Synthesis and Structure of Methylmercury(II) Complexes of 9-Methylguanine, including the *X*-Ray Structural Analysis of (9-Methylguanine)methylmercury(II) Nitrate

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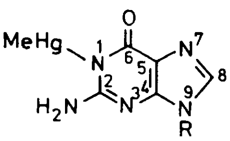
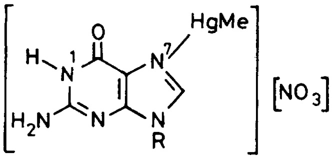
Methylmercury(II) nitrate reacts with 9-methylguanine (9-MeGua) in water to form solid complexes of stoicheiometry [HgMe(9-MeGuaH$_{-1}$)], [HgMe(9-MeGua)][NO$_3$], [HgMe(9-MeGua)][NO$_3$]·H$_2$O, and [(HgMe)$_2$(9-MeGuaH$_{-1}$)][NO$_3$]. Comparison of i.r. spectra of the solid complexes and ^{1}H n.m.r. spectra of [^{2}H$_6$]dimethyl sulphoxide-soluble (ionic) complexes with spectra of analogous guanosine (Guo) complexes indicates that complexes of 9-MeGua and Guo with similar stoicheiometry have the same mode of binding of Hg^{II}Me to the purine ring. The spectra indicate that [HgMe(9-MeGuaH$_{-1}$)] and [(HgMe)$_2$(9-MeGuaH$_{-1}$)][NO$_3$] have Hg^{II}Me bonded to N(1) and both N(1) and N(7), respectively, and the complexes [HgMe(9-MeGua)][NO$_3$] and [HgMe(9-MeGua)][NO$_3$]·H$_2$O have Hg^{II}Me bonded to N(7) with retention of a proton at N(1). Crystals of [HgMe(9-MeGua)][NO$_3$] are monoclinic, with a = 4.196(1), b = 15.060(4), c = 18.288(5) Å, β = 90.17(2)°, Z = 4, and space group $P2_1/c$. The structure has been solved by conventional Patterson and Fourier methods and refined by least-squares techniques to R 0.061 for 1 152 reflections collected by diffractometer. The complex has Hg^{II}Me bound to N(7) with Hg–C 2.06(2), Hg–N(7) 2.09(2) Å, and C–Hg–N(7) 175(1)°. Mercury interacts weakly with nearby nitrate ions, with Hg · · · O 2.75(2) and 2.99(2) Å; the purine ring is planar with the Hg^{II}Me group slightly tilted from this plane, Hg being −0.168(1) and the carbon atom −0.411(25) Å from the plane.

METHYLMERCURY(II) ion is often used in the characterization or separation of polynucleotides,[1] and the first sites of reaction of Hg^{II}Me with native DNAs are believed to be N(3) of thymine bases and N(1) of guanine bases.[2,3] Ultraviolet and Raman studies of aqueous solutions of Hg^{II}Me with uridine (u.v. absorption,[4] Raman [5]), and thymidine monophosphate (dThd-5'-*P*)[‡] (Raman),[3] indicate that Hg^{II}Me replaces the proton of the base at N(3). In support of this assignment i.r. and ^{1}H n.m.r. spectra of the solid complex [HgPh(dThdH$_{-1}$)]·H$_2$O indicate the same mode of binding.[6] For the more complex nucleoside Guo and nucleotide Guo-5'-*P* containing a guanine base, analogous u.v.[4] and Raman [7] studies, respectively, and a subsequent study of solid complexes [6] indicate formation of one neutral and two cationic complexes with structures (1)—(3).



(1)



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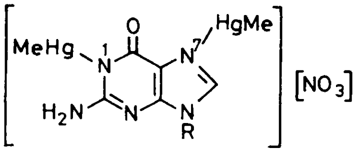

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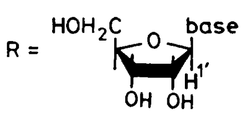

In view of the importance of these interactions in studies of polynucleotides, and in establishing i.r. and ^{1}H n.m.r. spectroscopic data for attack of an essentially unifunctional [8] electrophile at specific sites that can be used for interpretation of spectral changes on reaction with more complex electrophiles, *e.g. cis*- and *trans*-Pt^{II}(NH$_3$)$_2$, it is appropriate to confirm these structures using *X*-ray crystallography. Unfortunately, the Guo complexes are not crystalline but we have found that analogous 9-methylguanine (9-MeGua) complexes can be prepared and that of these one forms crystals suitable for *X*-ray crystallography. The synthesis and characterization of 9-MeGua complexes, evidence that they have structures analogous to Guo complexes, and the crystal and molecular structure of [HgMe(9-MeGua)][NO$_3$] are presented here.

EXPERIMENTAL

Methylmercury(II) nitrate was prepared as described previously,[6] and 9-methylguanine (Vega Biochemicals) was used as received. Microanalyses were performed by the Purdue Departmental Microanalytical Laboratory. Infrared spectra (400—4 000 cm^{-1}) of complexes in Nujol and halogenocarbon mulls were recorded with a Beckman Acculab 6 spectrophotometer, and ^{1}H n.m.r. spectra with a Varian A-60A spectrometer.

Preparation of Complexes.—All preparations were carried out at ambient temperature in a well ventilated fume hood, with an inverted beaker placed over reaction vessels to ensure slow evaporation of solvent.

[HgMe(9-MeGuaH$_{-1}$)]. A solution of methylmercury(II) nitrate (0.144 g, 0.519 mmol) and 9-methylguanine (0.085 g, 0.515 mmol) in water (30 cm^3) was filtered to remove a small amount of insoluble 9-methylguanine, and sodium hydroxide (0.19 mol dm^{-3}; 2.72 cm^3, 0.517 mmol) added. After slow evaporation over 24 h a white precipitate was collected and dried over P$_2$O$_5$ (0.112 g, 57%) (Found: C, 22.0; H, 2.7; Hg, 52.9; N, 18.4. C$_7$H$_9$HgN$_5$O requires C, 22.1; H, 2.4; Hg,

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[‡] The I.U.P.A.C.–I.U.B. abbreviations for nucleosides, *etc.* are employed throughout; see *Biochemistry*, 1970, **9**, 4022.

52.8; N, 18.4%). Infrared absorption: 3 330m(br), 3 170m(br), 1 665m, 1 619s, 1 574s, 1 534m, 1 494s, 1 421vw, 1 389w, 1 351m, 1 280w, 1 225vw, 1 182w, 1 131w, 1 092vw, 1 051vw, 1 030w, 820vw, 803vw, 784w, 756vw, 741vw, 720w, 632w, 563w, 541w(br), and 426w cm^{-1}.

[HgMe(9-Gua)][NO$_3$]·H$_2$O *and* [HgMe(9-MeGua)][NO$_3$]. A solution of methylmercury(II) nitrate (0.198 g, 0.713 mmol) and 9-methylguanine (0.118 g, 0.714 mmol) in water (20 cm^3) was filtered to remove a small amount of insoluble 9-methylguanine and allowed to evaporate slowly. After 2 d, crystals of the monohydrate were collected (0.107 g, 61%) (Found: C, 18.1; H, 3.0; Hg, 43.6; N, 18.5. $C_7H_{12}HgN_6O_5$ requires C,18.3; H, 2.7; Hg, 43.5; N, 18.2%). Infrared absorption: 3 520w(br), 3 310m(br), 3 125s(br), 1 699s, 1 672s, 1 635w, 1 592s, 1 546m, 1 494m, 1 430m, 1 330s(vbr), 1 220vw, 1 180m, 1 088vw, 1 072w, 1 049vw, 1 026vw, 859vw, 820w, 778w, 730m, 698w, 670vw, 621vw, 523vw, and 427vw cm^{-1}. On slow evaporation to dryness the filtrate gave long needles of [HgMe(9-Gua)][NO$_3$] (Found: C, 19.6; H, 2.6; Hg, 45.5; N, 19.3. $C_7H_{10}HgN_6O_4$ requires C, 19.0; H, 2.3; Hg, 45.3; N, 19.0%). Infrared absorption: 3 450w, 3 328m, 3 216m, 3 165w, 3 120m, 2 380vw, *ca.* 1 705m(sh), 1 681s, 1 637s, 1 596s, 1 545m, 1 488w, 1 431w, 1 410w, 1 375m, 1 330s(br), 1 220vw, 1 178m, 1 086vw, 1 061vw, 891vw, 822w, 803vw, 774m, 730m, 682w, 624w, and 490vw(br) cm^{-1}.

[(HgMe)$_2$(9-MeGuaH$_{-1}$)][NO$_3$]. Sodium hydroxide (0.19 mol dm^{-3}; 2.58 cm^3, 0.49 mmol) was added to a solution of methylmercury(II) nitrate (0.272 g, 0.98 mmol) and 9-methylguanine (0.81 g, 0.49 mmol) in water (30 cm^3). The solution was filtered, and after 2 d of slow evaporation a white precipitate was collected (0.102 g, 31%) (Found: C, 14.8; H, 2.0; Hg, 61.3; N, 12.9. $C_8H_{12}Hg_2N_6O_4$ requires C, 14.6; H, 1.8; Hg, 61.0; N, 12.8%). Infrared absorption: 3 346m, 3 193m, 3 111vw, 3 060w, 3 015vw, 2 929vw, 1 666m, 1 637s, 1 600s, 1 547w, 1 502s, 1 430m, 1 380s(sh), 1 330s(br), 1 187m, 1 130w, 1 094w, 1 066w, 1 042w, 907vw, 820w(sh), 805w, 780m, 722m, 622w, 569w, and 437vw cm^{-1}.

Crystal Data for [HgMe(9-MeGua)][NO$_3$].—$C_7H_{10}HgN_6O_4$, $M = 422.78$, Monoclinic, $a = 4.196(1)$, $b = 15.060(4)$, $c = 18.288(5)$ Å, $\beta = 90.17(2)°$, $U = 1\,155.65$ Å^3, $D_m = 2.56(1)$ g cm^{-3} (by flotation in a CH$_3$I–CHBr$_3$ mixture), $Z = 4$, $D_c = 2.54$ g cm^{-3}, $F(000) = 824$, space group $P2_1/c$ (no. 14, C^5_{2h}) from systematic absences $h0l$ with l odd and $0k0$ with k odd, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 12.84 mm^{-1}. Unit-cell parameters were determined using a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator, as described previously.[9]

Intensity Measurements.—Intensity data were collected using the diffractometer above and a white crystal of dimensions 0.01 × 0.03 × 0.06 mm (optimum size 0.15 mm) that had been checked for cracking or twinning using a polarizing microscope. The crystal was mounted on a silica capillary using ' Resiweld ' epoxy-cement and centred on the goniometer using high-angle reflections selected from an initial rapid data collection. Three standard reflections monitored at 2 h intervals showed no significant systematic variation in intensity.

Data were collected by the ω-scan technique with a symmetric scan width of ±0.55° in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0.05° s^{-1}. The Mo-K_α radiation was monochromatized with a flat graphite crystal and no reflection was sufficiently intense to warrant the insertion of an attenuation filter. The data were processed with a program written specifically for the PW 1100 diffractometer.[10] The background-corrected intensities were assigned standard deviations according to $\sigma(I) = [C_T + (t_c/t_b)^2(B_1 + B_2) + (qI)^2]^{\frac{1}{2}}$ where C_T is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = C_T - (t_c/t_b)(B_1 + B_2)$; q was 0.04 and is an allowance for ' machine errors'. Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects. An absorption correction was applied based on the indexed crystal faces (1 0 2), ($\bar{1}$ 0 2), (0 1 0), (0 $\bar{1}$ 0), (0 0 1), and (0 0 $\bar{1}$), and direction cosines calculated for the PW 1100 data. Maximum and minimum values of the transmission factors were 0.879 9 and 0.682 4, respectively. The total number of reflections measured to 2θ(Mo-K_α) 60° was 3 881, of which 134 were rejected as being systematically absent or having zero F or I and 408 were multiple observations [the measure of agreement between these, R, was 0.048 where R is given by $(\Sigma\{N\Sigma[w(F_{av.} - F)^2]\}/\Sigma[(N - 1)\Sigma(wF^2)])^{\frac{1}{2}}$ (the inner summations are over the N equivalent reflections averaged to give $F_{av.}$, and the outer summations are over all unique reflections) [11]]. This left 3 339 unique reflections of which 1 171 obeyed the condition $I \geqslant 3\sigma(I)$, and 19 reflections were considered as poorly calculating, very weak reflections and were omitted during the refinement. Thus, 1 152 reflections were used in the final refinement.

Structure Determination and Refinement.—The Patterson synthesis enabled location of the mercury atom by standard methods; its position was refined and all non-hydrogen atoms were located in the subsequent difference-Fourier synthesis. The function minimized in full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight $[1/\sigma^2(F_o)]$ and F_o and F_c are the observed and calculated structure factors, respectively. Several cycles, with the mercury atom refined anisotropically and other non-hydrogen atoms refined isotropically, resulted in R 0.079, where $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. Absorption corrections were applied and several cycles of full-matrix least-squares refinement led to R 0.061 and R' 0.056 (for observed reflections), where $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$. The final difference-Fourier synthesis revealed some hydrogen-atom positions but these were not included in refinement, and had no major characteristic greater than 1.92 e Å^{-3}, this being in the vicinity of the mercury atom.

TABLE 1

Final fractional co-ordinates for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Hg	2 368(3)	1 814(1)	3 577(1)
C	4 060(62)	1 166(15)	4 488(12)
C(2)	−5 748(56)	1 478(13)	1 042(11)
C(4)	−2 830(54)	2 507(14)	1 648(10)
C(5)	−1 609(52)	1 937(13)	2 152(10)
C(6)	−2 489(66)	1 011(16)	2 086(13)
C(8)	323(54)	3 246(14)	2 415(11)
C(9)	−2 267(66)	4 165(14)	1 426(13)
N	−2 657(53)	3 657(14)	4 017(10)
N(1)	−4 432(47)	820(11)	1 490(9)
N(2)	−7 468(51)	1 222(12)	515(10)
N(3)	−4 689(45)	2 323(10)	1 078(8)
N(7)	356(47)	2 383(12)	2 643(9)
N(9)	−1 545(39)	3 329(10)	1 828(8)
O(1)	−1 488(54)	4 350(14)	4 197(11)
O(2)	−1 613(49)	2 966(11)	4 299(10)
O(3)	−4 723(58)	3 625(12)	3 546(11)
O(6)	1 749(41)	414(10)	2 553(8)

Final observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22732 (9 pp.).[*] Parameters for all non-hydrogen atoms are listed in Table 1, together with their estimated standard deviations derived from the inverse least-squares matrix. The atom-numbering scheme follows the conventional numbering for purine rings [see structure (1)]. Atomic scattering factors for neutral atoms and corrections for anomalous dispersion were taken from refs. 12 and 13.

Calculations.—All calculations were performed on the Monash University B6700 computer. The major programs used were SHELX-76,[11] ORFFE,[14] MEANPL,[15] and Figures were drawn using ORTEP.[16]

RESULTS AND DISCUSSION

Preparation and Characterization of Complexes.—Complexes of 9-methylguanine were obtained from water by employing the same reaction procedures developed for synthesis of the analogous guanosine complexes. The

$$\mathrm{HgMe(NO_3)} + \mathrm{Na[OH]} + \text{9-MeGua} \longrightarrow \mathrm{[HgMe(9\text{-}MeGuaH_{-1})]} + \mathrm{Na[NO_3]} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{HgMe(NO_3)} + \text{9-MeGua} \longrightarrow \mathrm{[HgMe(9\text{-}MeGua)][NO_3]{\cdot}H_2O} \quad (2)$$

$$2\mathrm{HgMe(NO_3)} + \mathrm{Na[OH]} + \text{9-MeGua} \longrightarrow \mathrm{[(HgMe)_2(9\text{-}MeGuaH_{-1})][NO_3]} + \mathrm{Na[NO_3]} + \mathrm{H_2O} \quad (3)$$

monohydrate formed as crystals, and the filtrate from this reaction gave crystals of the anhydrous complex $[\mathrm{HgMe(9\text{-}MeGua)}][\mathrm{NO_3}]$ on slow evaporation to dryness.

The complexes have different i.r. spectra (Figure 1), and the nitrates have strong, broad, absorption in the region 1 300—1 400 $\mathrm{cm^{-1}}$ characteristic [17] of free or very weakly co-ordinated nitrate ion. For organomercury guanosine complexes, spectra in the region 1 500—1 800 $\mathrm{cm^{-1}}$ were found to be characteristic of structures involving retention of a proton at N(1) of Guo in $[\mathrm{HgR(Guo)}][\mathrm{NO_3}]$, or deprotonation to give $[\mathrm{HgR(GuoH_{-1})}]$, $[\mathrm{(HgR)_2(GuoH_{-1})}][\mathrm{NO_3}]$ (R = Me or Ph), and $\mathrm{Na[GuoH_{-1}]{\cdot}H_2O}$. In this region, spectra of analogous 9-MeGua and Guo complexes are very similar (Figure 1),[†] particularly for $[\mathrm{HgMe(9\text{-}MeGua)}][\mathrm{NO_3}]$ and $[\mathrm{HgMe(Guo)}][\mathrm{NO_3}]$ which have three intense absorptions at 1 681, 1 637, and 1 596 $\mathrm{cm^{-1}}$, and 1 705, 1 641, and 1 603 $\mathrm{cm^{-1}}$, respectively.

Absorption near 1 700 $\mathrm{cm^{-1}}$ for guanosine,[‡] primarily ν[C(6)=O] involving some coupling with ring modes,[§] is lowered on deprotonation to form $\mathrm{Na[GuoH_{-1}]{\cdot}H_2O}$ (*ca.* 1 560—1 675 $\mathrm{cm^{-1}}$)[¶] and organomercury complexes (*ca.* 1 600—1 669 $\mathrm{cm^{-1}}$),[§] consistent with increased electron delocalization in the base resulting in a decreased bond order for the carbonyl group. Similarly, intense absorption of 9-MeGua at 1 686 $\mathrm{cm^{-1}}$ is lowered on formation of $[\mathrm{HgMe(9\text{-}MeGuaH_{-1})}]$ and $[\mathrm{(HgMe)_2(9\text{-}MeGuaH_{-1})}][\mathrm{NO_3}]$ (Figure 1).

Proton n.m.r. spectra for ionic complexes of 9-MeGua and analogous Guo complexes in $[^2\mathrm{H_6}]$dimethyl sulphoxide are given in Table 2. The compounds 9-MeGua and $[\mathrm{HgMe(9\text{-}MeGuaH_{-1})}]$ are insoluble in this solvent, and both $[\mathrm{HgMe(9\text{-}MeGua)}][\mathrm{NO_3}]$ and its monohydrate have similar spectra. Analogous 9-MeGua and Guo complexes have similar spectra. The spectra confirm i.r. evidence that the proton at N(1) is retained on formation of $[\mathrm{HgMe(L)}][\mathrm{NO_3}]$ and removed on formation of $[\mathrm{(HgMe)_2(LH_{-1})}][\mathrm{NO_3}]$ (L = 9-MeGua or Guo). The $\mathrm{Hg^{II}Me}$ moiety in analogous complexes has an almost identical

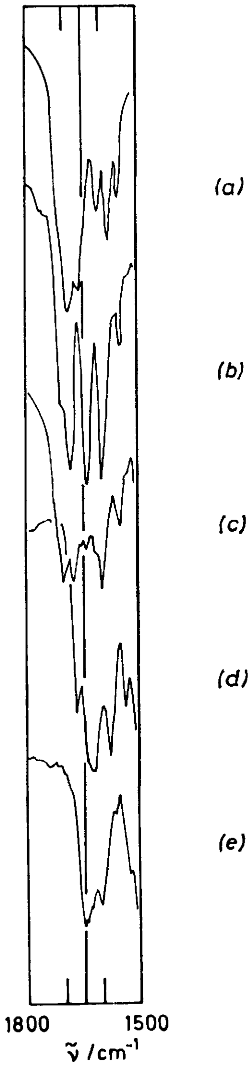

FIGURE 1 Infrared spectra of (*a*) 9-MeGua, (*b*) $[\mathrm{HgMe(9\text{-}MeGua)}][\mathrm{NO_3}]$, (*c*) $[\mathrm{HgMe(9\text{-}MeGua)}][\mathrm{NO_3}]{\cdot}\mathrm{H_2O}$, (*d*) $[\mathrm{HgMe(9\text{-}MeGuaH_{-1})}]$, and (*e*) $[\mathrm{(HgMe)_2(9\text{-}MeGuaH_{-1})}][\mathrm{NO_3}]$ as Nujol mulls in the region 1 500—1 800 $\mathrm{cm^{-1}}$

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

[†] For Guo complexes a Figure similar to that of Figure 1 is given in ref. 6.

[‡] Guanosine occurs in at least two crystalline forms (M. Tsuboi, Y. Kyogoku, and T. Shimanouchi, *Biochim. Biophys. Acta*, 1962, **55**, 1). These authors found that form I has absorption at 1 730 $\mathrm{cm^{-1}}$ and form II at 1 730 and 1 692 $\mathrm{cm^{-1}}$.

[§] See ref. 6 for a discussion of this assignment.

[¶] Part of broad absorption containing both ν[C(6)=O] and $\mathrm{NH_2}$ deformation modes.[6]

coupling constant $|^2J(^1H-^{199}Hg)|$, reflecting [6,*] bonding to N(7) in $[HgMe(L)][NO_3]$, and both N(1) and N(7) in $[(HgMe)_2(LH_{-1})][NO_3]$.

Close similarity between i.r. and ^1H n.m.r. spectra of Guo and 9-MeGua complexes indicates that the mode of bonding of $Hg^{II}Me$ to 9-MeGua in $[HgMe(9\text{-}MeGua)][NO_3]$ discussed below is identical to that in the Guo analogue $[HgMe(Guo)][NO_3]$.

Crystal and Molecular Structure of $[HgMe(9\text{-}MeGua)][NO_3]$.—Aspects of the molecular geometry are given in Tables 3—5, and two different views of the structure are given in Figures 2 and 3.

TABLE 2

Hydrogen-1 n.m.r. data (δ/p.p.m.) for guanosine and ionic complexes of guanosine and 9-methylguanine [a]

Compound	δ[N(1)H]	$\delta(NH_2)$	δ[H(8)]	δ[H(1′) or NMe] [b]	δ(MeHg)	$|^2J(^1H-^{199}Hg)|$/ Hz [c]
Guo [d]	10.79	6.47	7.96	5.47(d)		
$[HgMe(Guo)][NO_3]$ [d]	11.45	7.02	8.69	5.90(d)	0.89	229
$[HgMe(9\text{-}MeGua)][NO_3]$	11.37	6.94	8.40	3.74	0.87	227
$[HgMe(9\text{-}MeGua)][NO_3]\cdot H_2O$ [e]	11.34	6.93	8.39	3.73	0.87	227
$[(HgMe)_2(GuoH_{-1})][NO_3]$		6.97	8.60	5.88(d)	0.85	221
$[(HgMe)_2(9\text{-}MeGuaH_{-1})][NO_3]$		6.96	8.31	3.71	0.83	220

[a] For dimethyl sulphoxide solutions. Hydrogen-1 shifts are downfield from internal tetramethylsilane. 9-Methylguanine and $[HgMe(9\text{-}MeGuaH_{-1})]$ are insoluble. [b] H(1′) of Guo, N(9)Me of 9-MeGua. [c] Coupling to the methyl protons; the sign of the coupling constant is assumed to be negative (F. A. L. Anet and J. L. Sudmeier, *J. Magnetic Resonance*, 1969, **1**, 124; H. F. Henneike, *J. Amer. Chem. Soc.*, 1972, **94**, 5945). [d] From ref. 6. [e] Water protons at 3.38 p.p.m.

The crystal structure is composed of $[HgMe(9\text{-}MeGua)]^+$ cations and nitrate anions. The $Hg^{II}Me$ group is bonded to N(7) of the purine ring, with the Hg–N(7) bond length [2.09(2) Å] similar to that in $[(HgMe)_2(AdeH_{-1})][NO_3]$ which has Hg–N(7) 2.09 and Hg–N(9) 2.08 Å.[18] The oxygen O(6) of the purine ring is well removed from mercury [3.31(2) Å], so the purine is acting as a unidentate ligand *via* N(7).

TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

(*a*) Mercury environment			
Hg–C	2.06(2)	Hg · · · O(2)	2.75(2)
Hg–N(7)	2.09(2)	Hg · · · O(3^i)	2.99(2)
(*b*) 9-Methylguanine group			
C(2)–N(1)	1.40(3)	C(5)–N(7)	1.39(3)
C(2)–N(2)	1.26(3)	C(6)–O(6)	1.28(3)
C(2)–N(3)	1.35(3)	C(6)–N(1)	1.39(3)
C(4)–N(3)	1.33(3)	C(8)–N(7)	1.37(3)
C(4)–C(5)	1 36(3)	C(8)–N(9)	1.33(3)
C(4)–N(9)	1.39(3)	C(9)–N(9)	1.49(3)
C(5)–C(6)	1.45(3)		
(*c*) Nitrate group			
N–O(1)	1.20(3)	N–O(3)	1.22(3)
N–O(2)	1.24(3)		

Symmetry code: i, $1 + x, y, z$.

The nearest atom to mercury, except for C and N(7), is the nitrate O(2) at 2.75(2) Å, *ca.* 0.1—0.4 Å less than the sum of van der Waals radii, 2.9 Å [Hg 1.5,[19] O 1.4 Å (ref. 20)] or 3.13 Å using Grdenić's [19] upper limit of 1.73 Å for the radius of Hg. Consistent with the presence of an Hg · · · O(2) interaction the angle C–Hg–N(7) is 175(1)° with C and N(7) bent away from O(2) and approximately coplanar with Hg and O(2) [sum of angles at Hg 350°, Hg is −0.090(1) Å out of the C, N(7), O(2) plane], although this interaction must be very weak as the nitrate ion is regular (within 1σ in bond lengths and angles). The next-nearest oxygen is O(3) of a symmetry-related nitrate ion at 2.99(2) Å from mercury.

The $Hg^{II}Me$ group is slightly out of the plane of the purine ring (Table 5), with Hg and C −0.168(1) and −0.411(25) Å removed from the plane, respectively. The torsion angle C–Hg–N(7)–C(5) is −17(10), and C–Hg–N(7)–C(8) is 155(9)°, where the sign of the angle follows accepted convention.[21] The purine ring is planar with deviations of atoms from the plane within 3σ, except for N(1) and O(6) which are 0.071(19) and −0.067(16) Å from the mean plane.

TABLE 4

Angles (°), with estimated standard deviations in parentheses

(*a*) About mercury			
C–Hg–N(7)	175(1)	N(7)–Hg–O(2)	84(1)
C–Hg–O(2)	97(1)		
(*b*) 9-Methylguanine group			
C(2)–N(1)–C(6)	123(2)	C(5)–C(6)–N(1)	114(2)
N(1)–C(2)–N(3)	121(2)	C(5)–C(6)–O(6)	124(2)
N(1)–C(2)–N(2)	117(2)	N(1)–C(6)–O(6)	121(2)
N(2)–C(2)–N(3)	121(2)	C(5)–N(7)–C(8)	105(2)
C(2)–N(3)–C(4)	115(2)	C(5)–N(7)–Hg	125(2)
C(5)–C(4)–N(3)	128(2)	C(8)–N(7)–Hg	130(1)
C(5)–C(4)–N(9)	105(2)	N(7)–C(8)–N(9)	110(2)
N(3)–C(4)–N(9)	127(2)	C(4)–N(9)–C(8)	110(2)
C(4)–C(5)–C(6)	117(2)	C(8)–N(9)–C(9)	126(2)
C(4)–C(5)–N(7)	111(2)	C(4)–N(9)–C(9)	124(2)
C(6)–C(5)–N(7)	132(2)		
(*c*) Nitrate group			
O(1)–N–O(2)	118(2)	O(2)–N–O(3)	121(2)
O(1)–N–O(3)	121(2)		

Hydrogen bonding does not occur between guanine bases, but may occur between the base and a symmetry-related nitrate ion ($\bar{x} - 1, y - \frac{1}{2}, \frac{1}{2} - z$) with N(1) · · · O(1) 3.07(3) and N(2) · · · O(1) 2.90(3) Å, and another

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[*] In $Hg^{II}Me$ complexes of pyridine and substituted pyridines, $[HgMe(L)][NO_3]$, the coupling constant increases with decreasing basicity of the pyridine donor (A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425; A. J. Canty, P. Barron, and P. C. Healy, *J. Organometallic Chem.*, 1979, **179**, 447). Consistent with structures (1) and (2), $[HgMe(GuoH_{-1})]$ has a coupling constant of 206.5 Hz, while $[HgMe(Guo)][NO_3]$ has a coupling constant of 229 Hz as N(7) is less basic than N(1). The complex $[(HgMe)_2(GuoH_{-1})][NO_3]$ has $^2J(^1H-^{199}Hg)$ 221 Hz, intermediate between these two values, consistent with rapid exchange of $Hg^{II}Me$ between N(1) and N(7).

symmetry-related nitrate ion ($x - 1, \frac{1}{2} - y, z - \frac{1}{2}$) with $N(2) \cdots O(2)$ 3.07(3) Å.

This work was supported by a Public Health Service Grant from the National Institute for Arthritis, Metabolism, and Digestive Diseases, by grants from the National Science Foundation (to R. S. T.), the Australian Research Grants Committee (to B. M. G.), and the Australian Development Assistance Plan (to N. C.).

TABLE 5

Equations of mean planes and deviations (Å) of individual atoms from planes in square brackets. X, Y, Z are orthogonal co-ordinates and are related to the fractional co-ordinates x, y, z in the crystal system by the equation:

$$\begin{pmatrix} 4.196\,000 & 0.000\,000 & -0.053\,942 \\ 0.000\,000 & 15.060\,000 & 0.000\,000 \\ 0.000\,000 & 0.000\,000 & 18.287\,920 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

(*a*) Mean plane through the 9-methylguanine group [C(2), C(4), C(5), C(6), C(8), C(9), N(1), N(2), N(3), N(7), N(9), O(6)]

$0.7925X - 0.1763Y - 0.5839Z + 3.3607 = 0$

[C(2) −0.061(22), C(4) −0.013(21), C(5) 0.004(21), C(6) 0.029(27), C(8) 0.017(22), C(9) −0.028(26), N(1) 0.071(19), N(2) 0.001(20), N(3) 0.029(18), N(7) 0.013(19), N(9) 0.003(16), O(6) −0.067(16), Hg −0.168(1), C −0.411(25)]

(*b*) Mean plane through the nitrate group [N, O(1), O(2), O(3)]

$0.6941X - 0.0815Y - 0.7152Z + 6.4773 = 0$

[N −0.015(20), O(1) 0.005(21), O(2) 0.005(19), O(3) 0.005(22)]

(*c*) Direction cosines

9-MeGua plane:	0.7925	−0.1763	−0.5839
Nitrate plane:	0.6941	−0.0815	−0.7152

(*d*) Angle between planes: 10.87°

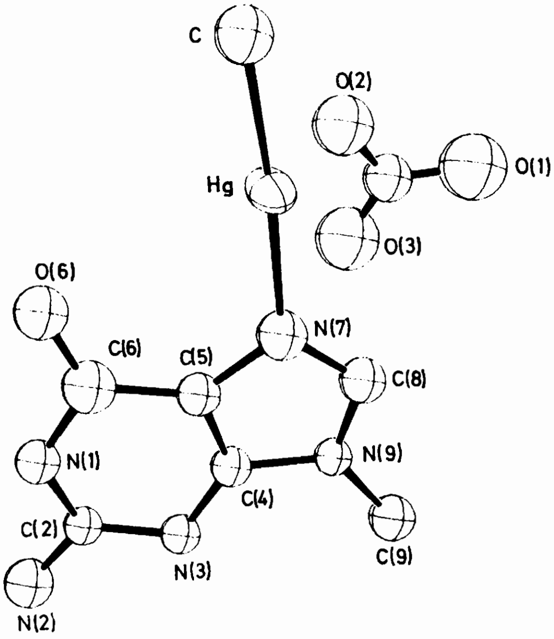

FIGURE 2 Molecular structure of [HgMe(9-MeGua)][NO_3] showing the atom-numbering scheme used

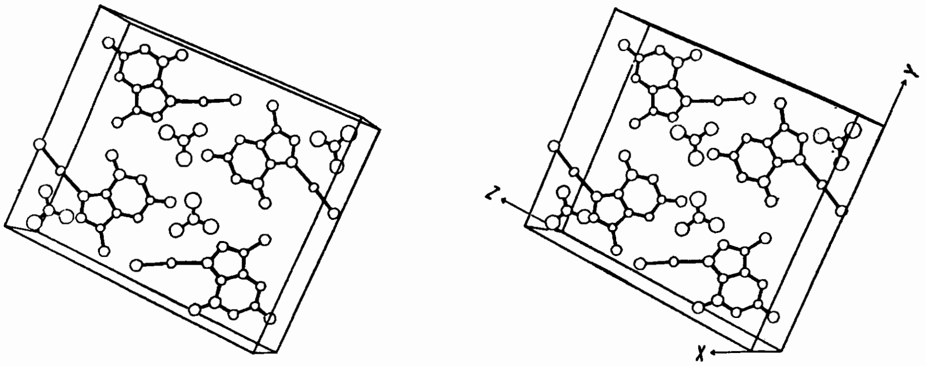

FIGURE 3 Packing of the ions [HgMe(9-MeGua)]$^+$ and NO_3^- in the unit cell

[9/1539 *Received*, 26*th September*, 1979]

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