X-RAY CRYSTAL STRUCTURE OF $[Cu(adenineH)_2Br_2]Br_2$; A COPPER COMPLEX INVOLVING NON-BRIDGING ADENINE

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SUMMARY

X-ray studies have shown that in the compound $[Cu(adenineH)_2Br_2]Br_2$ the adenine molecules coordinate to the metal ion via N(9) only, with the copper atom adopting a flattened tetrahedral coordination geometry.

INTRODUCTION

Copper(II) ions are known (1) to denature DNA in a reversible manner. This observation has resulted in an increasing interest in the possible modes of binding of metal ions with adenine, guanine, cytosine and thymine. Detailed determination by X-ray methods of the coordination sites of these bases, which would permit a clearer understanding of the influence of metal ions on the key hydrogen bonds in biological molecules, is as yet limited to very few systems.

The structures of three copper-adenine (ade) complexes have recently been reported, the inner complex $[Cu(C_5H_4N_5)_2H_2O]_2.6H_2O$ (2), $[Cu(ade)_2Cl]_2Cl_2.6H_2O$ (3), and $Cu_3Cl_8(adeH)_2.4H_2O$ (4), and in all three adenine acts as a bridging ligand coordinating via N(3) and N(9). We report the crystal structure of a new complex in which adenine is monodentate, coordinating via N(9) only.

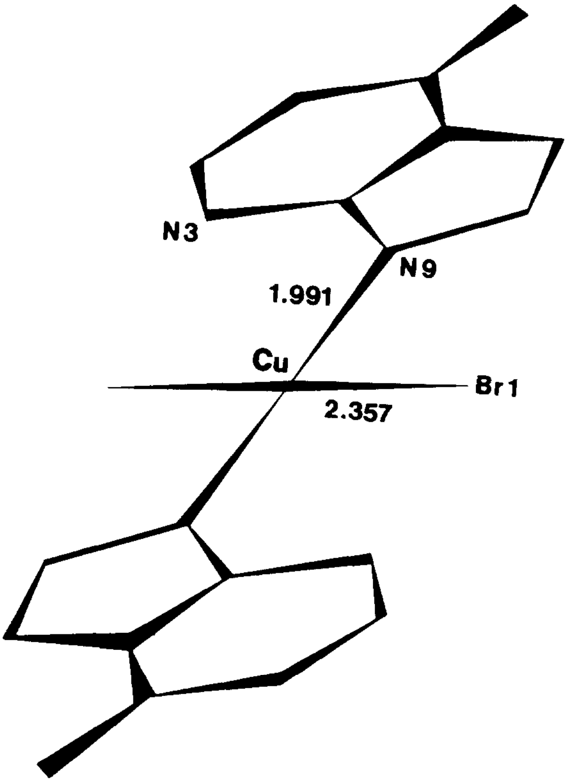
RESULTS AND DISCUSSION

Dark brown, monoclinic crystals of the title compound, $CuBr_4(C_5H_6N_5)_2$, were obtained from 4:1 mole ratios of cupric bromide and adenine in aqueous acidic solution. The unit-cell dimensions are $\underline{a}$ = 18.649, $\underline{b}$ = 8.731,

c = 12.028Å, β = 113°14', V = 1791.1Å^3, D_m = 2.50, Z = 4, D_c = 2.43g. cm^{-3}, space group $C2/c$.

Three-dimensional X-ray data were collected on a Siemens four-circle diffractometer. Using Cu-Kα radiation a total of 1109 independent reflections were measured (to $\theta = 55^\circ$) of which 9 were judged to be unobserved. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached R = 0.068.

The structure contains complex ions $[Cu(ade)_2Br_2]^{2+}$ and bromide ions. The complex ion, in which the central copper atom lies on a diad, is shown in the Figure. The copper atom is coordinated to two N(9) atoms of adenine ligands at a distance of 1.991Å, and two terminal bromine atoms at a



A schematic view of the $[Cu(adeH)_2Br_2]^{2+}$ ion looking down the diad axis through the copper atom. Standard deviations are Cu–Br, 0.003; Cu–N, 0.010Å.

distance of 2.357Å. The Cu-N distance is normal, and is possibly fractionally shorter than those found in the bridging-adenine complexes. The coordination about the copper atom is a flattened tetrahedron where the angle between the planes containing Cu, N(9), N(9)' and Cu, Br(1), Br(1)' is ca. 49° (this should be 90° for tetrahedral, and 0° for square-planar coordinations). The site of protonation of the adenine ligand has not yet been determined unequivocally.

In coordinating via N(9) in this complex adenine behaves similarly to guanine (gua) in the two complexes for which structural information is available, $Cu(guaH)Cl_3$ (5) and $Zn(guaH)Cl_3$ (6). On the other hand, the mode of coordination of adenine not only differs from that in the other copper-adenine complexes studied hitherto, but also from that of the only other complex known to involve monodentate adenine $Zn(adeH)Cl_3$ (6). This last has adenine bound to zinc via N(7).

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