The Crystal Structure and Absolute Configuration of a Novel Tetradentate Ligand in a Cobalt(III) Ion Complex

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Summary The absolute configuration of the title complex has been shown by *X*-ray anomalous dispersion to be *trans*-[dichloro-{*NN'*-bis-(*S*-2-amino-3-phenylpropyl)-*trans*-*R*-cyclohexane-1,2-diamine δλδ}cobalt(III)] perchlorate.

RECENTLY, a new tetradentate ligand with four optical centres having two different relative configurations has been reported.[1] In a Co^{III} complex, the ligand is strongly stereoselective for the *trans*-isomer (Figure 1), and the only other isomer observed, the L-*cis*-β, readily isomerizes to the *trans*-geometry. Initially, a D-*cis*-α-isomer was predicted by analogy with LL-αα'-Me_2(trien) which complexes with Co^{III} to give 95% D-*cis*-α, 4% L-*cis*-β, and 1% *trans*-isomers.[2] As in the new ligand, the backbone of this (trien) molecule has a configuration opposite to that in the two arms, both of which have the same configuration. We report here the three-dimensional *X*-ray structure study of the perchlorate

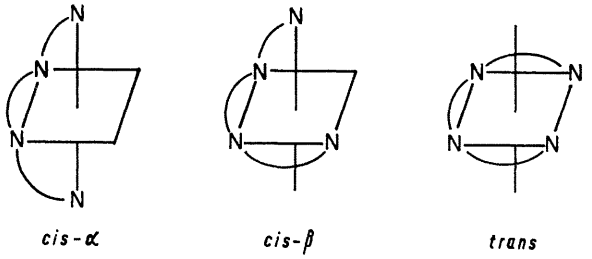

FIGURE 1. *Geometric isomers in an octahedral complex*: cis-*forms occur as enantiomeric pairs giving a total of five possible isomers.*

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salt of a Co^{III} ion complex of the new ligand, *NN'*-bis-(L-2-amino-3-phenylpropyl)-*trans*-D-cyclohexane-1,2-diamine.

The green crystals of $CoC_{24}H_{36}Cl_3N_4O_4$ are in space group C_2^2—$P2_1$. A least-squares fit of the Picker automatic diffractometer setting angles for twelve reflections gave $a = 13{\cdot}237(2)$, $b = 16{\cdot}671(3)$, $c = 12.988(2)$Å, $\beta = 94{\cdot}806(8)°$, and $Z = 4$ from which $D_c = 1{\cdot}416$ g cm^{-3}. There are two formula units in the asymmetric unit. Intensities for 2277 reflections above background were measured on the automatic diffractometer using Cu-K_α radiation (1·5418Å) and a graphite monochromator. Transmission coefficients ranged from 0·389 to 0·658 for $\mu = 74{\cdot}93$ cm^{-1}, and a general absorption correction was applied. The structure was solved by the heavy-atom method and refined by least squares with anomalous dispersion effects included, and with thermal parameters anisotropic for Co and Cl and isotropic for all other atoms, to a final value of $R = 0{\cdot}096$.

The average Co–N distances of 1·96(2) in molecule (I) and 1·98(2)A in molecule (II) are in agreement with recently published values.[3–5] The four Co–Cl distances average to 2·260(8)Å, at the low end of the range of values previously reported.[6,7] All C–C and C–N distances in the structure appear normal. The eight Cl–O bond distances in the two perchlorate ions average to 1·41(3)Å, in agreement with a recently observed value of 1·43Å,[8] but show a wide range of values, attributed to the observed large thermal motion in these ions.

The two independent molecules in the structure have identical configurations but their conformations are different (see Figure 2) as a result of crystal packing requirements, leading to small differences in their geometries. The cobalt co-ordination octahedron is somewhat distorted by the stiffness of the large ligand molecule so that the N–Co–N' angle for the terminal NH_2 groups has a value of 103·0° in molecule (I) and 107·8° in molecule (II), while the other angles in the equatorial plane vary from 83·5 to 87·2°. In addition, the four nitrogen atoms deviate from their average plane by approximately 0·1Å. The axial Cl–Co–Cl' angles are 174·1 and 177·7°.

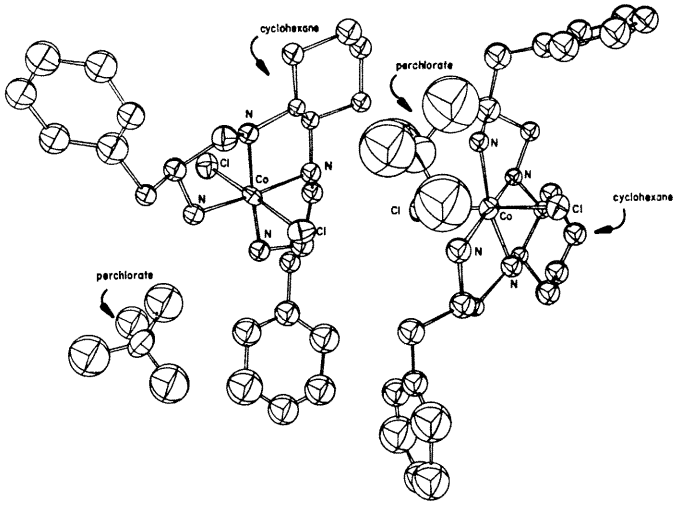

FIGURE 2. *Perspective view of one asymmetric unit of dichloro-{NN'-bis-(L-2-amino-3-phenylpropyl)-*trans*-D-cyclohexane-1,2-diamine}cobalt(III) perchlorate.*

Analysis of the anomalous dispersion data shows the absolute configuration to be $(+)_{589}$-*trans*-[dichloro-{$(-)_{589}$-*NN'*-bis-(*S*-2-amino-3-phenylpropyl)-*trans*-*R*-cyclohexane-1,2-diamine δλδ}cobalt(III)] perchlorate where the nomenclature combines recent usage.[9,10] This result confirms, by a direct method, the D-configuration assigned to (−)-*trans*-cyclohexane-1,2-diamine on the basis of o.r.d. curve comparisons.[11]

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