

Structure, Conformational Analysis, and Properties of Diastereoisomeric Forms of β_1 -Glycinatotriethylenetetraminecobalt(III) Ions¹

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Abstract: The synthesis and characterization of $\Delta(-)_{\beta_1}-(RR)$ - and $-(RS)\text{-}\beta_1\text{-[Co(triethylenetetramine)(glycinate)]}_2$ are described. An X-ray structural analysis of a single crystal containing both diastereoisomers defines the geometry of the ions ($P1$, $a = 8.544(2)$, $b = 8.475(2)$, $c = 12.351(3)$ Å, $\alpha = 101.67(2)$, $\beta = 91.89(2)$, $\gamma = 109.98(2)^\circ$, $R = 0.029$ from 4126 diffractometric data). The geometries are also adequately reproduced by strain energy minimization calculations and the latter are correlated with the stability relationships. The kinetics of mutarotation (k_{inv}) of the two species were compared with proton exchange (k_{ex}) at the pertinent asymmetric N center giving $k_{ex}/k_{inv} \sim 10^6$. The absolute configurations of the two isomers are also assigned using the anomalous dispersion method coupled with the circular dichroism of the isolated isomers.

As part of a general program designed at understanding the detailed stereochemistries and relative stabilities of polyamine metal complexes²⁻⁴ we have now examined the $[\text{Co}(\text{trien})(\text{gly})]^{2+}$ ion (trien = triethylenetetramine, gly = glycinate anion). This ion provides a wealth of stereochemical detail, and all ten possible configurational isomers have been isolated.⁵ Also, some of the isomers can be rapidly equilibrated under alkaline conditions. This allows comparisons to be made between the relative thermodynamic stabilities in solution and those for calculated structures of minimum energy. Such comparisons are important for the successful prediction of the detailed molecular structures of coordination complexes by computational methods.²⁻⁴

In this paper we describe the results of an X-ray determination of the structures of the $\Delta(-)_{\beta_1}-(RR)$ - and $\Delta(-)_{\beta_1}-(RS)\text{-[Co(trien)(gly)]}^{2+}$ cations, and give an account of their physical properties and the dynamics and thermodynamics of their interconversion. The structural and thermodynamic results are then compared with those obtained from calculations leading to the structures of minimum strain energy. In following papers similar detailed accounts will be given for the β_2 - and $\alpha\text{-[Co(trien)(gly)]}^{2+}$ ions.

Experimental Section

Analytical reagents were used for kinetic measurements without further purification. Glycine ethyl ester hydrochloride was made

(1) Nomenclature: β_1 refers to the unsymmetrical topology of the trien ligand with the glycinate oxygen atom trans to a secondary nitrogen: A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967); D. A. Buckingham and L. G. Marzilli, *ibid.*, **6**, 1042 (1967). R and S refer to the configuration of the sec-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, *ibid.*, **6**, 1032 (1967). Δ and Λ refer to the configuration defined by the terminal chelate rings of trien related to Δ - and $\Lambda\text{-[Co(en)}_2\text{X}_2]^+$ isomers: *ibid.*, **9**, 1 (1970).

(2) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970).

(3) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

(4) D. A. Buckingham and A. M. Sargeson, *Top. Stereochem.*, **6**, 219 (1971).

(5) R. J. Dellaca, V. Jansson, W. T. Robinson, D. A. Buckingham, L. G. Marzilli, K. R. Turnbull, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 57 (1972).

by treating glycine in ethanol with SOCl_2 . The free base was obtained by treating a finely divided ether suspension of the hydrochloride with NH_3 (10 min), drying with anhydrous Na_2CO_3 , filtering, and removing the ether by vacuum evaporation.

Spectrophotometric rate data and visible spectra were collected on Cary 14 or 16K spectrophotometers. Polarimetric rate data and optical rotatory dispersion curves were obtained on a Perkin-Elmer P22 spectropolarimeter ($\pm 0.002^\circ$) using a 10-cm cell. H-Exchange data and pmr spectra were collected at 34° on a Varian HA-100 spectrometer using TMS external lock. 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. Circular dichroism measurements were obtained using a Jouan Dichrographe.⁶ Molecular rotations have the units $\text{deg } M^{-1} \text{ m}^{-1}$.

Buffer solutions (0.05, 0.10, and 0.20 M) were made up to unit ionic strength with NaClO_4 . For measurements in D_2O , pD was calculated using the empirical expression $\text{pD} = \text{pH} + 0.4$.⁷ pH was measured using Radiometer 26, or TTTlc plus A630T scale expander instruments with a salt bridge containing NH_4NO_3 (1.6 M) and NaNO_3 (0.2 M).

Kinetic Measurements. Samples of complex (*ca.* 10 mg) were dissolved in 1 M NaClO_4 solutions at 25° and immediately mixed with an equal volume of buffer solution. Reactions were followed in thermostated cells at $25.0 \pm 0.05^\circ$. For H-exchange about 200 mg of complex was dissolved quickly in 0.5 ml of D_2O buffer, and the solution was filtered into an nmr tube. Spectra were run at various times and peak areas measured with a planimeter.

Equilibrium Measurements. Weighed amounts of complex (*ca.* 100-200 mg) were equilibrated in buffer solutions, or in 0.01 M NaOH (1 M NaClO_4), 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 1 M NaClO_4 , pH 4, and eluted with 1-2 M HCl . Visible spectra were recorded and cobalt was estimated by atomic absorption.

Preparations. Racemic $\beta_1\text{-[Co(trien)(gly)]}_2 \cdot 2\text{H}_2\text{O}$ was prepared and resolved as previously described.⁸ The only method found to give pure β_1 products was the reaction of a freshly prepared solution of $\beta\text{-[Co(trien)OH(H}_2\text{O)](ClO}_4)_2$ with glycine ethyl ester at room temperature. *Anal.* Calcd for $\text{CoC}_8\text{H}_{22}\text{N}_5\text{O}_2 \cdot 2\text{H}_2\text{O}$: C, 16.88; H, 4.61; N, 12.31. Found: C, 16.6; H, 4.5; N, 12.3. This material consists of approximately equal amounts of the $(RR + SS)$ and $(RS + SR)$ diastereoisomers. Treatment of α - or $\beta\text{-[Co(trien)Cl}_2\text{]Cl}$ or $\beta\text{-[Co(trien)Cl(H}_2\text{O)](ClO}_4)_2$ with glycine or glycine ethyl ester at 25° , or at higher temperatures,

(6) By courtesy of S. F. Mason and C. J. Hawkins.

(7) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

(8) D. A. Buckingham and L. G. Marzilli, *Inorg. Chem.*, **6**, 1042 (1967).

gave mixtures of α , β_1 and β_2 products.⁹ Although the β_1 iodide is less soluble than the β_2 iodide we have been unable to obtain pure β_1 product after ten recrystallizations of a mixture containing *ca.* 30% β_2 iodide.

The β_1 diastereoisomers were separated by ion exchange on a column (5 cm \times 100 cm) using 1 M NaClO₄, or NH₄Cl, pH 4, as eluent. No appreciable separation occurred below pH 2 and above pH 8. In a typical experiment, the iodide salt (5 g) was dissolved in water (1 l.) and sorbed on the resin. The two bands, (*RS* + *SR*) and (*RR* + *SS*) in order of elution, separated over 24–48 hr using 1 M NaClO₄ (pH 4). They were eluted with 1–2 M HCl and the eluents quickly reduced to dryness on a rotatory evaporator. The (*RR* + *SS*) iodide was crystallized readily from water using NaI, and the (*RS* + *SR*) isomer from aqueous methanol (50:50) with NaI. They were recrystallized and air dried at room temperature. *Anal.* Found for β_1 -(*RR* + *SS*)-[Co(trien)gly]I₂·2H₂O: C, 16.6; H, 4.5; N, 12.3. Found for β_1 -(*RS* + *SR*)-[Co(trien)gly]I₂·2H₂O: C, 16.7; H, 4.6; N, 12.3. *Calcd.* C, 16.88; H, 4.61; N, 12.31. The red (*RS* + *SR*) chloride was also induced to crystallize from a concentrated aqueous solution by adding methanol. *Anal.* *Calcd.* for β_1 -(*RS* + *SR*)-[Co(trien)gly]Cl₂·5H₂O: C, 26.75; H, 6.45; N, 19.50. *Found:* C, 27.0; H, 6.3; N, 19.5. The orange (*RR* + *SS*) chloride was obtained by a similar procedure. *Anal.* *Calcd.* for anhydrous salt: C, 27.43; H, 6.33; N, 20.00. *Found:* C, 27.2; H, 6.0; N, 19.6. Both salts were very soluble in water.

The β_1 -(*RR* + *SS*)-[Co(trien)(gly)]I₂·2H₂O salt was resolved as follows. The complex (2.75 g) in water (30 ml) was treated with AgSbO-(+)-tartrate (3.9 g) and the mixture agitated for 5 min at *ca.* 25°. AgI was removed and the filtrate reduced to dryness on a rotatory evaporator. The residue was taken up in water (10 ml) and methanol added slowly when, on scratching, orange crystals of (+)- β_1 -(*SS*)-[Co(trien)(gly)](+)-SbOtart₂ separated. Further fractions of lower and then opposite rotatory power were obtained after cooling the solution and by adding more methanol. Fractions of the same sign were combined and fractionally crystallized to constant rotation. A 0.1% solution of the least soluble diastereoisomer (1.02 g) gave $\alpha_{589} = 0.368^\circ$, and for the most soluble fraction (0.21 g) $\alpha_{589} = -0.142^\circ$. Addition of NaI and cooling in an ice bath gave (+)- β_1 -(*SS*)-[Co(trien)(gly)]I₂·2H₂O, $[\alpha]_{589}^{25} 323^\circ$. *Anal.* *Found:* C, 16.6; H, 4.3; N, 12.4. The (-)- β_1 -(*RR*) iodide gave $[\alpha]_{589}^{25} -279^\circ$ indicating that it was optically impure. The (+)- β_1 -(*SS*)-iodide was chromatographed on cation exchange resin and eluted as a single band.

Crystallography of Δ -(*RR* + *RS*)-[Co(trien)(gly)]I₂·0.5H₂O. Crystals were prepared as previously described.⁸ *Anal.* *Calcd.* for [Co(trien)(gly)]I₂·0.5H₂O: C, 17.72; H, 4.28; N, 12.92. *Found:* C, 17.68; H, 4.28; N, 12.76. Precession photography, using Mo K α radiation, on several samples did not reveal any symmetry, and thus the crystals appeared to belong to the triclinic system. Unit cell dimensions were obtained at 25° by the least-squares procedure described below. A density of 2.18 (± 0.03) g cm⁻³ was obtained by flotation in methyl iodide-phenyl bromide solution. This implied that there were two molecules of [Co(trien)(gly)]I₂ per unit cell. Since the sample was optically active, the space group had to be noncentrosymmetric (*P*1-*C*₁) with two independent molecules per unit cell. *Crystal data:*¹⁰ CoC₆N₃O₂H₂I₂·0.5H₂O, molecular weight 542.2; triclinic with *a* = 8.544 (2), *b* = 8.475 (2), *c* = 12.351 (3) Å, α = 101.67 (2), β = 91.89 (2), γ = 109.98 (2)°; *V* = 818.0 Å³; *d*_{obsd} = 2.18 (± 0.03) g cm⁻³; *Z* = 2; *d*_{calcd} = 2.20 g cm⁻³; μ (Mo K α) = 50.4 cm⁻¹.

Diffraction data were collected from a well-formed crystal of noncentric habit and of average diameter 0.2 mm; the nine boundary faces were (001), (00 $\bar{1}$), ($\bar{1}$ 10), ($\bar{1}$ 00), (10 $\bar{1}$), (1 $\bar{1}$ 0), ($\bar{1}$ 01), (0 $\bar{1}$ 1) and (1 $\bar{1}$ 1). The crystal was mounted in a random orientation on a Hilger and Watts computer-controlled four-circle diffractometer. Twelve reflections from this crystal were accurately centered in a 1.5 mm diameter circular receiving aperture. The setting angles of these reflections were data used for a least-squares refinement¹¹ of cell parameters and crystal orientation, in which the wavelength

of Mo K α_1 radiation was taken as 0.70930 Å. The mosaicity of the crystal was examined by means of open-counter ω scans at a take-off angle of 3°. The width at half-height for a typical strong, low-angle reflection was 0.13°.

The intensity data were collected with Zr-filtered Mo K α radiation at a take-off angle of 3°. The circular receiving aperture, positioned 23 cm from the crystal, was 5 mm in diameter. Data were collected by the θ - 2θ scan technique. A symmetric scan range of 1.28° in 2θ , centered on the calculated peak position (λ (Mo K α) = 0.7107 Å), was composed of 64 steps of 1 sec duration. Stationary-crystal, stationary-counter background counts of 16 sec were measured at each end of the scan range. Attenuation was not required as the intensity of the diffracted beam did not exceed 7000 counts/sec for any reflection.

The intensities of 4819 reflections, consisting of the Friedel non-equivalent pairs *hkl* and $\bar{h}\bar{k}\bar{l}$, were recorded within a 2θ limit of 46°. Three reflections monitored at regular intervals showed only the deviations from their mean intensities predicted by counting statistics. There were a reasonable number of reflections above background at values of $2\theta > 46^\circ$.

Data processing¹² included the application of Lorentz polarization corrections and the calculations of $\sigma(I) = [C + 0.25(t_o/t_b)^2 \cdot (B_1 + B_2) + (pI)^2]^{1/2}$. Initially the value of *p* was selected as 0.07; prior to the final refinement the data were reprocessed with a value of 0.0375. After averaging the 239 reflections which had been measured more than once, the data set consisted of 4563 reflections of which 4126 had $F^2 > 3\sigma(F^2)$. An absorption correction was then applied¹³ using Gaussian integration (6³ grid points) with transmission factors ranging from 0.53 to 0.64.

Results

Solution and Refinement of Crystal Structure. The structure of (-)- β_1 -(*RR* + *RS*)-[Co(trien)(gly)]I₂·0.5H₂O was solved and refined in space group *P*1. Positions for four iodine and cobalt atoms were obtained from a sharpened, three-dimensional Patterson synthesis. An iodine atom was assigned to (000) to fix the origin of the unit cell. Full-matrix least-squares refinement was begun using those data for which $F^2 > 3\sigma(F^2)$. 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 I⁻ were taken from Cromer and Waber,¹⁴ those for H from Stewart, *et al.*,¹⁵ and those for all other atoms from the usual tabulation.¹⁶ The effects of anomalous dispersion were included in F_c ; values of $\Delta f'$ and $\Delta f''$ for I and Co were taken from Cromer's tabulation.¹⁸ The initial least-squares refinement, in which all atoms were assigned variable isotropic vibrational parameters, gave agreement factors $R_1 = 0.162$ and $R_2 = 0.211$, where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and R_2 (the weighted *R* factor) = $(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

Two subsequent difference Fourier syntheses revealed the positions of all O, N, and C atoms of the cations, as well as the O of a water molecule. The second maps also showed regions of high electron density (up to 4.5 e/Å³) around the four iodine atoms. Accordingly, in the next least-squares refinement, the

(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(13) Programs for the IBM 360/44 used in the crystal structure analysis include local modifications of Busing and Levy's ORFFE function and error program, Zalkin's FORNAP Fourier program, Johnson's ORTEP thermal ellipsoid plotting program, and Coppens' DATAPH absorption program.

(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(16) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England.

(17) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(9) C. Y. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Lett.*, **4**, 15 (1968); *Inorg. Chim. Acta*, **4**, 3 (1970).

(10) Here, and throughout the crystallography sections, the uncertainties given in parentheses are estimated standard deviations in the least significant digit quoted.

(11) W. R. Busing, Paper I2, International Summer School on Crystallographic Computing, Ottawa, Canada, 1969; W. R. Busing and H. A. Levy, ORNL-4054, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Table I. Positional and Thermal Parameters for $\Delta\text{-}\beta_1\text{-}[\text{Co}(\text{trien})(\text{gly})]_2 \cdot 0.5\text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	0	0	0	0.0271 (2)	0.0192 (2)	0.00549 (5)	0.0134 (1)	0.00153 (7)	0.00381 (7)
I(2)	0.3526 (1)	-0.3079 (1)	-0.24226 (7)	0.0133 (1)	0.0108 (1)	0.00576 (5)	0.00333 (9)	0.00133 (6)	0.00253 (6)
I(3)	-0.4664 (1)	-0.5273 (1)	0.17032 (7)	0.0156 (1)	0.0223 (2)	0.00527 (5)	0.0112 (1)	0.00199 (6)	0.00196 (7)
I(4)	-0.1890 (1)	-0.2234 (1)	-0.44623 (7)	0.0127 (1)	0.0097 (1)	0.00710 (6)	0.00369 (9)	0.00346 (6)	0.00212 (6)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Co(1)	0.1741 (2)	-0.2235 (2)	0.2827 (1)	1.90 (2)	Co(11)	-0.4392 (2)	0.2367 (2)	-0.3433 (1)	1.84 (2)
O(1)	0.1232 (8)	0.1886 (8)	0.4655 (5)	3.2 (1)	O(11)	-0.3853 (7)	0.1031 (8)	-0.6582 (5)	3.0 (1)
O(2)	0.2027 (7)	-0.0334 (7)	0.4040 (4)	2.2 (1)	O(12)	-0.4005 (7)	0.1097 (7)	-0.4800 (5)	2.2 (1)
N(1)	0.3061 (9)	-0.0760 (9)	0.1879 (6)	2.5 (1)	N(11)	-0.6617 (9)	0.0638 (9)	-0.3479 (6)	2.4 (1)
N(2)	0.1521 (8)	-0.4147 (9)	0.1603 (6)	2.3 (1)	N(12)	-0.4899 (9)	0.3622 (9)	-0.2109 (6)	2.6 (1)
N(3)	0.0393 (9)	-0.3985 (8)	0.3582 (6)	2.3 (1)	N(13)	-0.2151 (9)	0.4160 (9)	-0.3143 (6)	2.5 (1)
N(4)	0.3706 (9)	-0.2489 (9)	0.3554 (6)	2.3 (1)	N(14)	-0.3372 (9)	0.1047 (9)	-0.2682 (6)	2.3 (1)
N(5)	-0.0314 (9)	-0.1832 (9)	0.2354 (6)	2.5 (1)	N(15)	-0.5227 (9)	0.3555 (9)	-0.4391 (6)	2.5 (1)
C(1)	0.335 (1)	-0.189 (1)	0.0888 (8)	3.2 (2)	C(11)	-0.735 (1)	0.133 (1)	-0.2590 (8)	3.6 (2)
C(2)	0.180 (1)	-0.352 (1)	0.0564 (9)	3.3 (2)	C(12)	-0.631 (1)	0.246 (1)	-0.1642 (8)	3.1 (2)
C(3)	-0.013 (1)	-0.549 (1)	0.1591 (7)	3.0 (2)	C(13)	-0.336 (1)	0.467 (1)	-0.1359 (8)	3.1 (2)
C(4)	-0.029 (1)	-0.572 (1)	0.2772 (8)	3.4 (2)	C(14)	-0.206 (1)	0.543 (1)	-0.2101 (7)	2.8 (2)
C(5)	0.149 (1)	-0.395 (1)	0.4569 (7)	2.7 (2)	C(15)	-0.094 (1)	0.325 (1)	-0.3116 (8)	3.1 (2)
C(6)	0.317 (1)	-0.383 (1)	0.4199 (7)	2.7 (2)	C(16)	-0.153 (1)	0.199 (1)	-0.2375 (8)	3.0 (2)
C(7)	-0.036 (1)	-0.023 (1)	0.3051 (7)	2.9 (2)	C(17)	-0.470 (1)	0.321 (1)	-0.5515 (7)	2.5 (2)
C(8)	0.105 (1)	0.055 (1)	0.4004 (7)	2.2 (2)	C(18)	-0.413 (1)	0.167 (1)	-0.5664 (6)	1.9 (1)
OW	-0.359 (1)	0.124 (1)	-0.0156 (8)	6.3 (2)					

^a The expression used for the atomic temperature factor was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Positional Parameters for Hydrogen Atoms^a of $\Delta\text{-}\beta_1\text{-}[\text{Co}(\text{trien})(\text{gly})]_2 \cdot 0.5\text{H}_2\text{O}$

Atom	$\Delta\text{-}\beta_1\text{-RR}$ Cation ^b			$\Delta\text{-}\beta_1\text{-RS}$ Cation ^b		
	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
H(1)	0.4162	0.0022	0.2307	-0.6503	-0.0442	-0.3345
H(2)	0.2432	-0.0060	0.1655	-0.7253	0.0394	-0.4224
H(3)	0.4347	-0.2181	0.1060	-0.8365	0.0341	-0.2332
H(4)	0.3530	-0.1275	0.0265	-0.8155	0.1991	-0.2881
H(5)	0.2016	-0.4400	-0.0035	-0.5891	0.1756	-0.1227
H(6)	0.0813	-0.3274	0.0291	-0.6839	0.3151	-0.1121
H(7)	0.2404	-0.4625	0.1747	-0.5331	0.4442	-0.2396
H(8)	-0.0201	-0.6603	0.1084	-0.2982	0.3937	-0.0951
H(9)	-0.1050	-0.5126	0.1333	-0.3547	0.5617	-0.0810
H(10)	0.0357	-0.6444	0.2935	-0.0920	0.5806	-0.1688
H(11)	-0.1497	-0.6293	0.2866	-0.2252	0.6442	-0.2292
H(12)	-0.0573	-0.3669	0.3854	-0.1919	0.4784	-0.3476
H(13)	0.0993	-0.5027	0.4846	0.0195	0.4107	-0.2807
H(14)	0.1609	-0.2925	0.5179	-0.0901	0.2616	-0.3881
H(15)	0.3089	-0.4966	0.3718	-0.1300	0.2629	-0.1577
H(16)	0.4005	-0.3527	0.4860	-0.0925	0.1157	-0.2494
H(17)	0.4393	-0.2822	0.2971	-0.3922	0.0865	-0.1990
H(18)	0.4394	-0.1369	0.4065	-0.3566	-0.0093	-0.3192
H(19)	-0.1327	-0.2820	0.2432	-0.4771	0.4825	-0.4061
H(20)	-0.0311	-0.1736	0.1562	-0.6482	0.3131	-0.4447
H(21)	-0.1461	-0.0492	0.3376	-0.3745	0.4248	-0.5602
H(22)	-0.0270	0.0617	0.2581	-0.5656	0.2961	-0.6085

^a Calculated (see text). ^b Atom labels are defined in Figures 3 and 4.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Minimum	Intermediate	Maximum
I(1)	0.179 (1)	0.217 (1)	0.301 (1)
I(2)	0.175 (1)	0.206 (1)	0.214 (1)
I(3)	0.177 (1)	0.206 (1)	0.270 (1)
I(4)	0.170 (1)	0.181 (1)	0.246 (1)

iodine atoms were assigned anisotropic vibrational parameters, while the remaining 33 atoms were included with isotropic vibrational parameters. This refinement, using 4126 data which had $F^2 > 3\sigma(F^2)$, converged to give agreement factors $R_1 = 0.033$ and $R_2 = 0.045$. Preliminary diagrams drawn at this stage showed that both cations had the same *absolute* configuration about the cobalt atom, but were catoptric to

each other with respect to one of the secondary N centers. The absolute configuration had earlier been assigned at Δ . Refinement with both cations in the Δ configuration produced the significantly higher agreement factors $R_1 = 0.036$ and $R_2 = 0.050$. Thus, the absolute configuration was taken to be Δ .

A further difference Fourier synthesis showed peaks of height up to $1 \text{ e}/\text{\AA}^3$ around the iodine atoms, as well as regions of positive electron density in most expected hydrogen atom positions. In the next cycles of refinement, the 44 hydrogen atoms of the cations were included in their calculated positions (assuming $d(\text{N-H}) = d(\text{C-H}) = 1.00 \text{ \AA}$, $\text{H-X-H} = 109.5^\circ$, $B = 4.0 \text{ \AA}^2$); no parameters were varied for these atoms. This calculation converged at $R_1 = 0.029$ and $R_2 = 0.040$. Examination of average values of the minimized

Table IV. Comparison of Crystal Structure and Minimized Structure

$\Delta\text{-}\beta_1\text{-(RR)-[Co(trien)gly]}^{2+}$			$\Delta\text{-}\beta_1\text{-(RS)-[Co(trien)gly]}^{2+}$		
	Crystal	Minimized		Crystal	Minimized
(a) Interatomic Distances (Å)					
Co(1)–O(2)	1.906 (5)	1.894	Co(11)–O(12)	1.914 (6)	1.893
Co(1)–N(1)	1.980 (7)	1.966	Co(11)–N(11)	1.955 (7)	1.967
Co(1)–N(2)	1.931 (7)	1.946	Co(11)–N(12)	1.911 (7)	1.946
Co(1)–N(3)	1.965 (7)	1.961	Co(11)–N(13)	1.963 (7)	1.957
Co(1)–N(4)	1.974 (7)	1.967	Co(11)–N(14)	1.976 (7)	1.984
Co(1)–N(5)	1.991 (7)	1.985	Co(11)–N(15)	1.960 (7)	1.973
O(1)–C(8)	1.205 (9)	1.220	O(11)–C(18)	1.223 (9)	1.220
O(2)–C(8)	1.304 (9)	1.287	O(12)–C(18)	1.276 (9)	1.287
N(1)–C(1)	1.47 (1)	1.50	N(11)–C(11)	1.51 (1)	1.50
N(2)–C(2)	1.48 (1)	1.49	N(12)–C(12)	1.49 (1)	1.49
N(2)–C(3)	1.48 (1)	1.49	N(12)–C(13)	1.47 (1)	1.49
N(3)–C(4)	1.51 (1)	1.51	N(13)–C(14)	1.48 (1)	1.51
N(3)–C(5)	1.50 (1)	1.50	N(13)–C(15)	1.49 (1)	1.50
N(4)–C(6)	1.47 (1)	1.49	N(14)–C(16)	1.50 (1)	1.50
N(5)–C(7)	1.47 (1)	1.50	N(15)–C(17)	1.48 (1)	1.50
C(1)–C(2)	1.52 (1)	1.51	C(11)–C(12)	1.47 (1)	1.51
C(3)–C(4)	1.51 (1)	1.51	C(13)–C(14)	1.52 (1)	1.51
C(5)–C(6)	1.50 (1)	1.51	C(15)–C(16)	1.51 (1)	1.50
C(7)–C(8)	1.52 (1)	1.50	C(17)–C(18)	1.52 (1)	1.50
(b) Bond Angles (deg)					
O(2)–Co(1)–N(1)	93.5 (3)	93.7	O(12)–Co(11)–N(11)	91.6 (3)	91.8
O(2)–Co(1)–N(2)	178.3 (3)		O(12)–Co(11)–N(12)	176.7 (3)	
O(2)–Co(1)–N(3)	94.9 (3)	92.7	O(12)–Co(11)–N(13)	95.7 (3)	93.9
O(2)–Co(1)–N(4)	87.2 (3)	87.7	O(12)–Co(11)–N(14)	86.5 (3)	87.8
O(2)–Co(1)–N(5)	84.5 (3)	85.6	O(12)–Co(11)–N(15)	84.5 (3)	85.9
N(1)–Co(1)–N(2)	85.7 (3)	87.5	N(11)–Co(11)–N(12)	86.3 (3)	87.3
N(1)–Co(1)–N(3)	171.5 (3)		N(11)–Co(11)–N(13)	171.4 (3)	
N(1)–Co(1)–N(4)	94.5 (3)	91.7	N(11)–Co(11)–N(14)	90.6 (3)	89.9
N(1)–Co(1)–N(5)	91.0 (3)	90.2	N(11)–Co(11)–N(15)	92.6 (3)	92.5
N(2)–Co(1)–N(3)	85.8 (3)	86.1	N(12)–Co(11)–N(13)	86.6 (3)	87.4
N(2)–Co(1)–N(4)	91.3 (3)	90.9	N(12)–Co(11)–N(14)	96.0 (3)	97.1
N(2)–Co(1)–N(5)	97.0 (3)	95.8	N(12)–Co(11)–N(15)	93.1 (3)	89.2
N(3)–Co(1)–N(4)	85.8 (3)	88.9	N(13)–Co(11)–N(14)	85.4 (3)	86.0
N(3)–Co(1)–N(5)	89.9 (3)	89.9	N(13)–Co(11)–N(15)	92.6 (3)	92.2
N(4)–Co(1)–N(5)	170.3 (3)		N(14)–Co(11)–N(15)	170.5 (3)	
N(1)–O(2)–C(8)	117.9 (5)	115.3	Co(11)–O(12)–C(18)	116.4 (5)	115.5
Co(1)–N(1)–C(1)	108.4 (5)	108.1	Co(11)–N(11)–C(11)	108.8 (5)	108.2
Co(1)–N(2)–C(2)	109.4 (5)	106.9	Co(11)–N(12)–C(12)	110.2 (5)	107.0
Co(1)–N(2)–C(3)	107.5 (5)	105.6	Co(11)–N(12)–C(13)	110.7 (6)	106.3
C(2)–N(2)–C(3)	115.2 (7)	114.6	C(12)–N(12)–C(13)	117.8 (7)	114.9
Co(1)–N(3)–C(4)	109.7 (5)	109.8	Co(11)–N(13)–C(14)	109.0 (5)	108.8
Co(1)–N(3)–C(5)	107.4 (5)	105.1	Co(11)–N(13)–C(15)	106.1 (5)	106.1
C(4)–N(3)–C(5)	113.6 (6)	112.2	C(14)–N(13)–C(15)	114.5 (6)	113.0
Co(1)–N(4)–C(6)	110.6 (5)	107.3	Co(11)–N(14)–C(16)	111.2 (5)	111.6
Co(1)–N(5)–C(7)	110.1 (5)	109.0	Co(11)–N(15)–C(17)	110.1 (5)	110.0
N(1)–C(1)–C(2)	108.4 (7)	109.3	N(11)–C(11)–C(12)	109.0 (8)	109.2
C(1)–C(2)–N(2)	104.2 (7)	106.7	C(11)–C(12)–N(12)	106.7 (7)	106.6
N(2)–C(3)–C(4)	106.9 (7)	107.3	N(12)–C(13)–C(14)	105.8 (7)	107.1
C(3)–C(4)–N(3)	110.0 (7)	110.2	C(13)–C(14)–N(13)	111.8 (7)	110.4
N(3)–C(5)–C(6)	107.5 (7)	109.0	N(13)–C(15)–C(16)	108.2 (7)	109.1
C(5)–C(6)–N(4)	109.2 (7)	108.5	C(15)–C(16)–N(14)	107.7 (7)	109.0
N(5)–C(7)–C(8)	111.9 (7)	109.2	N(15)–C(17)–C(18)	109.7 (7)	109.3
O(1)–C(8)–O(2)	123.9 (7)	120.4	O(11)–C(18)–O(12)	123.4 (7)	120.3
O(1)–C(8)–C(7)	121.6 (8)	120.8	O(11)–C(18)–C(17)	120.0 (7)	120.7
O(2)–C(8)–C(7)	114.5 (7)	118.9	O(12)–C(18)–C(17)	116.6 (7)	119.0
(c) Torsion Angles ^a (deg)					
Co(1)–N(1)–C(1)–C(2)	35.6	29.9	Co(11)–N(11)–C(11)–C(12)	–32.1	–29.9
Co(1)–N(2)–C(2)–C(1)	45.4	44.9	Co(11)–N(12)–C(12)–C(11)	–40.5	–45.1
Co(1)–N(2)–C(3)–C(4)	–48.0	–48.9	Co(11)–N(12)–C(13)–C(14)	41.0	46.2
Co(1)–N(3)–C(4)–C(3)	–15.3	–14.1	Co(11)–N(13)–C(14)–C(13)	22.3	21.3
Co(1)–N(3)–C(5)–C(6)	–43.4	–42.1	Co(11)–N(13)–C(15)–C(16)	–48.0	–46.6
Co(1)–N(4)–C(6)–C(5)	–27.7	–33.3	Co(11)–N(14)–C(16)–C(15)	–22.1	–18.9
Co(1)–N(5)–C(7)–C(8)	–6.3	–14.5	Co(11)–N(15)–C(17)–C(18)	16.1	5.5
Co(1)–O(2)–C(8)–O(1)	–171.4	–178.5	Co(11)–O(12)–C(18)–O(11)	177.0	179.2
N(1)–C(1)–C(2)–N(2)	–52.7	–49.5	N(11)–C(11)–C(12)–N(12)	46.6	49.6
N(2)–C(3)–C(4)–N(3)	40.9	41.3	N(12)–C(13)–C(14)–N(13)	–40.9	–44.6
N(3)–C(5)–C(6)–N(4)	46.7	51.0	N(13)–C(15)–C(16)–N(14)	45.8	42.2
N(5)–C(7)–C(8)–O(2)	–0.6	8.9	N(15)–C(17)–C(18)–O(12)	–8.2	–3.0
(d) Nonbonded Interactions ^b (>0.3 kcal mol ^{–1})					
H(6)···H(20)	2.18 (0.5)	2.11 (0.6)	H(5)···H(17)	2.15 (0.5)	2.10 (0.7)
H(9)···H(19)	2.19 (0.4)	2.18 (0.5)	H(8)···H(15)	2.04 (0.9)	2.1 (0.6)
H(12)···H(19)	2.19 (0.4)	2.25 (0.3)	H(7)···H(9)	2.17 (0.5)	2.32 (0.23)

Table IV (Continued)

	$\Delta\text{-}\beta_1\text{-}(RR)\text{-[Co(trien)gly]}^{2+}$		$\Delta\text{-}\beta_1\text{-}(RS)\text{-[Co(trien)gly]}^{2+}$		
	Crystal	Minimized	Crystal	Minimized	
H(9)···H(21)	2.17 (0.5)	2.21 (0.4)	H(19)···H(21)	2.19 (0.4)	2.22 (0.4)
H(20)···H(22)	2.16 (0.5)	2.22 (0.4)	H(20)···H(22)	2.19 (0.4)	2.22 (0.4)
H(7)···H(17)	2.23 (0.3)	2.29 (0.2)	H(10)···H(13)	2.23 (0.4)	2.30 (0.2)
H(11)···H(12)	2.25 (0.3)	2.24 (0.3)	H(11)···H(12)	2.22 (0.4)	2.25 (0.3)
C(5)···H(10)	2.56 (0.3)	2.50 (0.4)	C(5)···H(10)	2.51 (0.4)	2.56 (0.3)

^a The torsion angle A-B-C-D is defined as that angle between the planes containing A, B and C and B, C and D with normal sign convention. ^b Energy of interaction in kcal mol⁻¹ in parentheses following distance in Å. ^c Hydrogen atom positions for crystal structure are here based on local tetrahedral C_{2v} symmetry around nitrogen and carbon N-H 1.03 Å, and C-H 1.09 Å.

function over ranges of $|F_o|$ and $\lambda^{-1} \sin \theta$ showed that the intense reflections were being underweighted. Accordingly, the data were reprocessed with a value for p of 0.375. Following recalculation of the H atom positions, two cycles of least-squares refinement, in which a single scale factor and 165 positional and vibrational parameters were varied, produced final agreement factors of $R_1 = 0.029$ and $R_2 = 0.034$.

Average values of the minimized function obtained after the final cycle of refinement show little dependence on $|F_o|$ or on $\lambda^{-1} \sin \theta$, which indicates that the relative weighting scheme is reasonable. The error in an observation of unit weight is 1.16 electrons. A final difference Fourier map still shows peaks of height up to 0.9 e/Å³ around the iodine atoms, although the electron density does not rise above 0.4 e/Å³ elsewhere. Structure factor calculations for the 436 reflections having $F_o^2 > 3\sigma(F_o)^2$ showed no anomalously high values of F_o . No correction was made for secondary extinction.

The positional and vibrational parameters and their esd's obtained from the final cycle of least-squares refinement are listed in Tables I and II. In Table III are presented the root-mean-square amplitudes of vibration of the iodine atoms. Listings of final values of $10|F_o|$ and $10|F_c|$ (in electrons) for the 4126 reflections used in the refinement will appear following these pages in the microfilm edition of this journal (see paragraph at end of paper regarding supplementary material).

Description of the Crystal Structure. The crystals contain an equimolar mixture of two diastereoisomers of the $\beta_1\text{-Co}[(\text{trien})(\text{gly})]^{2+}$ cation, along with iodide ions and water molecules. A perspective view of each complex cation showing the absolute configuration and atom numbering system is given in Figure 1. Both cations have the same chirality with respect to the overall configuration of the β -trien ligand but have opposite configurations at the "planar" secondary nitrogen atom; designated as $\Delta\text{-}\beta_1\text{-}(RR)\text{-[Co(trien)(gly)]}^{2+}$ and $\Delta\text{-}\beta_1\text{-}(RS)\text{-[Co(trien)(gly)]}^{2+}$. Intramolecular bond lengths and angles for the cations are presented in Table IV. The absolute configuration for each complex, Δ , as determined from the anomalous scattering of X-rays, is in agreement with that anticipated from the rotatory dispersion and circular dichroism spectra; see below. Moreover, this assignment is consistent with those given to related cobalt(III) β -trien complexes by the X-ray method.^{4, 19, 20}

The cations are hydrogen bonded to each other *via* their glycinato oxygens and primary nitrogen atoms. Figure 2, which is a stereo pair of the contents of the

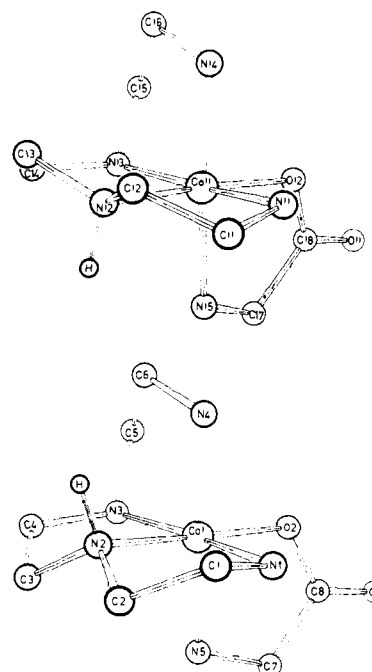


Figure 1. Perspective view of the crystallographic structures of $\Delta\text{-}\beta_1\text{-}(RR)\text{-[Co(trien)(gly)]}^{2+}$ (lower) and $\Delta\text{-}\beta_1\text{-}(RS)\text{-[Co(trien)(gly)]}^{2+}$ (upper) cations.

unit cell projected onto (100), shows such a pair of cations. The water molecule is associated with the $\Delta\text{-}\beta_1\text{-}RS$ complex cation through a hydrogen bond with N(14). Interatom distances and angles for the H bonds are listed in Table V; the bonds are drawn in Figure 2 as

Table V. Hydrogen Bonds in $\Delta\text{-}\beta_1\text{-Co}[(\text{trien})(\text{gly})]_2 \cdot 0.5\text{H}_2\text{O}$ Crystal^a

Atoms X-H···Y	$d(\text{X} \cdots \text{Y})$, Å	Atoms X-H···Y	$d(\text{X} \cdots \text{Y})$, Å
N(1)-H···O(11)	2.94	N(15)-H···O(1)	2.95
N(4)-H···O(12)	3.22	N(11)-H···O(2)	3.08
		N(14)-H···OW	3.11

Atoms	Angle, deg	Atoms	Angle, deg
C(18)-O(11)···N(1)	112	C(8)-O(1)···N(15)	109
Co(1)-N(1)···O(11)	98	Co(11)-N(15)···O(1)	116
C(1)-N(1)···O(11)	111	C(17)-N(15)···O(1)	90
Co(11)-O(12)···N(4)	132	Co(1)-O(2)···N(11)	135
C(18)-O(12)···N(4)	82	C(8)-O(2)···N(11)	103
Co(1)-N(4)···O(12)	110	Co(11)-N(11)···O(2)	103
C(6)-N(4)···O(12)	109	C(11)-N(11)···O(2)	121
		C(16)-N(14)···OW	86
		Co(11)-N(14)···OW	119

^a With respect to values in Table I, the coordinates of atoms in this table are x, y, z for $\Delta\text{-}\beta_1\text{-}(RR)\text{-[Co(trien)(gly)]}^{2+}$ and $1 + x, y, 1 + z$ for $\Delta\text{-}\beta_1\text{-}(RS)\text{-[Co(trien)(gly)]}^{2+}$ and OW.

(19) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **9**, 649 (1970).

(20) H. C. Freeman, L. G. Marzilli, and I. E. Maxwell, *Inorg. Chem.*, **9**, 2408 (1970).

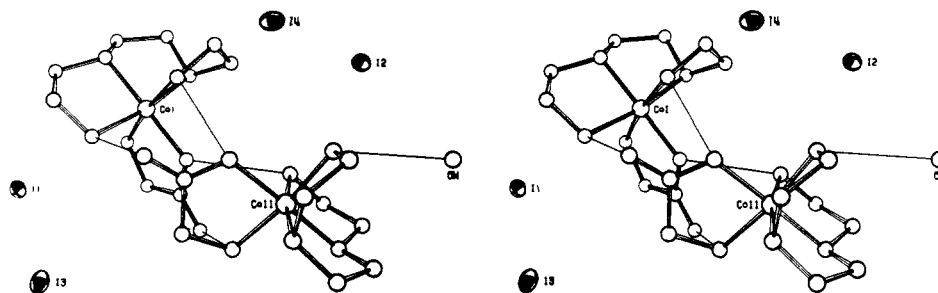


Figure 2. Stereo pair of the contents of a unit cell projected down [100]; possible hydrogen bonds are indicated.

solid lines. Excluding hydrogen atoms, intermolecular contacts other than those between the atoms in Figure 2 are all greater than 3.45 Å.

The mean Co(III)-N(trien) bond distances are 1.963 and 1.951 Å in the Δ - β -*RR* and Δ - β -*RS* isomers, respectively. Comparable distances for related complexes are 1.955 Å in Δ - β -(*SSS*)-[Co(trien)(*S*-pro)]-[ZnCl₄],²⁰ 1.96 Å in Δ - β -(*RRS*)-[Co(trien)(*S*-pro)]₂·2H₂O,¹⁹ and 1.93 Å in β -[Co(trien)ClH₂O][ClO₄]₂²¹ (*S*-pro = (*S*)-proline). However, for the present complexes there are some significant deviations from the mean values. For the Δ - β -*RR* cation the Co(1)-N(2) bond length of 1.931 (7) Å is 4 σ smaller than the mean, while for the Δ - β -*RS* complex the corresponding Co(11)-N(12) bond distance of 1.911 (7) Å is 5 σ smaller than the mean value. Rather surprisingly, the Co(III)-N(gly) bond lengths for the two cations differ by 4 σ (Co(1)-N(5), 1.991 (7) Å and Co(11)-N(15), 1.960 (7) Å). The comparable Co(III)-N(pro) bond distance in Δ - β -(*SSS*)-[Co(trien)(*S*-pro)][ZnCl₄]²⁰ is 1.980 (9) Å, and strain energy minimization calculations indicated it was lengthened because of steric effects. For both cations in the present structure to Co(III)-O(gly) distances are equal to within 2 σ (Co(1)-O(2), 1.906 (5) Å (*RR*) and Co(11)-O(12), 1.914 (6) Å (*RS*)). These bond lengths may be compared with a Co(III)-O(pro) distance of 1.924 (7) Å in Δ - β -(*SSS*)-[Co(trien)(*S*-pro)][ZnCl₄].²⁰

Polarization of the coordinated amino acid carboxyl group in each cation is evident, with mean values of 1.214 (6) Å (for C(8)-O(1) and C(18)-O(11)) and 1.290 (6) Å (for C(8)-O(2) and C(18)-O(12)). While little significance can be attached to the relative differences in the two cations (0.048 (18) Å) this difference in means (8 σ) indicates a consistent drift of electron density toward the metal ion. A similar effect was found for the proline carboxyl group in Δ - β -(*SSS*)-[Co(trien)(*S*-pro)][ZnCl₄]²⁰ where the comparable distances are 1.22 (1) and 1.29 (1) Å. In the present structure, mean C-N bond distances are 1.483 (16) and 1.488 (12) Å, and mean C-C bond lengths are 1.515 (12) and 1.505 (25) Å for the Δ - β -*RR* and Δ - β -*RS* cations, respectively.

Significant angular distortions occur in both cations at the secondary nitrogens of the β -trien ligand: C(2)-N(2)-C(3), 115.2 (7) $^\circ$; C(12)-N(12)-C(13), 117.8 (7) $^\circ$; C(4)-N(3)-C(5), 113.6 (6) $^\circ$; C(14)-N(13)-C(15), 114.5 (6) $^\circ$. Strain free angles at the sec-N atoms would be expected to be close to the regular tetrahedral value, 109.5 $^\circ$. The significance of bond angle and bond length distortions in the cations will be discussed in the following section.

(21) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969).

As is evident in Figures 1 and 2, the β -trien chelate rings are considerably puckered. Torsion angles about the C-C bonds, and chiralities¹ of the five-membered rings, are: C(1)-C(2), 52.6 (9) $^\circ$, λ ; C(3)-C(4), 40.9 (9) $^\circ$, δ ; C(5)-C(6), 46.7 (8) $^\circ$, δ ; C(11)-C(12), 46.6 (9) $^\circ$, δ ; C(13)-C(14), 40.9 (9) $^\circ$, λ ; C(15)-C(16), 45.8 (9) $^\circ$, δ . For the "in-plane" chelate rings the conformations are determined primarily by the configuration at the "planar" secondary nitrogen atom. Strain energy minimization calculations indicate that the "apical" chelate ring of β -trien is less free to adopt the λ conformation (\sim 2 kcal) in both [Co(trien)gly]²⁺ cations. The present result is consistent with the proposal²² that the δ conformation for this chelate ring is in general more stable in Δ - β -Co(III)(trien) complexes.

The glycinate groups show significant differences in terms of planarity. In the Δ - β -*RR* isomer the best weighted mean plane contains all five glycinate heavy atoms with the cobalt atom 0.23 Å out of plane (Table VI, plane 1). The usual chi-squared test indicates these atoms are coplanar to better than the 50% confidence level. In contrast, no set of four or more atoms in the Δ - β -*RS* isomer are near coplanar. The best plane involves the carboxyl part of the anion (O(11), O(12), C(18), and C(17)); the cobalt atom is 0.11 Å below and the nitrogen atom N(15), 0.22 Å above this plane (4, Table VI).

Strain Energy Minimization Calculations. As the method of calculation differs from previous work^{3,23} by the addition of new terms and strategy a summary will be presented here. Total strain energy U is assumed to be represented by a six-term summation. The first and

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

second terms are bond length and bond angle deformation energies, respectively. Both are assumed to have the harmonic form, $U(\theta_{ijk}) = k_{ijk}^\theta/2 (\theta_{ijk}^0 - \theta_{ijk})^2$ and $U(r_{ij})_b = k_{ij}^r/2 (r_{ik}^0 - r_{ij})^2$, where k_{ijk}^θ and k_{ij}^r are bond angle and bond length force constants, and θ_{ijk}^0 , r_{ij}^0 are the strain free values, respectively. The third term described nonbonded interactions and is a function of the Buckingham form, $U(r_{ij})_b = a_{ij} \exp(-b_{ij} \cdot r_{ij}) - c_{ij}/r_{ij}^3$, where a_{ij} , b_{ij} , and c_{ij} are constant terms for any particular type of atom-atom interaction.

The coefficients a_{ij} , b_{ij} , and c_{ij} have been tabulated.³ For reasons outlined previously^{2,3} all geminal 1,3 and cobalt nonbonding interactions are excluded. How-

(22) D. A. Buckingham, H. C. Freeman, I. E. Maxwell, and A. M. Sargeson, *Inorg. Chem.*, **9**, 1921 (1970).

(23) R. H. Boyd, *J. Chem. Phys.*, **49**, 2754 (1968).

Table VI. Weighted Mean Planes^a for Δ - β -[Co(trien)(gly)]I₂·0.5H₂O

No.	Atoms defining plane ^b	Other atoms	Equation coefficients ^c			
			A	B	C	D
1	N(5), 0.007; C(7), -0.009; C(8), -0.006; O(1), 0.005; O(2), -0.001	Co(1), 0.23	0.4642	0.6663	-0.5838	-2.9934
2	Co(11), -0.001; O(12), 0.007; C(18), 0.030; O(11), -0.016	N(15), 0.42; C(17), 0.155	-0.8309	-0.5247	-0.1852	2.8416
3	O(1), 0.001; O(2), 0.001; C(7), 0.002; C(8), -0.004	N(11), -1.34; N(15), 1.19	0.4623	0.6633	-0.5886	-3.0184
4 ^d	O(11), 0.002; O(12), 0.001; C(17), 0.002; C(18), -0.008	{N(1), 2.57; N(4), 2.47 Co(11), -0.11; N(15), 0.22}	-0.7863	-0.5835	-0.2033	-4.5420

^a Method of B. M. Blow, *Acta Crystallogr.*, **13**, 168 (1960); program written by M. E. Pippy, NRC-22, Ottawa, Canada. ^b Distance of atom from plane in ångströms follows atom labels. ^c The orthogonal system of axes has X (Å) along the a axis, Y (Å) in the (a, b) plane, and Z (Å) along the c axis: the equation of the plane is $AX + BY + CZ = D$. ^d Coordinates of atoms converted to same asymmetric unit (see footnote a, Table V).

ever, recent studies have shown that variations in energy may be created by the previous² limiting criterion (ii) for nonbonded interactions: $[d_{ij} - p(w_i + w_j)] > 0$ where d_{ij} is the nonbonded distance between i th and j th atoms, p is a limiting factor (1.1–1.2), and w_i and w_j are van der Waals radii.²⁴ Minor modifications of p (or w_i , w_j) can give rise to significant changes in the relative strain energy of diastereoisomers. For example, the difference in strain energy for the *lel* and *ob* isomers of Δ -(cobalt(propylenediamine))₃³⁺ can vary as much as 0.7 kcal mol⁻¹, compared with the total calculated difference of 1.0 kcal mol⁻¹.²⁵

Such errors occur because there are small variations in the nonbonded intramolecular contact profiles of closely related isomers. Different interaction sets are generated by the above criterion and so the strain energy sums are biased. Upon correction, no significant changes occur in the final minimized coordinates, although final energies may be altered. We suggest two further criteria are therefore required: (1) the same set of interactions should be used for each stereoisomer in a related set; (2) any limits based on an atomic contact radii or a standard set criterion should be checked against the nonbonded interaction energy profiles for each stereoisomer. To restrict the number of interactions at early stages of analyses, it is preferable to use values of w for the above equation based on the minima of the respective Buckingham equations (Table VII).

Table VII. "Buckingham Radii" for Nonbonding Interaction Limits (see text)

Atom type	W_i^B , radii (Å)
H	1.48
C	1.75
N	1.63
O	1.63
Cl	1.90

The complete interaction set may then be used in final refinements. The Co···H and Co···O nonbonding interactions are excluded because suitable Buckingham parameters are not known. Over-estimates for these parameters have been shown not to affect the relative energies or final geometries for the isomers studied in this paper.

The fourth term, $U(\phi_{ijk})$, allows for the restricted

(24) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1967).

(25) G. J. Gainsford, unpublished results.

rotation about specific bonds and is modified from the usual form for a torsion potential, where ϕ_{ijk} is the

$$U(\phi_{ijk}) = \frac{1}{2}U_{ijkl} \phi_{ijk} [1 + \cos n(\phi + C_2)]$$

dihedral angle between planes i, j, k and j, k, l (with the normal sign convention), U_{ijkl} is the potential energy barrier to n -fold rotation about the bond jk less the differences in nonbonded interaction energies,² and C_1 and C_2 are "stiffening" and phase shift constants, respectively, as outlined by Wiberg and Boyd.²⁶ Variation of C_1 permits refinement to a particular value for ϕ_{ijk} . One torsion interaction is automatically generated per bond except for the weak² 12-fold barriers around Co–O and Co–N bonds which are excluded.

Both fifth and sixth terms allow one atom to be constrained to the plane of three others. They are simple harmonic functions: $U_{ijk}(\Delta_i) = \frac{1}{2}k_{ijk}(\Delta_i)^2$ and $U(\delta_{ijkm}) = \frac{1}{2}k_{ijkm}(\delta_{ijkm})^2$ where Δ_i is the distance of the i th atom from the plane of atoms j, k , and m , δ_{ijkm} is the angle between the vector jm and the plane ijk ;²³ k_{ijk} and k_{ijkm} are constants. Similar angular-dependent terms have been used by Allinger and co-workers.²⁷

Apart from the r_{ij}^0 values for the C–O and Co–N bonds, which have been revised in the light of consistent X-ray structural evidence,²⁸ most of the constants (Table VIII) concerning the trien ligand are identical with those used in previous studies.^{2,3} The glycinato force field poses some problems concerning both the types and barriers of its torsional interactions. Currently, these consist of one standard threefold C–N rotation barrier, 2.5 kcal mol⁻¹ (N(5)–C(7)), a sixfold rotation barrier of 0.5 kcal mol⁻¹ minimizing ϕ (by phase shift) to 0° (C(7)–C(8)), and a twofold rotation barrier of 6 kcal mol⁻¹ minimizing ϕ to 0° also (O(2)–C(8)). An out of plane distance constraint (Δ_i) such that C(7) is held in the plane of C(8), O(2), and O(1) completes the model (see Figure 1). Coupled with the other types of interactions, these potential functions reflect the apparent demand for planarity of amino acid ring systems in experimental²⁹ and theoretical studies.³⁰

Minimization of the total strain energy was achieved

(26) K. B. Wiberg and R. H. Boyd, *J. Amer. Chem. Soc.*, **94**, 8426 (1972).

(27) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

(28) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Inorg. Chem.*, **9**, 1921 (1970).

(29) H. C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).

(30) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972).

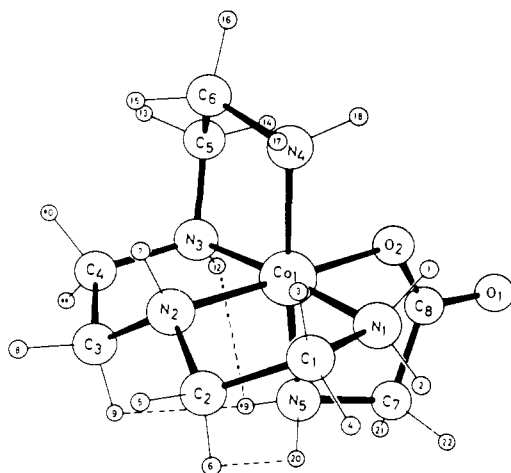


Figure 3. $\Delta\text{-}\beta_1\text{-(RR)-[Co(trien)(gly)]}^{2+}$ isomer drawn using minimized coordinates and showing major nonbonding interactions.

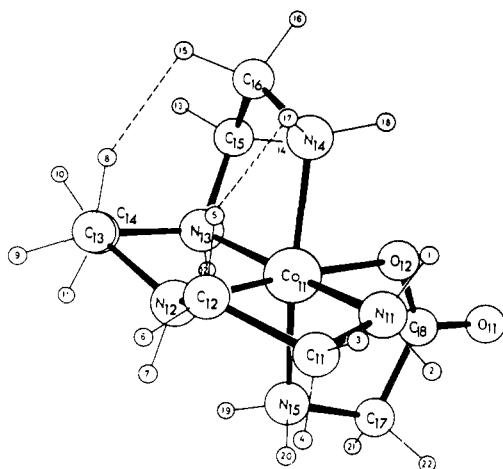


Figure 4. $\Delta\text{-}\beta_1\text{-(RS)-[Co(trien)(gly)]}^{2+}$ isomer drawn using minimized coordinates showing major nonbonding interactions.

using a modified Newton-Raphson method of optimization as developed by Boyd.²³ The advantages of this method are that the changes in atomic coordinates are calculated directly, and the likelihood of local minima is small. The computational method was similar to that used previously^{2,3} except that provision was made to change the interactions list between iterations. The calculated shifts were damped for early cycles to avoid divergence and minimization was terminated when the coordinate shift for each atom was less than 0.002 Å. Calculations were carried out on a UNIVAC 1108 computer with 196K words of core storage. Our program uses overlay procedures to reduce core requirements to 48K words with cycle times for these cations averaging less than 15 sec (698 interactions, 108 variables). Line diagrams were drawn³ on a CDC 3600 connected to a Calcomp incremental plotter.

Trial coordinates for the $\Delta\text{-}\beta_1\text{-(RR)-}$ and $\Delta\text{-}\beta_1\text{-(RS)-}$ [Co(trien)(gly)]²⁺ isomers were obtained from the crystal structure analysis, and hydrogen atoms were placed at calculated positions by approximating to C_{2v} symmetry at each carbon and nitrogen center (N-H 1.03 Å; C-H 1.09 Å). It has been shown² that the final minimized geometry is not dependent on the trial coordinates. However, it seems that good trial coordinates reduce the computation time and the possibility of refining to

Table VIII. Force Field Potential Function Constants^a

Bond type	Bond Length Force Constants ^b		Ref
	k_{ij}^r	r_{ij}^0 , Å	
N-H	5.64	1.03	<i>e</i>
C-H	5.0	1.09	<i>d</i>
C-C	5.0	1.50	<i>d</i>
C-N	6.0	1.49	
Co-N	1.75	1.95	<i>e</i>
Co-O	1.75	1.90	
C=O	9.0	1.22	<i>h-k</i>
C=O ⁿ	8.0	1.29	

Bond angle type	Bond Angle Force Constants, k_{ijk}^{θ}		Ref
	k_{ijk}^{θ}	θ_{ijk}^0 , radians	
H-C-H	0.52	1.911	<i>d</i>
H-N-H	0.53	1.911	<i>e</i>
N-C-H	0.65	1.911	
C-N-H	0.55	1.911	
C-C-H	0.65	1.911	<i>d</i>
C-C-N	1.00	1.911	
N-Co-N	0.68	1.571	<i>e</i>
N-Co-O	0.68	1.571	<i>e</i>
Co-N-H	0.20	1.911	<i>e</i>
Co-N-C	0.40	1.911	
C-N-C	1.0	1.911	
C-C-C	1.0	1.911	<i>d</i>
O-C-O	1.0	2.095	
O-C-C	1.0	2.095	
Co-O-C	0.40	2.095	
N-C-C=	0.80	1.911	
H-C-C=	0.55	1.911	

Nonbonded atoms	Nonbonded Potential Function Constants ^c			Ref
	a_{ij}	b_{ij} , Å ⁻¹	c_{ij}	
H...H	45.8	4.08	0.341	<i>k</i>
C...H	218	4.20	0.84	<i>k</i>
N...H	195	4.32	0.69	<i>l</i>
C...C	1640	4.32	2.07	<i>k</i>
C...N	1472	4.44	1.695	<i>l</i>
N...N	1295	4.55	1.39	<i>l</i>
O...H	195	4.32	0.69	<i>l</i>
O...C	1472	4.44	1.695	<i>l</i>
O...N	1295	4.55	1.39	<i>l</i>

Bond type	Torsional Force Constants ^a		
	U_{ijkl}^{ϕ}	n	C_2 , radians
C-C	0.0173	3	0.0
C-N	0.0107	3	0.0
C=O ⁿ	0.0420	2	1.571
C-C=	0.0035	6	0.5237

In plane atoms	Out-of-Plane Constant ^b		Ref
	Constrained atom	k_{ijkl}^0	
O(1)O(2)C(8)	C(7)	1.0	
O(11)O(12)C(18)	C(17)	1.0	<i>m</i>

^a Constants which are not referenced have been estimated and in some instances fitted to give best agreement with the structural data. ^b Force constants are given in 10⁶ dyn cm⁻¹ molecule⁻¹. ^c The units for parameters a_{ij} and c_{ij} , respectively, are 10⁻¹¹ erg molecule⁻¹ and 10⁻¹¹ erg Å⁶ molecule⁻¹. ^d J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963). ^e I. Nakagawa and T. Shimanouchi, *ibid.*, **22**, 759, 1707 (1966). ^f Force constants are given in 10⁻¹¹ ergs radian⁻² molecule⁻¹. ^g Force constants are given in 10⁻¹¹ ergs molecule⁻¹. ^h O. Thomas, *Discuss. Faraday Soc.*, No. 9, 339 (1950); H. H. Jensen and S. Y. Cyvin, *Acta Chem. Scand.*, **23**, 3168 (1969). ⁱ R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965). ^k J. L. De Coen, G. Elefante, A. M. Liquori, and A. Damiani, *Nature (London)*, **216**, 910 (1967). ^l A. M. Liquori, A. Damiani, and G. Elefante, *J. Mol. Biol.*, **33**, 439 (1968). ^m C. W. F. Pistorius, *J. Chem. Phys.*, **29**, 1174 (1958). ⁿ Oxygen atom bound to cobalt ion.

Table IX. Minimized Coordinates

	$\Delta\text{-}\beta_1\text{-}(RR)\text{-}[\text{Co}(\text{trien})\text{gly}]^{2+}$			$\Delta\text{-}\beta_1\text{-}(RS)\text{-}[\text{Co}(\text{trien})\text{gly}]^{2+}$ ^a		
	x	y	z	x	y	z
Co(1)	0.000	0.000	0.000	0.000	0.000	0.000
N(1)	1.966	0.000	0.000	1.967	0.000	0.000
N(2)	0.085	1.944	0.000	0.091	1.944	0.000
N(3)	-1.948	0.219	0.019	-1.942	0.180	-0.165
N(4)	-0.059	-0.029	-1.966	0.004	-0.245	-1.969
N(5)	-0.006	-0.200	1.975	-0.087	0.031	1.970
O(2)	-0.123	-1.889	-0.044	-0.061	-1.885	0.162
O(1)	-0.012	-3.694	1.165	-0.267	-3.535	1.565
C(1)	2.432	1.421	-0.089	2.436	1.421	0.087
C(2)	1.415	2.319	0.565	1.419	2.318	-0.569
C(3)	-1.084	2.398	0.808	-1.084	2.419	-0.785
C(4)	-2.296	1.658	0.296	-2.284	1.639	-0.301
C(5)	-2.403	-0.221	-1.338	-2.332	-0.626	-1.363
C(6)	-1.453	0.322	-2.373	-1.397	-0.307	-2.495
C(7)	0.222	-1.639	2.320	-0.275	-1.358	2.497
C(8)	0.023	-2.477	1.092	-0.202	-2.333	1.360
H(1)	2.306	-0.535	-0.812	2.327	-0.434	-0.862
H(2)	2.335	-0.439	0.855	2.317	-0.540	0.805
H(3)	2.551	1.707	-1.135	3.399	1.527	-0.416
H(4)	3.395	1.530	0.415	2.555	1.708	1.134
H(5)	1.636	3.361	0.327	1.445	2.193	-1.650
H(6)	1.440	2.199	1.647	1.641	3.361	-0.334
H(7)	0.005	2.330	-0.952	0.023	2.317	0.959
H(8)	-1.226	3.472	0.674	-0.925	2.281	-1.852
H(9)	-0.933	2.203	1.869	-1.242	3.483	-0.599
H(10)	-2.664	2.156	-0.602	-3.112	1.779	-0.998
H(11)	-3.085	1.702	1.049	-2.591	2.028	0.671
H(12)	-2.373	-0.394	0.731	-2.404	-0.212	0.670
H(13)	-3.416	0.134	-1.536	-3.360	-0.406	-1.654
H(14)	-2.402	-1.311	-1.386	-2.263	-1.689	-1.125
H(15)	-1.562	1.403	-2.459	-1.682	0.634	-2.965
H(16)	-1.678	-0.125	-3.344	-1.469	-1.091	-3.250
H(17)	0.608	0.642	-2.374	0.525	0.488	-2.466
H(18)	0.179	-0.971	-2.309	0.471	-1.144	-2.162
H(19)	-0.912	0.087	2.371	-0.874	0.623	2.275
H(20)	0.728	0.365	2.422	0.782	0.431	2.352
H(21)	-0.480	-1.957	3.093	-1.250	-1.447	2.981
H(22)	1.240	-1.783	2.687	0.504	-1.593	3.224

^a For $\Delta\text{-}\beta_1\text{-}RS$ isomer, atom labels are obtained by adding 10 to corresponding nonhydrogen atom number, e.g., for N(2) read N(12) (see Figures 3 and 4).

local minima. For convenience, and to resolve redundancy,³ the trial coordinates were transformed from the crystal system to a Cartesian coordinate system for the molecule. A set of Cartesian axes X , Y , and Z were defined by the following vectors: $X = U$; $Y = (U \cdot V) \cdot U$; $Z = U \cdot V$; where $U = \text{Co} \rightarrow \text{N}(1)$, $V = \text{Co} \rightarrow \text{N}(2)$, and the cobalt ion was placed at the origin.

A total of 698 interactions (41 bonded; 88 angular, 556 nonbonded, 12 torsional, and 1 planar-constraint) were generated for both $\Delta\text{-}\beta_1\text{-}RR$ and $\Delta\text{-}\beta_1\text{-}RS$ cations. The refinements converged in 15 and 19 cycles to strain energies of 7.0 and 7.8 kcal mol⁻¹, respectively. Nonbonding contracts longer than 4.85 Å could have been excluded without affecting the final geometry and energies according to energy profile studies. Figures 3 and 4 give perspective views of the cations plotted from the minimized coordinates given in Table IX. A breakdown of the final energy terms is given in Table X and a comparison of the minimized and crystal structures in terms of bond lengths, bond angles, dihedral angles, and major nonbonding interactions (>0.3 kcal/mol) is made in Table IV.

Isomer Separation and Properties. The two β_1 isomers were prepared as outlined above. The isolated iodide salt, $\beta_1\text{-}[\text{Co}(\text{trien})(\text{gly})]\text{I}_2 \cdot 2\text{H}_2\text{O}$ (ϵ_{348} 162 and ϵ_{348} 125 M⁻¹ cm⁻¹), contained the equilibrium distribution of ($RR + SS$) and ($RS + SR$) diastereoisomers, 56

Table X. Final Energy Terms (kcal mol⁻¹) for Minimized Structures

	$\Delta\text{-}\beta_1\text{-}(RR)\text{-}[\text{Co}(\text{trien})\text{gly}]^{2+}$	$\Delta\text{-}\beta_1\text{-}(RS)\text{-}[\text{Co}(\text{trien})\text{gly}]^{2+}$
Bond length deformations	0.5	0.5
Nonbonded interactions	-3.1	-3.3
Valence angle deformations	3.9	4.4
Torsional terms	5.7	6.2
Out of plane deformation	0.0	0.0
Total strain energy	7.0	7.8

$\pm 2\%$ ($RR + SS$) and $44 \pm 2\%$ ($RS + SR$). Fractional recrystallization of either the iodide or chloride salts proved unsuccessful in separating the diastereoisomers. The racemate mixture of ($RR + SS$) and ($RS + SR$) diastereoisomers was resolved about the cobalt center using $\text{Na}(+)\text{[Co(en)(C}_2\text{O}_4)_2]$.⁸ The optically pure product, $(-)\text{[Co}(\text{trien})(\text{gly})]\text{I}_2 \cdot 0.5\text{H}_2\text{O}$ ($[\alpha]_{589} -330^\circ$; $[\alpha]_{546} -665^\circ$) contains equal amounts of the $(-)\text{-}\beta_1\text{-}RR$ and $(-)\text{-}\beta_1\text{-}RS$ diastereoisomers (*vide supra* X-ray structure). These could not be separated by recrystallization either as their iodide or chloride salts.

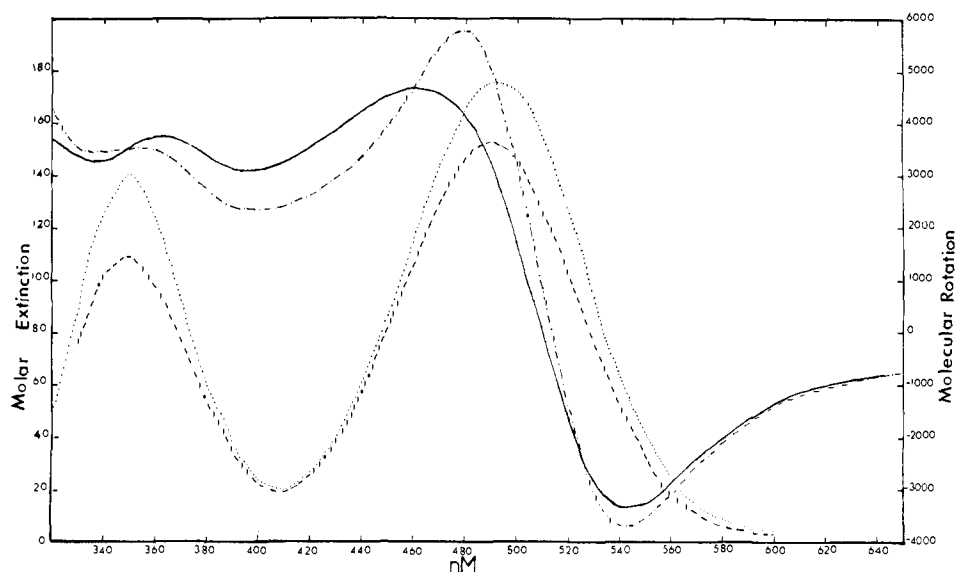


Figure 5. Visible spectra and RD curves for $\Delta(-)_{589}\text{-}\beta_1\text{-(RR)-[Co(trien)gly]Cl}_2$ (---- and - · - · - ·, respectively), and $\Delta(-)_{589}\text{-}\beta_1\text{-(RS)-[Co(trien)gly]Cl}_2 \cdot 0.5\text{H}_2\text{O}$ (····· and ———, respectively), in water at 25°.

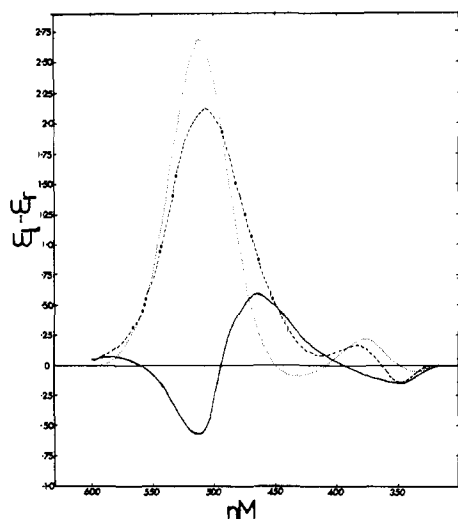


Figure 6. CD curves for $\Delta(-)_{589}\text{-}\beta_1\text{-(RR)-[Co(trien)(gly)]I}_2 \cdot 2\text{H}_2\text{O}$ (----), $\Delta(-)_{589}\text{-}\beta_1\text{-(RS)-[Co(trien)(gly)]I}_2 \cdot 2\text{H}_2\text{O}$ (·····) in water at 25° and the difference curve (— · — · —) for the two isomers.

The diastereoisomers were separated using cation exchange resin, and recovered as their chloride and iodides salts; $\beta_1\text{-(RR + SS)-[Co(trien)(gly)]I}_2 \cdot 2\text{H}_2\text{O}$ (ϵ_{488} 168, ϵ_{348} 133), $\beta_1\text{-(RS + SR)-[Co(trien)(gly)]I}_2 \cdot 2\text{H}_2\text{O}$ (ϵ_{492} 179, ϵ_{349} 142). Visible absorption spectra of the chloride salts are given in Figure 5. Similarly ion exchange chromatography of the optically pure $(-)_{589}\text{-(RR + RS)-[Co(trien)(gly)]I}_2 \cdot 0.5\text{H}_2\text{O}$ complex resulted in the separation of the $(-)_{589}\text{-}\beta_1\text{-RR}$ and $(-)_{589}\text{-}\beta_1\text{-RS}$ cations, and these were crystallized as their iodide salts ($[\text{M}]_{589} - 1825^\circ$, -1735° and $[\text{M}]_{546} - 3706^\circ$, -3345° , respectively).

Alternatively the racemate $\beta_1\text{-(RR + SS)}$ iodide was resolved using $\text{AgSbO-(+)}\text{tartrate}$ as above, resulting finally in optically pure $(+)_{589}\text{-}\beta_1\text{-(SS)-[Co(trien)(gly)]I}_2 \cdot 2\text{H}_2\text{O}$ ($[\text{M}]_{589}$ 1838°; $[\text{M}]_{546}$ 3721°).

Rotatory dispersion (RD) and circular dichroism (CD) spectra for the $(-)_{589}\text{-}\beta_1\text{-RR}$ and $(-)_{589}\text{-}\beta_1\text{-RS}$ ions are given in Figures 5 and 6, respectively. It is apparent that the chiral cobalt center is the dominating

feature, but the configuration about the secondary N center and the accompanying changes in ring conformations provide a significant perturbation. This is particularly apparent in the CD spectra with the absorptions about 435 nm having opposite sign. The CD difference curve, Figure 6, clearly demonstrates the effect of a change in chirality about the secondary N center. Its overall shape in the visible region is not unlike that for $(-)_{436}\text{-[Co(NH}_3)_4\text{(sar)]}^{2+}$ (sar = sarcosine anion) which has the R configuration about the coordinated secondary N center,³¹ and supports the assignment of isomers in the present instance. It has previously been asserted that such difference curves (CD or RD) substantially remove the contribution made by the asymmetric cobalt center.^{32,33} Both the visible and CD spectra obtained in this study substantiate that previous workers⁹ were dealing with a mixture of the $\Delta\text{-RR}$ and $\Delta\text{-RS}$ β_1 isomers.

Pmr spectra (100 MHz) are given in Figure 7. The broad absorptions below 5.0 ppm in D_3O^+ solution are characteristic of N-H protons; in neutral D_2O solution they vanish due to rapid exchange with the solvent protons. The methylene protons of glycine and triethylenetetramine absorb at about 4.0 and 3-4 ppm, respectively, the former changing from a triplet in D_3O^+ to a single on deuteration of the glycine amino group, and the latter showing more fine structure due to the same property. The major chemical shift difference between the $(\text{RR} + \text{SS})$ and $(\text{RS} + \text{SR})$ diastereoisomers occurs with the N-H absorptions at lowest field. These are assigned to the secondary N-H protons of triethylenetetramine. The asymmetric absorption at 7.1-7.2 ppm (2 protons) in the $(\text{RS} + \text{SR})$ ions is split into two single N-H absorptions at 6.5 and 7.3 ppm in the $(\text{RR} + \text{SS})$ ions, Figure 7A and C. Those at 7.2 and 6.5 ppm in the two isomers, respectively, are involved in the mutarotation process (*vide infra*) and are assigned to the "planar" N proton. The chemical shift is consistent with a change in configuration about the nitrogen center.

(31) S. Larsen, K. J. Watson, A. M. Sargeson, and K. R. Turnbull, *J. Chem. Soc., Chem. Commun.*, 847 (1968).

(32) D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, 5, 1649 (1966).

(33) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 3, 1356 (1964).

The correspondence between these shifts and those observed on the related β_2 isomers of known absolute configuration³⁴ supports the CD assignment of absolute configuration about the N centers.

Kinetics and Thermodynamics of Equilibration. The rates of mutarotation of the Δ - β_1 -RR and Δ - β_1 -RS isomers were followed polarimetrically at 510 nm in Tris or glycine buffers. Rotational changes of 0.03–0.07° were observed and plots of $\log(\alpha_\infty - \alpha_t)$ vs. time were linear for at least 3 half-lives. The data (Table XI)

Table XI. Rate Data for Mutarotation of Δ - β_1 -(RR)- and Δ - β_1 -(RS)-[Co(trien)(gly)]I₂ in Tris Buffer (0.1 M) at 25°, $\mu = 1.0$ (NaClO₄)

pH	10 ⁶ [HO ⁻] ^a	10 ³ k _{obsd} , sec ⁻¹	10 ⁻³ k _{obsd} / [HO ⁻], M ⁻¹ sec ⁻¹
β_1 -RR Isomer			
7.57	0.64	0.72	1.13
8.36	3.89	3.98	1.03
β_1 -RS Isomer			
8.74 ^b	9.33	11.3	1.21
8.38	4.07	4.13	1.01

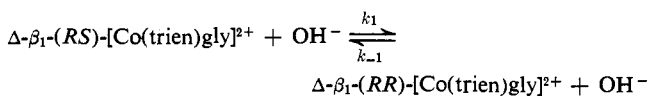
^a Calculated using $pK_w = 13.77$. ^b 0.2 M glycine buffer.

show that mutarotation follows the rate law

$$v = k[\text{complex}][\text{OH}^-]$$

with $k = 1.11 \pm 0.05 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° and $\mu = 1.0$.

The product of mutarotation is the equilibrium mixture of the Δ - β_1 RS and Δ - β_1 -RR isomers, with $K = 1.22 \pm 0.05$ for the



interconversion at 25° in 1 M NaClO₄. The data, Table XII, were obtained by separating the diastereoisomers on the cation exchange resin and spectrophotometric and/or atomic absorption analysis of the eluted fractions; racemic material was used in some experiments to conserve optically pure material. In one experiment the equilibrium constant was calculated from polarimetric data using known specific rotations for the two isomers and this agreed with the chromatographic separation. To investigate the effect of temperature with more precision a $1.40 \times 10^{-3} \text{ M}$ solution of (-)₅₈₉- β_1 -RS iodide was equilibrated at pH 8.74 (0.2 M Tris buffer, $\mu = 1.0$ (NaClO₄)) for 6 min at 25° and then quenched to pH ~4 with HOAc. A separate solution was similarly treated for 3 min at $85 \pm 1^\circ$. The resulting RD spectra for the two solutions at 25° were identical, with $[\alpha]_{510} 0.113^\circ$, consistent with a 46:54 distribution of the RS and RR diastereoisomers. Based on the known specific rotations of the separated isomers a 2% change in the isomer distribution would result in a 0.004° change in rotation at 510 nm. Thus the equilibrium constant was essentially temperature independent with $|\Delta H^\circ| < 0.3 \text{ kcal mol}^{-1}$.

Combination of the measured values of K and the

(34) D. A. Buckingham, P. J. Cresswell, G. J. Gainsford, V. Janson, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, and A. M. Sargeson, unpublished results.

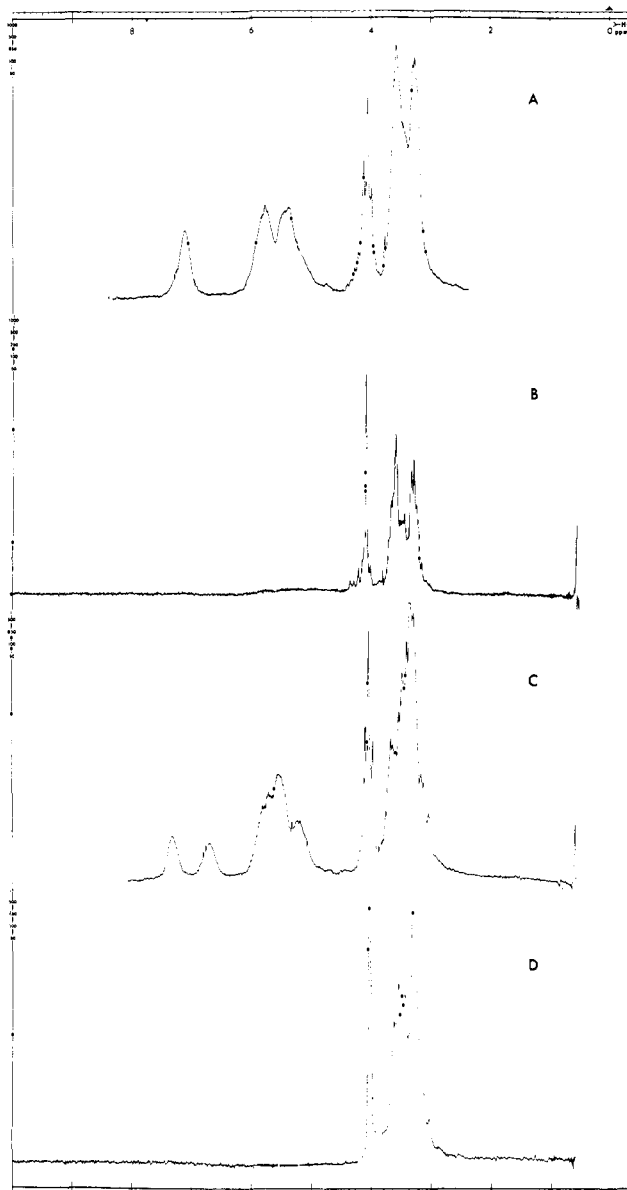


Figure 7. Pmr spectra (100 MHz) of β_1 -(RS + SR)-[Co(trien)gly]Cl₂·0.5H₂O in 0.02 M DCl (A) and D₂O (pD ~7) (B) and β_1 -(RR + SS)-[Co(trien)(gly)]Cl₂ in 0.05 M DCl (C) and D₂O (pD ~7) (D).

rate constant for mutarotation, $k = k_1 + k_{-1}$, gives $k_1 = 5.0 \pm 0.3 \times 10^2 \text{ M}^{-2} \text{ sec}^{-1}$ and $k_{-1} = 6.1 \pm 0.4 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$, 25°, $\mu = 1.0$.

Kinetics of H-Exchange. Rate data for H-exchange for the secondary NH groups and some of the primary NH₂ groups were obtained by pmr spectroscopy in dilute DCl or D₂O buffers at 34°. Data are given in Table XIII. The HDO signal at 5 ppm interfered only with the NH₂ absorptions at highest field. The β_1 -(RR + SS) isomer was most suitable for following deuteration of the secondary NH groups as the two absorptions are well separated, Figure 7C; in such cases plots of $\log(\text{peak height})_t$ against time were linear for at least 3 half-lives. For the β_1 -(RS + RS) isomer the secondary NH absorptions are not well separated and plots of $\log\{(\text{area})_t - (\text{area})_\infty\}$ against time were used. The β_1 -(RS + SR) isomer was more convenient for following exchange of the primary NH₂ protons since these signals were better separated than in the β_1 -(RR + SS) ion.

Table XII. Equilibrium Data for β_1 -(RR + SS)- and β_1 -(RS + SR)-[Co(trien)(gly)]I₂ at 25°, $\mu = 1.0$ (NaClO₄)

Isomer	[HO ⁻], ^a M	[β_1 -(RR, SS)], mol	[β_1 -(RS, SR)], mol	[β_1 -(RR + SS)/ β_1 -(RS + SR)]
β_1 -(RR + SS)	4.27×10^{-4} ^d	1.41×10^{-3}	1.18×10^{-3}	1.20
Δ - β_1 -RR	5.75×10^{-7} ^{a,b}			1.27
	10^{-2} ^c	1.79×10^{-3}	1.51×10^{-3}	1.19
β_1 -(RS + SR)	10^{-2} ^c	1.29×10^{-3}	1.03×10^{-3}	1.25
Δ - β_1 -RS	9.33×10^{-6} ^a	1.11×10^{-3}	9.41×10^{-4}	1.18

^a 0.2 M Tris buffer. ^b RR/RS ratio calculated from known $[\alpha]_{589}$ values for the pure isomers. ^c 0.01 M NaOH for 30 sec. ^d 0.1 M glycine buffer. ^e Measured pH values, $K_w = 13.77$.

Table XIII. Rate Constants for Proton Exchange at 34.3° ^d

[D ⁺]	$10^4 k_{\text{obsd}}$, sec ⁻¹	$10^{-8} k_{\text{ex}}$, ^e M ⁻¹ sec ⁻¹
β_1 -(RR + SS)-[Co(trien)(gly)]Cl ₂		
0.0011 ^{a,c}	2.76	8.01
1.55×10^{-2} ^a	2.10	8.54
5.30×10^{-3} ^a	6.08	8.30
5.58×10^{-4} ^a	57.8	8.49
6.81×10^{-6} ^b	3.50	0.063
β_1 -(RS + SR)-[Co(trien)(gly)]Cl ₂		
9.77×10^{-3} ^a	3.12	8.03
1.41×10^{-3} ^a	2.20	8.16
5.68×10^{-5} ^b	1.93	0.035

^a NH proton at 6.5 ppm in β_1 -(RR + SS) isomer, and 7.2 ppm in β_1 -(RS + SR) ^b NH proton at 7.3 ppm in β_1 -(RR + SS) isomer and 7.1 ppm in β_1 -(RS + SR). ^c 0.0011 M DCl. ^d In NaOD/DOAc buffers (0.1 M), pD = pH + 0.4. ^e $k_{\text{ex}} = k_{\text{obsd}}[D^+]/3.80 \times 10^{-16}$.

At pD 4.63 half-lives were ca. 60 min for the absorptions at 5.45 and 5.8 ppm, and the -CH₂- of glycine at ~4.0 ppm had collapsed to a singlet within 5 min at the same pD.

The derived rate constants k_{ex} (Table XII) were calculated using $k_{D_2O} = 3.80 \times 10^{-15}$, ³⁵ and it is clear that the exchange processes follow a rate law, $v = k_{\text{ex}} \cdot [\text{complex}][\text{OD}^-]$. It is also apparent that one secondary NH proton deuterates more than 10²-fold faster than the other and that the latter exchanges at a rate similar to that for the NH₂ protons of triethylenetetramine. The rapidly exchanging proton is the only one which has a significant chemical shift difference in the two isomers and is assigned to that attached to the N atom connecting ethylenediamine residues in the same plane.

Discussion

The occurrence of the two diastereoisomeric cations in the same crystal provides a unique opportunity for the detailed comparison of molecular geometries differing only in the conformations of the chelate rings. Moreover, the relatively high accuracy to which the structure parameters have been determined allows some significance to be attached to the comparison of the crystal structure geometries with those obtained by minimization of the intramolecular strain energy. In the discussion which follows the structural and thermodynamic aspects are considered before the dynamics of H-exchange and the inversion process.

Comparison between Observed and Minimized Molecular Geometries. (a) The Δ - β_1 -(RR)-[Co(trien)(gly)]²⁺ Cation. The most important steric repulsions occur between the protons on the amino acid nitrogen atom, N(5), and protons on β_1 -trien carbon atoms C(2) and

C(3): H(6)···H(20) 2.11 Å, 0.6 kcal mol⁻¹, H(9)···H(19) 2.18 Å, 0.5 kcal mol⁻¹ (see Table IV and Figure 3). Twisting of the glycinate ring is prevented by further interactions notably with the proton on nitrogen atom N(3): H(12)···H(19) 2.25 Å, 0.3 kcal mol⁻¹. These interactions are relieved by bond angle bending at the metal ion: minimized N(2)-Co(1)-N(5) 95.8°, 0.5 kcal mol⁻¹ (crystal 97.0 (3)°, 0.7 kcal mol⁻¹) and by a small but significant amount of bond stretching: Co(1)-N(5) 1.985 Å (crystal 1.991 (7) Å), both 0.2 kcal mol⁻¹.

Further angular distortion occurs at N(2), the trien "planar" secondary nitrogen atom (C(2)-N(2)-C(3), 114.6°, 0.6 kcal mol⁻¹ (minimized) 115.2 (7)° 0.7 kcal mol⁻¹ (crystal), Table IV(b). Angular strain at this center has the effect of shortening the Co-N(2) bond and again this is found for both minimized (1.946 Å) and crystal structure 1.931 (7) Å. Agreement of crystal and minimized torsion angles about C-C, C-N, and C-O bonds (Table IV(c)) is close indicating the calculations have adequately reproduced the observed chelate ring conformations. The minor differences reflect either the inadequacies of the glycinate force field (O(2)-C(8)-178.5° minimized, -171.4° crystal) or the hydrogen-bonding found in the crystal (N(1)-C(1) 29.9° minimized, 35.4° crystal). The mean plane data (Table VI) show the deviations are consistent with the expected (attractive) effects of hydrogen bonds (Table V).

(b) The Δ - β_1 -(RS)-[Co(trien)(gly)]²⁺ Cation. The major steric repulsions for this isomer occur within the β -trien ligand: H(5)···H(17), 2.10 Å, 0.7 kcal mol⁻¹; H(8)···H(15), 2.13 Å, 0.6 kcal mol⁻¹, Table IV and Figure 4. As might be anticipated, this results in bond angle bending at the metal ion: N(12)-Co(11)-N(14) 97.1°, 0.8 kcal mol⁻¹ (minimized), 96.0 (3)°, 0.5 kcal mol⁻¹ (crystal). As for the Δ - β_1 -RR isomer, bond angle strain is evident at the trien "planar" secondary atom, C(12)-N(12)-C(13), 114.9°, 0.7 kcal mol⁻¹ (minimized), 117.8(7)°, 1.5 kcal mol⁻¹ (crystal). The Co-N(12) bond length is shortened in the calculated structure (1.946 Å) although less than in the crystal (1.911 (7) Å), 0.2 kcal mol⁻¹.

The torsion angle agreement is again good, but the largest deviations between calculated and observed values occur for the torsion angles about the C(12)-N(12), N(12)-C(13), and C(13)-C(14) bonds. For these bonds the crystal structure dihedral angles are smaller than those calculated. Hydrogen bonds in the crystal would not be expected to cause these deviations in contrast to some in the Δ - β_1 -RR isomer above. Examination of Figure 4 suggests that further shortening of the Co(11)-N(12) bond, as in the crystal, would increase the major nonbonding interactions H(5)···H(17) and H(8)···H(15). This would flatten the trien chelate

(35) W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).

rings further, thus reducing the appropriate torsion angles. It seems that a choice of one strain-free Co–N bond length (1.95 Å) can lead to minor disagreements. Differences between crystal and minimized torsion angles about C(17)–C(18) and N(15)–C(17) bonds, which reflect puckering at N(15) of the glycinate group (Table V), may result from hydrogen bonds in the former approximately normal to the N(15)–C(17)–C(18)–O(12) plane (see Figure 2).

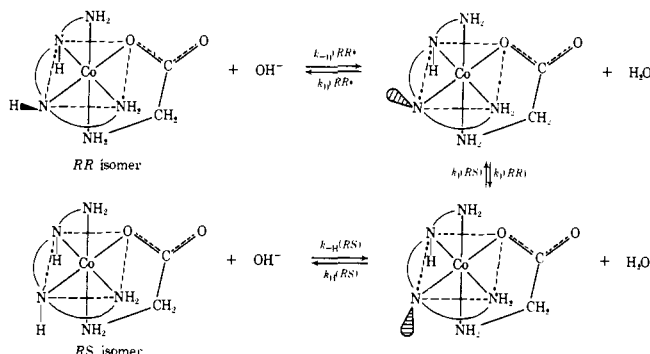
For both Δ - β_1 -*RR* and Δ - β_1 -*RS* isomers, calculations were carried out on both conformations of the slightly puckered amino acid chelate ring. Interconversion between these two conformations involves rotation through a small torsion angle for the N(5)–C(7) and N(15)–C(17) bonds and hence passage over a small energy barrier, so presumably interconversion at room temperature would be rapid. The minimization method calculated the same minimum strain energy configurations for Δ - β_1 -*RR* and Δ - β_1 -*RS* forms from trial coordinates of both possible glycine chelate conformations. However, the difference between the initial and final minimized strain energies after interconversion was only 0.1 \rightarrow 0.4 kcal mol⁻¹. These small energy differences for quite wide variations in the glycinate ring geometry allow the ring to deform easily to accommodate the different modes of H-bonding of the two isomers in the crystal.

Relative Stabilities of Δ - β -[Co(trien)(gly)]²⁺ Isomers. The total strain energy difference between Δ - β_1 -*RR* and Δ - β_1 -*RS* isomers is calculated as 0.8 kcal mol⁻¹ in favor of the *RR* isomer, Table X. Bond angle and torsional terms make the most significant contributions to the energy difference. The measured ΔH difference, obtained from the temperature dependence of the equilibrium constant, is <0.3 kcal mol⁻¹, which is in reasonable agreement with the calculated value at this stage of the development of the force field. Furthermore, ΔG_{25}° is about 0.1 kcal mol⁻¹ in favor of the *RR* isomer. In a following paper³⁴ describing the analogous Δ - β_2 -*RR* and Δ - β_2 -*RS* ions, the comparable energy difference for the structures of minimum energy is calculated at 3.5 kcal mol⁻¹ in favor of the Δ - β_2 -*RR* isomer, and this is compared with measured ΔG_{25}° and ΔH_{25}° (calorimetric) values of 1.3 and 1.1 kcal mol⁻¹, respectively. Thus the calculations correctly predict for both the β_1 and β_2 systems that the *RR* isomer is more stable, but by a smaller margin for the β_1 isomers. This smaller margin is due to the increased strain in the β_1 -*RR* isomer relative to the β_2 -*RR* isomer and decreased strain for the β_1 -*RS* isomer relative to the β_2 -*RS* isomer. Increased bond angle and torsional strain occur for the β_1 -*RR* isomer as a result of steric interaction between hydrogen atoms on the amino acid nitrogen and β -trien carbon atoms.

H-Exchange and Inversion. H-Exchange for the protons at 6.5 and 7.2 ppm in the β_1 -(*RR* + *SS*) and β_1 -(*RS* + *SR*) isomers, respectively, follows the rate law $k_{\text{obsd}} = k(\text{OD}^-)$ with similar values of $k = 8.2 \pm 0.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 34.3°. These protons are assigned to the planar NH group on the basis of their integrated intensity, characteristically low field position and chemical shift difference in the two isomers. They are also more than 10² times more labile than the remaining secondary NH proton and the primary NH₂ protons of triethylenetetramine. When compared to the second-order rate constants for mutarotation $\sim 10^3 \text{ M}^{-1} \text{ sec}^{-1}$

at 25° the retention factor for proton exchange over inversion is 10⁶. A similar high retention factor was observed for proton exchange and racemization of *sym*-[Co(trien)N₃]²⁺ and was ascribed to the necessity to invert the conformation of the two coupled chelate rings synchronously with the N center.³⁶ The same argument holds for the present ions. For the [Co(NH₃)₄(N-Meen)]³⁺ and *trans,trans*-[Co(NO₂)₂(N-Meen)₂]⁺ ions, where only one conformational ring inversion is required to invert the N center, a value of 10⁴–10⁵ is observed.³⁷

These results are consistent with the mechanism given below involving a common deprotonated intermediate for exchange and inversion.



Since k_{-H} and k_H are all much greater than $k_{I(RS)}$ or $k_{I(RR)}$ and since $k_{-H} \ll k_H$ the derived rate law for mutarotation takes the form

$$\frac{k_{\text{obsd}}}{[\text{OH}^-]} = \left(\frac{k_{I(RS)}k_{-H(RS)}}{k_H(RS)} + \frac{k_{I(RR)}k_{-H(RR)}}{k_H(RR)} \right)$$

No evidence exists for significant concentrations of the deprotonated species even in 1 M OH⁻ and the deprotonated amine is therefore a stronger base than OH⁻; K_b is probably between 1 and 10².³⁸ Under such conditions reprotonation should be close to diffusion control, i.e., $k_H \approx 10^9$ – 10^{10} sec^{-1} ^{39,40} for both ions. Also since the H-exchange rate constants for the two ions are approximately equal it follows that $k_{-H(RS)} \approx k_{-H(RR)}$. Using the value of the equilibrium constant

$$K = \frac{[RR]}{[RS]} = \frac{k_{-H(RS)}k_{I(RS)}k_H(RR)}{k_{-H(RR)}k_{I(RR)}k_H(RS)} = 1.22$$

we deduce $k_{I(RS)} \approx k_{I(RR)}$ and the deprotonated diastereoisomers have similar stability. The estimate for their interconversion using the estimated $\text{p}K_a$ and the mutarotation rate constant is 10³–10⁵ sec⁻¹ which is similar to that deduced for other Co(III) amine complexes.³⁸

Supplementary Material Available. A table of $10|F_o|$ and $10|F_c|$ for Δ - β_1 -(*RR* + *RS*)-[Co(trien)(gly)]₂·0.5H₂O will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1713.

(36) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).

(37) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 825 (1967).

(38) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6028 (1968).

(39) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

(40) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965).