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A Three-coordinate Mercury Complex: X-Ray Crystal Structure of Dichloro(9-methylhypoxanthine)mercury(II)

N. BARBA BEHRENS, B. A. CARTWRIGHT, D. M. L. GOODGAME and A. C. SKAPSKI

Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, U.K.

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One feature of current interest concerning the binding of metal ions to nucleic acids and their components is the question of the possible coordination of exocyclic oxygen atoms of the pyrimidine or purine bases [1, 2]. As part of our own studies in this area we have examined the coordination behaviour of the toxic metal mercury with various nucleic acid components.

Mercury(II) is known to coordinate weakly to O4 of uracil in the compounds dichlorobis(uracil)mercury(II) and dichlorobis(dihydrouracil)mercury(II) [3], and strongly to N3 and weakly to O2 of 1-methylcytosine in di-μ-chloro-bis[chloro(1-methylcytosine)mercury(II)] [4]. On the other hand, strong metal–oxygen bonding to O4 has recently been reported in dichlorobis(1,3-dimethyluracil)copper(II) [5].

The interaction of equimolar amounts of mercury(II) chloride with 9-methylhypoxanthine (9Mehyp) in 1:1 acetone/water gave a complex of composition Hg(9Mehyp)Cl_2 (*Anal.*: Found C, 17.15; H, 1.35; N, 12.79; calc. C, 17.11; H, 1.43; N, 13.30%). The low frequency vibrational spectra of the complex had bands in the region expected for terminal ν(Hg–Cl) [I.R. 275w, 325s, cm^{-1}; Raman 276s, 325w cm^{-1}] but no bands assignable to modes involving bridging chlorines.

The formation of a polymeric structure involving 9-methylhypoxanthine bridges, linking metal atoms via N1 and N7, of the type known to exist in related complexes with 9-methyladenine [6–8] would require proton migration from its normal position on N1 in the hypoxanthine base. Alternative possibilities were: (a) chelation via N7 and O6, (b) polymerisation via N3 and N7, or (c) the presence of three-coordinate mercury(II). As good crystals of Hg(9Mehyp)Cl_2 could be obtained we have determined its structure by X-ray diffraction methods.

Colourless needles of the title complex are monoclinic, with a = 10.204(1), b = 13.671(1), c = 7.167(1) Å, β = 98.24(1)° (at 12 °C), space group $P2_1/c$ and Z = 4. Intensity data were collected on a Siemens off-line four-circle automatic diffractometer to θ = 70°. A total of 1846 independent reflections were measured, of which 104 were judged to be unobserved. The structure was solved by Patterson and Fourier methods, and full-matrix least-squares refinement has now reached R = 0.055.

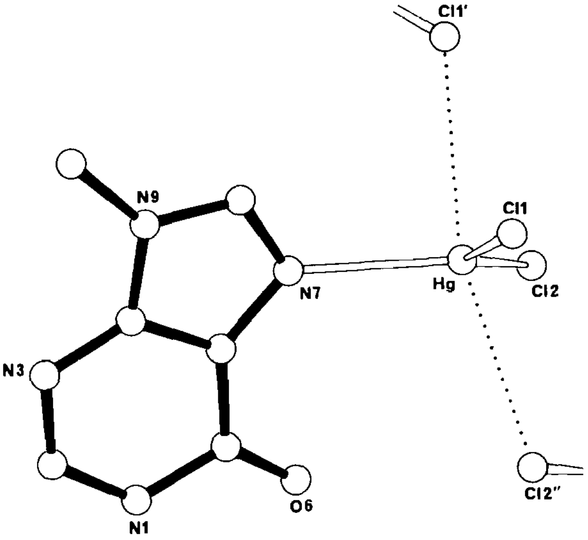

Figure 1. Molecular structure of Hg(9-methylhypoxanthine)-Cl_2. Dotted lines indicate possible weak interactions to neighbouring molecules.

Figure 1 shows the molecular structure, in which the mercury atom is coordinated to the N7 position on the hypoxanthine base. Two chlorine atoms complete the distorted trigonal-planar coordination about the metal atom. The Hg–N distance is 2.299(7) Å and the two Hg–Cl distances are Hg–Cl1, 2.401(2) Å, and Hg–Cl2, 2.353(3) Å. While the two Hg–Cl bond lengths are unexceptional, the Hg–N distance is rather long compared to 2.17 Å found in di-μ-chloro-bis[chloro(1-methylcytosine)mercury(II)] [4] and 2.16 Å in *catena*-(μ-chloro)-chloro(guanosine)mercury(II) [9]. Although the coordination is planar, there is considerable angular distortion within the plane (compared to sp^2 geometry). Thus the three angles centered on mercury are: N7–Hg–Cl1, 101.4(2), N7–Hg–Cl2, 118.0(2), and Cl1–Hg–Cl2, 140.5(1)°. The coordination plane is twisted relative to that of the purine ring system, and the angle between the two planes is *ca.* 60°.

Apart from the primary three-coordination, there are two further possible Hg...Cl interactions which link the complex molecules together, with Hg...Cl1′ of 2.979(3) Å and Hg...Cl2″ of 2.925(3) Å, and a Cl1′–Hg–Cl2″ angle of 165.8(1)°. If one were to include these secondary interactions in the coordination sphere, the geometry becomes intermediate between trigonal bipyramidal and square pyramidal.

The most common coordination geometries found for Hg(II) are linear *sp* and tetrahedral sp^3. Trigonal-planar geometry is comparatively rare, but is found in compounds such as $[(CH_3)_3S]^+(HgI_3)^-$ [10] and $[(CH_3)_4N]^+(HgX_3)^-$, (where X = Cl, Br or I) [11, 12]. These compounds also have two further weak Hg...X interactions forming a pseudo trigonal-bipyramidal coordination.

One common feature of mercury(II) in low-coordination environments is the presence of weak secondary interactions. In the crystal structure of the title compound these are achieved by intermolecular Hg...Cl links, but the exocyclic O6 atom, with an intramolecular Hg...O distance of 3.84 Å, is not involved.

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