

The Absolute Configurations and Conformations of Chlorocobalt(III) Tetraethylenepenta-amine Complexes

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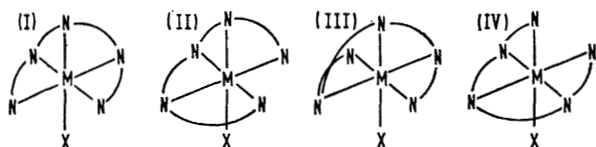
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Summary The absolute configurations, circular dichroism spectra, crystal structure, equilibria, and the results of energy minimization calculations are presented for a pair of diastereoisomeric chlorocobalt(III) tetraethylenepenta-amine complexes.

THE modes of co-ordination of 1,4,7,10,13-penta-azatri-decane (tetraethylenepenta-amine \equiv tetraen) are depicted in (I), (II), (III), and (IV).† Of these structures (I) has a



plane of symmetry and (II), (III), and (IV) are asymmetric. In addition to the stereochemistry generated by the topology of the co-ordinated ligand, there is the possibility of the existence of diastereoisomeric forms arising from alternative nitrogen atoms which fuse chelate rings in the same plane. From this source structure (II) could exist in two diastereoisomeric forms while structure (IV) could exist as four diastereoisomers. Structure (III) however could only exist in one form: the different orientations of the central proton are achieved by a rotation about the NCoX axis.

Several isomers of cobalt(III) complexes $[\text{Co tetraen Cl}]^{2+}$ have been isolated^{1,2} and we report the structures and absolute configurations of two optically active forms. The isomers are diastereoisomeric forms of structure (II) having the same topological arrangement of the ligand about the cobalt ion, and enantiomorphic arrangements about the secondary nitrogen centre joining the coplanar chelate rings. In basic solution the chloro-complexes hydrolyse rapidly and the $\text{D}\alpha\beta\text{R}\dagger$ isomer is converted substantially into the $\text{D}\alpha\beta\text{S}$. Under these conditions proton exchange is rapid at the N centre which inverts and the results require the $\text{D}\alpha\beta\text{S}$ hydroxo-ion to be *ca.* 1.5 kcal./mole more stable than the $\text{D}\alpha\beta\text{R}$ hydroxo-form. A similar stability relationship was established for this type of isomerism in the structurally related $\beta\text{-}[\text{Co trien}(\text{OH}_2)_2]^{3+}$ isomers.^{3,4}

The two isomers $\text{D}\alpha\beta\text{S}$ $[\text{Co tetraen Cl}](\text{ClO}_4)_2$ and $\text{D}\alpha\beta\text{R}$ $[\text{Co tetraen Cl}](\text{ClO}_4)_2$ both have the space group $P2_12_12_1$ and the structures, Figures 1 and 2, were each determined from *ca.* 1500 reflections with a full-matrix least-squares refinement to a residual of *ca.* 13% for the observed reflections. The unit cell parameters are $(\text{D}\alpha\beta\text{S})a = 17.37(1)$,

$b = 12.44(1)$, $c = 8.43(1)$ Å; $(\text{D}\alpha\beta\text{R})a = 17.26(2)$, $b = 12.03(1)$, $c = 8.72(3)$ Å. The absolute configurations were determined by anomalous scattering of $\text{Cu-K}\alpha$ X-rays by cobalt. The IUPAC symbol⁵ is given for each chelate ring

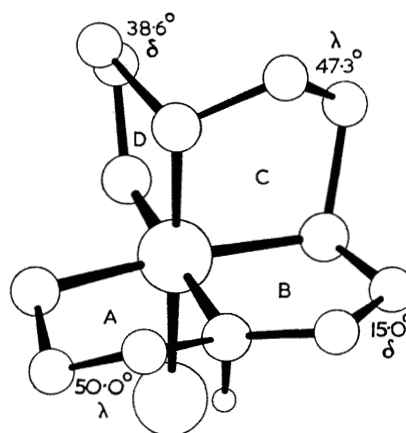


FIGURE 1. Structure of the $\text{D}\alpha\beta\text{R}$ $[\text{Co tetraen Cl}]^{2+}$ cation showing the values of dihedral angles at the C-C bonds.

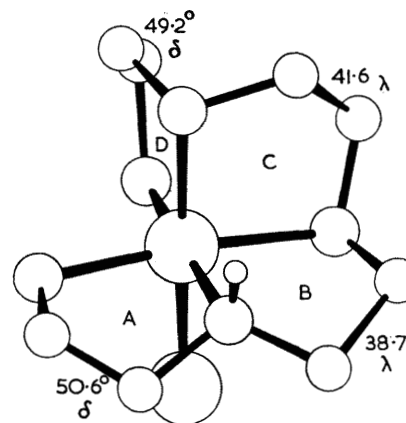


FIGURE 2. Structure of the $\text{D}\alpha\beta\text{S}$ $[\text{Co tetraen Cl}]^{2+}$ cation showing the values of dihedral angles at the C-C bonds.

together with the observed dihedral angles about the C-C bonds.

† The trivial $\alpha\beta$ nomenclature is extended from that used for the trien complexes.³ The tetraen ligand viewed from the two ends has either α , β , or *trans* characteristics *i.e.* (I) $\alpha\alpha$, (II) $\alpha\beta$, (III) $\beta\beta$, (IV) β *trans*. R and S refer to the configuration about the N atom fusing the chelate rings in the same plane and conform to the IUPAC rules.

Both isomers were submitted to the strain energy minimization procedure of Boyd⁶ using force constants^{7,8} and nonbonded potentials^{9,10} from the literature. With the exception of the dihedral angles the internal co-ordinates of the isomers were reproduced to within two standard deviations of the observed crystal values [$\sigma(\angle \text{NCC})$ vary between 2 and 4°]. The dihedral angles at the C-C bonds agreed within 5° except in the case of the ring (B) in $\alpha\beta R$ which minimized close to 45° for several sets of force constants. A close contact by perchlorate oxygen (3.08 Å) is made to a ring carbon of this ring consistent with holding it to the low dihedral angle of 15°. The strain energy differences between the two isomers obtained for these gas-phase calculations were in the range 1.5–2.4 kcal./mole depending on the force constants chosen.

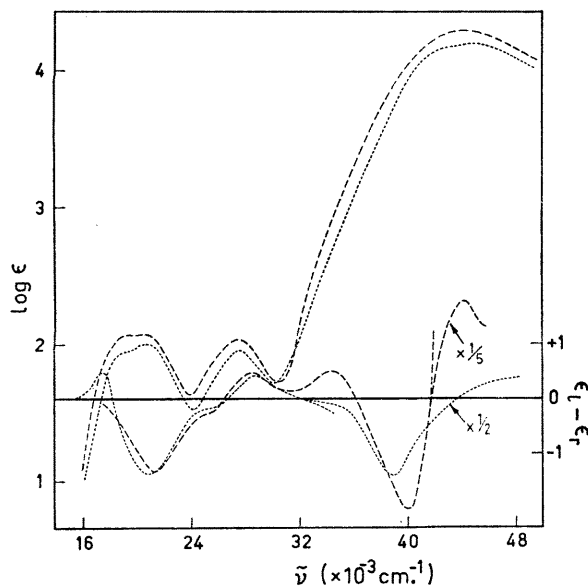
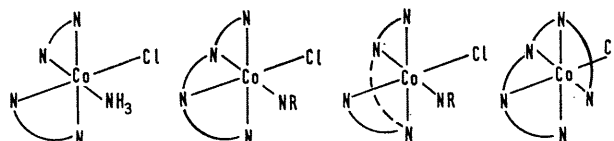


FIGURE 3. Absorption spectra and c.d. curves for $L(+)\text{-}420\alpha\beta R[\text{Co tetraen Cl}]$ (—) and $L(-)\text{-}540\alpha\beta S[\text{Co tetraen Cl}]$ (---) in $0.1M \text{HClO}_4$.

The source of the stability differences are distributed approximately equally between bond angle distortions and nonbonded interactions throughout the majority of the 280 interactions considered in minimization.

The c.d. and spectra Figure 3 show that the $L\alpha\beta S$ form coincides with that described previously as β and confirms House and Garner's structural assignment.¹ Also the $L\alpha\beta R$ form is the α isomer described by these authors¹ but in this instance their structural assignment was in error. The c.d. curves of the chloro-species in the vicinity of the first ligand-field band reflect the same configuration of the ligand about the metal ion. The minor differences may be attributed to the change in configuration at the asymmetric secondary nitrogen centre and the chelate conformations. This analysis is consistent with the relatively large magnitude of the c.d. bands associated with dissymmetry about cobalt centres in amine complexes relative to those associated solely with asymmetric co-ordinated N centres.

It is pertinent to draw attention to the correlation between c.d. curves and configurations for these and related penta-amine complexes. For example $D(+)\text{-}589[\text{Co en}_2\text{NH}_2\text{-Cl}]^{2+}$, $D(+)\text{-}589\alpha[\text{Co trien NH}_2\text{CH}_2\text{CO}_2\text{R Cl}]^{2+}$, $D(+)\text{-}589\beta[\text{Co trien NH}_2\text{CH}_2\text{CO}_2\text{R Cl}]^{2+}$ ¹¹ and the D antipodes of the present compounds all show a dominant positive c.d. band in the region of the first ligand-field band, ca. 20,000 cm^{-1} . The structural correlation can be drawn as follows from the



assigned configurations^{11,12} ($\text{NR} = \text{NH}_2\text{CO}_2\text{R}$). The configuration correlation between these complexes is exact if chelate pairs are chosen which are not adjacent. This is true irrespective of which end of the tetraen ligand is chosen. Numerous correlations of this nature between rotatory dispersion, c.d. and configuration have been noted for bis(en) and trien complexes where the absolute configuration is known or assigned with certainty.^{3,12,13} We would assert that there are now too many examples for this correlation to be accidental. It appears that the principal feature in determining the sign of the dominant dichroism for the first ligand-field band in these amine complexes is the orientation of non-adjacent pairs of chelate rings relative to that in the parent complex $D(+)\text{-}589[\text{Co en}_3]^{3+}$.

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