N–Co–N angles in the two terminal chelate rings (85.94 (9) and 85.79 (8)°) are typical of values found for all three rings in the β-trien structures (85.8°).[2,3,26] In the present complex, the angle to the central ring (N2–Co–N3 = 88.06 (8)°) has been opened up by some 2° relative to the values in the terminal rings. C–C and C–N distances average 1.502 and 1.492 Å, respectively, and all three rings are significantly puckered with the central ring slightly flattened vis-a-vis the terminal rings (torsion angles ϕ(C3–C4) = –39°, ϕ(C1–C2) = 42.7°, ϕ(C5–C6) = 45.2°). Perpendicular distances (Å) of the carbon atoms from the chelate N–Co–N planes are, respectively, C1 –0.045, C2 0.478, C3 0.309, C4 –0.211, C5 0.548, and C6 –0.047.

Bond distances and bond angles in the glycinate ring are characteristic of those observed in the β-$[Co(trien)(glyO)]^{2+}$ complexes.[2,3] As expected[27,28] some polarization of the carboxyl group is evident with the uncoordinated oxygen–carbon distance (C8–O1, 1.225 (3) Å) being 0.06 Å shorter than the corresponding distance to the coordinated oxygen (C8–O2, 1.289 (3) Å). The $-CCO_2$ moiety is planar but the metalloglycinate ring as a whole exhibits significant puckering (torsion angle ϕ(N5–C7) = –12.3°; atom distance from the $-CCO_2$ plane, Co 0.190 and N5 0.294 Å, respectively). The observed torsion angle (–12.3°) does not agree well with that predicted from strain energy minimization calculations (–22.5°). Similar results are observed in the β_1-$[Co(trien)(glyO)]^{2+}$ ions (ϕ(N5–C7), *RR* isomer, –6.3° (obsd), –14.5 (calcd); *RS* isomer, 16.1° (obsd), 5.5° (calcd))[2] and β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]^{2+}$ (ϕ(N5–C7), $\delta\lambda\delta$ conformer, 4.4° (obsd), –29.2° (calcd); $\lambda\lambda\delta$ conformer, 9.1° (obsd), 28.8° (calcd))[3] ions. Clearly, the extent of glycinate ring puckering is substantially dependent on factors such as intermolecular nonbonding contacts, Table IV, whose effects are not included in the strain energy calculations.

Figure 5 shows the packing arrangement in the crystal, and Table IV lists the closest cation–anion contacts (<3.7 Å) and intermolecular hydrogen bonds within the crystal. The closest cation–cation approach is 3.431 Å (O1–C5).

As can be seen from Figure 5, the three independent water molecules, together with their centrosymmetric equivalents, form hydrogen bonded cyclic hexamers with a chair conformation. These in turn are linked together through hydrogen bridges (O4–O1–O5) involving the carbonyl oxygen of the cation to form infinite ribbons parallel to the [110] direction. There is a further weak hydrogen bond (3.065 Å) between O5 and the secondary nitrogen N4 attached to the adjacent chain which serves to bind neighboring ribbons into cation, water, cation "sandwich-like" sheets perpendicular to the *c* axis. In

Table III. Bond Lengths and Angles, Nonbonded Interatomic Distances, and Torsion Angles for the Four Minimized Λ-α-(*RR*)$[\mathrm{Co(trien)(glyO)}]^{2+}$ Conformers and for the Crystal Structure Cation[a]

(i) Bond Lengths, Å

		Minimized			
Atoms	δλδ crystal	δλδ	δλλ	λλδ	δδδ
*Co-N1	1.958 (2)	1.972	1.971	1.968	1.967
Co-N2	1.950 (2)	1.951	1.953	1.963	1.964
Co-N3	1.954 (2)	1.952	1.968	1.956	1.956
*Co-N4	1.963 (2)	1.975	1.965	1.978	1.969
Co-N5	1.965 (2)	1.970	1.971	1.971	1.974
Co-O2	1.892 (2)	1.893	1.894	1.895	1.896
N1-C1	1.491 (3)	1.496	1.498	1.493	1.498
N2-C2	1.487 (4)	1.498	1.498	1.503	1.497
N2-C3	1.500 (4)	1.500	1.501	1.497	1.500
N3-C4	1.493 (3)	1.500	1.497	1.501	1.499
N3-C5	1.492 (3)	1.497	1.501	1.497	1.496
N4-C6	1.491 (3)	1.495	1.492	1.497	1.500
*N5-C7	1.476 (3)	1.496	1.497	1.496	1.497
O1-C8	1.225 (3)	1.220	1.220	1.220	1.220
O2-C8	1.289 (3)	1.289	1.289	1.289	1.288
C1-C2	1.507 (4)	1.504	1.505	1.503	1.509
C3-C4	1.507 (4)	1.510	1.509	1.511	1.499
C5-C6	1.493 (4)	1.502	1.501	1.502	1.510
C7-C8	1.509 (4)	1.503	1.503	1.503	1.502

(ii) Nonbonded Interatomic Distances, Å, and Energies, kcal mol^{-1} [b]

	Minimized			
Atoms	δλδ	δλλ	λλδ	δδδ
O2· · ·H14	2.71	3.84	2.57	2.42 [0.3]
C2· · ·H9	2.57	2.57	2.58	2.52 [0.3]
C3· · ·H6	2.64	2.64	2.48 [0.4]	2.60
C4· · ·H13	2.66	2.49 [0.4]	2.67	2.63
C5· · ·H10	2.56	2.57	2.55 [0.3]	2.55 [0.3]
H1· · ·H3	2.25 [0.3]	2.23 [0.3]	2.35	2.22 [0.4]
H1· · ·H19	2.20 [0.4]	2.26 [0.3]	3.04	2.31
H2· · ·H4	2.27 [0.3]	2.26 [0.3]	2.31	2.23 [0.3]
H2· · ·H12	2.25 [0.3]	2.38	2.20 [0.4]	2.23 [0.3]
H3· · ·H19	3.44	3.18	2.08 [0.7]	2.98
H4· · ·H9	2.94	2.93	4.54	2.17 [0.5]
H4· · ·H11	2.12 [0.6]	2.10 [0.7]	3.94	4.26
H5· · ·H7	2.29	2.30	2.25 [0.3]	2.35
H5· · ·H19	2.34	2.25 [0.3]	3.35	2.17 [0.5]
H6· · ·H9	2.24 [0.3]	2.25 [0.3]	2.33	2.51
H6· · ·H11	3.44	3.43	2.25 [0.3]	4.67
H7· · ·H8	2.25 [0.3]	2.25 [0.3]	2.32	2.28 [0.3]
H7· · ·H17	2.34	2.29	2.50	2.27 [0.3]
H8· · ·H15	2.10 [0.7]	4.01	2.11 [0.7]	4.53
H10· · ·H13	2.25 [0.3]	2.32	2.28 [0.3]	2.63
H11· · ·H12	2.25 [0.3]	2.31	2.25 [0.3]	2.31
H12· · ·H14	2.29	2.24 [0.3]	2.32	2.36
H15· · ·H17	2.28 [0.3]	2.36	2.27 [0.3]	2.23 [0.4]
H16· · ·H18	2.25 [0.3]	2.37	2.22 [0.4]	2.20 [0.4]
H19· · ·H21	2.24 [0.3]	2.23 [0.3]	2.29	2.23 [0.4]
H20· · ·H22	2.26 [0.3]	2.26 [0.3]	2.26 [0.3]	2.27 [0.3]

(iii) Torsion Angles, Deg, and Energies, kcal mol^{-1} [c]

		Minimized			
Atoms	δλδ crystal	δλδ	δλλ	λλδ	δδδ
Co-N1-C1-C2	−26.4	−26.9 [0.9]	−18.1 [1.2]	43.8 [0.3]	−11.5 [1.4]
Co-N2-C2-C1	−39.7	−40.4 [0.4]	−41.8 [0.3]	20.2 [1.2]	−45.0 [0.2]
Co-N2-C3-C4	31.2	28.3 [0.8]	27.4 [0.9]	41.6 [0.3]	−31.9 [0.7]
Co-N3-C4-C3	28.1	26.6 [0.9]	39.6 [0.4]	23.6 [1.0]	−39.7 [0.4]
Co-N3-C5-C6	−43.3	−42.2 [0.3]	20.0 [1.2]	−45.4	−45.9 [0.2]
Co-N4-C6-C5	−26.1	−27.6 [0.9]	49.2	−19.1 [1.2]	6.1 [1.5]
Co-N5-C7-C8	−12.3	−22.5 [1.1]	−21.2 [1.1]	25.8 [0.9]	−21.9 [1.1]
Co-O2-C8-O1	174.1	173.0	173.8	−174.5	174.5
Co-O2-C8-C7	−7.2				
N1-C1-C2-N2	42.7	44.6 [0.4]	39.3 [0.7]	−42.1 [0.5]	37.4 [0.8]
N2-C3-C4-N3	−39.0	−36.4 [0.8]	−45.0 [0.4]	−43.8 [0.4]	47.3 [0.3]
N3-C5-C6-N4	45.2	46.1 [0.3]	−45.8 [0.3]	42.2 [0.5]	26.1 [1.5]
N5-C7-C8-O2	13.1	21.1	19.5	−22.4	19.5

Table III (*Continued*)

(iv) Crystal Structure Bond Angles, Angular Deformations, Deg, and Energies, kcal mol^{-1}

Atoms	$\delta\lambda\delta$ crystal	Minimized			
		$\delta\lambda\delta$	$\delta\lambda\lambda^c$	$\lambda\lambda\delta^c$	$\delta\delta\delta^c$
N1-Co-N2	85.94 (9)	87.7			
N1-Co-N3	93.13 (8)	91.9	93.0	92.6	95.0 [0.4]
N1-Co-N4	178.83 (8)				
N1-Co-N5	91.03 (9)	91.0			
N1-Co-O2	88.50 (8)	88.5			
N2-Co-N3	88.06 (8)	88.8			
N2-Co-N4	94.48 (9)	93.1	93.7	94.6 [0.3]	95.2 [0.4]
N2-Co-N5	96.85 (9)	92.8			
N2-Co-O2	173.81 (9)				
N3-Co-N4	85.79 (8)	87.3	86.2	86.0	83.9 [0.6]
N3-Co-N5	173.78 (9)				
N3-Co-O2	89.55 (7)	91.6			
N4-Co-N5	90.01 (9)	89.8			
N4-Co-O2	91.03 (9)	90.6			
N5-Co-O2	85.94 (8)	87.1			
Co-N1-C1	111.9 (2)	109.4			
Co-N2-C2	108.7 (2)	107.0			
Co-N2-C3	109.2 (2)	109.2			
Co-N3-C4	109.8 (1)	109.4			
Co-N3-C5	107.5 (1)	106.8			
Co-N4-C6	111.4 (2)	109.6			
Co-N5-C7	109.2 (1)	107.2			
Co-O2-C8	116.3 (2)	113.4 [0.4]	113.8 [0.3]	113.4 [0.4]	114.1 [0.3]
N1-C1-C2	107.7 (2)	109.2			
C1-C2-N2	109.5 (2)	109.6			
C2-N2-C3	114.6 (2)	113.4 [0.3]	113.2 [0.3]	110.5	110.4
N2-C3-C4	110.3 (2)	111.1			
C3-C4-N3	110.4 (2)	111.0			
C4-N3-C5	115.2 (2)	113.5 [0.4]	110.8	113.2 [0.3]	110.6
N3-C5-C6	109.0 (2)	109.2			
C5-C6-N4	107.8 (2)	108.6			
N5-C7-C8	111.0 (2)	108.8			
C7-C8-O1	121.5 (2)	120.8			
C7-C8-O2	116.1 (2)	118.8			
O1-C8-O2	122.4 (2)	120.4			

[a] In the crystal structure determined dimensions, figures in parentheses are the estimated standard deviations in the least significant figure. [b] Energies ≥ 0.3 kcal mol^{-1} are given in brackets. [c] Only angles in which one or more of the structures have a strain energy component ≥ 0.3 kcal mol^{-1} are given.

the *c* direction, these sheets are held together by normal van der Waal's packing forces with the iodide ions fitting into interstices between the cations.

Strain Energies and Minimized Structures. Four conformational modifications of the triethylenetetramine ligand in the Λ-α-(RR)-$[Co(trien)(glyO)]^{2+}$ cation were of sufficient inherent stability to exhibit distinct minima in their strain energy profiles. The energy contributions are listed in Table V and the minimized structures are given in Figure 6. Comparisons of bond lengths and angles, nonbonded interatomic distances, and the torsional angles for the minimized and crystal structure cations are listed in Table III. Good correspondence between the crystal and minimized $\delta\lambda\delta$ structures is obtained except about the glycinato chelate ring, with bond lengths agreeing to better than 0.03 Å and angles to better than 3°.

Of the four conformers minimized, the $\delta\lambda\delta$ structure found in the crystal has the lowest total strain energy, Table V. The energy difference between $\delta\lambda\delta$ and $\delta\lambda\lambda$ ions, however, is not large (0.3 kcal mol^{-1}). Also, the puckered glycinate chelate ring (ϕ(N5–C7) 21–26° Table III(iii)) is stabilized in all four conformers but in the $\delta\lambda\delta$ ion a "planar" form (ϕ(N5–C7) 0°) minimized to an energy only 0.45 kcal mol^{-1} higher than that of the puckered form. The crystal cation has a slightly puckered glycinate chelate (ϕ(Co–N5–C7–C8) −12.3°) and calculations[29] show a low-energy barrier (1.5 kcal mol^{-1}) for the interconversion of the two extremes. This supports the analysis given in the previous section that this part of the molecule reponds readily to crystal packing requirements.

Compared with the similar β_1- and β_2-(RR) and -(RS) cations,[30] the total angular component to the strain energy is lower, Table V, but this is offset by an increase in the nonbonded and torsional terms. For the $\delta\lambda\delta$ and $\delta\lambda\lambda$ ions the former result can be traced to the release of strain in changing from the "planar" to the "angular" arrangement of the ethylenediamine fragments about N2, and the latter result to the introduction of unfavorable dihedral angles about N2–C3 and N1–C1 and the intrahydrogen contacts H4···H11 and H6···H9.

The two most stable ions have a δ N1–C1–C2–N2 chelate ring. The major close contact H3···H19 (2.08 Å, 0.7 kcal mol^{-1}) found in the λ conformation is relieved at the expense of increases in the H1···H3 and H1···H19 repulsions. The central N2–C3–C4–N3 chelate adopts a λ conformation in the three most stable structures. The unstable $\delta\delta\delta$ structures has two close contacts H4···H9 (2.17 Å, 0.5 kcal mol^{-1}) and C2···H9 (2.5 Å, 0.3 kcal mol^{-1}) which are minimized at the expense of some twisting toward the glycinate ring, H5···H19 (2.17 Å, 0.5 kcal mol^{-1}) ϕ(N1–C1) (−11.5°, 1.4 kcal mol^{-1}). The remaining apical N3–C5–C6–N4 ring appears to have no uniquely favored conformation with only 0.3 kcal mol^{-1} separating the $\delta\lambda\delta$ and $\delta\lambda\lambda$ structures, but inter-ring 1–4 type interactions tend to destabilize the δ conformation (H16···H18, H15···H17). Also the $\delta\delta$ combination for the central and apical chelates is destabilized relative to the $\lambda\delta$ combination largely as a result of unfavorable torsional strain (ϕ(C5–C6), 26.1°, 1.5 kcal mol^{-1}; ϕ(N4–C6), 6.1°, 1.5 kcal mol^{-1}) and angle deformations about the central Co atom (N3–Co–N4,

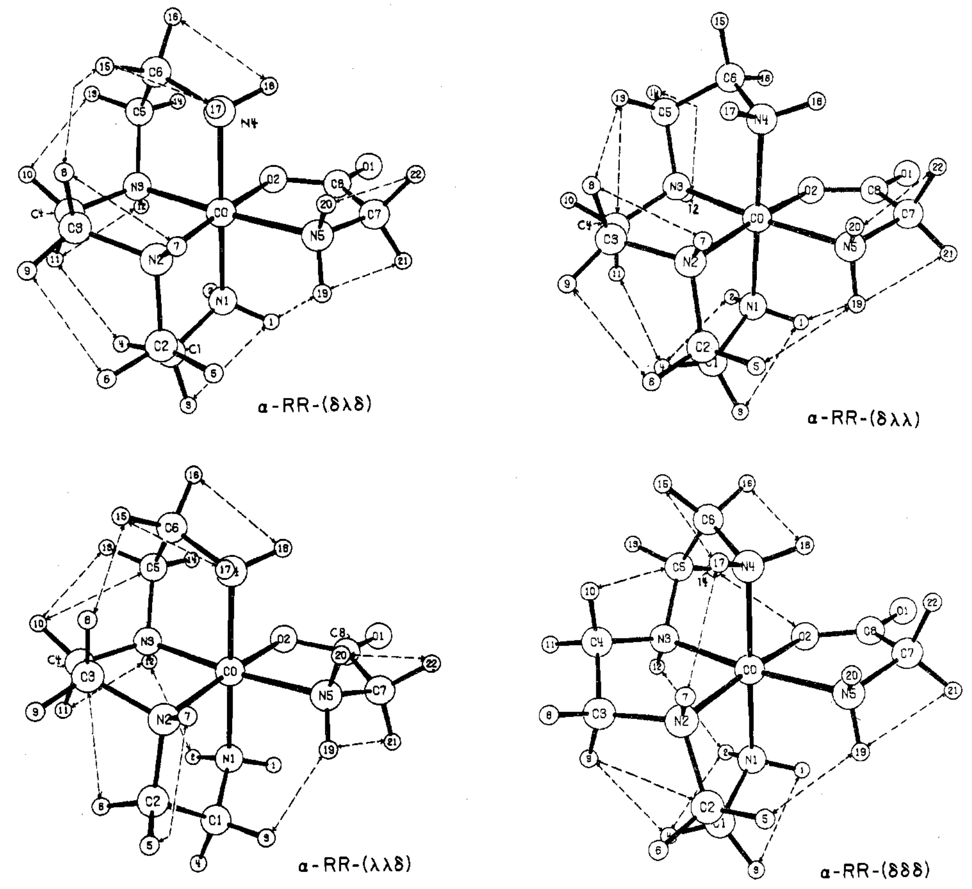


Figure 6. Structures of the four energy minimized Λ-α-(*RR*)-[Co(trien)(glyO)]$^{2+}$ cations showing major nonbonded repulsions (---) (>0.3 kcal mol^{-1}).

Table IV. Intermolecular contacts (<3.7 Å) in α-(*RR,SS*)-[Co(trien)(glyO)]$I_2 \cdot 3H_2O$

Atoms A···B	*d*(A···B), Å	Symmetry operation^a
I1···N1	3.528 (2)	*x*, 1 + *y*, *z*
I1···N5	3.655 (2)	*x*, *y*, *z*
I2···N2	3.537 (2)	*x*, *y*, *z*
I2···N1	3.560 (2)	*x* − 1, *y*, *z*
I2···O3	3.624 (3)	*x*, *y*, *z*
N4···O5	3.065 (4)	1 − *x*, 1 − *y*, −*z*
N4···O3	3.491 (4)	*x*, *y*, *z*
N4···O4	3.533 (4)	*x*, *y*, *z*
N5···O3	3.131 (4)	*x*, *y*, *z*
C5···O1	3.431 (4)	1 − *x*, −*y*, −*z*
C5···O4	3.601 (4)	−*x*, −*y*, −*z*
C6···O1	3.570 (4)	1 − *x*, −*y*, −*z*
C6···O1	3.670 (4)	*x* − 1, *y*, *z*
C7···O4	3.226 (4)	1 − *x*, 1 − *y*, −*z*
C7···O5	3.392 (4)	1 − *x*, 1 − *y*, −*z*
C7···O3	3.447 (4)	*x*, *y*, *z*
C8···O5	3.249 (4)	1 − *x*, 1 − *y*, −*z*
C8···O5	3.427 (3)	*x*, *y* − 1, *z*
C8···O4	3.591 (3)	1 + *x*, *y*, *z*
O1···O4	2.776 (3)	1 + *x*, *y*, *z*
O1···O5	2.941 (3)	*x*, *y* − 1, *z*
O1···O5	3.569 (4)	1 − *x*, 1 − *y*, −*z*
O2···O5	3.125 (3)	*x*, *y* − 1, *z*
O2···O5	3.524 (3)	1 − *x*, 1 − *y*, −*z*
O3···O4	2.753 (5)	*x*, *y*, *z*
O3···O5	2.875 (4)	*x*, *y*, *z*
O4···O5	2.753 (4)	1 − *x*, 1 − *y*, −*z*
O4···O4	3.444 (6)	−*x*, 1 − *y*, −*z*

^{a} To move atom B into contact with atom A.

Table V. Final Energy Terms for the Λ-α-(*RR*)-[Co(trien)glycinato)]$^{2+}$ Conformers (kcal mol^{-1})

Conformation	δλδ	δλλ	λλδ	δδδ
Bond def	0.43	0.44	0.51	0.48
Angle def	2.78	2.96	3.36	3.80
Nonbonded interactions	−3.15	−2.84	−2.28	−1.78
Torsional strain	6.98	6.78	6.67	8.25
Out-of-plane def	0.00	0.00	0.00	0.00
Total strain energy	7.05	7.35	8.27	10.75
Energy differences	0.0	0.3	1.2	3.7

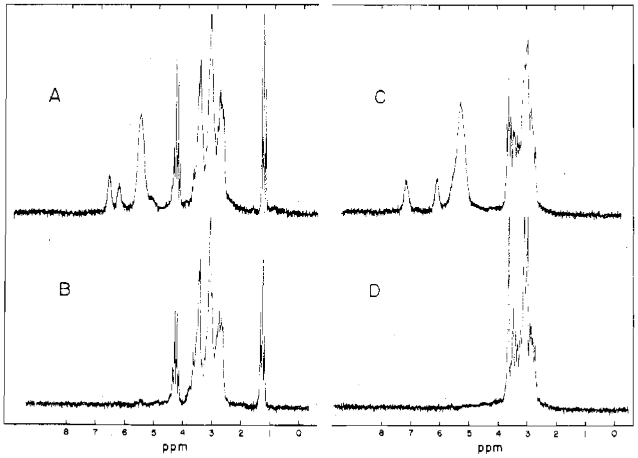


Figure 7. ^{1}H NMR spectra of α-[Co(trien)(glyOEt)Cl](ClO$_4$)Cl in (A) ~10^{-3} M DCl and (B) D$_2$O, pH ~7 after 10 min, and for α-[Co(trien)(glyO)]Cl$_2$ in (C) ~10^{-3} M DCl and (D) D$_2$O, pH ~8.

83.9°, 0.6 kcal mol^{-1}; N2–Co–N4, 95.2°, 0.4 kcal mol^{-1}; N3–Co–N1, 95.0°, 0.4 kcal mol^{-1}).

Proton Magnetic Resonance Spectra and H Exchange. ^{1}H NMR spectra for α-[Co(trien)(glyOEt)Cl]Cl$_2$ and α-[Co(trien)(glyO)]Cl$_2$ in acidic and slightly alkaline D$_2$O solutions are given in Figure 7. It is clear that the two sets of conditions correspond to retention of H, and D for H exchange, of the

Table VI. H-Exchange Data for α-[Co(trien)(glyOEt)Cl]Cl_2 in D_2O at 34 °C

	$10^6[D^+]$, M	$10^5 k_{obsd}$, s^{-1}	$10^{-5} k_H$,[f] M^{-1} s^{-1}
NH[a]	10^4[d]	4.13	1090
	10^3[d]	43.6	1150
NH[b]	61.7[e]	5.5	8.9
	7.08[e]	38.5	7.2
	4.41[e]	82.5	9.6
NH_2[c]	61.7[e]	3.4	5.5
	7.08[e]	30.0	5.6
	4.41[e]	48.1	5.6

[a] NH proton at 6.6 ppm. [b] NH proton at 6.9 ppm. [c] NH_2 protons of triethylenetetramine. [d] DCl solutions. [e] 0.1 M NaOAc/DOAc buffers; pD = pH + 0.4. [f] $k_H = k_{obsd}[D^+]/(3.80 \times 10^{-15})$.

Table VII. H-Exchange Data for α-[Co(trien)(glyO)]Cl_2 in D_2O at 26 °C

	$10^6[D^+]$,[e] M	$10^3 k_{obsd}$, s^{-1}	$10^{-5} k_H$,[f] M^{-1} s^{-1}
NH[a]	2.63	4.44	30.8
	7.94	1.583	33.2
	15.14	0.84	33.4
NH[b]	2.63	1.185	8.2
	7.94	0.40	8.4
	15.14	0.218	8.7
NH_2[c]	10.5	1.05	29
	52.5	1.05	145
	52.5	0.236	33
NH_2[d]	2.63	0.753	5.2
	15.14	0.135	5.4

[a] NH proton at 6.3 ppm. [b] NH proton at 7.4 ppm. [c] NH_2 protons of glycinate chelate; two rate processes are involved (see Figure 8). [d] NH_2 protons of triethylenetetramine moiety. [e] NaOAc/DOAc buffers (0.1 M), pD = pH + 0.4. [f] $k_H = k_{obsd}[D^+]/(3.80 \times 10^{-15})$.

coordinated amine functions, respectively; concomitant collapse of the glycine CH_2 triplet to a singlet occurs in alkaline D_2O. In acidic conditions the broad resonances at 6.6 and 6.9 ppm in α-[Co(trien)(glyOEt)Cl](ClO_4)Cl, Figure 7a, integrate for single protons and are assigned to the secondary amine protons of triethylenetetramine trans to Cl and trans to the glycinate NH_2 group, respectively. A similar assignment is given to the absorptions at 6.3 (trans to O) and 7.4 ppm (trans to N) in α-[Co(trien)(glyO)]Cl_2, Figure 7c. This assignment is based on the observed upfield shift of amine functions trans to electronegative groups, e.g., [Co(NH_3)$_5$X]$^{2+}$ (X^- = Cl^-, Br^-, NCS^-, $OCONH_2^-$),[31] and on their relative rates of H exchange.

Tables VI and VII give kinetic data for H exchange of the amine functions in α-[Co(trien)(glyOEt)Cl]$^{2+}$ and α-[Co(trien)(glyO)]$^{2+}$, respectively. Peak areas (A) or peak heights (P) were measured as a function of time for the primary and secondary amine protons of the triethylenetetramine moiety and the collapse of the glycinate triplet to a singlet was used to follow exchange in the NH_2 function of the amino acid. The data gave linear plots of log A_t or log $(P_t - P_\infty)$ vs. time for at least 2 half-lives and it is clear that rate laws of the form $k_{obsd} = k_H[OD^-]$ are closely followed in each case. Two exchange rates were observed for the NH_2 protons of the glycinate chelate in the α-[Co(trien)(glyO)]$^{2+}$ ion, Table VII. Exchange was followed by monitoring the CH_2 signal and, from Figure 8, it is clear that the original triplet collapses to approach a doublet which more slowly changes into the singlet of the fully exchanged material. Even allowing for a statistical factor of 2, the latter rate is slower. This may arise from either deuterium substitution reducing the acidity of the remaining NHD proton[32] or to their nonequivalence resulting from the asymmetric environment.

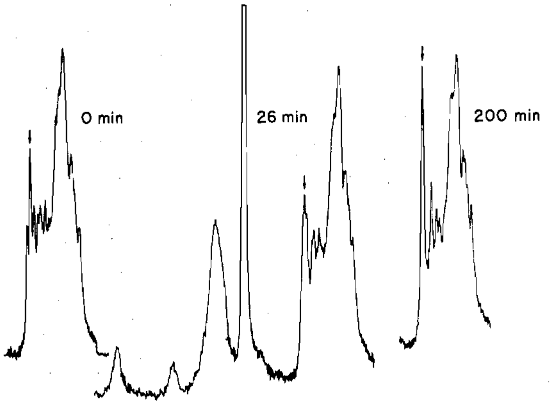


Figure 8. Collapse of the CH_2 resonance of glycine in [Co(trien)(glyO)]Cl_2 at pD 4.28, 26 °C.

Table VIII. Rate Data for Hg^{2+}-Catalyzed Aquation of α-(*RR,SS*)-[Co(trien)(glyOEt)Cl](ClO_4)Cl at 25 °C (550 nm, [Co] ≃ 10^{-4} M)

[Hg^{2+}], M	[$HClO^4$], M	μ, M	$10^3 k_{obsd}$, s^{-1}	$10^2 k$,[b] M^{-1} s^{-1}
0.037	0.39	1.3	0.89	2.4
0.10	0.15	1.3	2.30	2.3
0.15	0.55	1.3	3.30	2.2
0.30	0.1	1.3	6.08[a]	2.0
0.10	0.10	0.4	0.71	0.7

[a] Obtained from initial slope. [b] $k = k_{obsd}[Hg^{2+}]$.

The relative H-exchange rates are worth commenting on. The primary NH_2 protons of triethylenetetramine have similar rates in both complexes, $k_H \simeq 5.5 \times 10^5$ M^{-1} s^{-1}, as do the secondary NH protons at lowest field (trans to N), $k_H \simeq 8 \times 10^5$ M^{-1} s^{-1}. The NH_2 protons of the glycinate chelate in α-[Co(trien)(glyO)]$^{2+}$ are considerably more labile than the other primary amine protons, probably due to their proximity to the carboxyl function. The similar protons in α-[Co(trien)(glyOEt)Cl]$^{2+}$ were not studied. The most striking difference, however, occurs in the secondary NH protons trans to N, O, and Cl. In [Co(trien)(glyO)]$^{2+}$ that at 6.3 ppm (trans to O) is some four times more labile than that at 7.4 ppm (trans to N) and in [Co(trien)(glyOEt)Cl]$^{2+}$ that trans to Cl is ca. 100 times more labile than that trans to N. Polarization by the trans O and Cl atoms probably makes them more acidic although their chemical shift position suggests that they are shielded relative to the NH protons trans to N. However, other factors are important in relating chemical shifts and electron densities.[33] This lability of amine protons trans to some electronegative groups is common in Co(III) chemistry and has been used to advantage in propagating regiospecific condensations of deprotonated amine functions with adjacent electrophiles.[34]

Hg^{2+}-Catalyzed Aquation of α-(*RR,SS*)-[Co(trien)(glyOEt)Cl]$^{2+}$. Rate data collected spectrophotometrically at 550 nm are given in Table VIII. Optical density changes of ~0.4 were observed and plots of log $(D_t - D_\infty)$ vs. time were linear for up to 3 half-lives except for the run at 0.3 M Hg^{2+} where some subsequent curvature occurred. The data fit the rate law $k_{obsd} = k[Hg^{2+}]$ with $k = (2.2 \pm 0.2) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C, μ = 1.3. The rates are [H^+] independent but decrease threefold on reducing the ionic strength to 0.4. The reaction product was identified spectrophotometrically and by ion-exchange chromatography as >95% α-(*RR,SS*)-[Co(trien)(glyO)]$^{2+}$.

Treatment of a 0.1% solution of optically pure $(-)_{546}$-α-(*SS*)-[Co(trien)(glyOEt)Cl]$^{2+}$ ($[\alpha]_{589}$ −129°) with 0.3 M Hg^{2+} solution gave optically pure $(-)_{589}$-α-(*SS*)-[Co(trien)(glyO)]$^{2+}$ ($[M]_{589}$ −1720°). The visible and RD curves for this product

Scheme I

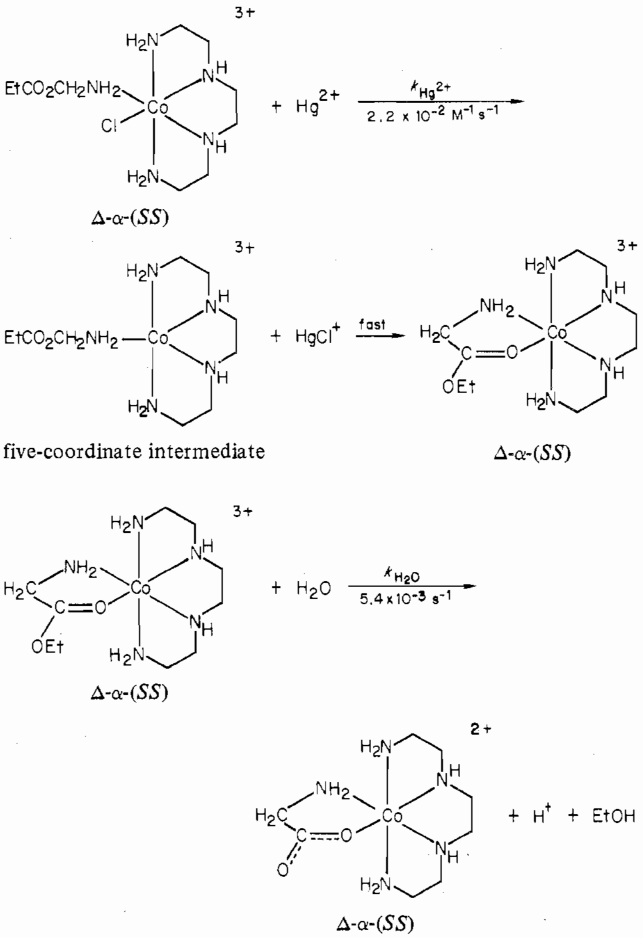


Table IX. Rate Data for Base Hydrolysis of α-[Co(trien)(glyOEt)Cl](ClO$_4$)Cl at 25 °C, μ = 1.0 M (NaClO$_4$)

pH[a]	$10^4 k_{\text{obsd}}$, s^{-1}	k_{OH},[b] $M^{-1}\ s^{-1}$
10.02[c]	133	75
9.50[d]	43.7	81
9.40[c]	30.1	71
9.17[c]	18.8	75
9.09[c]	15.0	72
8.59[c]	4.6	70

[a] pH at conclusion of run. [b] $k_{\text{OH}} = k_{\text{obsd}}[\text{H}^+]/K_w$, $K_w = 1.7 \times 10^{-14}$ in 1 M NaClO$_4$. [c] 0.1 M glycine buffer; followed spectrophotometrically at 560 nm. [d] pH-stat controlled; followed spectrophotometrically at 560 nm. [e] Optically pure $(+)_{589}$ complex; pH-stat controlled.

were identical (apart from sign) with those observed for separately resolved $(+)_{589}$-α-(*RR*)-[Co(trien)(glyO)]I$_2$, Figure 3. The product was also homogeneous on the ion-exchange column under conditions (0.5 M phosphate buffer, pH 6.8) where the α, β_1, and β_2 isomers can be separated.[3] Thus the Hg^{2+} reaction involves retention of both the optical and geometric configuration, and the absolute configuration of the $(-)_{546}$-α-(*SS*)-[Co(trien)(glyOEt)Cl]$^{2+}$ ion is Δ, the same as that for the $(-)_{589}$-α-(*SS*)-[Co(trien)(glyO)]$^{2+}$ ion.

Also the anions HSO$_4^-$ (or SO$_4^{2-}$) and NO$_3^-$ do not compete (<2%) during the Hg^{2+}-catalyzed reaction since no [Co(trien)(glyOEt)SO$_4$]$^+$ or [Co(trien)(glyOEt)NO$_3$]$^{2+}$ was detected spectrophotometrically or by ion exchange when the reaction was carried out in 0.1 M H$_2$SO$_4$ + 0.9 M Li$_2$SO$_4$ and 1 M NaNO$_3$, respectively. This also suggests that water is not involved as a competitor for the five-coordinate intermediate generated on removal of Br[35] and that α-[Co(trien)(glyOEt)(H$_2$O)]$^+$ is not formed. Since these observations are similar to those found for the [Co(en)$_2$(glyOC$_3$H$_7$)Br]$^{2+}$ + Hg^{2+} reaction[36,37] it was decided that direct verification of the noninvolvement of water by ^{18}O-tracer studies was unnecessary.

At the higher Hg^{2+} concentrations (0.3, 0.4, 0.5 M) a reaction subsequent to that described above was observed. This was followed using an absorbance scale 0–0.1 [Co] ≃ 10^{-3} M, 480 nm, and was shown to be [Hg^{2+}] independent with $k_{\text{obsd}} = 5.4 \times 10^{-3}\ s^{-1}$. This reaction almost certainly results from hydrolysis of the chelated ester in the rapidly formed intermediate α-[Co(trien)(glyOEt)]$^{3+}$ and is similar to that found by Alexander and Busch[38] in the analogous reactions of *cis*-[Co(en)$_2$(glyOR)Br]$^{2+}$ (R = CH$_3$, C$_2$H$_5$, *i*-C$_3$H$_7$). For the conditions used in this study only the pH-independent path will contribute to k_{obsd},[36,39] and the rate agrees well with that found for [Co(en)$_2$(glyOEt)]$^{3+}$,[38] viz., $7 \times 10^{-3}\ s^{-1}$. Scheme I accommodates all these observations; a similar mechanism has been proposed for the Hg^{2+}-catalyzed reaction of β_2-(*RR,SS*)-[Co(trien)(glyOEt)Cl]$^{2+}$.[35]

Base Hydrolysis of α-(*RR,SS*)-[Co(trien)(glyOEt)Cl]$^{2+}$. The rates of base hydrolysis were followed spectrophotometrically and by pH-stat titration in the presence and absence of buffers, respectively. In glycine buffers isosbestic points occurred at 507, 410, 364, and 321 nm. Linear first-order plots of log ($A_\infty - A_t$) vs. time were obtained at 550 nm over at least 3 half-lives. The results given in Table IX show that the rate law $k_{\text{obsd}} = k_{\text{OH}}[\text{OH}^-]$ is followed with $k_{\text{OH}} = 74 \pm 4\ M^{-1}\ s^{-1}$ at μ = 1 M (NaClO$_4$) and 25 °C. No buffer dependence was observed.

Visible and rotatory dispersion curves of the product solution suggested that the base hydrolysis reaction was not stereospecific, and when the products were chromatographed on cation-exchange resin using 0.5 M NaHPO$_4$–0.5 M NaH$_2$PO$_4$ eluent (pH ~6.8) two bands clearly separated. These were identified by visible spectra, Co analyses, and polarimetry as α-[Co(trien)gly]$^{3+}$ and β_2-[Co(trien)(gly)]$^{2+}$ in order of elution. No β_1 products (Figure 1b, c) were found. The product analysis results given in Table X show that the α:β_2 ratio, 63:37, is independent of [OH$^-$], ionic strength, and the presence of "Tris" buffer. Recoveries were >98%. The results of base hydrolysis of optically pure $(+)_{589}$-α-(*RR*)-[Co(trien)(glyOEt)Cl](ClO$_4$)Cl were as follows

Table X. Products from Base Hydrolysis of α-[Co(trien)(glyOEt)Cl](ClO$_4$)Cl at 25 °C under Different Conditions and Reaction Times

Conditions	Time, min	% α-[Co(trien)-(glyO)]$^{2+}$	% β_2-[Co(trien)-(glyO)]$^{2+}$
1. Tris buffer (0.1 M), pH 9.24, μ = 1 (NaClO$_4$)	70	63	37
2. 0.1 M NaOH, μ = 1 (NaClO$_4$)	1	64	36
3. pH 9.17, pH-stat, μ = 1 (NaClO$_4$)[a]	56	64	36
4. 0.1 M NaOH	1	63	37
5. 0.1 M NaOH	180	63	37
6. pH 9.5, radiometer controlled	150	62	38

[a] $(+)_{589}$-*RR* complex.

$$\underset{[M]_{589}\ +660^{\circ}}{\alpha\text{-}(RR)\text{-}[Co(trien)(glyOEt)Cl]^{2+}} \xrightarrow[\text{pH 9.17}]{(OH^-)}$$

$$\underset{[M]_{546}\ +3470^{\circ}}{\alpha\text{-}(RR)\text{-}[Co(trien)(glyO)]^{2+}\ (64\%)\ +}$$

$$\beta_2\text{-}(RR)\text{-}[Co(trien)(glyO)]^{2+}\ (32\%)\ +$$

$$\underset{[M]_{546}\ -2860^{\circ}}{\beta_2\text{-}(RS)\text{-}[Co(trien)(glyO)]^{2+}\ ({\sim}4\%)}$$

With phosphate eluent the β_2-(*RR*) and β_2-(*RS*) isomers do not separate by ion exchange,[3] and the relative amounts were calculated from the observed extinction coefficient (ϵ_{480} 131) and molecular rotation ($[M]_{546}$ −2860°). Authentic β_2-(*RR*)-$[Co(trien)(glyO)]^{2+}$ has ϵ_{479} 130, $[M]_{546}$ −2950°, and β_2-(*RS*)-$[Co(trien)(glyO)]^{2+}$, ϵ_{484} 142, $[M]_{546}$ −2470°, in 1 M HCl. The calculated ratio β_2-(*RR*):β_2-(*RS*) of 8 agrees well with the value of 9 found for the mutarotated mixture under alkaline conditions. Clearly full retention of optical activity obtains in both the α-(*RR*) and β_2 products.

In a separate experiment $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyO)]I_2 \cdot H_2O$ ($[\alpha]_{589}$ +320°) was shown to be optically stable for 3 days in pH 10.0 dimethylamine buffer (0.1 M, 25 °C). In 0.1 M NaOH some decomposition takes place, but after 2 h the ion-exchanged product (single band) was shown to be the optically pure starting material. These experiments demonstrate the inability of the secondary NH triethylenetetramine protons to undergo mutarotation in α-$[Co(trien)(glyO)]^{2+}$ and also that the β_2 products of base hydrolysis of α-(*RR*)-$[Co(trien)(glyOEt)Cl]^{2+}$ do not derive from an isomerization in the α-glycinato product.

The base hydrolysis reaction differs in two major respects from that found for the β_2-$[Co(trien)(glyOEt)Cl]^{2+}$ ion.[35] The rate is about 3000 times slower, being similar to that found for *cis*-$[Co(en)_2(glyOEt)Cl]^{2+}$,[41] Table XI, and both optically pure α and β_2 products result, Table X. In the former reaction, the β_2 stereochemistry is exclusively retained. A comparison of the rate constants for base hydrolysis (k_{OH}), and for H exchange (k_H), is instructive, Table XI. If k_H reflects the acidity of the amine protons, then the similarity in the k_H values for the most acidic secondary amine proton[42] in the α and β_2 ions suggests that the conjugate base of the β_2 ion loses Cl ion more rapidly than the similar deprotonated α complex. At least two pieces of information support the contention that removal of the most acidic proton in these ions results in the reactive conjugate bases leading to hydrolysis. Firstly, inversion about the planar secondary amine center in the β_2-(*RR*,*SS*)-$[Co(trien)(NH_3)Cl]^{2+}$ ion (to *RS*,*SR*) results in a sixfold increase in both k_H and k_{OH},[43] Table XI, suggesting that the two situations are related, and secondly, base hydrolysis of β_2-(*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$ leads to 32% inversion about the "planar" secondary N center during or after loss of Cl^- and before entry of the carbonyl function.[47] The latter result requires the proton trans to Cl to be absent during or after the removal of Cl. In the α ions the evidence relating k_H for the most acidic proton trans to Cl and k_{OH} is less substantial although a good body of evidence for other Co(III)–acido complexes,[44] and the above evidence for the β_2 species, suggests that such is the case.

It is not clear why the β_2-conjugate base is more reactive than the similar α ion. It could result, at least in part, from the greater steric strain about the deprotonated "planar" N atom. Strain energy calculations on the β_1- and β_2-Co(trien) complexes[2,3,7,45] show that this part of the molecule is in a distorted condition, and relief of strain may well be achieved in the transition state leading to the five-coordinate intermediate. Such effects and their influence on the rates of base hydrolysis have previously been observed in the $(NH_2R)_5CoCl^{2+}$ ions (R = CH_3, Bu).[46]

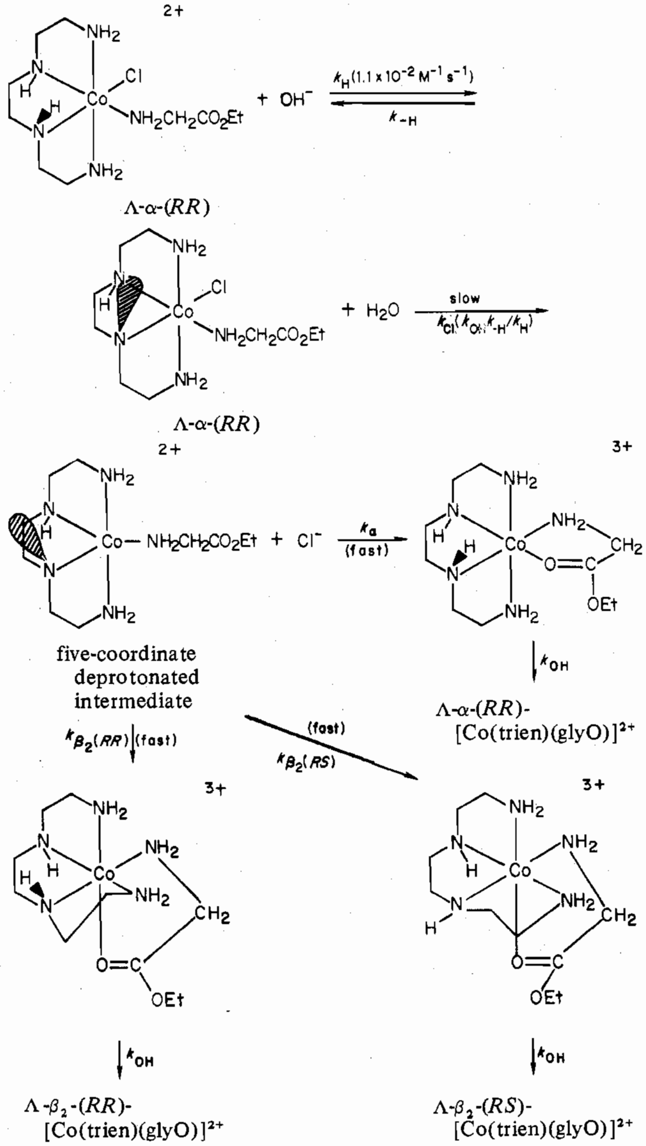
It is also possible to rationalize the stereochemical change accompanying base hydrolysis of the less labile α-$[Co(trien)(NH_2R)Cl]^{2+}$ ions (R = H, CH_2CO_2Et) as resulting from distortion toward the B_2-trien configuration in the transition state leading to the five-coordinate intermediate. This is depicted in Scheme II. Both equilibrium measurements and strain energy minimization calculations[3,43] show that the β_2 structure in the products of base hydrolysis

Table XI. Rate Data ($M^{-1}\ s^{-1}$) for H Exchange and Base Hydrolysis in some $[N_5CoCl]^{2+}$ Ions

	k_H[a]	k_{OH}[b]
α-(*RR*,*SS*)-$[Co(trien)(NH_3)Cl]^{2+}$	3×10^7	10
α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$	1.1×10^8	74
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	1.1×10^7	3.3
cis-$[Co(en)_2(glyOEt)Cl]^{2+}$		70
β_2-(*RR*,*SS*)-$[Co(trien)(NH_3)Cl]^{2+}$	0.8×10^7	4.8×10^4
β_2-(*RS*,*SR*)-$[Co(trien)(NH_3)Cl]^{2+}$	5×10^7	2.3×10^5
β_2-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$	2.5×10^8 (25 °C)	2.2×10^5

[a] For the α-trien and $(en)_2$ systems, k_H refers to the amine function trans to Cl; for the β_2-trien systems, it refers to the "planar" secondary NH function which is also trans to Cl. Data at 34 °C.
[b] 25 °C in 1 M $NaClO_4$.

Scheme II



($[Co(trien)(NH_3)(OH)]^{2+}$ and $[Co(trien)(glyO)]^{2+}$) is stabilized by some 2 kcal mol^{-1} over the corresponding α structure. This energy difference may well provide the driving force for stereochemical change. No β_1-$[Co(trien)(glyO)]^{2+}$ is formed and a complex stereochemical rearrangement would be required to produce it. Also, the similar product distributions resulting from α-$[Co(trien)(NH_3)Cl]^{2+}$ (27% β_2, 73% α)[43] and α-$[Co(trien)(glyOEt)Cl]^{2+}$ (37% β_2, 63% α) suggest some stereochemical rigidity in the five-coordinate intermediate with well-defined directions for entry of the sixth ligand.

Further details on the mechanism depicted in Scheme II have not been obtained. Thus ^{18}O-tracer experiments to distinguish between water and carbonyl oxygen entry in the five-coordinate intermediate have not been carried out. For the $[Co(en)_2(glyOC_3H_7)Br]^{2+}$ ion such paths contribute about equally[36] whereas for the β_2-$[Co(trien)(glyOEt)Cl]^{2+}$ ion at least 17% of the reaction occurs via intramolecular hydrolysis by coordinated hydroxide.[35] Also, although both the β_2-(*SS*,*RR*) and β_2-(*SR*,*RS*) ions appear as products of base hydrolysis, mutarotation between them is rapid under the experimental conditions, so it is not possible to determine the immediate β_2-(*SS*,*RR*)/β_2-(*SR*,*RS*) ratio on loss of chloride. This situation does not occur with the analogous β_2-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$ or β_2-(*RR*,*SS*)-$[Co(trien)(glyO)Cl]^+$ ions, and nonequilibrium product ratios (66/34, 37/63, respectively)[40,47] result.

Registry No. α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl](ClO_4)Cl$, 64043-36-3; $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyOEt)Cl](As_2((+)\text{-tart})_2)$, 64043-38-5; $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyOEt)Cl](ClO_4)Cl$, 64043-43-2; $(-)_{589}$-α-(*SS*)-$[Co(trien)(glyOEt)Cl](ClO_4)Cl$, 64043-45-4; α-(*RR*,*SS*)-$[Co(trien)(glyO)]I_2$, 54984-40-6; $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyO)](As_2((+)\text{-tart})_2)$, 64043-46-5; $(-)_{589}$-α-(*SS*)-$[Co(trien)(glyO)](As_2((+)\text{-tart})_2)$, 64044-00-4; $(+)_{589}$-α-(*RR*)-$[Co(trien)(glyO)]I_2$, 64010-56-6; $(-)_{589}$-α-(*SS*)-$[Co(trien)(glyO)]I_2$, 64043-47-6; α-(*RR*,*SS*)-$[Co(trien)(glyO)]Cl_2$, 63988-84-1; α-(*RR*,*SS*)-$[Co(trien)(NH_3)Cl]^{2+}$, 64043-48-7; *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$, 15392-82-2; β_2-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]^{2+}$, 64043-49-8; α-$[Co(trien)CO_3]ClO_4$, 36994-86-2; β_2-$[Co(trien)(glyO)]^{2+}$, 51022-66-3; α-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]Cl_2$, 64043-50-1.

Supplementary Material Available: Table II, a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Nomenclature: trien = triethylenetetramine; glyO = glycinate anion; glyOEt = ethyl glycinate; β and α refer to the unsymmetrical and symmetrical topology of the trien ligand, respectively (A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967)). β_1 and β_2 refer to the two configurational isomers obtained using different or unsymmetrical donor ligands in the remaining octahedral sites. For glycinate, β_1 refers to the isomer with O trans to the secondary N atom and β_2 to O trans to NH_2 (D. A. Buckingham and L. G. Marzilli, *Inorg. Chem.*, **6**, 1042 (1967)). *R* and *S* refer to the configurations about the secondary N centers in the order "angular" then "planar" where the N atom joins chelates not in the same plane, or in the same plane, respectively (D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967)). Δ and Λ refer to the configuration about the central metal atom defined by the terminal chelate rings of trien related to Δ- and Λ-$[Co(en)_2X_2]^+$. δ and λ define the conformations of the five-membered chelate rings (*Inorg. Chem.*, **9**, 1 (1970)).

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