The Crystal Structure of Two Diastereoisomeric β_2-Cobalt(III)–Triethylenetetramine-*S*-proline Complexes

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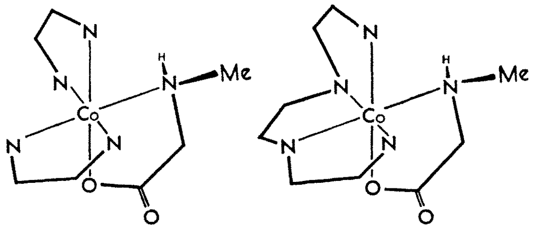
Summary The crystal structures of two diastereoisomeric β_2-cobalt(III)–triethylenetetramine-*S*-proline complexes are presented and the relative stabilities of the two complexes are exemplified by bond angle distortions in the less stable isomer.

THE degree of stereospecificity for the coordination of *N*-methylglycine (sarcosine), *S*-alanine and *S*-valine has recently been examined for some cobalt(III) triethylenetetramine and bis(ethylenediamine) complexes.[1–5] It was deduced that the configuration about the asymmetric N-centre in sarcosine was determined by the steric interactions between the chelate rings and the methyl group, and complete stereospecificity, for a given configuration about the cobalt ion, was established for the structures shown in Figure 1.

The alternative configuration about cobalt requires the mirror image configuration at the asymmetric N-centre. The possibility of detecting the less stable configuration at the *N*-methyl centre was eliminated by the lability of the N-proton under the conditions for the preparations.

These factors lead to the possibility of a completely stereospecific synthesis if the N-centre can be forced to adopt a fixed configuration which directs only one configuration for the cobalt centre. This situation is realised in *S*-proline where a five-membered ring couples the asymmetric C and N centres. A given configuration about C allows only one configuration for the co-ordinated secondary N group. The protons on the asymmetric C and N atoms of the amino-acid must be *cis* relative to the plane of the ring. Using this rationale we expected to prepare exclusively L$(-)_{589}$-β_2-*RRS*-[Co(trien)(*S*-Pro)]$^{2+}$ by reacting *S*-proline with β-[Co trien (OH)(OH$_2$)]$^{2+}$. However, the synthesis conducted under kinetically controlled conditions showed little stereospecificity.[6] Two iodide salts, fractionated from the reaction product, gave o.r.d. and c.d. curves which indicated that they were catoptric in relation to the configuration about the cobalt centre.



(I) (II)

FIGURE 1. (I) L$(-)_{589}$-*S*-[Co en$_2$scarocinato]$^{2+}$ *ion* (II) L$(-)_{589}$-β_2-*RRS*-[Co triensarcosinato]$^{2+}$ *ion* (*en = ethylenediamine, trien = triethylenetetramine*).

The foregoing analysis, however, indicates that one isomer should be considerably more stable than the other. In fact, in one instance the non-bonded interactions between trien and the proline ring should be almost prohibitive. To examine these interactions and also to remove any doubts arising from the several other possible sources of isomerism, crystal-structure analyses of both complexes were carried out.

Crystals of L$(-)_{589}\beta_2$(triethylenetetramine-*S*-proline) cobalt(III) diiodide dihydrate, L$(-)_{589}$-β_2-[Co trien (*S*-Pro)]I$_2$, 2H$_2$O, are orthorhombic; $a = 9{\cdot}12$, $b = 14{\cdot}43$, $c = 14{\cdot}90$ Å, $D_m = 2{\cdot}03 \pm 0{\cdot}03$ g. cm.$^{-3}$, $Z = 4$, $D_c = 2{\cdot}06$ g. cm.$^{-3}$; space group $P2_12_12_1$; 1828 *X*-ray reflections (408 unobservably weak). The structure has been refined by full-matrix least-squares incorporating anisotropic temperature factors to a residual $R = 0{\cdot}066$ for the observed reflections. In the final cycle of refinement no parameter shift was greater than 0·5 standard deviations.

Crystals of D$(+)_{589}$-β_2-(triethylenetetramine-*S*-proline) cobalt(III) tetrachlorozincate, D$(+)_{589}$-β_2-[Co trien -*S*- Pro)]-ZnCl$_4$, are monoclinic; $a = 7{\cdot}01$, $b = 15{\cdot}58$, $c = 9{\cdot}66$, $\beta = 109{\cdot}9°$, $D_m = 1{\cdot}76 \pm 0{\cdot}02$, $Z = 2$, $D_c = 1{\cdot}76$ g. cm.$^{-3}$; space group $P2_1$; 1785 *X*-ray reflections (91 unobservably weak). In the last cycle of full-matrix least-squares refinement, incorporating anisotropic temperature factors and hydrogen atoms in calculated positions, the maximum parameter shift was less than 0·4 standard deviations; and the residual $R = 0{\cdot}055$ for the observed reflections.

The configuration of the two β_2-[Co trien (*S*-Pro)]$^{2+}$ ions (Figure 2) are diastereoisomeric: catoptric with respect to the arrangement of the chelates about cobalt but with the same configuration for both proline residues. Both complexes have the β_2 configuration of the trien ligand as predicted and an analysis of the Bijvoet pairs for the L$(-)_{589}$-β_2-*RRS*-[Co trien (*S*-Pro)]$^{2+}$ isomer confirmed the assignment of absolute configuration to proline and also to the complexes.[7]

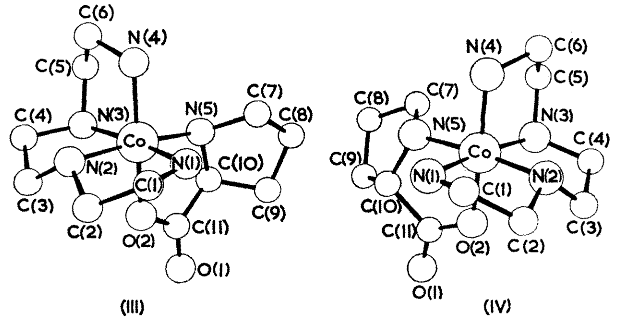


FIGURE 2. (III) L$(-)_{589}$-β_2-*RRS*-[Co trien(*S*-Pro)]$^{2+}$ *ion* (IV) D$(+)_{589}$-β_2-*SSS*-[Co trien(*S*-Pro)]$^{2+}$ *ion*.

The relative stability of the two isomers is almost certainly associated with abnormal angles involving the metal and the asymmetric N centre of proline. The angular distortions in D$(+)_{589}$-β_2-*SSS*-[(Co trien (*S*-Pro)]$^{2+}$ involve N-5–Co–N-3 (99·2°, $\sigma = 0{\cdot}4°$) and N-5–Co–N-1 (90·9°, $\sigma = 0{\cdot}4°$). The corresponding angles in L$(-)_{589}$-β_2-*RRS*-[Co trien (*S*-Pro)]$^{2+}$ [N-5–Co–N-3 (94·2°, $\sigma = 0{\cdot}9°$) and N-5–Co–N-1 (94·6°, $\sigma = 0{\cdot}9°$)] are significantly different. The increased N-5–Co–N-3 angle (and associated decrease in the N-5–Co–N-1 angle) in the "unstable" form minimises the non-bonded repulsions between the proline ring and the Co–N-4–C-6–C-5–N-3 chelate ring. Using the crystallographic co-ordinates, H-atom positions were calculated and a distance analysis indicated that no significant non-bonded interactions occur within the complex. Clearly, the energy required to distort the co-ordination angles must be considerably less than non-bonded repulsion energies implied by use of the Dreiding models. These factors are also relevant to the formation of the supposed least stable form since in the regular octahedral geometry the non-bonded interactions for the entry of the proline would be prohibitive. In the transition state significant angular distortion can be achieved for a relatively small energy change and the rate of formation of the less and more stable species need not be too different.

The relative degrees of distortion in the two species confirm the prediction that D$(+)_{589}$-β_2-*SSS*-[Co trien (*S*-Pro)]$^{2+}$ is less stable than L$(-)_{589}$-β_2-*RRS*-[Co trien (*S*-Pro)]$^{2+}$ but interconversion of the two isomers was not achieved. In basic media, H exchange at both the N and C asymmetric centres occurred but mutarotation was not obsevred before loss of the amino-acid anion. The slow rate of interconversion relative to ions such as [Co en $_2$(*S*-Val)]$^{2+}$ and [Co en $_2$(*S*-Ala)]$^{+\,5}$ is attributed to the need for

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† The nomenclature used is as follows: *R* and *S* designate the asymmetry about the "angular" and "planar" asymmetric N atoms of triethylenetetramine (ref. 3) and the secondary N atom of proline in that order and follow the rules suggested by C. K. Ingold, V. Prelog, and R. S. Cahn (*Angew. Chem. Intern. Edn.*, 1966, **5**, 385, and accepted by I.U.P.A.C).

deprotonation at both N and C centres before mutarotation is permitted. The concentration of this doubly deprotonated species must be exceedingly small.

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