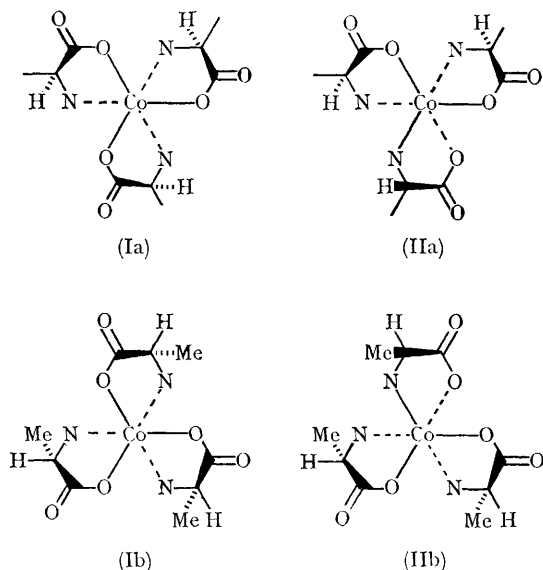# The Absolute Configuration of α-(+)-Tris-L-alaninatocobalt(III)

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THE diastereoisomeric metal complexes, D-[M(L)₃] and L-[M(L)₃], where L is an optically active ligand, have unequal stabilities: most evidence[1] relates to 1,2-diamines as ligands. Similar inequalities occur[2] for complexes of α-amino-acids. Tris-L-alaninato-cobalt(III) may be regarded as the parent compound The more easily obtained violet isomer is α-(+)-[Co(L-ala)₃], but its absolute configuration has not been related to those of the complexes of diamines, (+)-[Co(en)₃]³⁺ (Ref. 3) or (−)-[Co{(−)-pn}₃]³⁺ (Ref. 4), whose configurations were ascertained by X-ray anomalous scattering studies.[5] of the series of complexes of natural amino-acids.

The four possible isomeric forms of [Co(L-alaninate)₃] are shown in (Ia, Ib, IIa, IIb). The purple isomer cannot be represented by (Ia) or (Ib), since these possess a threefold axis of symmetry; on spectroscopic grounds[6,7] the purple isomers are less symmetric geometrically, and do not have threefold symmetry. An X-ray study now shows that the absolute configuration of α-(+)-[Co-(L-ala)₃] is represented by (IIa).

three "axial" methyl groups), must be excluded. It also appeared likely that a two-dimensional study would suffice for confirmation. Intensities of 266 reflexions in the *hk*0 zone were estimated visually from Weissenberg photographs taken with Mo-*K*α radiation. The centrosymmetric projection has been solved by Patterson and Fourier methods, and has revealed one molecule of solvated water. It also showed what appeared to be three "equatorial" methyl groups. However, no assumptions were made in interpreting the light-atom peaks. For the first full set of structure-factor calculations, the six atoms linked to the Co atom were given the mean scattering factor of nitrogen and oxygen, and the six outermost were given the mean of carbon and oxygen. Full-matrix least-squares isotropic refinement reduced R to 0·137. Figure 1 shows the atomic positions and the projected bond lengths.

It was noted that each ligand has one protruding bond with a projected length ≥ 1·50 Å (±0·05, ±0·05, ±0·05), and a second with a projected length ≤ 1·22 Å (±0·04, ±0·04, ±0·04). Clearly

(Ia)   (IIa)

(Ib)   (IIb)

The crystals are orthorhombic, space group $P2_12_12_1$, $a = 18\cdot550$, $b = 14\cdot459$, $c = 5\cdot09$ Å, $Z = 4$. With such a short *c*-axis it was virtually certain that the deeper form of the molecule, (IIb) (with
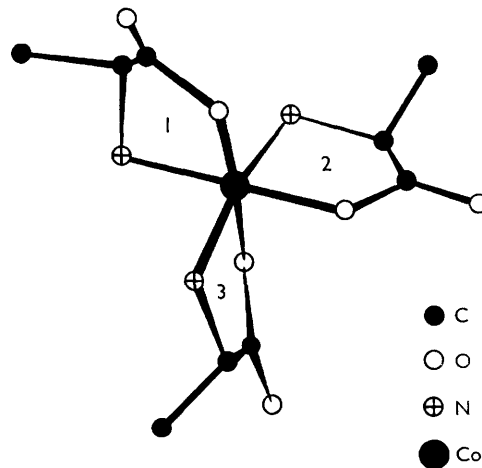

FIGURE 1

the first three are the C–Me's (1·54 Å), and the second three are the C=O's (1·25 Å). This assignment was confirmed when it was found that models of L-alanine could be projected unambiguously upon ligands 1, 2 in Figure 1; a step that distinguished between the nitrogens and oxygens of the two ligands, and also indicated which of them

is uppermost. The octahedral co-ordination then identified which of the two ligand atoms in ligand **3** is uppermost and made it possible unambiguously to place and project the third ligand. The result is (IIa). Full-matrix least-squares refinement using the correct form factors has reduced R to 0·127.

The configuration established for α-$(+)$-[Co-(L-ala)$_3$] may be called D by comparison with the $(+)$-[Co(en)$_3$]$^{3+}$ cation.[3] The configurations of a number of trisamino-acid complexes may be deduced by comparisons of Cotton effects; those

which have rotatory dispersion curves[2] of the same type as that of the isomer D-α-$(+)$-[Co(L-ala)$_3$] described here are: $(+)$-α-[Co(glycinate)$_3$] (the isomer less adsorbed on starch), $(+)$-α-[Co(L-valinate)$_3$] (the more stable isomer), and $(+)$-α-[Co(L-leucinate)$_3$] {again the more stable isomer, preponderating at equilibrium over $(-)$-α-[Co(L-leucinate)$_3$] by 4 : 1}. From this it can be predicted that the more stable isomer of α-[M (L-amino-acid)$_3$] will have the D-configuration, of Figure 1.

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