

A Case of Kinetic Stereoselectivity and its Origin

By J. H. DUNLOP,^a R. D. GILLARD,^b N. C. PAYNE,^b and G. B. ROBERTSON^c

(^a*Technische Hochschule, München, Germany*, ^b*The University of Kent at Canterbury*, ^c*The University of Warwick*)

KNOWN stereoselective effects¹ in complexes of metal ions with asymmetric ligands are thermodynamic in origin, and such effects in complexes of α -amino-acids are, in general, small.² However,

when L-glutamic acid (L-glut H₂) reacts with racemic carbonatobisethylenediaminecobalt(III) perchlorate, we find that the D-enantiomer of the bisaquobisethylenediaminecobalt(III) ion (formed from

the carbonato-complex in the acid conditions) reacts much more rapidly than does the L-bis-aquo-complex. Further, the first-formed diastereoisomer, D-[Co en₂ (L-glut)]ClO₄ is much less soluble in water than is L-[Co en₂ (L-glut)]ClO₄·H₂O, and may be crystallised from the mixture optically pure.

The deep orange crystals of D-[Co en₂ (L-glut)](ClO₄) are orthorhombic, space group *P*2₁2₁2₁, with *a* = 13.54, *b* = 12.08, *c* = 10.06; *Z* = 4 molecules per unit cell; *D*_c = 1.79; *D*_m = 1.79 (by flotation). Details of the crystal and molecular structure have been determined from three-dimensional X-ray diffraction data, and refined by the method of least squares. (*R* is at present 0.1 for 1085 independent reflections.) The stereochemistry of the cation together with metal-ligand bond distances is shown in Figure 1. Mean standard errors in these bond distances, estimated by inversion of the block diagonal least-squares matrix, are 0.02 Å for Co-N, and 0.015 for Co-O. The following structural features are noteworthy.

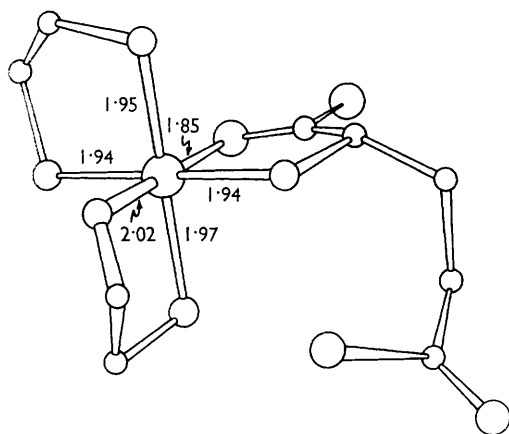


FIGURE 1. The D-[Co en₂(L-glut)]⁺ cation.

First, the polar side-arm of the L-glutamate ion interacts with an N-H group of an ethylenediamine chelate ring. The stereoselectivity in solution may well arise from this three-point attachment, which is sterically favourable only for the ion D-[Co en₂ (L-glut)]⁺ and not for L-[Co en₂ (L-glut)]⁺.

Secondly, the known absolute configuration of the asymmetric carbon atom in the L-glutamate chelate ring enables us to fix the absolute configuration of the whole molecule, which is D-[Co en₂ (L-glut)](ClO₄). By comparison of the circular dichroism spectrum of this isomer (see Figure 2) with that of any other optically active

complex of the type [Co en₂(α-amino-acid)]ⁿ⁺, the absolute configuration of the latter may be deduced.

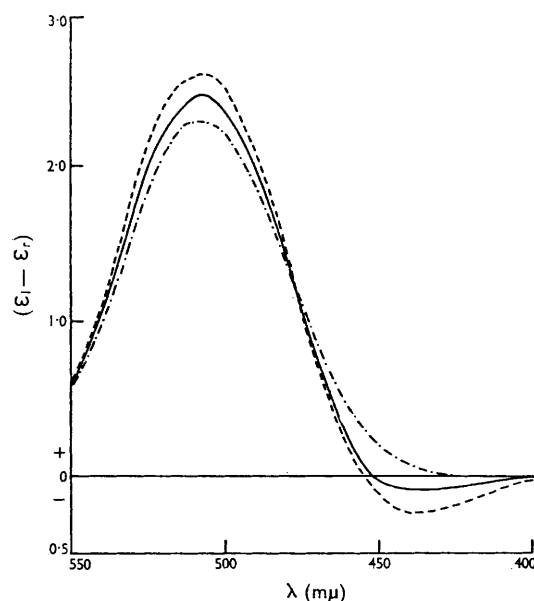
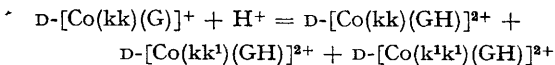


FIGURE 2. Circular dichroism spectra for D-[Co en₂ (L-glut)]ClO₄

----- pH 3; — pH 6; - · - · - pH 9.

A third, more subtle, point arises. The *cis*-complexes (Co en₂X₂) may exist (using the nomenclature³ of Corey and Bailar) as three pairs of enantiomers; D-[Co(kk)X₂] and L-[Co(k¹k¹)X₂]; D-[Co(kk¹)X₂] and L-[Co(k¹k)X₂]; and D-[Co(k¹k¹)X₂] and L-[Co(kk)X₂]. In the cases where X = Cl, etc., the various D-conformers will have very nearly the same energy, but in the present case, the intramolecular hydrogen bonding in solution will stabilise one conformation (presumably *kk*, since this is the conformation found in the solid). The variation of the circular dichroism shown in Figure 2 may possibly be explained in terms of a conformational equilibrium such as



the left-hand side being favoured by alkali, the right-hand side by acid, which will break the critical hydrogen bond between the γ -carboxylate of the glutamate ion, and the chiral nitrogen of the ethylenediamine ring.

Rather similar stereoselective effects arise with (+)-tartaric acid as a ligand, but not with α -alanine or with lactic acid, further supporting the

importance of three-point attachment as a source of stereoselectivity in metal complexes.

(Received, November 1st, 1966; Com. 843.)

¹ R. D. Gillard, "Progress in Inorganic Chemistry", Vol. 7, ed. F. A. Cotton, Interscience, 1966, p. 215 and references therein.

² J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, 1965, 6531.

³ E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.