Volume 14
Number 8
August 1975

Inorganic Chemistry

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Structures, Properties, and Relative Energies of $[Co(trien)(glyO)]^{2+}$ Ions. The β_2-(*RS*,*SR*)- and β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ Ions[1]

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Received October 24, 1974 AIC40739W

The synthesis, resolution into enantiomers, physical properties, and rates of H exchange of the Λ,Δ-β_2-(*SR*,*RS*)-$[Co(trien)(glyO)]^{2+}$ ions[1] (trien = triethylenetetramine, glyO = glycinato anion) are described. The structural assignment is confirmed by an X-ray analysis of Λ,Δ-β_2-(*SR*,*RS*)-$[Co(trien)(glyO)]Cl_2 \cdot H_2O$: the crystal contains two independent cations with mirror-imaged "apical" ring[1] conformations. The dynamics and thermodynamics of mutarotation to a mixture of the Λ,Δ-β_2-*SR*,*RS* and Λ,Δ-β_2-*SS*,*RR* ions are reported ($\Delta G_{25} = 1.3 \pm 0.1$ kcal mol^{-1}, $\Delta H_{25} = 1.2 \pm 0.1$ kcal mol^{-1}). Strain energy minimization calculations adequately predict the stereochemistry but overestimate the observed ΔH_{25} value (ΔH_{25}(calcd) = 3.8 kcal mol^{-1}). Equilibrations of the α, β_1, and β_2 cations on activated charcoal give the same products, 2.3 (6)% α-*RR*,*SS*, 93.2 (8)% β_2-*RR*,*SS* + β_2-*RS*,*SR*, and 4.5 (5)% β_1-*RR*,*SS* + β_1-*RS*,*SR* at 25° and this stability order is reproduced by the strain energy minimization calculations.

Introduction

Other papers concerning these ions have described the structures and properties of the Δ-β_1-(*RR*)- and Δ-β_1-(*RS*)-$[Co(trien)(glyO)]^{2+}$ cations[1,2] and the Δ,Λ-α-(*SS*,*RR*)-$[Co(trien)(glyO)]^{2+}$ cation[1,3] (trien = 1,4,7,10 tetraazadecane, glyO = glycinate anion). Both the structural and thermodynamic aspects compared favorably with the structures and energies calculated by an iterative strain energy minimization procedure.[4–6] In this paper we present similar results for the two remaining configurational isomers, Δ,Λ-β_2-(*RS*,*SR*)- and Δ,Λ-β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$. The combined results for the five independent structural isomers of the same cation represent the most extensive test so far reported for the computational approach to energy minimization in coordination complexes. The results described here demonstrate the value this approach has for a realistic evaluation of the detailed configurations and conformations of structural isomers in the solid state and of their relative energies in solution.

Although the preparation and resolution into enantiomers of β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ was described several years ago,[7] the chemistry of the β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]^{2+}$ ion is less well documented. A previous publication concerning the base hydrolysis of Λ-(+)$_{589}$-β_2-(*SS*)-$[Co(trien)(glyOEt)Cl]Cl_2$[8] described some 32% inversion about the "planar"[1] secondary N center of triethylenetetramine during hydrolysis and chelation of the glycinate moiety, but although the resulting Λ-(+)$_{589}$-β_2-(*SR*)-$[Co(trien)(glyO)]^{2+}$ ion was isolated in aqueous acidic solution, it was left to this publication to describe its properties and to defend its structural assignment. About the same time Lin and Douglas described the isolation of β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]I_2 \cdot H_2O$ following the treatment of α-$[Co(trien)Cl_2]Cl$ with aqueous NaOH and subsequently glycine at 60°.[9,10] The visible, infrared, and PMR spectra of this species were very similar to or identical with those found for the isomeric β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]I_2 \cdot H_2O$ and the circular dichroism spectra for the resolved cations differed only in their intensities at the absorption maxima. Their results differed significantly from ours and furthermore the stability relationships and solubility differences for the two isomers made it very unlikely that substantial yields of the β_2-*RS*,*SR* iodide could be obtained by their method. Therefore the preparation and properties of the β_2-(*SR*,*RS*)-$[Co(trien)(glyO)]^{2+}$ ions are described here in some detail.

Experimental Section

Analytical reagents were used for kinetic measurements without further purification.

Spectrophotometric rate data and visible spectra were collected on Cary 14 and 16K spectrophotometers. Rotatory power was measured with a Perkin-Elmer P22 spectropolarimeter using 1-dm cells and circular dichroism measurements were made with a Jouan Dichrographe[11] or a Cary 61 instrument. H-Exchange data and PMR spectra were recorded with a Jeol 100-MHz Minimar instrument at 25°. The calorimetric study on β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]I_2 \cdot H_2O$ was carried out on a LKB calorimeter.[12] Bio-Rad analytical Dowex 50W-X2 (200–400 mesh) ion-exchange resin was used for all cation-exchange separations. Cobalt concentrations were calculated from known extinction coefficients or were measured directly using a Techtron AA4 atomic absorption spectrometer. Glycine buffer solutions (0.1 *M*) were made up to unit ionic strength with $NaClO_4$. DOAc–NaOAc buffers (0.1 *M*) were prepared by titrating acetic anhydride in D_2O with a standard NaOD solution. The pD was calculated using the empirical expression pD = pH + 0.4,[13] and the pH was measured using a Radiometer 26 instrument equipped with a NH_4NO_3 (1.6 *M*)–$NaNO_3$ (0.2 *M*) salt bridge.

Kinetic Measurements. Samples of complex (ca. 10 mg) were dissolved in 1 *M* $NaClO_4$ solutions at 25° and immediately mixed with an equal volume of buffer solution. Reactions were followed in thermostated cells at 25.0 ± 0.1°. For H exchange ca. 200 mg of complex was dissolved quickly in DOAc–NaOAc buffer (0.5 ml) in the NMR tube. Spectra were run at time intervals and peak heights or areas (planimeter or weighing) measured.

Equilibrium Measurements. The β_2-*RR*,*SS*:β_2-*RS*,*SR* ratio was

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determined by equilibrating ca. 0.2 g of complex in the appropriate buffer or NaOH solution (1 *M* $NaClO_4$). The solution was quenched to pH 4 with glacial acetic acid, diluted to about 500 ml, and sorbed on the cation-exchange resin. The isomers were separated using 0.5 *M* HCl and eluted with 1 *M* HCl. Visible spectra of the fractions were recorded and cobalt concentrations were estimated by atomic absorption.

Equilibrium experiments using Norit A animal charcoal (ca. 1.5 g) were carried out with the complex iodide (1 g) dissolved in H_2O (100 ml). After equilibration in a thermostated bath overnight (~15 hr) the solution was filtered quickly and quenched to pH 4 with glacial HOAc. The products were sorbed onto cation-exchange resin, washed with water (pH ~4), and eluted with 0.5 *M* phosphate buffer at pH 6.2. The three orange bands containing 2+ ions were collected and estimated spectrophotometrically at their absorption maxima (480, 479, and 489 nm, respectively). The first bands from three such experiments were combined, diluted with water, sorbed onto fresh cation-exchange resin, washed with water, and eluted with 2 *M* HCl. The resulting solution was twice reduced to dryness from water and its PMR spectrum in D_2O was measured.

Preparation and Resolution of β_2-(*RS,SR*)-[Co(trien)(glyO)]-$Cl_2\cdot H_2O$. β_2-(*RR,SS*)-[Co(trien)(glyOEt)Cl]$(ClO_4)_2$[8] (5.4 g) was dissolved in water (200 ml) and 1 *M* NaOH was added to pH-Stat titration at pH 6.5 until base consumption was complete (10 ml). The solution was acidified to pH ~3 with $HClO_4$, diluted to 1 l., and absorbed on a large column of cation-exchange resin (7.5 cm × 50 cm) (Dowex 50W-X2). The two orange bands were separated using 0.5 *M* HCl and eluted with 1 *M* HCl. The eluents were taken to dryness on a rotary evaporator and reevaporated several times from water to remove excess acid. These two bands have previously been identified as the β_2-*RS,SR* and β_2-*RR,SS* isomers in order of elution from the column.[8] The chloride salt from the first band was crystallized from methanol containing some water by cooling in an ice bath and scratching. The orange crystals were washed with methanol and acetone and air-dried (0.7 g). Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]Cl_2\cdot H_2O$: C, 26.09; H, 6.57; N, 19.03. Found: C, 25.6; H, 6.5; N, 18.5. Addition of $LiClO_4$ to a concentrated aqueous solution of the chloride salt gave β_2-(*RS,SR*)-[Co(trien)-(glyO)]$(ClO_4)_2$. Anal. Calcd: C, 20.1; H, 4.64; N, 14.7. Found: C, 20.3; H, 4.6; N, 14.5. Addition of NaI to a concentrated aqueous solution of the chloride salt at pH ~4 and then addition of methanol resulted in the iodide salt. It was recrystallized from aqueous solution by adding NaI and then methanol and was air-dried. Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]I_2$: C, 18.02; H, 4.16; N, 13.14. Found: C, 18.1; H, 4.4; N, 13.0.

Resolution was achieved by treating β_2-(*RS,SR*)-[Co(trien)-(glyO)]$Cl_2\cdot 2H_2O$ (1.9 g) in 5 ml of water at pH 4 with 2 equiv of $(+)_{546}$-K[Co(EDTA)]$\cdot 2H_2O$ (4.22 g, $[\alpha]_{546}$ + 1000°) and cooling in an ice bath. On scratching, the mauve diastereoisomer $(+)_{520}$-β_2-(*SR*)-[Co(trien)(glyO)]Cl-$(+)_{546}$-[Co(EDTA)] slowly formed and after 1 hr was removed by filtration, washed with methanol, and air-dried (2.05 g). This was recrystallized from the minimum amount of warm water at pH 4 until no improvement in rotation was observed. Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]Cl[Co(C_{10}H_{12}N_2O_8)]\cdot 3H_2O$: C, 30.20; H, 5.63; N, 13.70. Found: C, 29.9; H, 5.6; N, 13.9. The resolving agent was removed using a small column of anion-exchange resin (Dowex 1-X8, 400 mesh, Cl^- form) and the recovered chloride salt was recrystallized from methanol containing a little water at pH ~4. The major fraction (0.65 g) gave α_{589} +0.246° and α_{546} +0.664° for a 0.1% solution, and the more soluble minor component gave α_{589} +0.180° and α_{546} +0.494°. No improvement in rotation was found on recrystallization of the major fraction. Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]Cl_2\cdot 2H_2O$: C, 24.85; H, 6.78; N, 18.4; Co, 15.24; Cl, 18.34. Found: C, 24.8; H, 6.9; N, 17.9; Co, 15.1; Cl, 18.3. The optically pure iodide was obtained by adding NaI to a concentrated aqueous solution of the chloride at pH 4 followed by methanol and scratching. It was recrystallized from water by adding methanol and was air-dried. Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]I_2$: C, 18.02; H, 4.16; N, 13.14. Found: C, 18.0; H, 4.2; N, 13.1.

Similarly, using $(-)_{546}$-K(Co(EDTA))$\cdot 2H_2O$ ($[\alpha]_{546}$ −990°), $(-)_{589}$-(*RS*)-[Co(trien)(glyO)]$Cl_2\cdot 2H_2O$ was obtained (0.6 g). Anal. Found: C, 24.7; H, 6.8; N, 18.0; Co, 15.2. $[\alpha]_{589}$ was −227° and $[\alpha]_{546}$ −619°.

Preparation and Resolution of β_2-(*RR,SS*)-[Co(trien)(glyO)]$I_2\cdot 2H_2O$. This complex was prepared and resolved as described previously.[7] Anal. Calcd for $[Co(C_6H_{18}N_4)(C_2H_4NO_2)]I_2\cdot 2H_2O$: C, 16.88; H, 4.61; N, 12.31; Co, 10.36; I, 44.60. Found for racemate (*RR,SS*): C, 16.7; H, 4.5; N, 12.2; Co, 10.2; I, 44.2. Found for $(+)_{589}$-*SS* isomer: C, 16.9; H, 4.7; N, 12.1; Co, 10.3; I, 44.8.

Crystallography of Racemic β_2-(*RS,SR*)-[Co(trien)(glyO)]$Cl_2\cdot H_2O$. Crystals were prepared as described above. Preliminary precession photographs taken with Ni-filtered Cu Kα radiation indicated that the crystals were monoclinic. The conditions limiting possible reflections among all recorded spectra ($h0l$ absent for $h + l \neq 2n$; $0k0$ absent for $k \neq 2n$) are uniquely consistent with space group C_{2h}^5-$P2_1/c$. Unit cell dimensions at 24° were obtained by the least-squares procedure described below. A density of 1.65 (±0.03) g cm^{-3}, obtained by gradient-tube measurement, indicated there were two independent molecules of [Co(trien)(glyO)]$Cl_2\cdot H_2O$ in each asymmetric unit.

Crystal Data:[14] $CoC_8N_5O_2H_{22}Cl_2\cdot H_2O$, mol wt 368.2; monoclinic with $a = 8.349$ (3), $b = 14.927$ (8), $c = 24.31$ (9) Å; $\beta = 103.58$ (2)°; $V = 2945.3$ Å^3; $d_o = 1.65$ (±0.03) g cm^{-3}; $Z = 8$; $d_c = 1.66$ g cm^{-3}; μ(Mo Kα) = 15.8 cm^{-1}.

For data collection a crystal with approximate dimensions 0.19 × 0.38 × 0.094 cm^3 and bounding faces (010), (0$\bar{1}$0), (001), (001), (100), and ($\bar{1}$00) was mounted on a thin glass fiber in a random orientation on a Hilger–Watts computer-controlled four-circle diffractometer. Eleven reflections from this crystal were accurately centered in a 1.5-mm diameter receiving aperture using a takeoff angle of 3°. These reflections formed the basis for the least-squares refinement of cell constants and the orientation defining matrix,[15] in which the wavelength of Mo Kα_1 radiation was taken as 0.7093 Å. Open-counter ω scans, at a takeoff angle of 3.0°, on several low-angle reflections had peak widths at half-height of approximately 0.2° which is normal for crystals suitable for intensity experiments.[16]

Intensity data were collected with Zr-filtered Mo Kα radiation. The circular receiving aperture, diameter 5 mm, was positioned 23 cm from the crystal. The data were collected by the θ–2θ scan technique; a symmetric scan of 0.6° based on the calculated peak position was composed of 60 steps of 1-sec duration. Stationary-counter background counts of 16 sec were taken at each end of the scan range. No attenuators were needed as the diffracted beam intensity did not exceed 7000 counts sec^{-1} during any scan.

During the data collections, the intensities of three standard reflections in diverse regions of reciprocal space were monitored periodically to check on electronic and crystal stability. The three standards showed different degrees of variation in intensity during the 4 days required to collect the data (average decrease, 80%), probably due to small crystal movements. The final variation range of 33% may have resulted from crystal decomposition. The average scale factors derived from these standards[17b] were used to correct relative intensities for the 3448 intensities recorded in a unique quadrant of reciprocal space. Lorentz and polarization corrections and standard deviations for the intensities were calculated as previously described.[18] An absorption correction was applied[17a] using gaussian integration (4^3 points), the transmission factors ranging from 0.55 to 0.76. The final data set consisted of 1726 refinements of which 963 had $F^2 > 3\sigma(F^2)$ and these were the data used in least-squares refinements.

Solution and Refinement of the Crystal Structure. The structure was solved by means of symbolic addition procedures using a local version of NRC-4.[17c] Two cobalt and four chlorine atom positions were obtained from one of two calculated E maps.

The function $\sum w(|F_o| - |F_c|)^2$ was minimized where the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$; $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors of Co^{3+}, Cl^-, O, N, and C were taken from Cromer and Waber.[19] The effects of anomalous dispersion were included in F_c;[20] values of $\Delta f'$ and $\Delta f''$ for Co and Cl were taken from Cromer's tabulation.[21] The initial least-squares refinement, in which all atoms were assigned variable isotropic vibrational parameters, gave agreement factors R_1 = 0.44 and R_2 = 0.46, where $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$ and R_2 (the weighted R factor) = $(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

All nonhydrogen atoms belonging to the two independent molecules were located using difference Fourier syntheses. Residual electron density was observed around Co and Cl atoms. Accordingly, the final refinement cycles were run with the cobalt and chlorine atoms assigned anisotropic vibrational parameters, while the remaining 16 atoms retained isotropic vibrational parameters. The refinement using 963 data converged to give $R_1 = 0.068$, $R_2 = 0.072$ (ratio of variables

Table I. Final Atomic Parameters with Their Esd's for β_2-(*RS*)-$[Co(trien)(glyO)]Cl_2 \cdot H_2O$

Atom	x	y	z	B_{11} or B^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co1	0.7237 (5)	0.1641 (3)	0.2344 (1)	0.0040 (8)	0.0032 (3)	0.0011 (1)	−0.0007 (5)	0.0012 (2)	0.000 (1)
Co11	0.1676 (5)	0.2282 (3)	0.4967 (2)	0.0055 (7)	0.0034 (3)	0.0012 (1)	0.0003 (4)	−0.0010 (2)	0.0001 (1)
Cl1	0.2159 (9)	0.5643 (5)	0.0713 (3)	0.009 (2)	0.0041 (6)	0.0015 (2)	0.0002 (9)	−0.0008 (5)	0.0001 (1)
Cl2	0.7119 (9)	0.1633 (6)	0.0506 (3)	0.008 (2)	0.0073 (7)	0.0016 (2)	−0.001 (1)	−0.0009 (5)	0.0005 (3)
Cl3	0.830 (1)	0.5318 (6)	0.1612 (4)	0.010 (2)	0.0061 (7)	0.0036 (3)	−0.000 (1)	−0.0007 (6)	−0.0009 (3)
Cl4	0.164 (1)	0.0865 (6)	0.1383 (3)	0.008 (2)	0.0066 (7)	0.0021 (2)	−0.0011 (9)	−0.0003 (6)	0.0002 (3)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
N1	0.597 (3)	0.278 (2)	0.2379 (8)	2.0 (5)	N11	0.225 (3)	0.102 (2)	0.4793 (8)	2.9 (5)
N2	0.614 (3)	0.116 (1)	0.2892 (8)	3.0 (5)	N12	0.370 (3)	0.267 (1)	0.4740 (8)	3.5 (5)
N3	0.822 (3)	0.040 (1)	0.2351 (9)	2.1 (5)	N13	0.126 (3)	0.361 (2)	0.5043 (9)	2.4 (6)
N4	0.559 (3)	0.124 (2)	0.1648 (8)	2.1 (5)	N14	0.019 (3)	0.234 (2)	0.4211 (8)	3.0 (6)
N5	0.863 (3)	0.220 (2)	0.1864 (8)	2.6 (6)	N15	−0.015 (3)	0.188 (1)	0.5310 (8)	2.4 (5)
O1	1.127 (2)	0.279 (1)	0.3229 (7)	2.8 (4)	O11	0.305 (2)	0.185 (1)	0.6593 (7)	3.6 (5)
O2	0.892 (2)	0.206 (1)	0.2993 (7)	3.1 (5)	O12	0.301 (2)	0.220 (1)	0.5721 (7)	2.8 (5)
C1	0.507 (4)	0.267 (2)	0.284 (1)	3.6 (8)	C11	0.402 (4)	0.104 (2)	0.471 (1)	3.3 (9)
C2	0.450 (3)	0.169 (2)	0.286 (1)	1.6 (7)	C12	0.405 (4)	0.191 (2)	0.436 (1)	2.5 (8)
C3	0.592 (4)	0.015 (2)	0.284 (1)	2.1 (8)	C13	0.357 (4)	0.356 (2)	0.451 (1)	2.2 (8)
C4	0.761 (4)	−0.014 (2)	0.278 (1)	2.5 (8)	C14	0.284 (3)	0.408 (2)	0.495 (1)	3.8 (7)
C5	0.782 (4)	0.006 (2)	0.176 (1)	1.9 (8)	C15	−0.018 (3)	0.389 (2)	0.460 (1)	4.1 (7)
C6	0.593 (3)	0.028 (2)	0.150 (1)	3.6 (8)	C16	−0.096 (4)	0.312 (2)	0.421 (1)	5.7 (7)
C7	1.011 (4)	0.263 (2)	0.222 (1)	2.8 (8)	C17	0.050 (3)	0.158 (2)	0.591 (1)	3.3 (7)
C8	1.014 (4)	0.245 (2)	0.285 (1)	3.2 (8)	C18	0.236 (4)	0.184 (2)	0.608 (1)	2.8 (7)
O21	0.192 (3)	0.935 (1)	0.2267 (8)	5.4 (6)	O22	0.651 (3)	0.360 (2)	0.1233 (9)	6.6 (6)

[a] The form of the anisotropic temperature parameter is $\exp[(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

to observations 1:5.3). An analysis of the weighting scheme in ranges of $|F_o|$ and $(\sin \theta)/\lambda$ indicated the relative weights were satisfactory.

The observed bond lengths and angles in the two independent cations reflected the low quality of the data set. The final difference Fourier synthesis showed peaks of 1.6 e/Å^3, about half the height of the last located atoms. No attempt was made to add hydrogen atoms to the refinement. Table I lists the atomic coordinates and temperature factors of atoms as in the structure.

Strain Energy Minimization Calculations. The method and parameters are the same as those used previously for the β_1-$[Co(trien)(glyO)]^{2+}$ ions.[2] In summary, the total strain energy (U) is expressed (eq 1) as a summation of terms representing bond length deformations, $(r_{ij})_b$, bond angle deformations, θ_{ijk}, nonbonded interatomic interactions, $(r_{ij})_{nb}$, torsional constraints, ϕ_{ijkl}, and out-of-plane terms (Δ_l, δ_m).[40] Minimization was achieved by an iterative

$$U = \sum_{ij} U(r_{ij})_b + \sum_{ijk} U(\theta_{ijk}) + \sum_{ij} U(r_{ij})_{nb} + \sum_{ijkl} U(\phi_{ijkl}) + \sum_{ijkl} U(\Delta_l) + \sum_{ijkm} U(\delta_m) \tag{1}$$

procedure and was terminated when the coordinate shifts for each atom were <0.002 Å. In this study the out-of-plane constraint for the glycinato ring minimized the angle between the vector C8–O1 and the plane through atoms O2, C8, and C7—the Δ-deformation type programmed by Boyd.[22] Also, the torsional barrier over atoms C7 and C8 was of the same magnitude as that used previously[2] but with zero phase shift; the previous barrier[2] favored planar amino acid rings whereas most structures show a slight out-of-plane buckling at the nitrogen atom.[23]

Results and Discussion

1. Preparation and Resolution of the Racemic β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]^{2+}$ Cation. This cation was prepared by pH-Stat-controlled base hydrolysis (pH 6–7) of β_2-(*RR*,*SS*)-$[Co(trien)(glyOEt)Cl]Cl_2$.[8] The method yields 32% of this ion, and separation from the remaining β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]^{2+}$ was achieved by ion-exchange chromatography. Similar hydrolysis of β_2-(*RR*,*SS*)-$[Co(trien)(glyOH)Cl]Cl_2$ results in ~65% of the β_2-*RS*,*SR* isomer, but the monodentate glycinate complex is more difficult to prepare.[24] Mutarotation at pH ≥10 of the easily obtained β_2-(*RR*,*SS*)-$[Co(trien)(glyO)]I_2$[7] is a useful method for the rapid synthesis of small amounts of material (≤200 mg) but the equilibrium mixture contains only ca. 9% of the required isomer (vide infra) and large ion-exchange columns and careful loading of them are required to achieve a clean separation.

Attempts to achieve higher yields of the β_2-*RS*,*SR* isomer using α- or β-$[Co(trien)Cl_2]Cl$[25] or β-$[Co(trien)(H_2O)_2]^{3+}$ [25] and glycine in alkaline solution resulted in mixtures of β_2-*RR*,*SS*, β_1-*RR*,*SS* and β_1-*RS*,*SR* isomers and fractional recrystallizations of the isolated iodide salt failed to achieve a complete separation. Ion-exchange chromatography on Dowex 50W-X2 resin using 0.5 *M* Na_2HPO_4–0.5 *M* NaH_2PO_4 as eluent (pH ~6.8) separated the β_1 and β_2 isomers while the *RR*,*SS* and *RS*,*SR* diastereoisomers could be separated using 1 *M* HCl. The preparative procedure used by Lin and Douglas for the β_2-*RS*,*SR* isomer[10] gave largely the β_2-*RR*,*SS* isomer together with small amounts of the β_1-*RR*,*SS* and β_1-*RS*,*SR* cations.

Racemic β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]I_2$ was resolved into the $(+)_{589}$-β_2-*SR* and $(-)_{589}$-β_2-*RS* enantiomers using Ag-$(+)_{589}$-[Co(EDTA)] and Ag-$(-)_{589}$-[Co(EDTA)], respectively, as resolving agents. Attempted resolutions using silver antimony (+)-tartrate in aqueous solution failed.

2. Structure of Racemic β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]Cl_2 \cdot H_2O$. The structure consists of two conformationally isomeric cations in equal abundance, together with chloride ions and water molecules, Figure 1. The space group symmetry, $P2_1/c$, also requires that each ion exist in Δ and Λ pairs giving an overall racemic crystal. For the Δ configuration about the metal the configurations and conformations of the triethylenetetramine ligands are *RS*-(δλδ) and *RS*-(λλδ). Although the accuracy of the molecular dimensions in each cation is limited, the overall features including the chelate ring conformations are clearly established.[26] The atom labeling scheme is illustrated in Figures 1, 10, and 11 and follows previous work.[2] This structure is the first in which mirror-imaged conformations of the out-of-plane β-trien ring ("apical" ring) have been found in independent cations. The general preference for the δ conformation in this ring for the Δ isomer has been noted previously[27] and is also observed for the two cations in crystals of Δ-β_1-(*RS* + *SS*)-$[Co(trien)(glyO)]I_2 \cdot 0.5H_2O$.[2] The present results imply however that the energy difference between the two apical conformers is not large in such ions.

Intramolecular dimensions are presented in Table II. Though not as internally consistent as we have observed in earlier work,[2] these values are clearly adequate in establishing the coexistence of two types of conformers (λλδ, δλδ) in the

Table II. Comparison of Crystal Structure and Minimized Structures for Δ-β_2-[Co(trien)(glyO)]$Cl_2 \cdot H_2O$

(i) Bonded Interatomic Distances, Å

	RS-δλδ		*RS*-λλδ[a]		*RR*-δδλ	*RR*-λδλ
Bond	Crystal	Minimized	Crystal	Minimized	Minimized	Minimized
Co1-N1	2.01 (2)	1.95	2.01 (2)	1.98	1.97	1.97
Co1-N2	1.92 (2)	1.93	1.98 (2)	1.95	1.95	1.95
Co1-N3	2.03 (2)	1.95	2.02 (2)	1.98	1.98	1.95
Co1-N4	2.00 (2)	1.96	1.96 (2)	1.97	1.97	1.97
Co1-N5	2.01 (2)	1.96	1.99 (2)	1.97	1.97	1.97
Co1-O2	1.95 (2)	1.90	1.91 (2)	1.90	1.90	1.90
N1-C1	1.50 (3)	1.50	1.54 (4)	1.50	1.50	1.50
N2-C2	1.57 (4)	1.49	1.53 (3)	1.49	1.49	1.50
N2-C3	1.53 (3)	1.49	1.44 (3)	1.49	1.49	1.50
N3-C4	1.49 (3)	1.50	1.56 (3)	1.50	1.51	1.50
N3-C5	1.49 (4)	1.50	1.47 (3)	1.50	1.50	1.50
N4-C6	1.53 (3)	1.50	1.51 (4)	1.49	1.50	1.50
N5-C7	1.48 (4)	1.50	1.50 (3)	1.50	1.50	1.50
O1-C8	1.27 (3)	1.22	1.24 (3)	1.22	1.22	1.22
O2-C8	1.30 (3)	1.29	1.25 (3)	1.29	1.29	1.29
C1-C2	1.54 (4)	1.50	1.56 (4)	1.51	1.50	1.50
C3-C4	1.51 (3)	1.51	1.56 (3)	1.51	1.51	1.52
C5-C6	1.58 (4)	1.50	1.53 (3)	1.50	1.51	1.50
C7-C8	1.53 (3)	1.50	1.56 (4)	1.50	1.50	1.50

(ii) Angles, Deg

	RS-δλδ		*RS*-δλλ[a]		*RR*-δδλ	*RR*-λδλ
Atoms defining angle	Crystal[b]	Minimized	Crystal[b]	Minimized	Minimized	Minimized
Co1-N1-C1	108	109.4	107	109.8	108.0	106.3
Co1-N2-C2	109	108.1	104	106.9	105.5	105.3
Co1-N2-C3	112	107.5	113	107.2	105.0	106.9
Co1-N3-C4	107	109.2	105	105.9	109.6	108.1
Co1-N3-C5	108	107.4	110	110.9	105.6	107.1
Co1-N4-C6	110	111.2	107	105.9	107.4	105.5
Co1-N5-C7	111	107.8	111	107.8	107.9	107.5
Co1-O2-C8	113	114.1[c]	116	114.6[c]	114.4[c]	114.1[c]
N1-Co1-N2	86.8	86.5	87.4	85.5[c]	87.5	88.8
N1-Co1-N4	91.3	90.5	88.5	90.6	92.1	91.4
N1-Co1-N5	93.2	91.7	92.8	93.1	91.9	93.3
N1-Co1-O2	89.0	91.6	91.6	92.9	89.2	90.3
N1-C1-C2	110	108.8	103	109.7	108.5	108.1
N2-Co1-N3	84.9	87.0	85.1	87.8	86.1[c]	83.3[c]
N2-Co1-N4	97.6	97.4[c]	96.8	97.3[c]	92.3	92.8
N2-Co1-O2	85.8	87.8	86.7	87.2	91.7	91.3
N2-C2-C1	102	105.9[c]	105	106.0[c]	106.6	107.2
N2-C3-C4	101	106.2[c]	102	105.5[c]	107.2	110.3
N3-Co1-N4	86.1	86.4[c]	87.6	85.1[c]	88.9	88.6
N3-Co1-N5	95.5	95.3[c]	95.3	94.3[c]	94.5[c]	94.7[c]
N3-Co1-O2	94.2	92.1	92.8	91.9	90.4	90.2
N3-C4-C3	113	109.8	111	108.5[c]	109.6	111.4
N3-C5-C6	107	109.1	113	110.2	109.0	108.5
N4-Co1-N5	90.4	89.9	91.5	91.0	90.7	90.3
N4-C6-C5	109	109.6	113.5	108.6	108.9	108.0
N5-Co1-O2	86.2	85.0[c]	84.8	84.6	85.3	85.6
N5-C7-C8	109	107.2	107	107.2	107.9	107.9
O1-C8-O2	118	120.8	121	120.8	120.6	120.7
O1-C8-C7	120	121.2	118	121.2	121.1	121.1
O2-C8-C7	121	118.0	119	118.1	118.3	118.2
C2-N2-C3	114	114.7[c]	117	115.9[c]	113.6[c]	113.0[c]
C4-N3-C5	117	112.2	110	110.3	111.5	111.9

(iii) Intramolecular Nonbonded Interactions[d] (>0.3 kcal mol^{-1})

	β_2-*RS*-δλδ			β_2-*RS*-λλδ[a]			β_2-*RR*-δδλ		β_2-*RR*-λδλ	
Atoms	Crystal	Minimized	SE	Crystal	Minimized	SE	Minimized	SE	Minimized	SE
O2···H7	2.31	2.39	0.4	2.40	2.39	0.3				
O2···H9							2.40	0.4		
O2···C3							2.90	0.1	2.83	0.3
C4···H13	2.68	2.63	0.1	2.34	2.46	0.5	2.61	0.2		
C5···H10		2.55	0.3	2.49	2.58	0.2	2.49	0.4	2.52	0.3
H1···H18		2.40	0.1	2.14	2.21	0.4				
H5···H8		2.41	0.1		2.46	0.1				
H6···H9							2.35	0.2	2.24	0.3
H5···H17	2.17	2.10	0.7	2.05	2.07	0.8				
H7···H17							2.33	0.2	2.18	0.5
H8···H10		2.41	0.1		2.47	0.1			2.25	0.3
H8···H15	1.91	2.13	0.6							
H8···H17		2.43	0.1	2.27	2.25	0.3				

Table II (*Continued*)

(iii) (*Continued*)

Atoms	β_2-*RS*-$\delta\lambda\delta$			β_2-*RS*-$\lambda\lambda\delta$[a]			β_2-*RR*-$\delta\delta\lambda$		β_2-*RR*-$\lambda\delta\lambda$	
	Crystal	Minimized	SE	Crystal	Minimized	SE	Minimized	SE	Minimized	SE
H9···H11	2.38	2.36	0.2		2.46	0.1	2.36	0.2	2.23	0.3
H11···H12									2.44	0.3
H10···H13	2.25	2.23	0.3	1.97	2.26	0.3	2.33	0.2		
H10···H15							2.28	0.3		
H12···H20									2.24	0.3
H14···H20	1.99	2.13	0.6				2.22	0.4		
H16···H20				2.36	2.20	0.4				
H1···H3	2.39	2.27	0.3	2.37	2.25	0.3	2.28	0.3	2.31	0.2
H2···H4	1.89	2.26	0.3	2.38	2.23	0.3	2.29	0.2	2.31	0.2
H11···H12	2.21	2.24	0.3	2.35	2.30	0.2	2.23	0.3		
H12···H14	2.34	2.32	0.2	2.19	2.23	0.3	2.32	0.3		
H15···H17	2.24	2.25	0.3	2.28	2.31	0.2	2.29	0.2	2.33	0.2
H16···H18	2.24	2.22	0.4	2.28	2.35	0.2	2.29	0.2	2.33	0.2
H19···H21	2.19	2.27	0.3	2.21	2.28	0.3	2.26	0.3		
H20···H22	2.24	2.30	0.2				2.28	0.3	2.26	0.3

(iv) Torsion Angles, Deg

Atoms defining dihedral angle	β_2-*RS*-$\delta\lambda\delta$			β_2-*RS*-$\lambda\lambda\delta$[a]			β_2-*RR*-$\delta\delta\lambda$		β_2-*RR*-$\lambda\delta\lambda$	
	Crystal	Minimized	SE	Crystal	Minimized	SE	Minimized	SE	Minimized	SE
Co-N1-C1-C2	−35.3	−28.9	0.8	−45.1	−21.2	1.1	30.0	0.8	36.2	0.5
Co-N2-C2-C1	−46.0	−45.4	0.2	−51.4	−49.2	0.1	47.8	0.2	44.3	0.3
Co-N2-C3-C4	45.4	46.1	0.2	46.7	44.1	0.3	−50.3	0.1	−35.7	0.5
Co-N3-C4-C3	30.2	23.8	1.0	34.4	38.1	0.5	−16.0	1.3	23.6	1.0
Co-N3-C5-C6	−45.8	−42.8	0.3	0.1	12.2	1.4	−40.6	0.4	35.3	0.5
Co-N4-C6-C5	−24.9	−18.0	1.2	31.3	47.3	0.2	−33.4	0.6	42.1	0.3
Co-N5-C7-C8	4.4	−29.2	0.8	9.1	28.8	0.8	−25.8	0.9	27.0	0.9
Co-O2-C8-O1	175.9	176.2	0.0	−171.4	−176.1	0.0	174.8	0.1	−174.0	0.1
N1-C1-C2-N2	52.1	48.1	0.2	61.6	45.7	0.3	−51.7	0.1	−54.2	0.1
N2-C3-C4-N3	−48.1	−45.5	0.3	−52.6	−54.8	0.0	43.5	0.4	7.8	2.4
N3-C5-C6-N4	46.6	39.6	0.7	−20.9	−39.1	0.7	50.0	0.2	−52.1	0.1
N5-C7-C8-O1	−176.8	−157.4	0.1	163.3	157.4	0.1	−158.6	0.1	157.2	0.1

[a] *RS*-λλδ atom labels (Table I, Figure 11) are obtained by adding 10 to the atom number of other isomers. [b] Esd's: N-Co-N, ~0.8°; Co-N-C, C-N-C, and N-C-C, ~1.7°. [c] Strain energy greater than 0.2 kcal mol^{-1}. [d] No entry means strain energy <0.04 kcal mol^{-1}.

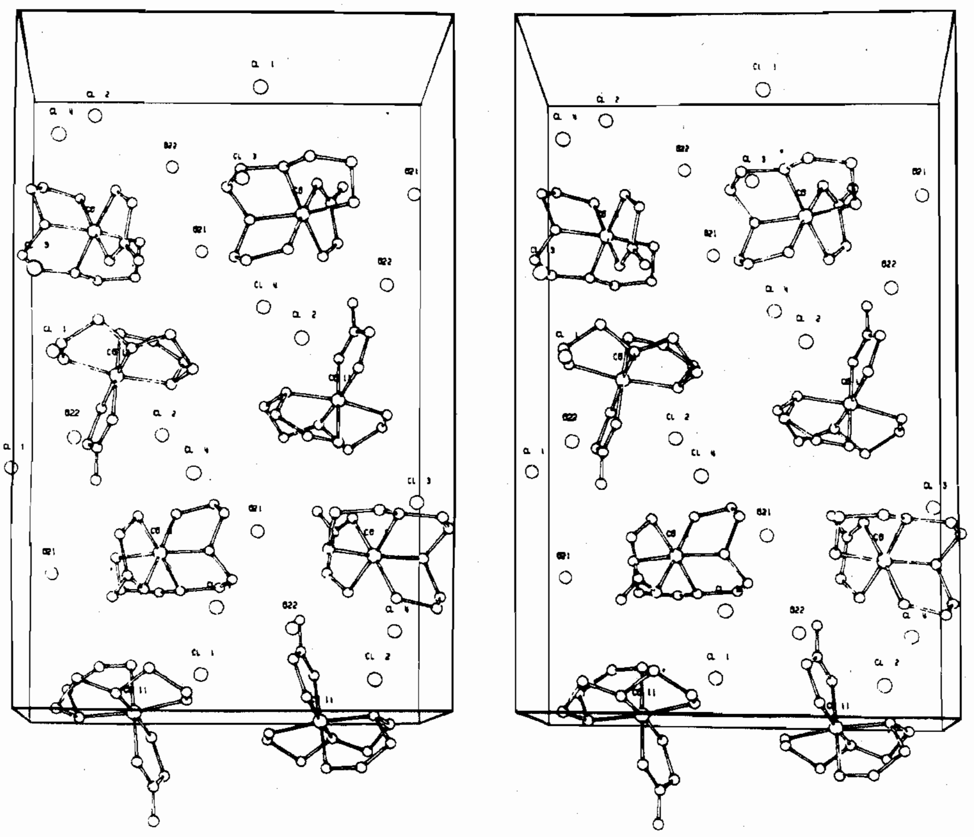

Figure 1. Stereoview of contents of unit cell of ΔΛ-β_2-(*RS,SR*)-[Co(trien)(glyO)]$Cl_2 \cdot H_2O$.

Table III. Hydrogen Bonding in *rac*-β_2-*RS*-[Co(trien)(glyO)]Cl·H_2O

No.	Atoms X···H-Y	*d*(X···Y), Å	Atoms	Angle, deg	Symmetry operations[a]
1	Cl1···H-N15	3.23	Cl1···N15-Co11	99	a
			Cl1···N15-C17	126	
2	Cl1···H-N14	3.24	Cl1···N14-Co11	100	a
			Cl1···N14-C16	102	
			N14···Cl1···N15	52	
3	Cl1···H-N11	3.35	Cl1···N11-Co11	121	b
			Cl1···N11-C11	106	
4	Cl1···H-N2	3.44	Cl1···N2-Co1	128	a′
			Cl1···N2-C2	108	
			Cl1···N2-C3	83	
5	Cl2···H-N12	3.19	Cl2···N12-Co11	130	b
			Cl2···N12-C12	109	
6	Cl2···H-N15	3.30	Cl2···N15-Co11	119	b′
			Cl2···N15-C17	100	
			Cl2···N15···Cl1	104	
7	Cl2···H-N5	3.35	Cl2···N5-Co1	109	
			Cl2···N5-C7	139	
8	Cl2···H-N4	3.37	Cl2···N4-Co1	109	
			Cl2···N4-C6	84	
			N5···Cl2···N4	50	
9	Cl3···H-O22	3.00	N5···O22···Cl3	105	
10	Cl3···H-O21	3.13	N1···O21···Cl3	106	a″
11	Cl3···H-N3	3.37	Cl3···N3-Co1	108	a
			Cl3···N3-C4	81	
			Cl3···N3-C5	132	
12	Cl4···H-O21	3.09	N1···O21···Cl4	137	c
			Cl4···O21···Cl3	105	
13	Cl4···H-N4	3.26	Cl4···N4-Co1	133	
			Cl4···N4-C6	91	
			Cl2···N4···Cl2	115	
14	Cl4···H-N13	3.29	Cl4···N13-Co11	110	b
			Cl4···N13-C14	99	
			Cl4···N13-C15	122	
15	O21···H-N1	2.94	O21···N1-Co1	114	a′
			O21···N1-C1	104	
16	O22···H-N5	2.93	O22···N5-Co1	104	
			O22···N5-C7	108	
			Cl2···N5···O22	68	
17	N1-H···O11	2.78	Co-N1···O11	122	a
			C1-N1···O11	91	
			N1···O11-C18	145	
			O11···N1···O21	114	
18	N14-H···O1	2.82	Co11-N14···O1	123	c′
			C16-N14···O1	98	
			N14···O1-C8	101	

[a] Symmetry operations (where necessary) to bring atom Y into contact with atom X are as follows: (a) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (a′) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (a″) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (b) $x, \frac{1}{2} - y, x - \frac{1}{2}$; (b′) $1 + x, \frac{1}{2} - y, x - \frac{1}{2}$; (c) $x, y - 1, z$; (c′) $1 - x, y, z$.

crystal and for comparisons with the calculated values for the strain energy minimized structures also given in Table II. The mean Co^{III}–N(trien) bond distances for the two isomers (1.99 (2), 1.99 (2) Å) are slightly longer than those for related compounds, 1.963 and 1.951 Å in the Δ-β_1-(*RR*)- and Δ-β_1-(*RS*)-[Co(trien)(glyO)]I_2·0.5H_2O isomers, respectively,[2] 1.955 Å in Λ-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)](ZnCl$_4$),[28] 1.96 Å in Λ-β_2-(*RRS*)-[Co(trien)((*S*)-Pro)]I_2·2H_2O,[29] and 1.93 Å in β-[Co(trien)(Cl)(H_2O)](ClO$_4$)$_2$.[30] The Co^{III}–N(gly) bond lengths are the same within experimental error for the two cations. The Co^{III}–O(gly) bond lengths (1.91 (2), 1.93 (3) Å) are comparable with 1.880 (14) Å in Δ-β_2-(*RS*)-[Co(trien)((*S*)-Pro)]I_2·H_2O[29] and 1.906 (5) and 1.914 (6) Å for the β_1-*RR* and β_1-*RS* cations in β_1-[Co(trien)(glyO)]I_2·0.5H_2O.[2] No significant difference in C–O bond lengths occurs, although the C8–O1 (1.29 Å) and C18–O11 (1.27 Å) bonds are longer than those found in β_1-(*RR* + *RS*)-[Co(trien)(glyO)]I_2·0.5H_2O[2] (1.21, 1.22 Å). Deviations from ideal values are discussed below.

The crystal packing incorporates a considerable network of hydrogen bonds linking the nitrogen and oxygen donor atoms to chloride ions and oxygens of an adjacent cation via water molecules, Figure 1. Table III lists the parameters associated with 18 hydrogen bonds that are suggested by the usual criteria.[31] At least *one* proton on each nitrogen is involved in a hydrogen bond, with *both* protons involved in the case of N15 (Cl1···N15···Cl2, 104°), N14 (O1···N14···Cl1, 124°), N1 (O11···N1···O21, 114°), and N4 (Cl2···N4···Cl2, 115°). The greater accessibility of protons on the terminal nitrogens N14, N15, N4, and N5 apparently allows the same chloride ions to hydrogen bond intramolecularly: N5···Cl2···N4, 50°; N14···Cl1···N15, 52°. The chloride ions also provide a link between the two isomers via water molecules, Table III. Two direct hydrogen bonds between the two isomers exist (entries 17 and 18 in Table III). One of the water molecules (O21) adds an interesting cross-linking pattern bonding both through its protons (to Cl4 and Cl3) and its oxygen (to N1). Similarly O22 is bonded to the δλδ cation and Cl3: N5···O22···Cl3, 105°. All other close intermolecular contacts result from these hydrogen bonds.

3. Visible, Optical Rotatory, Circular Dichroism, and Infrared Spectra. The visible ORD and CD spectra for $(+)_{589}$-β_2-(*SR*)-[Co(trien)(glyO)]I_2 in water at pH ~5 before and following mutarotation at pH ~12 (1 min) are compared in Figures 2–4. The spectra of the mutarorated solutions are very similar to those observed for optically pure $(+)_{589}$-β_2-(*SS*)-[Co(trien)(glyO)]I_2·2H_2O. This agrees with the lack of change previously found in the visible and ORD spectra of

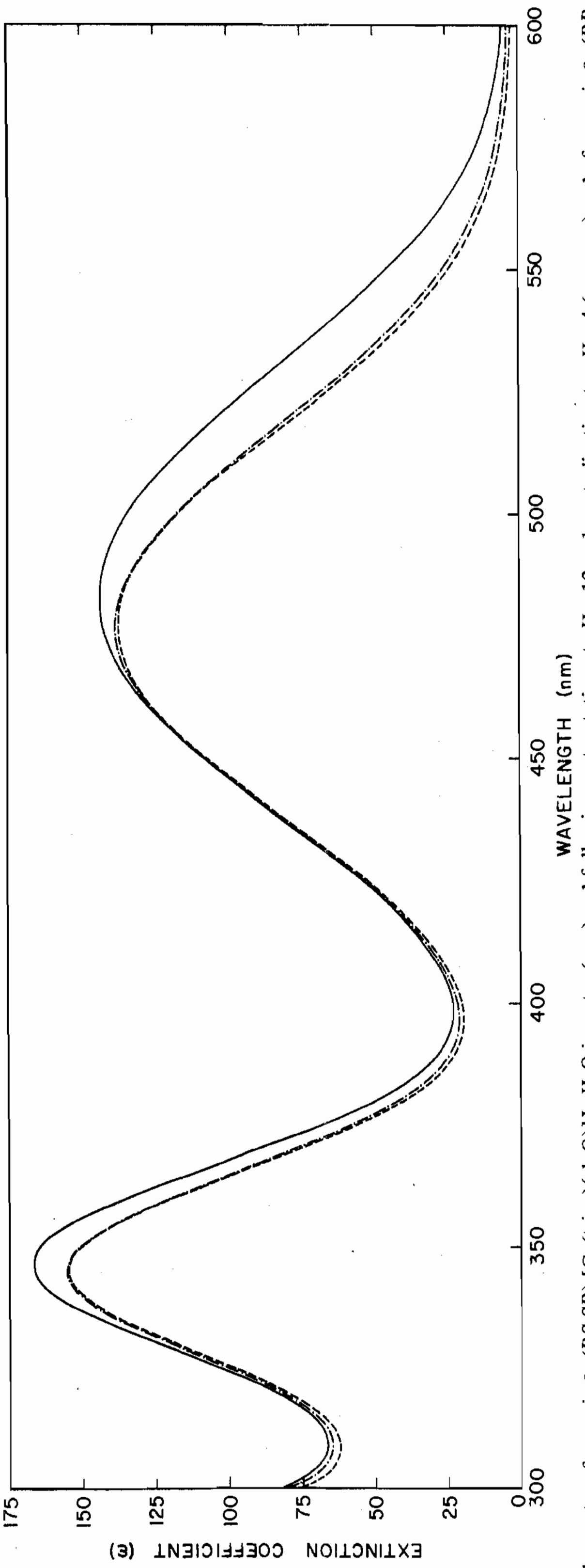

Figure 2. Visible spectra of racemic β_2-(*RS,SR*)-[Co(trien)(glyO)]$I_2 \cdot H_2O$ in water (——) and following mutarotation at pH ~12 and neutralization to pH ~4 (– · – · –) and of racemic β_2-(*RR,SS*)-[Co(trien)(glyO)]$I_2 \cdot 2H_2O$ in water (- - - - -) at 25°.

(+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyO)]$I_2 \cdot 2H_2O$ when treated with 0.01 *M* NaOH.[7] Previously this was argued in terms of stereospecific coordination about the "planar" secondary N atom in the β_2-*SS* ion,[7] but, as will be seen below, the β_2-*SS*:β_2-*SR* ratio is in fact about 0.1 under equilibrium-controlled conditions. These significant differences between the two β_2 diastereoisomers contrast with the similarity previously noted by Lin and Douglas.[9,10]

The CD difference curve, Figure 4, is similar in shape and is about twice the magnitude of that found for (−)$_{436}$-[Co(NH$_3$)$_4$(sar)](NO$_3$)$_2$ (sar = sarcosinate (or *N*-methylglycinate) anion),[32] for which the asymmetric center has the *R* configuration. A similar, but mirror-imaged, difference is obtained by subtracting the CD curves for the (−)$_{589}$-β_1-(*RS*)- and (−)$_{589}$-β_1-(*RR*)-[Co(trien)(glyO)]$^{2+}$ ions, Figure 5.[33] In this case the absolute configurations for both ions are known and the difference CD curve was interpreted as resulting from twice the contribution from the *S* configuration about the "planar" N atom of triethylenetetramine. The close similarity observed here with the β_2 ions supports the argument that such difference curves (CD, ORD) adequately remove contributions from the other common asymmetric centers even though the latter may dominate the total absorption. The residual curves therefore support the *R* and *S* assignments about the "planar" N atoms of triethylenetetramine in the (+)$_{589}$-β_2-(*SR*)- and (+)$_{589}$-β_2-(*SS*)-[Co(trien)(glyO)]$^{2+}$ ions, respectively. Also these properties, together with a substantial body of corroborative evidence on other trien complexes of known absolute configuration,[34] support the Λ configuration about the metal center in both ions.

Other differences between the β_2-*SS* and β_2-*SR* isomers are found in the infrared spectra, Figure 6A and B. This contrasts with the identical spectra noted by Lin and Douglas.[9,10] Both iodide salts show a complex pattern of absorptions in the 990–1100-cm^{-1} region attributable to the β-triethylenetetramine configuration[35] as do those for the corresponding β_1 iodides. By comparison, the α-(*RR,SS*)-[Co(trien)(glyO)]$I_2 \cdot 2H_2O$ complex spectrum is relatively simple in this region.

4. PMR Spectra and H Exchange. PMR spectra for the two β_2 diastereoisomers are given in Figure 7. In 10^{-3} *M* DCl all NH absorptions are observed but NH exchange with the solvent is rapid at pH ~6. Mutarotation of the β_2-*SR,RS* isomer at pH ~12 in H$_2$O, followed by recovery of the complex, results in a spectrum which is the same as that found for the β_2-*SS,RR* ion. The absorptions are assigned as follows (in ppm): β_2-*SR,RS* isomer, "planar" NH (7.05 ppm), "angular" NH (6.80), NH$_2$ of triethylenetetramine (5.6–4.8), NH$_2$ of glycinate (4.0), CH$_2$ of glycinate (3.6), and CH$_2$ of triethylenetetramine (3.6–2.6); β_2-*SS,RR* isomer, "angular" NH (6.85), "planar" NH (6.70), NH$_2$ of triethylenetetramine (5.4–4.7), NH$_2$ of glycinate (4.0), CH$_2$ of glycinate (3.6), and CH$_2$ of triethylenetetramine (3.4–2.4). The glycinate CH$_2$ triplet in the β_2-*SR,RS* isomer is well resolved and reduces to a sharp singlet on NH exchange. The similar absorption in the β_2-*SS,RR* ion is not as well resolved in acidic solution and reduces to a just resolved quartet on NH exchange indicating slight nonequivalence of the two protons.

The corresponding amine absorptions have similar chemical shifts except for that at 7.05 ppm (one proton) in the β_2-*SR,RS* ion which is observed at 6.7 ppm in the β_2-*SS,RR* isomer. This, together with the above mutarotation experiment and with the relatively fast rates of H exchange (see below), implies that this absorption corresponds to the unique "planar" NH proton. An even larger shift was observed for the corresponding proton in the β_1 ions (6.8 ppm (*RS,SR*), 6.1 ppm (*SS,RR*)).[36] In alkaline D$_2$O the triethylenetetramine CH$_2$ absorptions are sharp and differ significantly in the two ions.

Rate data for H exchange of the secondary NH protons and

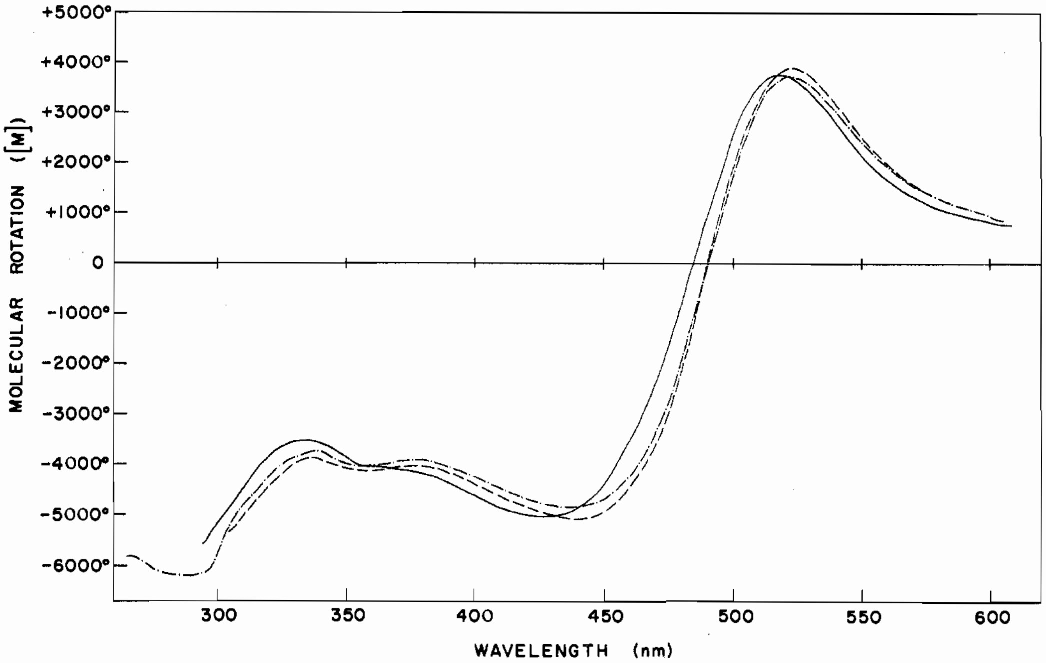

Figure 3. Optical rotatory dispersion spectra of Λ-β_2-(*SR*)-[Co(trien)(glyO)]I_2 in water (——) and following mutarotation at pH ~12 and neutralization to pH ~4 (– · – · – · – ·) and of Λ-β_2-(*SS*)-[Co(trien)(glyO)]$I_2 \cdot 2H_2O$ in water (- - - - - -) at 25°.

Table IV. Rate Data for NH Proton Exchange in β_2-(*RS,SR*)- and β_2-(*RR,SS*)-[Co(trien)(glyO)]$^{2+}$ Ions, at 25° in D_2O^a

	β_2-*RS,SR* isomer									β_2-*RR,SS* isomer				
	NH (7.05 ppm)		NH (6.8 ppm)		NH_2 (5.4 ppm)		NH_2 (5.1 ppm)			NH (6.7 ppm)		NH (6.85 ppm)	
pD	$10^3 k_{obsd}$, sec^{-1}	$10^{-7} k_H$, M^{-1} sec^{-1}	$10^4 k_{obsd}$, sec^{-1}	$10^{-5} k_H$, M^{-1} sec^{-1}	10^3 k_{obsd}, sec^{-1}	$10^{-6} k_H$, M^{-1} sec^{-1}	10^4 k_{obsd}, sec^{-1}	$10^{-5} k_H$, M^{-1} sec^{-1}	pD	10^3 k_{obsd}, sec^{-1}	$10^{-7} k_H$, M^{-1} sec^{-1}	10^4 k_{obsd}, sec^{-1}	$10^{-5} k_H$, M^{-1} sec^{-1}
4.13	0.84	1.6							4.32	4.2	5.4	0.77	9.7
4.52	2.5	2.0	0.38	3.0	0.23	1.8			4.37	5.8	6.5		
4.63	2.6	1.6							5.44			8.9	8.5
5.31	16.5	2.1	2.8	3.6	1.65	2.1	2.0	2.6					
5.63	34.6	2.1	5.9	3.6			3.85	2.3					
5.88			10.5	3.6			6.3	2.2					

[a] pD = pH + 0.4; $k_H = k_{obsd}[D^+]/3.80 \times 10^{-15}$; 0.1 *M* NaOD–DOAc buffers; [Co] $\simeq$0.3 *M*.

some of the NH_2 protons were obtained by PMR spectroscopy in 0.1 *M* DOAc buffers at 25°. Data are given in Table IV. Some data for the unique secondary NH proton at lowest field (6.95 ppm) in β_2-[Co(trien)Cl(glyOEt)]Cl_2 are also reported, Table V. For the two β_2-[Co(trien)(glyO)]$^{2+}$ ions the NH signals at lowest field are not well resolved and plots of log [(area)$_t$ − (area)$_\infty$] against time were used; for the other absorptions plots of log (peak height) against time sufficed. In all cases plots were linear for at least 2 half-lives. The derived rate constants k_H (Table IV) were calculated using $k_{D_2O} = 3.80 \times 10^{-15}$,[37] and it is clear that a rate law $v = k_H[\text{complex}][OD^-]$ is followed. It is also apparent that the unique protons at 7.05 ppm in the β_2-*SR,RS* ion and at 6.7 ppm in the β_2-*SS,RR* ion are ~10^2 times more labile than the others, with that for the β_2-*SS,RR* ion being ~3 times more labile than that in β_2-*SR,RS*. It was seen above that this proton is involved in the mutarotation process about the "planar" N center of triethylenetetramine. Although exchange of the glycinate NH_2 protons was not directly followed, the collapse of the CH_2 triplet in the β_2-*RS,SR* cation occurred at a rate similar to that found for the "slow" secondary NH proton, giving an estimate of ~3×10^5 M^{-1} sec^{-1} for this exchange.

5. Kinetics and Thermodynamics of Mutarotation. The rates of mutarotation of the β_2-*RS,SR* isomer were followed spectrophotometrically at 520 nm in glycine buffers. Optical density changes of ~0.1 were observed and plots of log (A_t − A_∞) vs. time were linear for at least 3 half-lives. The data, Table VI, show that mutarotation follows the rate law $v = k_M[\text{complex}][OH^-]$ with $k_M = 3.9 \times 10^2$ M^{-1} sec^{-1} at 25°. The product of the mutarotation process (2) is an equi-

Table V. Rate Data for Exchange of "Fast" Secondary NH Proton (6.95 ppm) in β_2-(*SS,RR*)-[Co(trien)(glyOEt)Cl]Cl_2 at 25°

[DCl], *M*	$10^5 k_{obsd}$, sec^{-1}	$10^{-8} k_H$,^{a} M^{-1} sec^{-1}
0.0058	14.4	2.2
0.0114	8.0	2.4
0.114	0.96	2.9

[a] $k_H = k_{obsd}[D^+]/3.80 \times 10^{-15}$.

Table VI. Spectrophotometric Rate Data for Mutarotation of β_2-(*RS,SR*)-[Co(trien)(glyO)]$^{2+}$ at 25° in 0.1 *M* Glycine Buffers, μ = 1.0 ($NaClO_4$)^a

pH	$10^3 k_{obsd}$, sec^{-1}	$10^{-2} k_M$, M^{-1} sec^{-1}
7.79	0.42	4.0
8.39	1.61	3.9
9.09	8.16	3.9
9.40	16.5	3.9

[a] $k_M = k_{obsd}/[OH^-]$; pK_w = 13.77; [Co] $\simeq 6 \times 10^{-3}$ *M*.

$$\beta_2\text{-}(SR,RS)\text{-}[\text{Co(trien)(glyO)}]^{2+} + OH^- \rightleftharpoons \beta_2\text{-}(SS,RR)\text{-}[\text{Co(trien)(glyO)}]^{2+} + OH^- \quad (2)$$

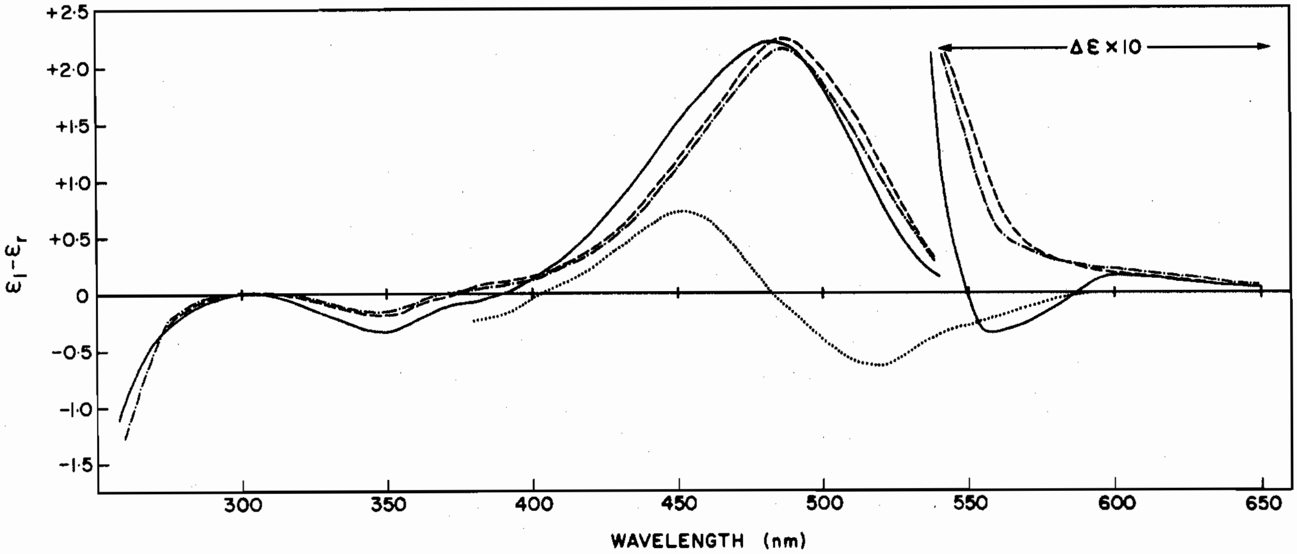

Figure 4. Circular dichroism spectra of Λ-β_2-(*SR*)-[Co(trien)(glyO)]$\mathrm{I_2}$ in water (——) and following mutarotation at pH ~12 and neutralization to pH ~4 (-·-·-·) and of Λ-β_2-(*SS*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot 2H_2O}$ in water (------) at 25°. The difference CD curve is for Λ-β_2-*SR* minus Λ-β_2-*SS* (······).

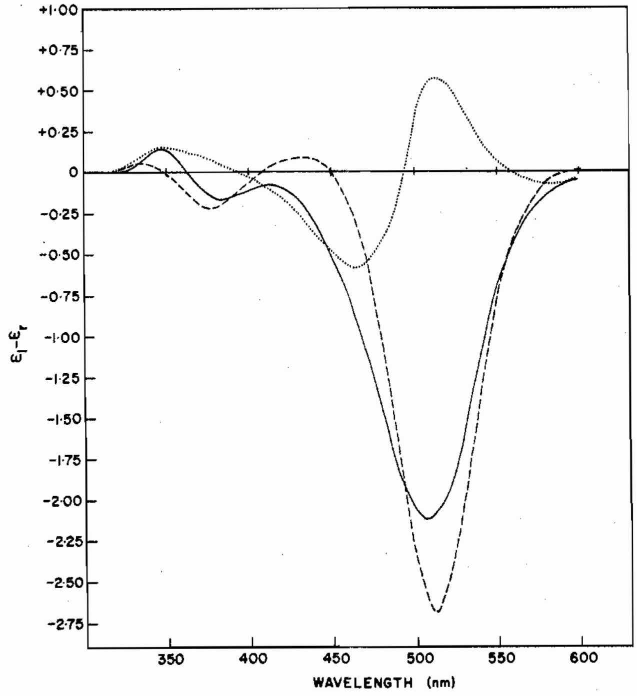

Figure 5. Circular dichroism spectra of Δ-β_1-(*RS*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot H_2O}$ (——) and of Δ-β_1-(*RR*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot H_2O}$ (-----) and the difference curve (Δ-β_1-*RS* minus Δ-β_1-*RR*) (······) in water at 25°.

librium mixture of the β_2-*SS,RR* and β_2-*SR,RS* diastereoisomers with ΔG_{25} = 1.3 ± 0.1 kcal mol^{-1} at 25° in 1 *M* NaClO$_4$, Table VII. These data were obtained by quenching the equilibrated solutions with acid, separating the diastereoisomers on the cation-exchange resin, and spectrophotometric (478, 484 nm) or atomic absorption analysis of the eluted fractions. In all cases >95% recoveries were obtained. One experiment using optically pure (+)$_{589}$-β_2-(*SR*)-[Co(trien)(glyO)]$\mathrm{Cl_2 \cdot 2H_2O}$ ([α]$_{589}$ +246°) gave 88% of optically pure (+)-β_2-(*SS*)-[Co(trien)(glyO)]$^{2+}$ ([M]$_{589}$ +1130°) and 12% of optically pure (+)-β_2-(*SR*)-[Co(trien)(glyO)]$^{2+}$ ([M]$_{589}$ +950°). Combination of the measured equilibrium constant with the rate constant for mutarotation, $k_M = k_1 + k_{-1}$, gives $k_1 = 3.5 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{-1} = 35\ M^{-1}\ \mathrm{sec}^{-1}$ for the processes given by eq 1.

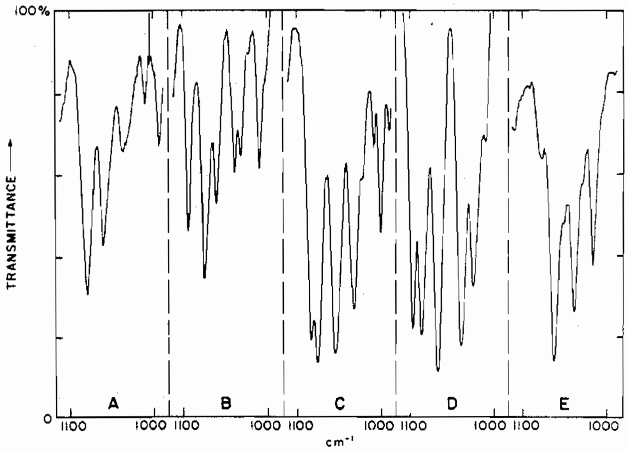

Figure 6. Infrared spectra from 990 to 1100 cm^{-1} of (A) Λ-β_2-(*SS*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot 2H_2O}$, (B) Λ-β_2-(*SR*)-[Co(trien)(glyO)]$\mathrm{I_2}$, (C) Λ-β_1-(*RR*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot H_2O}$, (D) Λ-β_1-(*RS*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot H_2O}$, and (E) $\Lambda\Delta$-α-(*SS,RR*)-[Co(trien)(glyO)]$\mathrm{I_2 \cdot 2H_2O}$ Nujol mulls.

Table VII. Products[f] of Mutarotation of β_2-(*SR,RS*)-[Co(trien)(glyO)]$\mathrm{Cl_2 \cdot H_2O}$ at 25° in 1 *M* NaClO$_4$

[OH$^-$], *M*	% β_2-*SS,RR*	% β_2-*SR,RS*	*K*[e]
0.01[c]	86	14	6.1
0.001[c]	90	10	9.0
4.3×10^{-5} [d]	88	12	7.3
1.05×10^{-6} [d]	90	10	9.0
1.05×10^{-6} [a,d]	88	12	7.3
1.05×10^{-6} [b,d]	91	9	10.1

[a] Using 0.5 g of (+)$_{589}$-β_2-(*SR*)-[Co(trien)(glyO)]$\mathrm{Cl_2 \cdot H_2O}$, [α]$_{589}$ 246°. [b] Using 1 g of β_2-(*SS,RR*)-[Co(trien)(glyO)$\mathrm{I_2 \cdot 2H_2O}$. [c] In NaOH solution for 10 sec; then quenched with HOAc to pH ~4. [d] 0.1 *M* glycine buffers, pK_w = 13.77. [e] K = [β_2-*SS,SR*] / [β_2-*SR,RS*]. [f] Corrected for 100% recovery.

The ΔH_{25} change for mutarotation was measured calorimetrically at 25.0° in 0.1 *M* glycine buffer, pH 9.21, using the isolated β_2-(*SR,RS*)-[Co(trien)(glyO)]$\mathrm{I_2}$ complex.[12] The measured value, 1.2 ± 0.1 kcal mol^{-1}, is substantially for the k_1 process and agrees well with the ΔG_{25} given above. Thus the entropy difference between the ions in aqueous solution is close to zero.

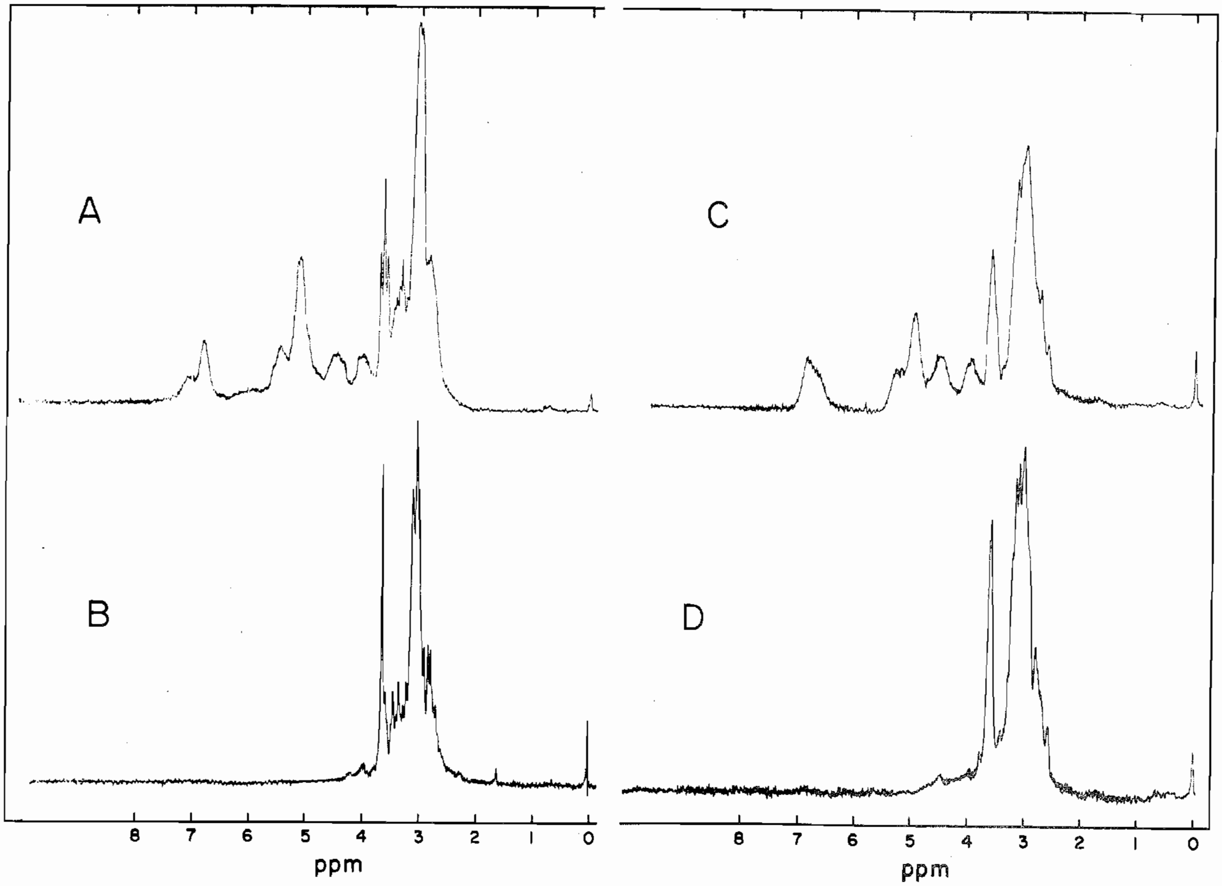

Figure 7. Proton magnetic spectra (100 MHz, reference of NaTPS at $\delta = 0$) of racemic β_2-(*RS,SR*)-[Co(trien)(glyO)]Cl_2 in (A) 10^{-3} *M* DCl and (B) pH ~7 D_2O and of racemic β_2-(*RR,SS*)-[Co(trien)(glyO)]Cl_2 in (C) 10^{-3} *M* DCl and (D) pH ~7 D_2O.

Table VIII. Products of Equilibration of [Co(trien)(glyO)]I_2 Isomers on Activated Charcoal

		% products[a]		
Starting isomer	Temp, °C	α-*RR,SS*	β_2-*RR,SS* + β_2-*RS,SR*	β_1-*RR,SS* + β_1-*RS,SR*
β_1-*RR,SS*	25	2.1	93.7	4.2
β_1-*RR,SS*	25	1.5	94.0	4.5
β_1-*RS,SR*	25	3.1	91.8	5.1
α-*RR,SS*	25	2.1	94.0	3.9
β_2-*RR,SS*	25	3.1	92.7	4.2
β_2-*RR,SS*	4[b]	1.2	95.3	3.5
β_2-*RR,SS*	25[b]	1.7	93.0	5.2
β_2-*RR,SS*	40[b]	2.9	91.3	5.8

[a] Adjusted to 100% recovery. [b] Set of experiments run in parallel.

It was also found possible to equilibrate each of the β_2-*RR,SS*, β_1-*RR,SS*, β_1-*RS,SR*, and α-*RR,SS* isomers on active charcoal. This process proceeds via the labile Co(II) oxidation state at the carbon surface and is known to equilibrate cobalt(III) complexes of this type.[38] The results of overnight equilibration (~12 hr) followed by ion-exchange separation are given in Table VIII. In trial experiments it was shown that 0.5 *M* Na_2HPO_4–0.5 *M* NaH_2PO_4 eluent (pH ~6.8) separated the α, β_2, and β_1 ions (in that order) without separating the internal diastereoisomers of the β_1 and β_2 sets. The product complexes were estimated spectrophotometrically against the authentic compounds in the same solvent. Total cobalt recoveries varied from 73 to 86%. The α-*RR,SS* product (~2%) was also identified by PMR spectroscopy; the secondary NH absorptions in dilute DCl^3 clearly distinguish this isomer from the β_2 ions. The results show that, within the order of reproducibility of the experiment, the product distribution is independent of the starting complex with the following distribution:[39] α, 2.3 (6)%; β_2, 93.2 (8)%; β_1, 4.5 (5)%. Thus ΔG_{25} values for the processes

$$\beta_2\text{-}(RR,SS)\text{-} + \beta_2\text{-}(RS,SR)\text{-}[\mathrm{Co(trien)(glyO)}]^{2+} \overset{K_3}{\rightleftharpoons} \alpha\text{-}(RR,SS)\text{-}[\mathrm{Co(trien)(glyO)}]^{2+} \quad (3)$$

$$\beta_2\text{-}(RR,SS)\text{-} + \beta_2\text{-}(RS,SR)\text{-}[\mathrm{Co(trien)(glyO)}]^{2+} \overset{K_4}{\rightleftharpoons} \beta_1\text{-}(RR,SS)\text{-} + \beta_1\text{-}(RS,SR)\text{-}[\mathrm{Co(trien)(glyO)}]^{2+} \quad (4)$$

are 2.2 ± 0.2 and 1.8 ± 0.1 kcal mol^{-1}, respectively. In one set of experiments using the β_2-*RR,SS* complex the equilibration temperature was varied. The small amounts of α and β_1 isomers do not allow accurate ΔH values but the estimates, $\Delta H_3 \approx 4$ kcal mol^{-1} and $\Delta H_4 \approx 3$ kcal mol^{-1}, for the processes given by eq 3 and 4, respectively, suggest that entropy contributions to the free energy differences are small.

6. Strain Energy Minimization. Figures 8–11 show the final minimized models for the four possible Δ-β_2 structures with nonbonded intraatomic interactions ≥0.3 kcal mol^{-1}, excluding those of the 1,4 type, shown as dotted lines. Table IX lists the final minimized coordinates and Table II contains relevant comparisons between the minimized geometry for each ion and that found in the crystal.

Three aspects of the results will be discussed in this section: (i) an analysis of the strain energy in the two possible conformers of the Δ-β_2-*RR* cation, (ii) a similar analysis of strain energy in the two Δ-β_2-*RS* conformers and a comparison of the minimized and crystal structure parameters, and (iii) a comparison of the calculated strain energies and observed stabilities for the five diastereoisomeric [Co(trien)(glyO)]$^{2+}$ cations.

(i) Δ-β_2-(*RR*)-[Co(trien-δδλ)(glyO)]$^{2+}$ and Δ-β_2-(*RR*)-[Co(trien-λδλ)(glyO)]$^{2+}$ Cations. Components of the overall

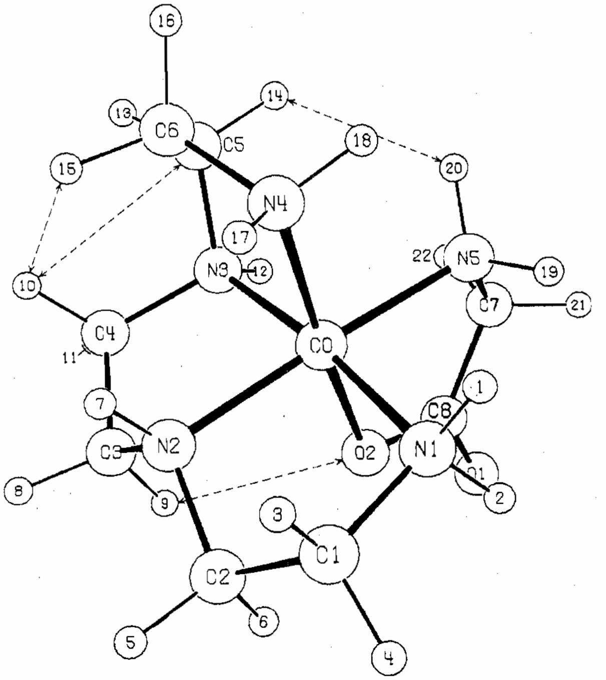

Figure 8. Strain energy minimized Δ-β_2-(*RR*)-[Co(trien-δδλ)-(glyO)]$^{2+}$ cation. Intra-ring nonbonded contacts ⩾0.3 kcal mol^{-1} are shown as dotted lines.

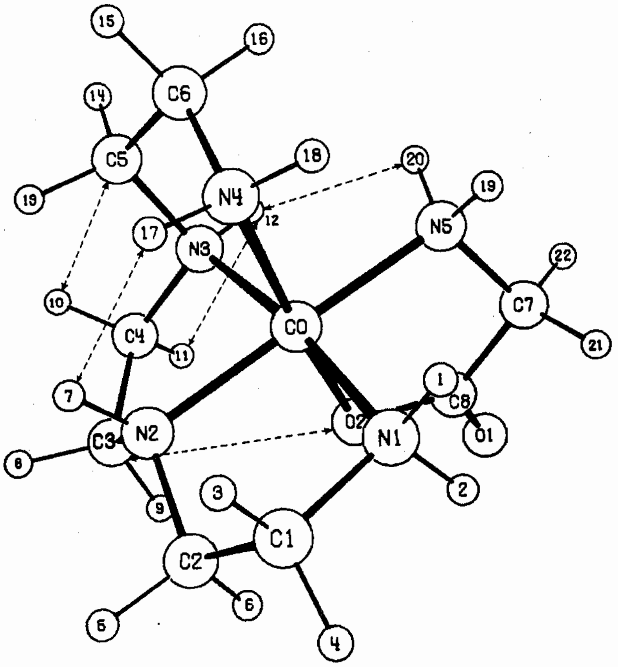

Figure 9. Strain energy minimized Δ-β_2-(*RR*)-[Co(trien-λδλ)-(glyO)]$^{2+}$ cation. Intra-ring nonbonded contacts ⩾0.3 kcal mol^{-1} are shown as dotted lines.

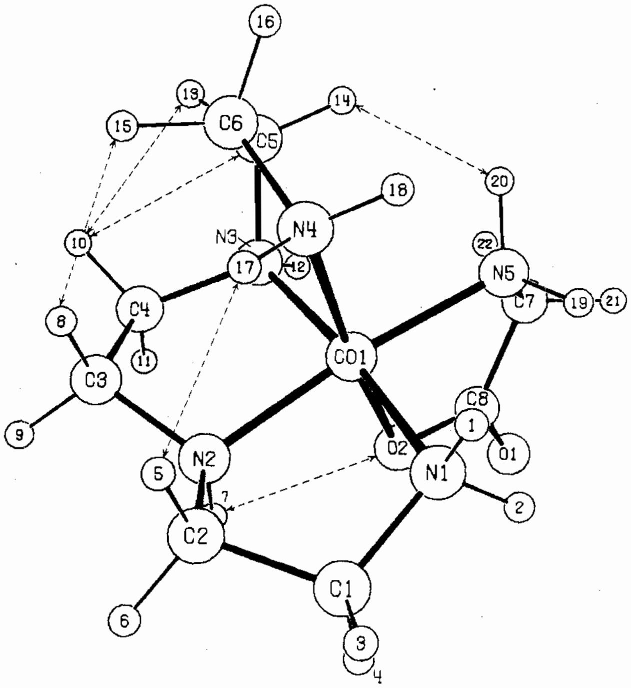

Figure 10. Strain energy minimized Δ-β_2-(*RS*)-[Co(trien-δλδ)-(glyO)]$^{2+}$ cation. Intra-ring nonbonded contacts ⩾0.3 kcal mol^{-1} are shown as dotted lines.

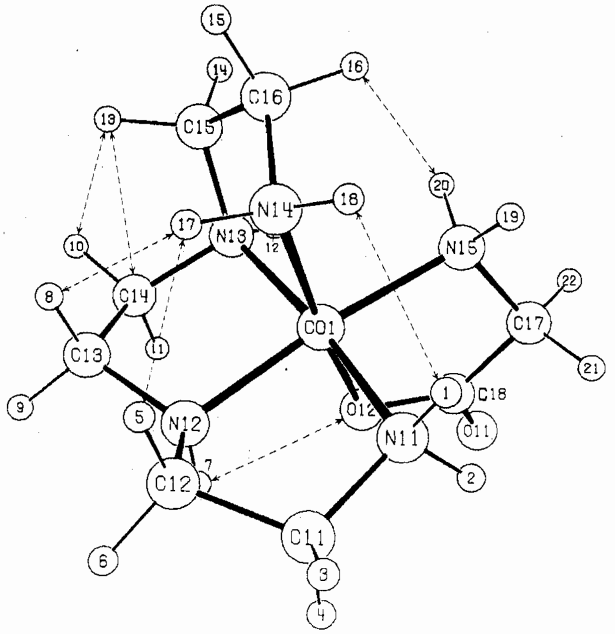

Figure 11. Strain energy minimized Δ-β_2-(*RS*)-[Co(trien-λλδ)-(glyO)]$^{2+}$ cation. Intra-ring nonbonded contacts ⩾0.3 kcal mol^{-1} are shown as dotted lines.

strain energy are given in Table X. Major contributions come from the nonbonded atom–atom interactions, angle deformations, and torsional terms with bond length and out-of-plane distortions small by comparison.

In the Δ-β_2-*RR*-δδλ conformer, Figure 8, major nonbonded interactions occur between the glycinato and triethylenetetramine ligands: O2···H9, 2.40 Å (0.4 kcal mol^{-1}); H14···H20, 2.22 Å (0.4 kcal mol^{-1}), Table II(iii). A similar observation was previously made for the Δ-β_1-(*RR*)-[Co(trien-δδλ)(glyO)]$^{2+}$ cation.[2] By contrast with the β_1 isomer where both glycinato nitrogen protons (H19, H20) interact significantly with trien protons, angular strain about the planar N2 nitrogen is partially relieved (C2–N2–C3, 113.6°, 0.4 kcal mol^{-1}, compared with 114.8°, 0.6 kcal mol^{-1} in the Δ-β_1-*RR* isomer[2]). Similar small differences are found in some torsional contributions; for example the dihedral angles about C3–C4 are 43.5° (0.4 kcal mol^{-1}) and 41.7° (0.5 kcal mol^{-1}) for the β_2 and β_1 cations, respectively. However the most significant torsional contribution remains about N3–C4, −16.1° (1.3 kcal mol^{-1}), Table II(iv) resulting from close contacts between H10 and C5 and H15 of the apical ring.

The Δ-β_2-(*RR*)-[Co(trien-λδλ)(glyO)]$^{2+}$ cation has more significant intra-trien and trien···glyO nonbonded repulsive contacts, Figure 9 and Table II. The central N2–C3–C4–N3 chelate adopts a nearly planar conformation (ϕ = 7.8°) in response to these effects. Thus the significant closing of the N2–Co–N3 angle (83.3°, 0.7 kcal mol^{-1}) occurs in response

Table IX. Final Minimized Coordinates (Å) for Δ-β_2-[Co(trien)(glyO)]$^{2+}$ Isomers

	RS-trien-δλδ			*RS*-trien-λλδ			*RR*-trien-δδλ			*RR*-trien-λδλ		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Co	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N1	1.952	0.000	0.000	1.975	0.000	0.000	1.968	0.000	0.000	1.965	0.000	0.000
N2	0.117	1.927	0.000	0.153	1.941	0.000	0.085	1.944	0.000	0.040	1.945	0.000
N3	−1.931	0.221	−0.137	−1.955	0.231	−0.178	−1.954	0.220	0.022	−1.935	0.269	−0.011
N4	−0.017	−0.252	−1.944	−0.022	−0.249	−1.958	−0.070	−0.076	−1.962	−0.049	−0.093	−1.965
N5	−0.057	−1.941	0.247	−0.106	−1.951	0.283	−0.066	−1.971	0.102	−0.112	−1.966	−0.106
O1	−0.337	−1.150	3.681	−0.064	−1.105	3.715	−0.097	−1.410	3.605	0.000	−1.406	3.604
O2	−0.054	0.077	1.901	−0.097	0.100	1.898	0.027	−0.057	1.901	0.009	−0.044	1.902
C1	2.449	1.411	0.064	2.483	1.406	−0.133	2.429	1.422	−0.061	2.384	1.417	−0.229
C2	1.434	2.311	−0.584	1.409	2.278	−0.730	1.401	2.287	0.615	1.406	2.312	0.482
C3	−1.065	2.447	−0.740	−1.105	2.483	−0.586	−1.087	2.383	0.813	−1.048	2.403	0.922
C4	−2.256	1.687	−0.216	−2.218	1.691	0.050	−2.296	1.663	0.277	−2.244	1.477	0.827
C5	−2.382	−0.526	−1.352	−2.420	−0.175	−1.549	−2.425	−0.225	−1.328	−2.341	0.488	−1.436
C6	−1.418	−0.267	−2.476	−1.325	−0.908	−2.271	−1.463	0.279	−2.373	−1.475	−0.366	−2.316
C7	−0.666	−2.212	1.585	0.362	−2.236	1.673	−0.540	−2.345	1.470	0.361	−2.370	1.466
C8	−0.338	−1.045	2.466	0.050	−1.028	2.502	−0.184	−1.224	2.402	0.101	−1.226	2.401
H1	2.315	−0.460	−0.847	2.344	−0.581	−0.766	2.327	−0.521	−0.813	2.336	−0.605	−0.746
H2	2.291	−0.518	0.824	2.312	−0.394	0.890	2.316	−0.447	0.861	2.329	−0.328	−0.906
H3	3.405	1.496	−0.458	3.366	1.425	−0.774	2.543	1.733	−1.101	2.379	1.639	−1.297
H4	2.589	1.707	1.105	2.758	1.793	0.850	3.391	1.526	0.445	3.389	1.579	0.164
H5	1.450	2.189	−1.665	1.322	2.094	−1.799	1.630	3.341	0.451	1.619	3.357	0.251
H6	1.657	3.353	−0.345	1.656	3.329	−0.576	1.396	2.083	1.687	1.494	2.157	1.558
H7	0.074	2.273	0.971	0.239	2.281	0.971	0.026	2.347	−0.947	−0.115	2.346	−0.936
H8	−0.948	2.312	−1.813	−1.118	2.368	−1.669	−1.223	3.461	0.715	−1.349	3.416	0.647
H9	−1.189	3.512	−0.537	−1.209	3.541	−0.338	−0.949	2.142	1.868	−0.693	2.427	1.953
H10	−3.116	1.866	−0.864	−3.181	1.987	−0.370	−2.631	2.160	−0.634	−3.097	2.018	0.413
H11	−2.502	2.056	0.782	−2.237	1.892	1.123	−3.104	1.723	1.009	−2.518	1.150	1.832
H12	−2.388	−0.179	0.696	−2.436	−0.327	0.543	−2.378	−0.371	0.752	−2.425	−0.553	−1.718
H13	−3.383	−0.205	−1.646	−2.713	0.692	−2.144	−3.425	0.163	−1.528	−2.217	1.535	−1.718
H14	−2.432	−1.594	−1.140	−3.290	−0.828	−1.459	−2.472	−1.313	−1.368	−3.389	0.211	−1.571
H15	−1.659	0.675	−2.968	−1.506	−0.862	−3.347	−1.557	1.360	−2.483	−1.654	−0.120	−3.365
H16	−1.516	−1.061	−3.219	−1.310	−1.957	−1.979	−1.693	−0.186	−3.334	−1.707	−1.420	−2.157
H17	0.521	0.474	−2.434	0.037	0.626	−2.492	0.598	0.590	−2.374	0.263	0.783	−2.407
H18	0.431	−1.156	−2.152	0.745	−0.865	−2.262	0.167	−1.021	−2.297	0.545	−0.859	−2.314
H19	0.905	−2.311	0.232	0.491	−2.450	−0.394	0.880	−2.350	−0.050	0.490	−2.400	−0.609
H20	−0.589	−2.433	−0.482	−1.077	−2.280	0.186	−0.694	−2.379	−0.603	−1.078	−2.294	−0.036
H21	−0.250	−3.128	2.009	−0.158	−3.108	1.685	−0.054	−3.266	1.797	1.430	−2.586	1.446
H22	−1.748	−2.315	1.497	−1.436	−2.424	2.075	−1.620	−2.492	1.472	−0.179	−3.256	1.804

Table X. Final Strain Energy Terms for Δ-β_2-[Co(trien)(gly)]$^{2+}$ Cations (kcal mol^{-1})

	N confign			
	RR	*RR*	*RS*	*RS*
trien ring conformn[a]	δδλ	λδλ	δλδ	λλδ
Bond length deformn	0.39	0.39	0.66	0.57
Angular deformn	3.43	3.76	5.07	5.46
Nonbonded interacn	−3.75	−3.49	−2.59	−2.56
Torsional term	5.11	6.79	5.88	5.83
Out-of-plane deformn	0.0	0.0	0.0	0.0
Total strain energy	5.2	7.5	9.0	9.3
Energy diff (based on *RR*)	0.0	2.3	3.8	4.1

[a] In the order C5–C6 ("apical"), C3–C4, C1–C2 ("planar").

to the following close contacts: O2···C3, 2.83 Å (0.3 kcal mol^{-1}); H6···H9, 2.24 Å (0.3 kcal mol^{-1}); H12···H20, 2.24 Å (0.3 kcal mol^{-1}). However this is counterbalanced to some extent by a decrease in the "planar"–"apical" trien ring interactions. Distortion of the glycinatio ring (ϕ(N5–C7) = 27.0°) also helps to alleviate the trien–glyO close contacts. The combined result is to destabilize the λδλ isomer through larger torsional (1.7 kcal mol^{-1}) angular strain (0.3 kcal mol^{-1}) and nonbonded (0.3 kcal mol^{-1}) contributions, Table X.

(ii) Δ-β_2-(*RS*)-[Co(trien-δλδ)(glyO)]$^{2+}$ and Δ-β_2-(*RS*)-[Co(trien-λλδ)(glyO)]$^{2+}$ Cations. Contributions to the total strain energy are given in Table X and, as for the *RR* isomers, nonbonded interactions and torsional and angle deformation contributions predominate. As observed in the Δ-β_1-(*RS*)-[Co(trien)(glyO)]$^{2+}$ ion,[2] the major structure-defining interactions occur between atoms in the "planar" and "apical" triethylenetetramine rings (Figure 10 and 11). The δλδ conformer, Figure 10, has three major contacts of this type: H5···H17, 2.10 Å (0.7 kcal mol^{-1}); H8···H15, 2.13 Å (0.6 kcal mol^{-1}); H10···H13, 2.23 Å (0.3 kcal mol^{-1}). For the λλδ isomer, Figure 11, there are five such contacts: H5···H17, 2.07 Å (0.8 kcal mol^{-1}); H8···H17, 2.25 Å (0.3 kcal mol^{-1}); C14···H13, 2.46 Å (0.5 kcal mol^{-1}); H10···H13, 2.26 Å (0.3 kcal mol^{-1}); H1···H18, 2.21 Å (0.4 kcal mol^{-1}). The apical ring in both isomers cannot twist to accommodate these intramolecular repulsions without incurring greater torsional strain within the ring itself or increased repulsive contacts with the glycinato nitrogen protons. As it is, both isomers have one close contact of this latter type: for δλδ H14···H20, 2.13 Å (0.6 kcal mol^{-1}); for λλδ H16···H20, 2.20 Å (0.4 kcal mol^{-1}). In both conformers the "planar" segment of the trien ligand is less able to distort than in the *RR* cations because of the opposed configurations about the secondary N centers. This results in an increase in strain energy about N2 and also the close contact between H7 (on N2) and O2 of the glycinate moiety.

Both isomers deviate from ideal bond lengths and angles in an attempt to alleviate these nonbonded contacts. Only minor bond length deformations occur with extensions of the Co–N5 and Co–N4 bonds of ~0.03 Å (0.15 kcal mol^{-1}). Angular distortions are considerably greater: for example, in the δλδ conformer N2–Co1–N4 = 97.4° (0.8 kcal mol^{-1}), Co–O2–C8 = 114.1° (0.3 kcal mol^{-1}), N2–C2–C1 = 105.9° (0.3 kcal mol^{-1}), and C2–N2–C3 = 114.7° (0.6 kcal mol^{-1}). The higher torsional strain about N4–C6 in the δλδ ion cannot be relieved because of the increased repulsions H8···H15 and H18···H20 (Figure 10). In the λλδ conformer alleviation of

Table XI. Final Strain Energy Terms for the Δ-$[Co(trien)(glyO)]^{2+}$ Isomers (kcal mol^{-1})

Isomer	β_2	β_2	β_2	β_2	β_1	β_1	β_1	β_1	α	α	α	α
N confign	*RR*	*RR*	*RS*	*RS*	*RR*	*RR*	*RS*	*RS*	*RR*	*RR*	*RR*	*RR*
trien conformn	$\delta\delta\lambda$	$\lambda\delta\lambda$	$\delta\lambda\delta$	$\lambda\lambda\delta$	$\delta\delta\lambda$	$\lambda\delta\lambda$	$\delta\lambda\delta$	$\lambda\lambda\delta$	$\delta\lambda\delta$	$\lambda\lambda\delta$	$\delta\lambda\lambda$	$\delta\delta\delta$
Strain energy	5.2	7.5	9.0	9.3	6.9	9.2	7.8	9.3	7.1	7.4	8.3	10.7
Strain energy diff	0	2.3	3.8	4.1	1.7	4.0	2.6	4.1	1.9	2.2	3.1	5.5
Obsd $\Delta G°$	0		1.3		1.8		1.8		2.2			
Obsd $\Delta H°$	0		1.2		~3		~3		~4			
Crystal structure information	No	No	Yes	Yes	Yes	No	Yes	No	Yes	No	No	No

the nonbonded strain is also not possible because protons on both sides of the apical ring are already in repulsive contact and further twisting of this ring would increase the torsional component. The overall strain energy difference between the $\lambda\lambda\delta$ and $\delta\lambda\delta$ isomers is small (0.3 kcal mol^{-1}, Table XI) and resides largely in the greater angular distortions associated with the close contacts of H17 and H8 and with H5 in the $\lambda\lambda\delta$ isomer, C12–N2–C13 = 115.9° (0.9 kcal mol^{-1}); this is partially offset by slightly lower torsional and bond length contributions.

The overall agreement between the energy-minimized structures and those found in the crystal is good (Table II) considering the limited accuracy of the crystal structure. Some sections of the crystal cations show deviations which are unexpected from other structural studies (e.g., N2–C2 = 1.57 (3) Å) and probably reflect the quality of the X-ray data. The major angle and torsional features in the cations agree to within the experimental error (3σ) except for those of the glycinato ring. The latter ring is much closer to being planar in the crystal. For the $\delta\lambda\delta$ isomer the differences are seen in the angular strain (Co–N5–C7 = 111° (crystal), 107.8° (minimized)), torsional angles (ϕ(N5–C7) = 4.4° (crystal), −29.2° (minimized)), and nonbonded contacts (H14···H20 = 1.99 Å (crystal), 2.13 Å (minimized)). Starting models with near-planar (ϕ(N5–C5) = 0–7°) glycinato conformation are unstable to refinement reverting to the puckered form shown in Figures 10 and 11. These differences are small in an energy sense (9.0 kcal mol^{-1} vs. 9.3 kcal mol^{-1}), and it is therefore not surprising that the two conformers cohabit in the crystal.

(iii) Relative Energies of the Five Diastereoisomeric $[Co(trien)(glyO)]^{2+}$ Cations. The final minimized strain energy differences for the α, β_1, and β_2 diastereoisomers are compared with the observed relative free energy differences in Table XI. The two sets of results substantially agree for the β_1-*RR* and α isomers but the minimized energy differences are somewhat larger than those observed for the β_1-*RS* and β_2-*RS* ions. All results are relative to the β_2-*RR* cation which is of lowest energy by both calculation and observation. Also given in Table XI are the measured ΔH differences which more correctly should be compared with the minimized strain energy differences. $\Delta(\Delta H)$ for the β_2-*RS*, β_2-*RR* (1.2 ± 0.1 kcal mol^{-1}) and β_1-*RS*, β_1-*RR* (<0.3 kcal mol^{-1})[2] pairs demonstrate that entropy contributions to the mutarotation processes are negligible. An accurate assessment of ΔH for equilibration of the α, β_1, and β_2 ions was not possible due to the small amounts of α and β_1 isomers at equilibrium, but the estimated values also suggest that entropy contributions to these processes are small. It is interesting to note that the only significant disagreements between the observed and calculated relative energies occur in the *RS* configurations of the β_1 and β_2 cations. This may well result from enhanced solvation compared to the other ions, and indeed H bonding of lattice water is observed in the β_1-*RS* cation but not in the β_1-*RR* cation.[2]

The calculations imply that the 1.8 kcal mol^{-1} energy difference between the Δ-β_2-*RR*-$\delta\delta\lambda$ and Δ-β_1-*RR*-$\delta\delta\lambda$ isomers results largely from interactions between protons on N5 of the glycinate moiety and protons of the "planar" N2–C3–C4–N3 and "apical" N4–C6–C5–N3 trien rings, respectively; the fixed conformation of the "planar" ring system is less able to accommodate these effects than the more flexible "apical" ring. In the Δ-β_2-*RS*-$\delta\lambda\delta$ and Δ-β_1-*RS*-$\delta\lambda\delta$ ions inversion about N2 has resulted in the elimination of all major interactions between the glycinato and trien rings in the β_1 ion whereas in the β_2 structure the major H20···H14 (0.6 kcal mol^{-1}) interaction cannot be avoided due to counterbalancing nonbonded interactions between the apical and planar trien rings. The result is a reversal in the stabilities of the β_2 and β_1 structures ($\beta_1 < \beta_2$). The greater strain in Δ-α-(*RR*)-$[Co(trien\text{-}\delta\lambda\delta)(glyO)]^{2+}$ compared to that of the Δ-β_2-*RR*-$\delta\delta\lambda$ ion resides largely in intra-trien contacts resulting in higher torsional strain about N2–C3 and N1–C1. Angular strain associated with N2 in the β structures is however relieved in the α cation resulting in a lower overall angular component to the total strain energy.

With the exception of the β_2-*RR* isomer where no structural information is available, the trien conformation of minimum energy is observed in the crystal. In the case of the β_2-*RS* isomer both the $\delta\lambda\delta$ and $\lambda\lambda\delta$ conformers are found and the strain energies differ by only 0.3 kcal mol^{-1}. The same difference is calculated for the $\delta\lambda\delta$ and $\lambda\lambda\delta$ α isomers but in racemic α-(*RR*,*SS*)-$[Co(trien)(glyO)]I_2$ only the minimum energy $\delta\lambda\delta$ conformer occurs.[3] For the β_1-*RR* and β_1-*RS* isomers the energy differences between the two possible trien conformations are ≥1.5 kcal mol^{-1} and only the conformer of minimum energy occurs in the crystal. The present force field used for the glycinato ring differs from that used previously[2] and can result in energy minima for both the "planar" (ϕ(N5–C7) = 0–7°) or "puckered" (ϕ(N5–C7) = 15–30°) glycinate rings. For example, recalculation for the Δ-β_1-*RR*-$\delta\delta\lambda$ and Δ-β_1-*RS*-$\delta\lambda\delta$ ions results in strain energies for the respective planar and puckered rings found in the crystalline state of 7.7 and 7.9 kcal mol^{-1}. However the Δ-β_1-*RR*-$\delta\delta\lambda$ ion will also minimize to a lower strain energy of 6.9 kcal mol^{-1} in which the glycinato ring has reverted to the puckered form (ϕ(N5–C7) = −15.2°). In both conformers of the β_2-*RS* isomer the planar glycinato ring is unstable with respect to the puckered form even though the amino acid rings are essentially planar in the crystal, Table II(iv). Hydrogen bonding may play a significant role in deciding the conformations of the glycinato ring in all five cations in the crystalline state and the resulting structural changes in this part of the molecule are not reproduced in the minimized structures. However H-bonding and other lattice effects apparently have less influence on the conformations and detailed structures of the trien rings. These areas of good agreement provide strong support for the force constants used and the minimization method.

Acknowledgment. Professor S. F. Mason and Dr. C. J. Hawkins provided some of the earlier CD results and Dr. E. R. Vance, Department of Solid State Physics, Research School of Physical Sciences, The Australian National University, provided Cary 61 facilities for data recorded in this paper.

Registry No. β_2-(*RS*,*SR*)-$[Co(trien)(glyO)]Cl_2 \cdot H_2O$, 54932-35-3; β_2-(*RS*,*SR*)-$[Co(trien)(glyO)](ClO_4)_2$, 51022-67-4; β_2-(*RS*,*SR*)-$[Co(trien)glyO]I_2$, 15137-38-9; $(+)_{520}$-β_2-(*SR*)-[Co(trien)(glyO)]-

Cl-$(+)_{546}$-[Co(EDTA)], 54932-33-1; Λ-β_2-(*SR*)-[Co(trien)(glyO)]Cl_2, 54932-31-9; Λ-β_2-(*SR*)-[Co(trien)(glyO)]I_2, 29132-12-5; Δ-β_2-(*RS*)-[Co(trien)(glyO)]Cl_2, 55028-49-4; β_2-(*RR*,*SS*)-[Co(trien)(glyO)]I_2, 54984-36-0; Λ-β_2-(*SS*)-[Co(trien)(glyO)]I_2, 29024-03-1; Δ-β_1-(*RS*)-[Co(trien)(glyO)]I_2, 52745-22-9; Δ-β_1-(*RR*)-[Co(trien)(glyO)]I_2, 36491-24-4; β_2-(*RS*,*SR*)-[Co(trien)(glyO)]Cl_2, 54932-30-8; β_2-(*RR*,*SS*)-[Co(trien)(glyO)]Cl_2, 54984-37-1; β_1-(*RR*,*SS*)-[Co(trien)(glyO)]I_2, 54984-39-3; β_1-(*RS*,*SR*)-[Co(trien)(glyO)]I_2, 33846-50-3; α-(*RR*,*SS*)-[Co(trien)(glyO)]I_2, 54984-40-6; β_2-(*SS*,*RR*)-[Co(trien)(glyOEt)Cl]Cl_2, 55056-57-0; β_2-(*RR*,*SS*)-[Co(trien)(glyOEt)Cl]$(ClO_4)_2$, 55056-55-8; β_2-(*RS*,*SR*)-[Co(trien)(glyO)]$^{2+}$, 51022-66-3; β_2-(*RR*,*SS*)-[Co(trien)(glyO)]$^{2+}$, 55028-48-3; Δ-β_2-(*RS*)-[Co(trien)(glyO)]$^{2+}$, 55028-50-7; Δ-β_2-(*RR*)-[Co(trien)(glyO)]$^{2+}$, 46468-07-9; Δ-β_1-(*RR*)-[Co(trien)(glyO)]$^{2+}$, 46468-10-4; Δ-β_1-(*RS*)-[Co(trien)(glyO)]$^{2+}$, 54932-34-2; Δ-α-(*RR*)-[Co(trien)(glyO)]$^{2+}$, 54984-38-2.

Supplementary Material Available. A listing of $|F_o|$ and $|F_c|$ 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 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 AIC40739W.

References and Notes

(1) Nomenclature: 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 configuration 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)). Λ and Δ 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)) and for the β topology of triethylenetetramine the order used is terminal "apical" ring, central ring, terminal "planar" ring. For a preliminary report of some of this work see R. J. Dellaca, V. Janson, W. T. Robinson, D. A. Buckingham, L. G. Marzilli, K. R. Turnbull, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 57 (1972).

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