

***cis-trans*-Isomerism of Bis-(α -alaninato)copper(II)**

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SINCE complexes of the cupric ion are kinetically labile in aqueous solution, solid compounds derived from such solutions are expected to contain the ion in its thermodynamically favoured form which is usually assumed to be that of the *trans*-configuration. No unequivocal example of *cis-trans*-isomerism in complexes of copper(II) has been previously reported.

Bis-(L-alaninato)copper(II) normally forms pale blue monoclinic crystals which have been shown¹ to contain the *trans*-bis-(L-alaninato)copper(II) unit with two long Cu-O bonds completing the expected tetragonally-distorted octahedral co-ordination around the metal. Crystals of bis-(D-alaninato)copper(II) are, as is to be expected, strictly isomorphous as indicated by X-ray powder

photographs. We have now prepared a second crystal modification of bis-(D- α -alaninato)copper(II) and of its enantiomer by ageing suspensions of the *trans*-complexes in water; these new crystals are deep blue and orthorhombic. While such properties as the optical rotatory dispersion and absorption spectra of aqueous solutions of the two polymorphs are identical, as would be expected from the known lability of amino-acid complexes of copper(II), a three-dimensional X-ray analysis ($R = 0.08$) of the new form of bis-(D- α -alaninato)-copper shows that the co-ordination of the cupric ion is very different from that described by Dijkstra and Vonk¹ for the other crystal modification. The stereochemistry of the dark-blue complex is shown in the Figure together with some

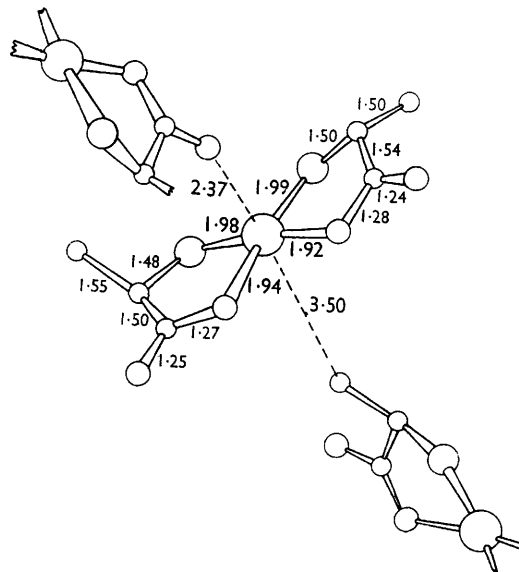
of the more important bond lengths; the average standard deviations of these values, as estimated from inversion of the block-diagonal least-squares matrix, are Cu-O, Cu-N, and Cu-C 0.012 Å and C-C, C-O, and C-N 0.02 Å.

Two features of the structure are noteworthy. The ligands are arranged in a *cis*-configuration around the metal so that the two independent analyses of the structure of bisalaninatocopper represent the first rigorous proof of *cis-trans*-isomerism in complexes of copper(II). The two known forms² of bisglycinatocopper(II) are thought to represent *cis-trans*-isomers but only the structure of the *cis*-complex has been determined.³ The other *cis*-complex of copper(II) reported⁴ is that of $[\text{Cu}(\text{NH}_3)_2\text{CO}_3]$.

The stereochemistry of the *cis*-complex is essentially that of a distorted square pyramid with carboxyl-oxygen atoms bridging copper ions in a polymeric structure. The sixth position of what would constitute octahedral co-ordination of the copper is filled by a methyl group of a neighbouring molecule. The Cu-C(H₃) distance of 3.50 Å may, at first sight, be thought of as being too large to constitute a bonding interaction; but an inspection of the geometry of the chelate rings, which are not strictly planar, shows that the two methyl groups are differently positioned with respect to the mean planes defined by the chelate rings to which they are bonded. The perpendicular displacement of the methyl carbon, which appears to interact with the metal, from the plane of its chelate ring is only 0.6 Å, the other methyl carbon being displaced 1.5 Å in the opposite sense. As a result of the Cu-C(H₃) distance of 3.50 Å, quite small metal-hydrogen distances may exist⁵

but the hydrogen atoms have not, as yet, been located. As in other copper complexes, the metal is not coplanar with the equatorial ligands but is displaced 0.1 Å towards the apical oxygen; the co-ordination symmetry is similar to that observed in glycylglycylglycinatocopper(II)⁶ and (β -alanyl-L-histidinato)copper(II) hydrate.⁷

Our results show that schemes⁸ describing amino-acid complexes of copper(II) in terms of *trans*-structures alone are over-restrictive and that other factors, as yet not understood, intervene to stabilise the *cis*-isomers.



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