

A Guanosine–Mercuric Chloride Complex, *catena*-(μ -Chloro)-chloro(guanosine- N^7)-mercury(II)

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Abstract. Orthorhombic, $P2_12_12_1$, $a = 11.152$ (6), $b = 20.565$ (9), $c = 6.561$ (2) Å, $Z = 4$ $C_{10}H_{13}Cl_2 \cdot HgN_5O_5$ formula units per cell, $D_c = 2.45$ g cm $^{-3}$. Hg is strongly bonded to one Cl and to N(7) of guanosine. The overall coordination sphere of Hg also includes two weaker Hg–Cl bonds, completing an irregular four-coordinate geometry. The carbonyl group is not involved in coordination. Infinite –Cl–Hg–Cl–Hg zigzag chains are centered on the 2_1 axis in the c direction. The structure is stabilized by base stacking and hydrogen bonding.

Introduction. Chelate formation *via* N(7) and carbonyl O(6) of guanine is believed to be an important mode of interaction of platinum anti-tumour drugs with DNA (Dehand & Jordanov, 1976; Millard, Macquet & Theophanides, 1975). In a previous paper (Authier-Martin & Beauchamp, 1977) we have reported that a Hg atom strongly bonded to a N atom of 1-methylcytosine showed some interaction with the nearby carbonyl group. The present complex was studied in order to determine whether guanosine would also act as a bidentate ligand for mercury.

The compound was prepared from stoichiometric amounts of guanosine and mercuric chloride in dilute hydrochloric acid ($pH \approx 3$, $80^\circ C$). The crystals obtained upon cooling were found to be suitable for X-ray work. The crystal used in this work had dimensions $0.58 \times 0.16 \times 0.025$ mm perpendicular to the $\{001\}$, $\{100\}$ and $\{010\}$ faces respectively.

Space group $P2_12_12_1$ was unambiguously determined from the systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) noted on precession and Weissenberg photographs. Accurate cell parameters were obtained by least-squares refinement of the setting angles 2θ , ω , and χ of 15 Mo $K\bar{\alpha}$ peaks automatically centered and indexed on a Syntex $P\bar{1}$ diffractometer [$\lambda(\text{Mo } K\bar{\alpha}) = 0.71069$ Å, graphite monochromator]. Intensities of 1629 reflections in two octants (hkl and $\bar{h}kl$) within a sphere $2\theta \leq 40^\circ$ were measured with the Syntex diffractometer. The scan rate was $1^\circ (2\theta) \text{ min}^{-1}$ for most reflections, but rates as high as $24^\circ \text{ min}^{-1}$ were selected for strong reflections by the auto-collection program. The scan range was from $[2\theta(K\bar{\alpha}_1) - 1.2]^\circ$ to $[2\theta(K\bar{\alpha}_2) + 1.2]^\circ$. Background was counted

at the limits of the scan. The counting time was adjusted in order to make the background-to-scan time ratio equal to 0.40. Three standard reflections were measured every 50 reflections. They showed fluctuations of $\pm 3\%$ during data collection.

Net intensities I were calculated from $I = (I_t - B/0.40)S$, where I_t is the total scan count, B is the total background count and S is the scan rate.

The standard deviations $\sigma(I)$ were calculated from $\sigma^2(I) = (I_t + B/0.16)S^2 + (0.02I)^2$ and the 219 measurements with $I/\sigma(I) < 2.0$ were assigned zero weight. An absorption correction based on the crystal faces was calculated at a later stage. Program *NRC-3* by Ahmed & Singh was used with $\mu = 110 \text{ cm}^{-1}$ and a grid of $10 \times 10 \times 10$. The transmission factor varied from 0.19 to 0.72. L_p corrections were applied, and in a first step equivalent hkl and $\bar{h}kl$ reflections were averaged. This set of 775 averaged nonzero reflections was initially used.

The structure was solved by the conventional heavy-atom method and refined by full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Isotropic refinement of all nonhydrogen atoms with unit weights converged to an R factor, $\sum |F_o| - |F_c| / \sum |F_o|$, of 0.12. Hg and Cl were then refined anisotropically and R reduced to 0.068. After absorption correction, R was further reduced to 0.047. Fully anisotropic refinement was deemed unjustified because the large number of parameters (208) to be refined would make the ratio of observations to parameters rather low (3.5). Some of the H atoms were visible on the Fourier map, but only those for which ideal positions could be calculated were introduced and fixed at those positions with temperature factors B of 6.0 \AA^2 . The real and imaginary contributions of Hg and Cl to anomalous dispersion were included in the structure-factor calculations. Those contributions introduced significant differences between hkl and $\bar{h}kl$ reflections which would be otherwise equivalent. For that reason, the rest of the refinement was carried out with a set of 1410 non-averaged hkl and $\bar{h}kl$ reflections. Isotropic refinement of light nonhydrogen atoms and anisotropic refinement of Cl and Hg led to an R factor of 0.040. Individual weights $w = 1/\sigma(F)^2$ (Stout & Jensen, 1968) were finally applied. The refinement

Table 1. Refined coordinates ($\times 10^3$; for Cl $\times 10^4$; for Hg $\times 10^5$)

	x	y	z
Hg	18845 (11)	-54481 (5)	-42783 (23)
Cl(1)	3336 (7)	-4457 (3)	-5097 (10)
Cl(2)	3120 (8)	-6317 (3)	-5212 (10)
N(1)	-240 (2)	-581 (1)	-428 (5)
C(2)	-317 (2)	-533 (1)	-440 (4)
N(2)	-429 (2)	-546 (1)	-445 (3)
N(3)	-284 (2)	-468 (1)	-442 (3)
C(4)	-164 (2)	-462 (1)	-439 (4)
C(5)	-79 (3)	-513 (1)	-433 (6)
C(6)	-118 (3)	-574 (1)	-428 (6)
O(6)	-48 (2)	-622 (1)	-412 (3)
N(7)	32 (2)	-483 (1)	-446 (4)
C(8)	15 (2)	-419 (1)	-460 (5)
N(9)	-100 (2)	-405 (1)	-451 (3)
C(1')	-158 (2)	-341 (1)	-465 (4)
C(2')	-108 (2)	-291 (1)	-307 (5)
O(2')	-152 (2)	-305 (1)	-111 (3)
C(3')	-160 (2)	-230 (1)	-401 (4)
O(3')	-285 (2)	-222 (1)	-373 (3)
C(4')	-141 (2)	-240 (1)	-634 (4)
O(1')	-129 (2)	-313 (1)	-656 (3)
C(5')	-28 (2)	-211 (1)	-703 (5)
O(5')	4 (1)	-234 (1)	-904 (3)

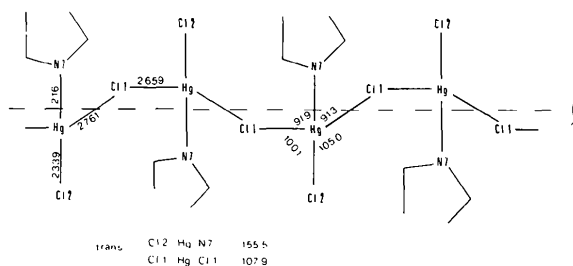
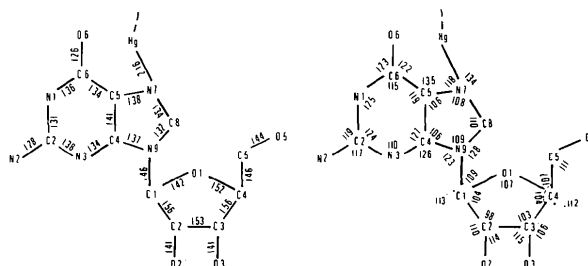
converged to $R = 0.040$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2} = 0.043$. The refined coordinates are given in Table 1.*

The R factor for the other enantiomorphous structure was much higher (0.057 compared with 0.040, unit weights), which indicates that the coordinates of Table 1 correspond to the absolute structure. This is further confirmed by the fact that the sugar has the expected *D*-configuration. In the final ΔF map, the general background was $\pm 0.5 \text{ e } \text{\AA}^{-3}$. A few higher peaks were found within 2.0 \AA from the Hg ($1.1 \text{ e } \text{\AA}^{-3}$) and a few more within 1.0 \AA from the O atoms ($0.7 \text{ e } \text{\AA}^{-3}$). Some of these latter peaks may correspond to the neglected H atoms.

The atomic scattering factors used were from Cromer & Waber (1965), except for those of H (Stewart, Davidson & Simpson, 1965). Anomalous dispersion terms were from Cromer (1965). The computer programs used are listed elsewhere (Authier-Martin & Beauchamp, 1977).

Discussion. The coordination sphere of Hg includes N(7) of guanosine and three Cl atoms, but the arrangement cannot be described in terms of a regular polyhedron (Fig. 1). N(7) and Cl(2) are strongly bonded with an N(7)—Hg—Cl(2) angle of $155.5 (6)^\circ$. The bond

* Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33004 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. Zigzag chain centered on the 2_1 axis in the c direction.Fig. 2. Bond lengths and angles in the guanosine ligand. The standard deviations are 0.02 – 0.04 \AA and 2 – 3° for bond lengths and bond angles respectively.

lengths [Hg—Cl(2) = $2.339 (7)$, Hg—N(7) = $2.16 (2) \text{ \AA}$] are typical of two-coordinate species (Authier-Martin & Beauchamp, 1977). The overall environment of Hg is completed with two crystallographically equivalent Cl(1) atoms forming weaker bonds [Hg—Cl(1) = $2.761 (7)$ and $2.659 (7) \text{ \AA}$] in a plane approximately perpendicular to the first two bonds. In a recently reported complex of 1-methylcytosine with Hg (Authier-Martin & Beauchamp, 1977), one chlorine of HgCl_2 was similarly displaced by a ring N and found as a bridging ligand in the complex. However, dimers were formed and two Hg atoms were joined by two symmetrically bridging Cl atoms. In the present case, unsymmetrical bridging results in an infinite 'square-wave' chain centered on the 2_1 axis in the c direction.

Guanosine was found to be coordinated *via* N(7) in a guanosine-platinum complex (Gellert & Bau, 1975) and in several compounds of divalent cations with guanosine monophosphate (Aoki, Clark & Orbell, 1976; Aoki, 1976; DeMeester, Goodgame, Skapski & Smith, 1974; DeMeester, Goodgame & Jones, 1974; DeMeester, Goodgame, Jones & Skapski, 1974). Mercury shows a similar preference for N(7) in the present compound. Carbonyl O(6) is not attached to mercury, even though ring closure would be favored by the small Hg—N(7)—C(5) [$118 (2)^\circ$] and large Hg—N(7)—C(8) angles [$134 (2)^\circ$]. However, the Hg—O(6) distance [$3.08 (2) \text{ \AA}$] is greater than the sum of the van der Waals radii (2.9 \AA , Grdenić, 1965; Cotton & Wilkinson, 1966). Bonding effects must therefore be vanishingly weak.

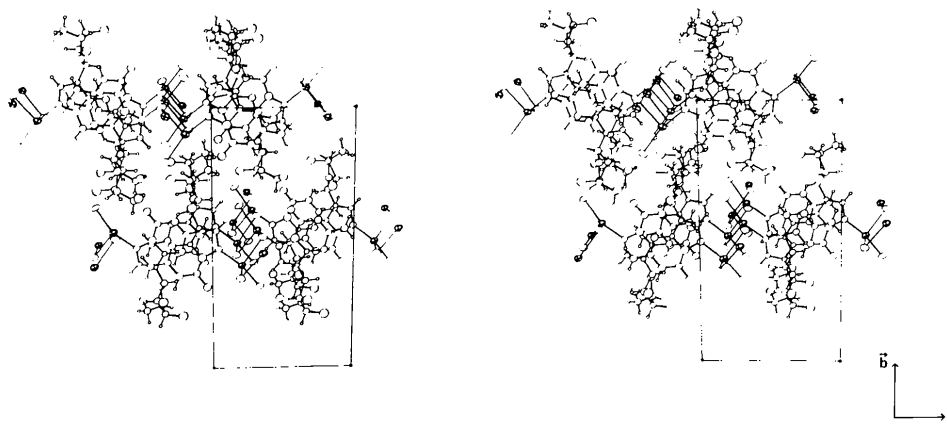


Fig. 3. A stereo diagram of the unit cell viewed down the c axis. The a axis is horizontal and b is vertical. The Hg atoms are represented by darker ellipsoids. The H atoms of the $-OH$ groups have not been found.

Table 2. Distances (\AA) and angles ($^\circ$) involved in hydrogen bonds

Symmetry code: (i) $x, y, 1 + z$; (ii) $\bar{x}, \frac{1}{2} + y, -\frac{3}{2} - z$; (iii) $-\frac{1}{2} - x, -1 - y, -\frac{1}{2} + z$; (iv) $-\frac{1}{2} - x, -1 - y, \frac{1}{2} + z$; (v) $-1 + x, y, z$; (vi) $\bar{x}, \frac{1}{2} + y, -\frac{1}{2} - z$.

O(2')—H(2')...O(5') ⁱ	2.65 (2)	C(2')—O(2')—O(5')	97 (1)
O(5')—H(5')...O(6) ⁱⁱ	2.66 (2)	C(5')—O(5')—O(6) ⁱⁱ	100 (1)
		C(6) ⁱⁱ —O(6) ⁱⁱ —O(5')	139 (2)
		C(5') ^j —O(5') ^j —O(2')	119 (1)
N(1)—H(1)...O(2') ⁱⁱⁱ	2.90 (2)	C(6)—N(1)—O(2') ⁱⁱⁱ	119 (2)
N(1)—H(1)...O(1') ^{iv}	3.17 (2)	C(2)—N(1)—O(2') ⁱⁱⁱ	108 (2)
		C(2') ⁱⁱⁱ —O(2') ⁱⁱⁱ —N(1)	134 (2)
		C(2') ^{iv} —O(2') ^{iv} —N(1)	97 (1)
		C(4') ^{iv} —O(1') ^{iv} —N(1)	134 (1)
		C(6)—N(1)—O(1') ^{iv}	122 (2)
		C(2)—N(1)—O(1') ^{iv}	105 (2)
N(2)—H(21)...Cl(1) ^v	3.38 (2)	C(2)—N(2)—Cl(1) ^v	130 (2)
N(2)—H(22)...Cl(2) ^v	3.42 (2)	C(2)—N(2)—Cl(2) ^v	159 (2)
		Hg ^v —Cl(1) ^v —N(2)	89.2 (4)
O(3')—H(3')...Cl(2) ^{vi}	3.20 (2)	C(3')—O(3')—Cl(2) ^{vi}	105 (1)
		Hg ^{vi} —Cl(2) ^{vi} —O(3')	100.3 (4)
		Hg ^v —Cl(2) ^v —Cl(2) ^{vi}	93.6 (4)

The interatomic distances and bond angles in the ligand are shown in Fig. 2. The results are not very accurate, but they agree within experimental error with accepted literature values for the purine base (Voet & Rich, 1970) and the ribose group (Aoki, 1976; Young, Tollin & Wilson, 1974; Chwang & Sundaralingam, 1974; Tougaard & Chantot, 1974; Brennan, Weeks, Shefter, Rao & Sundaralingam, 1972; Thewalt, Bugg & Marsh, 1970). The two-ring system of the base is planar within 2σ (0.05 \AA), and the substituents are significantly displaced from that plane: O(6) 0.09 (2), N(2) 0.10 (2) \AA . In the ribose group, O(1'), C(1'), C(3') and C(4') are coplanar within 2σ and C(2') is 0.72 (3) \AA distant from that plane on the same side as N(9). This corresponds to a C(2')-endo conformation. The torsion angle O(1')—C(1')—N(9)—C(8) is 60° and defines an *anti* configuration about the glycosidic bond. The C(5')—O(5') bond is in a *gauche-trans* conformation relative to the ribose ring: [O(1')—C(4')—

C(5')—O(5') = 52° ; C(3')—C(4')—C(5')—O(5') = 166°].

A packing diagram is shown in Fig. 3. The Hg—Cl chains of Fig. 1 are oriented along c and the purine rings, which are approximately parallel to the ab plane, are stacked in the same direction. Alternate piles of purine rings and Hg—Cl chains define layers parallel to the ac plane at $b \sim 0$ and $\sim \frac{1}{2}$. The interlayer region is occupied by ribose groups with their average planes oriented roughly parallel to bc . A list of potential hydrogen bonds is given in Table 2. Hydrogen bonding is probably not the predominant packing effect, although a few strong hydrogen bonds are formed. For instance, O(2')—H(2') of each ribose group is strongly hydrogen-bonded to O(5') in a group one unit cell further along c [O(2')—O(5') = 2.65 (2) \AA]. Both H atoms of the amino group are pointed towards Cl atoms, but hydrogen bonding must be very weak [N(2)—Cl(1) = 3.38 (2), N(2)—Cl(2) = 3.42 (2) \AA].

The N(1)—H(1) bond is aimed approximately halfway between O(2') and O(1') of adjacent molecules and forms a bifurcated hydrogen bond. The most important interlayer hydrogen bond involves O(5')—H(5') and carbonyl O(6) [O(5')—O(6) = 2.66 (2) Å].

The base-stacking pattern resembles those of 9-methyl- and 9-ethyladenine (Fig. 14*d,e*, Bugg, Thomas, Sundaralingam & Rao, 1971). Base stacking seems to be an important packing factor and it may have a determining effect in stabilizing this particular type of Hg—Cl chain, in which the pitch ($c/2 \sim 3.3$ Å) is equal to a normal interbase distance.

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Di- μ -chloro-bis[dichloro(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)oxomolybdenum(V)]

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Abstract. $C_{10}H_2F_{12}O_6Cl_4Mo_2$, $M_r = 779.8$, monoclinic, $a = 5.972$ (5), $b = 12.733$ (8), $c = 14.704$ (10) Å, $\beta = 91.23$ (7)°, $U = 1117.9$ Å³, $Z = 2$, $d_c = 2.32$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 13.9$ cm⁻¹. Space group $P2_1/n$ from systematic absences $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$. The centrosymmetric dimer contains a dichloro bridge [Mo—Cl 2.369 (4), 2.460 (4) Å]. The octahedral environment around each Mo is completed by a terminal O [Mo—O 1.648 (9) Å], a terminal Cl [Mo—Cl 2.305 (5) Å] and the bidentate hexafluoropentane-2,4-dionate ligand [Mo—O 2.07 (1), 2.17 (1) Å]. 1077 independent reflections measured on a diffractometer have been refined to an R of 0.062.

Introduction. Crystals of $Mo_2Cl_4O_2(hfac)_2$, $hfacH = 1,1,1,5,5,5$ -hexafluoropentane-2,4-dione, were prepared as follows. $hfacH$ (10 cm³) was distilled into $MoOCl_4$ (2 g) *in vacuo* and the resulting deep-red solution was filtered through the sintered disc of a double ampoule. Deep-red crystals formed over several months in the dark at 0°C. Excess $hfacH$ was removed and a suitable crystal was found for X-ray analysis. The crystal, 0.2 × 0.3 × 0.4 mm, was mounted with the a^* axis parallel to the instrument axis of a General Electric XRD-5 apparatus, which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height