The Absolute Configuration of the $(+)_{589}$-*trans*-Dichlorotriethylenetetraminecobalt(III) Ion

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IT has been shown recently[1] that the co-ordination of L-3,8-dimethyltriethylenetetramine, prepared from L-alanine, to cobalt(III) leads to the formation of $(+)_{589}$-*trans*-[Co(L-3,8-dimetrien)Cl_2]Cl, (I), in preference to the possible *cis*-isomers. The complex has a substantial optical rotatory power which was ascribed to the vicinal effect of the optically active ligand.[1] However, we find that, although the unsubstituted ligand, triethylenetetramine, is not optically active, the circular dichroism spectrum of the $(+)_{589}$-*trans*-[Co(trien)Cl_2]$^+$ ion (II) is similar in form and sign to that of (I) (Figure), suggesting that these complex ions have the same absolute configuration and that the optical rotatory power has an analogous origin in the two cases.

The dissymmetry of the complex ion (II), obtained by the rearrangement of (+)-*cis*-β-[Co(trien)Cl_2]ClO_4 in acidic methanol under reflux,[2] arises from the asymmetry of the co-ordinated secondary nitrogen atoms of the ligand, and from the chelate ring conformations, which are dependent upon the particular orientation of the secondary N–H bonds. The optical stability of the ion (II) is due to the inertness of the protons of these N–H bonds to exchange in dilute aqueous acid. In addition to the assymmetric carbon atoms of the ligand, similar elements of dissymmetry exist in the ion (I) and the form of the circular dichroism spectra (Figure) suggest that the chiral elements common to (I) and (II) are the major determinants of the rotatory power of these complex ions.

In the complex (I) the chelate ring conformations and the orientations of the secondary N–H bonds are governed by the steric requirements of the methyl groups. Numerous studies[3] of methyl substitution in cobalt(III) ethylenediamine ring systems show that the conformation in which the methyl group is most equatorial is preferred. Preliminary calculations indicate that the Cl · · · C and Cl · · · H non-bonded interactions are prohibitive in (I) if the methyl group is axial ($>$ 14 kcal./mole less stable than the equatorial form). As the ligand is derived from L-alanine,[1] the asymmetric carbon atoms of L-3,8-dimethyltriethylenetetramine have the *S*-configuration,[4] which requires the configuration (I) for the $(+)_{589}$-*trans*-$[Co(L\text{-}3,8\text{-}dimetrien)Cl_2]^+$ ion if the methyl groups are equatorially disposed in each of the substituted chelate rings. The corresponding circular dichroism bands of (I) and $(+)_{589}$-*trans*-$[Co(trien)Cl_2]^+$ have the same sign (Figure), which suggests the analagous configuration (II) for the latter complex ion.

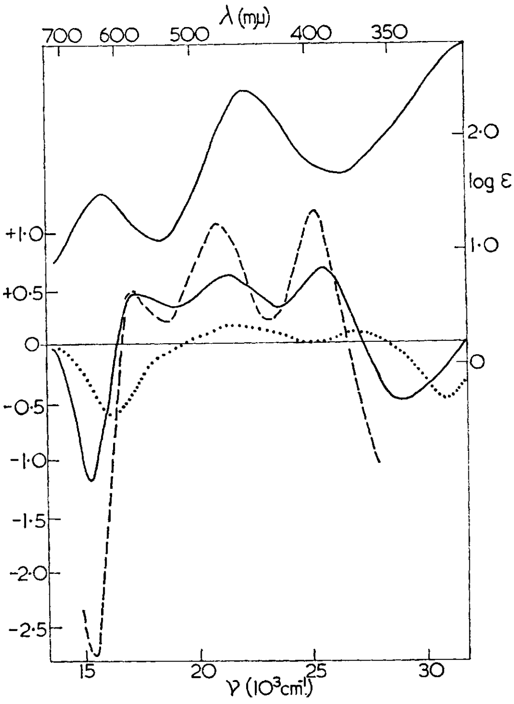
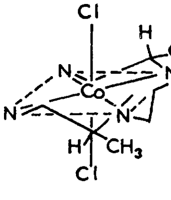
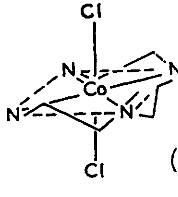


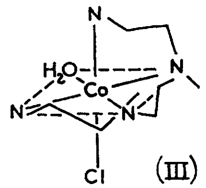
FIGURE. *The absorption spectrum (upper curve) and the circular dichroism (lower curve) of* $(+)_{589}$-*trans*-$[Co(trien)Cl_2]Cl$ (II) (——), *and the circular dichroism of* $(+)_{589}$-*trans*-$[Co(L\text{-}(+)\text{-}3,8\text{-}dimetrien)Cl_2]Cl$ (I) (— —), *and* $(+)_{546}$-*trans*-$[Co(+pn)_2Cl_2]Cl$ (IV) (···) *in aqueous solution.*



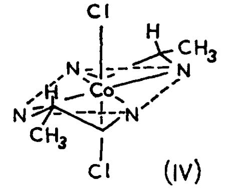
(I)



(II)



(III)



(IV)

These configurational assignments are supported by two additional and independent correlations. Firstly, it has been shown[2] that the complex ion (II) undergoes acid hydrolysis stereospecifically to the $(+)_{589}$-*cis*-β-$[Co(trien)(H_2O)Cl]^{2+}$ ion, which has been assigned the D-configuration (III) from a comparative study[5] of the Cotton effects given by the α- and β-*cis*-$[Co(trien)X_2]^{n+}$ ions and the corresponding *cis*-$[Co(en)_2X_2]^{n+}$ ions ($X = Cl$, H_2O, CO_3, NO_2).[6–8] Secondly, the circular dichroism spectra of the complexes (I) and (II) resemble that of the $(+)_{546}$-*trans*-$[Co(+pn)_2Cl_2]^+$ ion (Figure), which is known to have the configuration (IV) from a *X*-ray diffraction study of the enantiomeric complex.[9] The asymmetric carbon atoms in the complex (IV), as in the ion (I), have the *S*-configuration,[4] since (+)-propylenediamine is related chemically to L-alanine,[10] and the equatorial disposition of the methyl groups gives the chelate rings of the complex (IV) a preferred *Psc* (plus-synclinal)[4] conformation. In fact the *Psc* conformation of the *trans*-disposed chelate rings is the only element of dissymmetry common to the complex ions (I), (II), and (IV), and it is probable that this chiral element makes an important contribution to the rotatory power of these complexes.

The chelate ring joining the secondary nitrogen atoms in the complexes (I) and (II) has the enantiomeric *Msc* (minus-synclinal)[4] conformation and it imposes a major distortion from tetragonal symmetry upon the chromophore of these ions. The circular dichroism spectra show (Figure) that the effective ligand field has D_4 symmetry in the complex (IV), whereas the corresponding symmetry is only C_2 in the cases of the ions (I) and (II). All three complexes give a positive circular dichroism and at 21,000—22,000 cm.$^{-1}$, which is due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, where xy is the plane of the four nitrogen atoms and the metal ion, since the $A_{1g} \rightarrow T_{1g}$ band of the octahedral CoN_6 chromophore lies in this region. The other components of the transition to the T_{1g} octahedral state remain degenerate in D_4 symmetry but they are split in a C_2 ligand field, and it is found (Figure) that whilst the ion (IV) gives a single negative circular dichroism band in the red at 16,300 cm.$^{-1}$ the complexes (I) and (II) give two bands, one negative and the other positive, at 15,400 and 17,500 cm.$^{-1}$, respectively.

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