Structural and Chemical Studies Defining the Configurational Isomers of the Triethylenetetra-amineglycinatocobalt(III) Ion, $[Co(trien)(gly)]^{2+}$

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Summary The configurations of $\Delta(-)_{589}$-β_1-*RR*† and $\Delta(-)_{589}$-β_1-*RS* $[Co(trien)(gly)]^{2+}$, and of β_2-(*RR,SS*)$[Co(trien)(gly)]^{2+}$ in two conformational modifications, have been determined by *X*-ray techniques; the structures and the mutarotation and equilibrium studies allow all the β_1,β_2, and α configurations to be assigned, and the results are correlated with calculations on the structures of minimum energy and with a calorimetric study.

THE interest shown recently in $[Co(trien)(aa)]^{2+}$ complexes[1] (trien = triethylenetetra-amine; aa = amino acid anion) prompts us to report on one of the simplest of these systems, namely $[Co(trien)(gly)]^{2+}$ (gly = glycinato). The geometrical arrangement of the trien ligand about the cobalt centre, and the diastereoisomers arising from asymmetry about the Co and secondary N atoms of trien allow ten configurational isomers. All of these have now been obtained as crystalline salts, and this communication gives preliminary results of two structural analyses and some chemistry which allows an assignment of the configurational relationships for all the isomers.

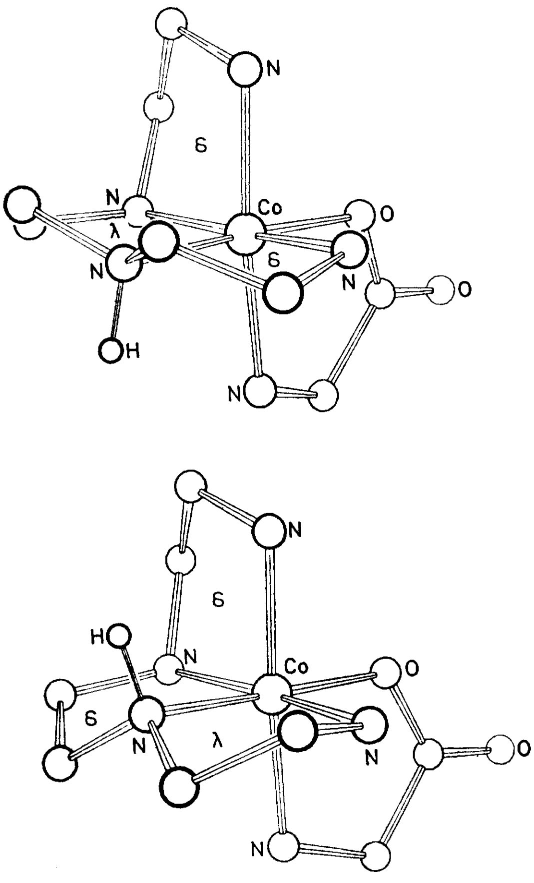

FIGURE 1. *Perspective view of cations in crystals of* $\Delta(-)_{589}$-β_1-$[Co(trien)(gly)]I_2,0{\cdot}5H_2O$. Top: Δ-β_1-*RS*-$[Co(trien)(\delta\lambda\delta)(gly)]^{2+}$; Bottom: Δ-β_1-*RR*-$[Co(trien)(\delta\delta\lambda)(gly)]^{2+}$.

For $\Delta(-)_{589}$-β_1-$[Co(trien)(gly)]I_2,0{\cdot}5H_2O$ reported previously,[2] the crystals are triclinic, space-group $P1$, with one *RR* and one *RS* cation in the unit cell, (Figure 1); $a = 8{\cdot}544(2)$, $b = 8{\cdot}475(2)$, $c = 12{\cdot}351(3)$ Å; $\alpha = 101{\cdot}67(2)$, $\beta = 91{\cdot}89(2)$, $\gamma = 109{\cdot}98(2)°$; $D_m = 2{\cdot}18 \pm 0{\cdot}03$ g cm^{-3}, $Z = 2$, $D_c = 2{\cdot}20$ g cm^{-3}. Intensity data were collected using a Hilger and Watts four-circle automatic diffractometer and Zr-filtered Mo-K_α *X*-radiation. Fourier analysis and full-matrix least-squares refinements using 4126 independent reflections established the co-ordinates for all atoms; conventional *R* factor 2·9%, (inverted configuration 3·6%). Both cations have been separated by ion-exchange chromatography and crystallized as the iodide salts: $\Delta(-)_{589}$-β_1-*RR*-$[Co(trien)(gly)]I_2,2H_2O$ ($\epsilon_{489} = 167$, $[\alpha]_{589} = -323°$ in 1M-NH_4Cl); $\Delta(-)_{589}$-β_1-*RS*-$[Co(trien)(gly)]I_2,2H_2O$ ($\epsilon_{492} = 180$, $[\alpha]_{589} = -305°$, 1M-NH_4Cl). Mutarotation ($RR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RS$) at the secondary N centre for both isomers was followed spectrophotometrically and polarimetrically over the pH range 7·5—8·7 giving a rate law $k_{obs} = (k_1 + k_{-1})[OH^-]$ with $k_1 + k_{-1} = 1{\cdot}11 \pm 0{\cdot}05 \times 10^3 M^{-1} s^{-1}$ (25°, μ= 1M-$NaClO_4$, Tris buffer). The equilibrium mixture contained 46 ± 2% and 54 ± 2% of the $\Delta(-)_{589}$-β_1-*RS* and *RR* isomers respectively, whence $\Delta G < 0{\cdot}1$ kcal mol^{-1}. The crystal-structure distortions from normal bond angles and torsion angles were also predicted by calculations of the structure of minimum energy[3] and the calculated energy difference of 1·1 kcal mol^{-1} also favoured the *RR* form.

Crystals of β_2-$[Co(trien)(gly)]Cl_2,H_2O$,[2] are monoclinic, space-group $P2_1/c$, $a = 8{\cdot}349(3)$, $b = 14{\cdot}927(8)$, $c = 24{\cdot}313(9)$ Å, $\beta = 103{\cdot}58(3)°$, $D_m = 1{\cdot}65 \pm 0{\cdot}03$ g cm^{-3}, $Z = 8$, $D_c = 1{\cdot}66$ g cm^{-3}. Intensity data were collected as described above and all 38 non-hydrogen atoms have been located. Full-matrix least-squares refinements using 1726 independent reflections resulted in a conventional *R* factor of 11·7%. In this case two independent $[Co(trien)(gly)]^{2+}$ cations are present in the unit cell, both having the same configuration about the secondary N centres but with mirror image conformations for the apical five-membered ring (Figure 2). This is the first example among several crystal structures of triethylenetetra-amine complexes where two different chelate ring conformations for the same configurational isomer have been observed, and it limits an

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† The IUPAC nomenclature (*Inorg. Chem.*, 1970, **9**, 1) is confined to the Co(trien) moiety. *R* and *S* refer to the configuration about the secondary amine N atoms.

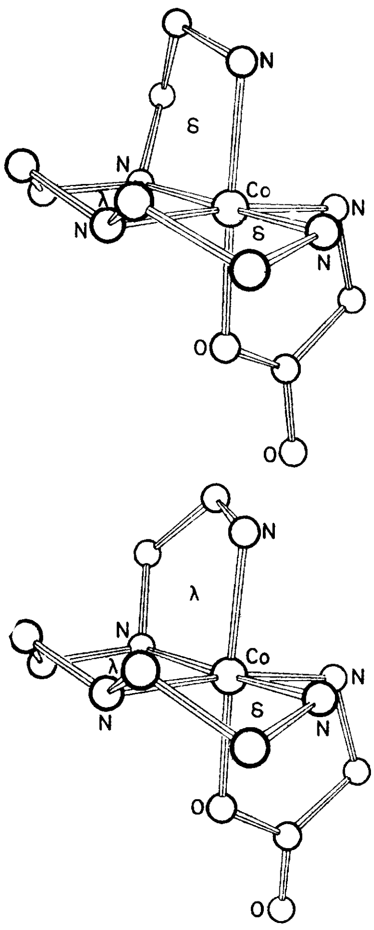

FIGURE 2. *Perspective view of cations in crystals of racemic* β_3-[Co(trien)(gly)]Cl_2,H_2O. Top: Δ-β_2-*RS*-[Co(trien)($\delta\lambda\delta$)(gly)]$^{2+}$; Bottom: Δ-β_3-*RS*-[Co(trien)($\lambda\lambda\delta$)(gly)]$^{2+}$.

earlier suggestion concerning probable rigidity in such chelates.[4] The conformations of the fused chelate rings in the same co-ordination plane are largely decided by the configuration about the central secondary N centre, but it appears that the apical chelate ring is more flexible and able to adopt either δ or λ conformations. The complex was resolved using Ag–SbO–(+)-tartrate and the absolute configurations of the $\Delta(-)_{589}$-β_2-*RR* and $\Lambda(+)_{589}$-β_2-*SS*-[Co(trien)(gly)]I_2,H_2O complexes ($[\alpha]_{589} = \pm 205°$; $\epsilon_{478} = 130$, $\epsilon_{347} = 145$ in 1M-NH_4Cl, pH 4) assigned by comparison of o.r.d. and c.d. spectra with those of the similar Δ-β_2-*RRS*-[Co(trien)(*S*-pro)]I_2[5] and Λ-β_2-*SSS*-[Co(trien)(*S*-pro)]I_2[6] complexes (pro = proline anion).

Equilibration of racemic β_2-(*RR* + *SS*)-[Co(trien)(gly)]I_2 at pH 10 and ion-exchange chromatography resulted in the isolation of β_2-(*RS* + *SR*)-[Co(trien)(gly)]$(ClO_4)_2$ ($\epsilon_{484} = 147$, $\epsilon_{348} = 166$ in 1M-NH_4Cl, pH 4). This complex was resolved using $(+)_{546}$-Na[Co(edta)] and both $\Delta(-)_{589}$-β_2-*RS* and $\Lambda(+)_{589}$-β_2-*SR* [Co(trien)(gly)]Cl_2,1·5H_2O isolated $[\alpha]_{589} = -227$ and 232° respectively). The optical purity and configurational relationships with the corresponding $\Delta\beta_2$-*RR* and $\Lambda\beta_2$-*SS* isomers were confirmed by mutarotation studies. Equilibration of these isomers over the pH range 7·8—9·4 (glycine buffers, 1M-$NaClO_4$) gave $K = 9{\cdot}0$ at 25° for $SR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SS$; this value is slightly temperature and ionic strength dependent, but pH independent. Spectrophotometric rate data followed the rate law $k_{obs} = (k_1 + k_{-1})[OH^-]$ with $k_1 + k_{-1} = 3{\cdot}87 \pm 0{\cdot}02 \times 10^{-2} M^{-1} s^{-1}$ at 25°. The enthalpy change substantially for the process $SR \rightarrow SS$ was measured as $\Delta H_{25°} = 1{\cdot}2 \pm 0{\cdot}1$ kcal mol^{-1} in glycine buffer ($\mu = 0{\cdot}1$) at pH 9 using a LKB calorimeter and the isolated racemic β_2-(*RS* + *SR*) iodide salt.‡ This value is close to that for $\Delta G_{25°}$ and shows that the entropy difference between the ions is small.

The crystal-structure distortions for the β_2-*RR* cation were also duplicated by a calculation of the structure of minimum energy,[3] and a similar calculation for the β_2-*RS* cation gave an energy difference of 3 kcal mol^{-1} in favour of the *RR* form. This value has the same sign as the measured $\Delta H_{25°}$ and $\Delta G_{25°}$, and it offers some hope that similar calculations for other complexes of this type may be fruitful in obtaining energy differences accurately.

These characterisations define eight of the ten possible isomers (excluding conformational isomers) in this system, Δ*RR*, Λ*SS*, Δ*RS*, Λ*SR*, for the β_1 and β_2 configurations all of which have been isolated. The remaining two isomeric forms Δ-(*SS*) and Λ-(*RR*) α-[Co(trien)(gly)]I_2 have been prepared from $(-)_{589}$ and $(+)_{589}$-α-[Co(trien)(glyOEt)-Cl](ClO_4)(Cl) using Hg^{2+} to remove the co-ordinated Cl^- ion ($[\alpha]_{589} = \pm 359°$, $\epsilon_{481} = 91$, $\epsilon_{347} = 121$ in 1M-NH_4Cl). These isomers are optically stable in alkaline solutions (pH < 12) and were recovered unchanged after three days at pH 10. In this instance the asymmetry about the secondary N atoms is controlled by the configuration of the quadridentate about cobalt. Linkages between adjacent N atoms are not long enough to allow inversion at the secondary N centres unless the coupled chelates are in the same plane. The absolute configurations have been assessed as $\Lambda(+)_{589}$-α-*RR* and $\Delta(-)_{589}$-α-*SS*-[Co(trien)(gly)]-I_2 by comparisons of o.r.d. and c.d. spectra with $\Delta(-)_{589}$-α-*SS*-[Co(trien)NH_3Cl]$(NO_3)_2$[7] and related disubstituted [Co(trien)X_2]$^{n+}$ ions of known absolute configuration.[8] A detailed account of this work is in preparation.

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