Structure of μ-(9-Methyladeninato-μ-N^6)-bis[methylmercury(II)], $C_8H_{11}Hg_2N_5$

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Abstract. $M_r = 578 \cdot 59$, triclinic, $P\bar{1}$, $a = 8 \cdot 701$ (6), $b = 9 \cdot 127$ (2), $c = 15 \cdot 043$ (2) Å, $\alpha = 82 \cdot 08$ (2), $\beta = 88 \cdot 86$ (4), $\gamma = 78 \cdot 15$ (4)°, $V = 1158 \cdot 0$ Å^3, $Z = 4$, $D_x = 3 \cdot 318$, $D_m = 3 \cdot 32$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å (graphite-monochromated), $\mu = 26 \cdot 45$ mm^{-1}, $F(000) = 1016$, $T = 293$ K, final $R = 4 \cdot 4\%$ for 2553 unique observed reflections. The asymmetric unit consists of two independent molecules, in which both NH_2 protons of 9-methyladenine have been substituted by linearly coordinated methylmercury groups. The $-N(HgCH_3)_2$ group is approximately in the plane of the ring.

Introduction. In an earlier report from this laboratory, it was noted that the CH_3Hg^+ ion smoothly displaces an amino H of 9-methyladenine (H_2mad)* in water, even under slightly acidic conditions (Prizant, Olivier, Rivest & Beauchamp, 1979). We have recently reported that under relatively mild conditions it is possible to displace both amino H atoms of adenine and 9-methyladenine (Charland, Simard & Beauchamp, 1983). A full report on the crystal structure of the 9-methyladenine complex $(CH_3Hg)_2$(mad) is presented here.

Experimental. Colorless crystals precipitated by slow cooling of a mixture of two mmol of CH_3HgOH (1M aqueous solution) and one mmol of H_2mad (0·15 g) dissolved in warm N,N-dimethylformamide. Composition was determined by elemental analysis: calc. for $C_8H_{11}N_5Hg_2$: C 16·61, H 1·92, N 12·11, Hg 69·36%; found: C 16·74, H 2·11, N 12·26, Hg 69·09%.

D_m measured by flotation in $CH_2I_2/C_2H_2Br_4$ mixture. Crystal dimensions between pairs of centrosymmetrically related faces: 0·60 mm [(10$\bar{1}$) and ($\bar{1}$01)], 0·10 mm [(0$\bar{1}$0) and (010)] and 0·14 mm [(001) and (00$\bar{1}$)]. Unit-cell parameters determined from 25 reflections (2·74 < θ < 20·03°) centered on an Enraf–Nonius CAD-4 diffractometer; these were identical with those deduced from a set of precession photographs (no systematic absences) and the Niggli parameters clearly showed that the lattice could not be described in higher symmetry. Data collected as described elsewhere (Bélanger-Gariépy & Beauchamp, 1980). $2\theta_{max} = 50°$. Range of *hkl*: $0 \leq h \leq 10$, $-10 \leq k \leq 10$, $-17 \leq l \leq 17$. Standards (e.s.d.): 034

(1·5%), 1$\bar{1}$5 (2·0%), 31$\bar{1}$ (1·6%). 4065 unique reflections measured, 2553 observed, 1512 unobserved [$I < 2 \cdot 5\sigma(I)$]. Corrections for the Lorentz effect, polarization and absorption (Gaussian integration, grid $8 \times 8 \times 8$, transmission range 0·030 − 0·119). Structure solved by the heavy-atom method. The centrosymmetric space group $P\bar{1}$ was assumed first, and this choice was confirmed by successful refinement. The four independent Hg atoms were located from a three-dimensional Patterson synthesis. The remaining nonhydrogen atoms (except H's) were positioned from a subsequent difference Fourier map. $\sum w(|F_o| - |F_c|)^2$ minimized in full-matrix least squares (isotropic), then in block-diagonal least squares. Parameters refined: coordinates (except H's), anisotropic temperature factors, overall scale, secondary extinction. The methyl H atoms were not detected. H atoms on C(21), C(22), C(81) and C(82) were fixed at their calculated coordinates ($C-H = 0 \cdot 95$ Å, sp^2 hybridization, isotropic $B = 5 \cdot 0$ Å^2). The H parameters were not refined, but the coordinates were recalculated after each cycle. $R = 4 \cdot 4\%$, $wR = 5 \cdot 0\%$, $S = 1 \cdot 67$; $w^{-1} = \sigma^2(F) = |\sigma^2(I) + (0 \cdot 02I)^2|/4\text{Lp}I$; $(\Delta/\sigma)_{max} = 0 \cdot 13$, $(\Delta/\sigma)_{ave} = 0 \cdot 01$; $\Delta\rho_{max} = 2 \cdot 74$, $\Delta\rho_{min} = -1 \cdot 79$ e Å^{-3}, both near Hg. Secondary-extinction value 2·8 (2) ×10^{-4}. Scattering curves from Cromer & Waber (1965) except for H (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion correction for Hg from Cromer (1965). The computer programs used are listed elsewhere (Hubert & Beauchamp, 1980).

Discussion. The final atomic coordinates and U_{eq} values are listed in Table 1.* The asymmetric unit includes two independent molecules, in which the two H atoms of the ligand N(6)† amino group have been substituted by CH_3Hg^+ ions (Fig. 1). The mean bond distances and angles are schematically represented in Fig. 2.

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† In the atom labels, the first digit corresponds to the position in the ring, whereas the two independent molecules (1 and 2) are distinguished by the second digit. In discussions dealing with the average geometry of both molecules, the second digit is omitted.

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* 9-Methyladenine: neutral form = H_2mad; dianionic form obtained by loss of the two amino hydrogens = mad.

Table 1. *Refined atomic coordinates* (×10³, Hg ×10⁵) *and equivalent isotropic thermal parameters* (Å² ×10³, Hg ×10⁴)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12}a^*b^*ab\cos\gamma + 2U_{13}a^*c^*ac\cos\beta + 2U_{23}b^*c^*bc\cos\alpha).$$

	x	y	z	U_{eq}
Hg(61A)	50713 (10)	76231 (11)	−4062 (5)	504
Hg(61B)	18274 (11)	108188 (10)	−5712 (5)	482
Hg(62A)	90486 (10)	20296 (10)	54269 (5)	451
Hg(62B)	70151 (10)	−10653 (10)	55930 (5)	463
N(11)	206 (2)	999 (2)	142 (1)	50
N(12)	681 (2)	−8 (2)	359 (1)	53
N(31)	278 (2)	895 (2)	294 (1)	49
N(32)	717 (2)	104 (2)	208 (1)	60
N(61)	330 (2)	907 (2)	16 (1)	46
N(62)	788 (2)	64 (2)	487 (1)	45
N(71)	535 (2)	672 (2)	156 (1)	58
N(72)	923 (2)	286 (2)	350 (1)	44
N(91)	494 (2)	676 (2)	301 (1)	48
N(92)	876 (2)	297 (2)	200 (1)	37
C(21)	193 (2)	992 (2)	229 (1)	56
C(22)	664 (3)	12 (2)	273 (1)	56
C(41)	386 (2)	794 (2)	256 (1)	41
C(42)	799 (2)	190 (2)	246 (1)	34
C(51)	410 (2)	788 (2)	168 (1)	39
C(52)	829 (2)	185 (2)	333 (1)	36
C(61)	317 (2)	897 (2)	105 (1)	40
C(62)	765 (2)	84 (2)	398 (1)	39
C(81)	580 (2)	610 (2)	240 (1)	53
C(82)	951 (2)	347 (2)	262 (1)	42
C(91)	518 (2)	642 (2)	401 (1)	48
C(92)	876 (3)	338 (3)	100 (1)	61
C(61A)	680 (3)	618 (3)	−99 (2)	82
C(61B)	36 (3)	1262 (3)	−131 (2)	72
C(62A)	1017 (3)	334 (3)	607 (2)	70
C(62B)	632 (3)	−295 (3)	633 (2)	64

The four independent Hg atoms show the linear two-coordination usually encountered for this element. Departure from linearity is significant in molecule (2) [C(62A)–Hg(62A)–N(62) 175·8 (8) and C(62B)–Hg(62B)–N(62) 174·9 (8)°], but such deviations are often found as a result of packing effects. The Hg–N (ave. 2·05 Å) and Hg–C (ave. 2·06 Å) bond lengths do not differ significantly from those reported for similar compounds (Prizant, Olivier, Rivest & Beauchamp, 1982; Olivier & Beauchamp, 1982). The accepted value for the van der Waals radius of Hg is 1·50 Å (Huheey, 1972). The Hg(61)···Hg(62) separations, averaging 3·605 Å, clearly indicate the absence of steric hindrance between the two Hg atoms of the disubstituted amino group. The angles about the N(6) amino atoms correspond to a trigonal-planar geometry. Therefore, even if both NH₂ protons have been substituted by CH₃Hg⁺ groups, the N(6) atoms retain their sp^2 hybridization, as in free H₂mad (Kistenmacher & Rossi, 1977).

The two nonequivalent ligands have the same geometry within experimental errors. Since light atoms make only a small contribution to the total electron density, the e.s.d.'s on bond lengths and angles are large and probably greater than the changes in ligand geometry resulting from complexation. No differences are observed between the average values given in Fig. 2 and those of free 9-methyladenine (Kistenmacher & Rossi, 1977) and other neutral adenine residues (Taylor & Kennard, 1982), except perhaps in the N(7)–

C(8)–N(9) portion, where the bond-length pattern observed here [N(7)–C(8) 1·37 (3), C(8)–N(9) 1·32 (3) Å] is opposite to that usually found [N(7)–C(8) 1·312 (2), C(8)–N(9) 1·376 (2) Å] (Taylor & Kennard, 1982). The individual rings in both molecules are planar within 2σ (0·04 Å). Dihedral angles of 1·5 (12) and 4·3 (11)° are found between the five-membered and the six-membered rings in molecules (1) and (2), respectively, the last value being somewhat higher than commonly found. The amino N atoms are essentially within the plane of their respective six-membered ring [N(61) displaced −0·03 (2) and N(62) 0·02 (2) Å], but the methyl groups slightly deviate from the planes calculated through the five-membered rings [C(91) −0·07 (2) and C(92) −0·05 (2) Å].

The two −N(HgCH₃)₂ groups, including the methylmercury C atoms, are planar, except in molecule (2) where C(62B) is tilted out its plane, with an atom-to-plane displacement of 0·19 (2) Å. Dihedral angles of 6·3 (13) and 4·8 (13)° are found between the planes calculated through the disubstituted amino groups and the corresponding six-membered rings. These small rotations about C(6)–N(6) can be ascribed to packing effects.
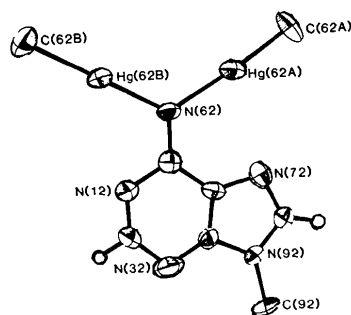

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the [(CH₃Hg)₂(mad)] molecule (molecule 2). The ellipsoids correspond to 50% probability. H atoms at C(2) and C(8) are shown as spheres of arbitrary size.

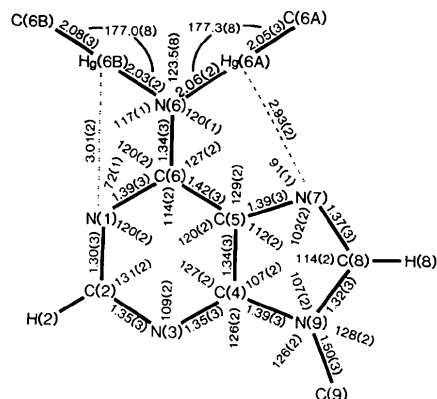Fig. 2. Interatomic distances (Å) and bond angles (°). The values averaged over the two independent molecules are given. Individual values have been deposited.
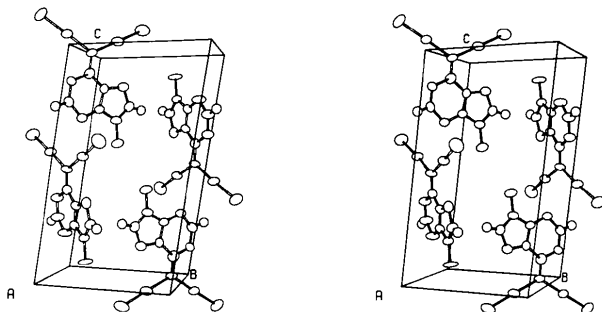
Fig. 3. Stereoview of the packing in the unit cell viewed down **a**.

Intramolecular distances in the range 2·90 (2)–3·02 (2) Å are observed between the amino-bonded Hg atoms and N(1) or N(7) (Table 3, deposited). These distances could indicate weak bonding interactions, but the angles are not favorable, the metal being far from the probable direction of the N(1) or N(7) lone pair: C(6)–N(1)–Hg(62) ave. 72, expected 120°; C(5)–N(7)–Hg(61) ave. 91, expected 129°.

A packing diagram is given in Fig. 3. The cell contains two independent pairs of centrosymmetrically related |(CH₃Hg)₂(mad)| molecules roughly perpendicular to the *ab* plane. Successive molecules along **c** are oriented 86° apart about the **c** direction and the

N(3) atom of one molecule is just above (or below) the mouth of the Y-shaped –N(HgCH₃)₂ group of the next molecule, producing intermolecular N(3)···Hg contacts in the range 3·03 (2)–3·16 (2) Å (Table 2, deposited). In the **a** and **b** directions, all intermolecular contacts are of the normal van der Waals type.

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Structure of Bis(diphenyl phosphato)tetrakis(imidazole)copper(II), [Cu{P(C₆H₅O)₂O₂}₂(C₃H₄N₂)₄]

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Abstract. $M_r = 834\cdot3$, monoclinic, $P2_1/c$, $a = 8\cdot264$ (3), $b = 25\cdot339$ (8), $c = 10\cdot216$ (3) Å, $\beta = 114\cdot82$ (4)°, $V = 1941\cdot6$ (8) Å³, $Z = 2$, $D_m = 1\cdot43$ (1), $D_x = 1\cdot43$ g cm⁻³, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu = 21$ cm⁻¹, $F(000) = 862$, $T = 295$ K. Final $R = 0\cdot033$ for 2284 unique observed reflections. The coordination of the Cu atom is tetragonally distorted octahedral with the basal plane defined by four coplanar imidazole N atoms and the axial sites occupied by unidentate diphenyl phosphato O atoms. The Cu atom lies very close to one of the two unique coordinated imidazole ring planes |Δ 0·049 (1) Å| but is much more displaced |Δ 0·104 (1) Å| from the other one. The discrete uncharged molecular units are held together *via* N–H(pyrrole)···O(phosphate) hydrogen bonds.

Introduction. Studies on mixed-ligand complexes containing bipyridyl, histamine, histidine and imidazole (Mohan, Bancroft & Abbott, 1979; Antolini, Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue, Pellacani & Saladini, 1982, and references cited therein) show that when metal ions are bound to these aromatic

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