Crystal Structure of a Dinuclear 2:1 Adenine–Copper Complex

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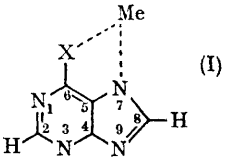
IN recent years there has been much effort in clarifying the ability of purine bases to form complexes with bivalent cations.[1,2] The most common opinion has been that the metal-ion binds to N(7) and the substituent on C(6), forming a 5-membered ring (I); a scheme similar to that found in copper(II)–8-hydroxyquinolinate.[3] However, the results from synthetic work on complexes of copper with different purine derivatives as ligands, indicate that N(3) and N(9) are the more probable binding sites for the metal ion.[2]

Bis-(6-aminopurine)–copper(II) was crystallized from water as intense blue-violet prisms and studied by *X*-ray crystallography. The space group is $P\bar{1}$ with two formula units in the cell: $a = 9{\cdot}458(2)$, $b = 10{\cdot}452(2)$, $c = 9{\cdot}410(3)$ Å, $\alpha = 102{\cdot}98(2)°$, $\beta = 116{\cdot}58(2)°$, $\gamma = 79{\cdot}81(2)°$. The compound loses its crystalline structure when dried over silica gel. The chemical analysis reported for the powdered substance[2] indicates three molecules of water per formula unit. The density of the crystals found by flotation in a mixture of carbon tetrachloride and tetrabromoethane was 1·677(10) g.cm.$^{-3}$ in good agreement with the calculated value of 1·661 g.cm.$^{-3}$ based on four molecules of crystal water per formula unit.



(I)

The crystal used for data collection on the diffractometer had dimensions 0·20 mm. × 0·15 mm. × 0·40 mm. Within the sphere of reflections, limited at sin $\theta/\lambda = 0{\cdot}6$, 2882 unique reflections were measured using Mo-K_α radiation. Of these, 356 were coded unobserved. The structure was solved by the heavy atom method and refined to an R of 0·075 by a full-matrix least-squares procedure applying anisotropic temperature factors to all non-hydrogen atoms.

The water molecules not co-ordinated to copper show both partial occupancy and disorder. Hydrogen atoms on these molecules are not yet located. The other hydrogen atoms have been included in the calculation but are not refined.

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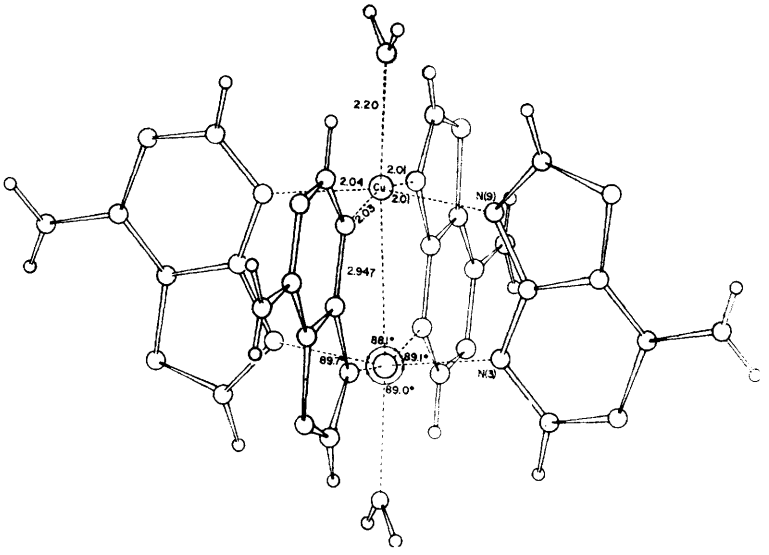

FIGURE. *The co-ordination around the copper ion, viewed along the* b-*axis.*

The co-ordination around the copper atom is shown in the Figure. A similar dimeric configuration has been found in copper(II) acetate dihydrate,[4] monopyridine copper(II) acetate,[5] and copper(II) succinate dihydrate.[6]

The rigid geometry of the adenine molecule with the chelating sites N(3) and N(9) only 2·41 Å apart, should be favourable for the formation of a short metal–metal bond. However, the copper–copper distance is found to be 2·947 ±0·002 Å which is appreciably longer than the distances (2·64, 2·64, and 2·61 Å) found in the compounds mentioned above. The copper atom is displaced by 0·27 Å from the equatorial plane of the octahedron. This displacement is significantly greater than that found in the other structures where the ligands have a more flexible geometry.

Numerous attempts have been made to describe the nature of the metal–metal bond in di-nuclear copper complexes. An excellent review is given by Kato *et al.*[7] The subnormal magnetic moment often found in this type of compound has been interpreted as spin pairing between the odd electrons on the copper atoms. Two different schemes have been proposed for this interaction: (1) a σ or δ type bonding between the copper atoms when the copper–copper distance is short (2·61—2·64 Å), and (2) a super-exchange mechanism which involves an electron transfer through one or more bridging atoms when the distance is too long for direct overlap between copper orbitals.

Thus far no measurement of the magnetic moment of the copper–adenine complex has been undertaken. The large copper–copper separation rules out the possibility of a direct overlap of copper orbitals. If any subnormal magnetic moment is found in this compound, this should be due to super-exchange. The copper atoms deviate only slightly from the least-squares planes of the purine rings so that a migration of electrons through the π-system of the ligands is very favourable.

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