Molecular Structure of the Binuclear Copper(II) Chelate Complex, Aquocopper(II)-μ-(triethylenetetra-aminehexa-acetato)-aquocopper(II) Heptahydrate: *X*-Ray Crystallography *versus* Electron Spin Resonance

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Summary An *X*-Ray crystal structure analysis of a binuclear metal chelate complex of the ligand triethylenetetra-aminehexa-acetic acid (ttha) shows the title compound to be in its fully open or extended molecular form, in apparent disagreement with earlier e.s.r. results.

RECENT developments in the e.s.r. theory of dipolar coupled copper(II) ions[1,2] have been used to determine the distance between the copper(II) ions in dinuclear chelate complexes. The e.s.r. spectrum observed at low field of an aqueous solution of the title compound [Cu_2(ttha),$7H_2O$] was attributed exclusively to dipolar coupling arising from the copper(II)–copper(II) separation of 5·5(5) Å[3]. Of the two major structural possibilities for this complex, Smith and Martell[3] preferred the closed form (Figure 1) to the open (or extended) form (Figure 2). They suggested, after examination of molecular models, that the separation of the copper(II) ions in the former was consistent with their experimentally determined distance, but in the latter was much larger.

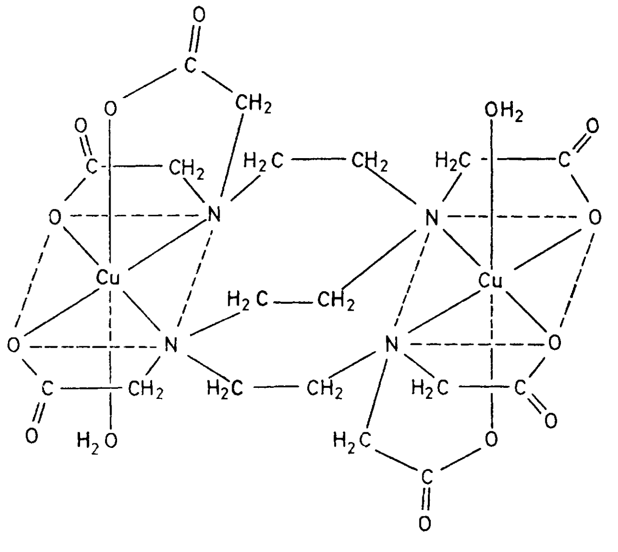

FIGURE 1. Proposed closed form of the Cu_2(ttha)$(H_2O)_2$ complex.

However, molecular models clearly show the predicted closed form to be highly strained and improbable. They also show that in the more feasible open form symmetric rotation of the two quinquedentate ends of the complex about the central ethylenediamine group can formally allow the copper(II)–copper(II) separation to contract from a maximum of *ca.* 7·5 Å to a minimum of *ca.* 5·5 Å. Excessive crowding in the latter case suggests the complex could not contract to give this minimum internuclear separation. The present *X*-ray study was undertaken to establish the exact nature of this binuclear copper(II)–(ttha) complex where it was felt that the molecular structure in the solid state would not differ greatly from that in aqueous solution. The analysis establishes the presence of the fully open form of the complex in the crystal.

Crystal data: Pale-blue prismatic crystals elongated along the [100] direction were grown from an aqueous solution of the complex. $C_{18}H_{26}Cu_2N_4O_{12},7H_2O$, $M = 743·7$, monoclinic, $a = 7·165$, $b = 13·137$, $c = 17·079$ Å; $\beta = 112·6°$; $V = 1486·2$ Å^3; $D_m = 1·67(1)$ g cm^{-3}; $Z = 2$; $D_c = 1·66$ g cm^{-3}; space group $P2_1/c$. The structure was solved from Patterson and electron density maps using 2209 observed reflections of 2803 unique reflections measured with graphite-monochromatized Mo-K_α radiation on a Philips PW1100 automatic diffractometer. It was refined to a conventional R of 0·068 assuming an anisotropic temperature factor for the Cu atom and isotropic temperature factors for the remaining non-hydrogen atoms. Hydrogen atoms were not found.

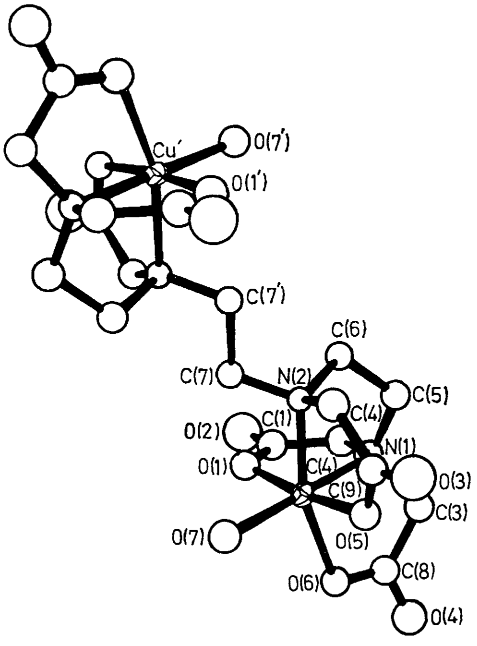

FIGURE 2. Molecular structure of Cu_2(ttha)$(H_2O)_2$; interatomic distances: Cu–O(1), 1·961(9); Cu–O(5), 1·949(9); Cu–O(6), 2·512(9); Cu–O(7), 1·988(8); Cu–N(1), 2·065(8); Cu–N(2), 2·262(9); O(1)–C(1), 1·26(1); C(1)–O(2), 1·25(1); C(1)–C(2), 1·52(2); C(2)–N(1), 1·49(2); N(1)–C(5), 1·51(2); C(5)–C(6), 1·48(2); C(6)–N(2), 1·50(1); N(2)–C(4), 1·47(1); C(4)–C(9), 1·53(2); C(9)–O(5), 1·25(1); C(9)–O(3), 1·27(1); O(6)–C(8), 1·19(1); C(8)–C(4), 1·33(1); C(8)–C(3), 1·52(2); C(3)–N(1), 1·49(2); N(2)–C(7), 1·51(2); C(7)–C(7′), 1·53(2) Å; angles: N(2)–Cu–O(6), 155·0(4)°, N(1)–Cu–O(7), 172·1(4)°; O(1)–Cu–O(5), 177·3(4)°.

The molecular structure is shown in Figure 2. together with some important bond lengths and angles. The molecule is centrosymmetric about the mid-point of the central ethylene group. The stereochemistry about the copper atom is distorted octahedral with a water molecule, O(7), filling the sixth co-ordination position. Major distortion is confined to one axial direction of the co-ordination polyhedron and can be attributed to a combination of Jahn–Teller and chelate effects. The dihedral angle O(6)–Cu–N(2) deviates some 25° from linear in order to relieve strain imposed by the chelating ethylenediamine group N(2), C(6), C(5), N(1) which itself is twisted out of plane into the *trans*-conformation. The copper atom is virtually coplanar with co-ordination square comprising O(1), N(1), O(5) and O(7) where all bond lengths and angles are normal. The Cu–O(6) distance is much longer than both the Cu–O(1) and Cu–O(5) distances indicating O(6) to be the protonated oxygen. This is further supported by the significantly longer C(8)–O(4) and shorter C(8)–O(6) distances. The intramolecular copper(II)–copper(II) distance is 7·655 (2) Å which indicates the binuclear complex is probably in its fully extended form.

Each binuclear complex is strongly linked at each end to a centrosymmetrically related molecule by a pair of similar hydrogen bonds, leading to a chain-like structure running through the crystal in the [100] or prism axis direction. The hydrogen bonds O(7)–H ···· O(1′) and O(7′)–H ···· O(1) have a length of 2·81(1) Å and result in an intermolecular copper(II)–copper(II) distance of 5·349(2) Å. The remaining water molecules (*ca.* 5 H_2O per complex) in the crystal were trapped during crystallization and partially occupy interchain positions.

The interpretation given by Smith and Martell[3] of the e.s.r. spectrum of this binuclear copper(II) complex requires an intramolecular copper(II)–copper(II) separation of 5—6 Å in aqueous solution. Although a copper(II)–copper(II) distance of this order does exist in the crystal (*viz.* 5·349 Å) it is not intramolecular but intermolecular and since it is sustained by hydrogen bonding it is unlikely to survive dissolution. In solution symmetric twisting about the central ethylenediamine group of the fully extended form of the complex (as found in the crystal) could formally move the copper atoms as much as 2 Å closer, *i.e.*, contraction of the intramolecular copper(II)–copper(II) separation from 7·655 to *ca.* 5·5 Å. This would seem to be energetically unfavourable and suggests the necessity for a re-examination of the e.s.r. results.

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