The Crystal Structure of Copper(II) Pyridoxylidene (±)-Valine Complex

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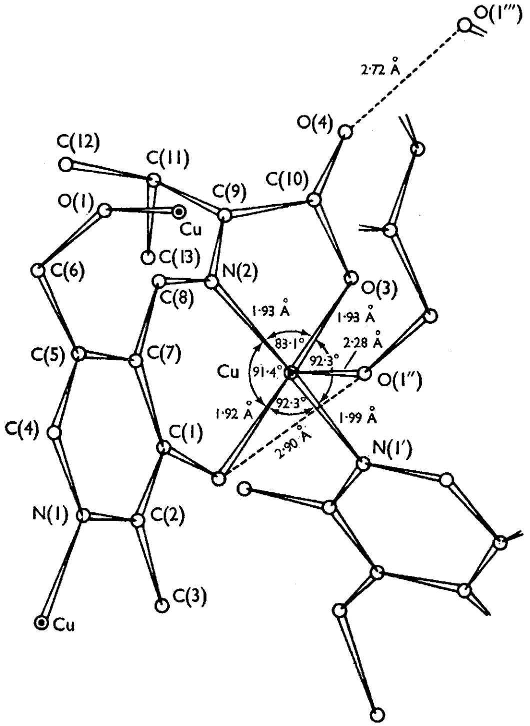
THE use of model systems in the study of complex enzymic reactions is well known and particular interest has been shown in systems set up to explain the role of vitamin B_6 as a catalyst for some reactions of amino-acids.[1-3] In many of these the further catalytic effect of added metal ions has been investigated[2,4,5] leading to the view that the roles of vitamin and metal are complementary, imine formation by the former being facilitated and sterically controlled by chelation with the latter.

Thus, in the copper chelate with pyridoxal (the aldehyde form of B_6) and amino-acid, a tridentate structure has been assigned in which the "vacant" fourth donor position is supposedly occupied by a solvent molecule. To substantiate these deductions and to provide detailed steric information a full three dimensional *X*-ray structural examination of the stable copper(II) pyridoxylidene (±)-valine complex, prepared as dark green crystals by the method of Christensen,[4] was undertaken.

The crystal data are: $a = b = 25{\cdot}53$, $c = 13{\cdot}32$Å, $Z = 18$, and the space group $= R\bar{3}$.

Intensity data were obtained with Cu-K_α *X*-radiation by conventional Weissenberg and precession camera photography. The structure determination was effected by three-dimensional Patterson and heavy-atom syntheses. Refinement of a model embodying all atoms except hydrogen is still proceeding by a least-squares procedure, the present R factor being 0·139 for all 1445 observed reflections. Individual temperature factors have been assumed.

The molecular structure of the complex is based on a five-co-ordinate copper atom with a square-pyramidal configuration. Three distinct units contribute towards this stereochemistry; the first fills three positions of the square plane as seen in the Figure, the heterocyclic nitrogen of a second unit occupies the remaining in-plane vacancy and the hydroxymethyl oxygen of a third group completes the pyramidal geometry. This fifth bond (2·28 Å) is elongated with respect to the other four in agreement with previous observations. Similarly the copper atom is displaced (by 0·14 Å) above the plane towards this particular donor. The structure is polymeric as a consequence of this ligand co-ordination, presenting a stable interlocked network which is further stabilised by hydrogen bonding between O(4) and O(1‴) (separation of 2·72 Å) and between O(2) and O(1″) (2·90 Å). (See Figure).



FIGURE

The molecule as a whole (excluding side-chains) is approximately planar although the pyridoxal ring and the large chelate ring (excluding copper) show minor deviations from their mean plane. Atom C(9) is twisted away, presumably by the close approach (less than 3·5 Å) of atoms C(11) and C(12) of a separate unit, and as a presumed consequence atoms C(10) and O(3) together with Cu and N(1′) from the neighbouring unit are slightly displaced in the opposite sense.

In the solid state at least, the intermediate has the essential planarity thought to be necessary in facilitating the reactions of the cofactor. Appropriate electron displacements leading to transamination, racemisation, decarboxylation, *etc.*, are clearly possible confirming that a primary function of the metal ion is to define and stabilise the required conjugated pathway in a steric sense. Its role as an activating group, modifying the action of pyridoxal, is not so immediately obvious but such an effect may also be safely inferred from the molecular geometry.

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