Basicity of Nitrogen Donors in an Amino-substituted Methylmercury Derivative of Adenine. Crystal Structure of μ-(Adeninato-μ-N^6,N^9)-bis[methylmercury(II)] · ethanol*

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Abstract

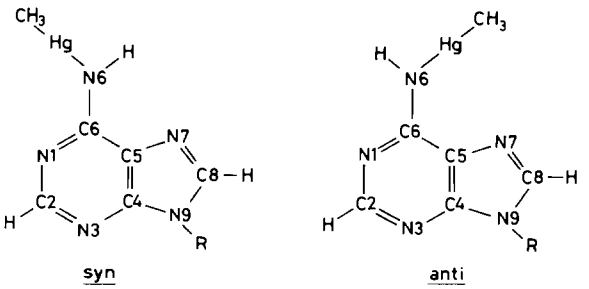
The compound $[(CH_3Hg)_2(Ad\text{-}H)]\cdot CH_3CH_2OH$ has been isolated from an ethanolic 2:1 solution of CH_3HgOH and adenine (HAd) and its structure has been established by X-ray diffraction. The title compound is monoclinic, $P2_1/c$, a = 7.999(3), b = 24.056(8), c = 14.625(2) Å, β = 90.56(2)°, Z = 8. The structure was solved and refined on 2203 observed reflections to R = 0.053. The asymmetric unit includes two independent, identically substituted molecules, in which the adenine base is coordinated at both N9 and N6. The monomercurated amino groups are found in the less sterically hindered *anti* orientation (Hg above N7). This is the first crystal structure of a methylmercury complex of adenine showing an intermolecular contact of N1 with Hg. Structural features discussed in this paper are relevant to the understanding of the relative basicities of the nitrogen donors in adenine and their modification upon metal coordination at N9 and N6.

Introduction

A convenient way of investigating the electronic structure of purine and pyrimidine bases of the nucleic acids and of classifying the affinities of their donor sites is to look at their interactions with metal ions. Metal ion complexes of DNA free bases, nucleosides, nucleotides [1] and, more recently, oligonucleotides and their duplexes [2] are also used and studied as model compounds to understand metal ion–nucleic acid interactions.

The CH_3Hg^+ ion, a uniligating Lewis acid with minimum steric effects, is a suitable cation to probe and characterize binding sites of DNA bases. Beauchamp *et al.* have shown that this ion can form series of complexes with free and blocked nucleic acid bases as they are known to exist in DNA [3–11]. Structural studies of CH_3Hg^+ complexes of adenine (HAd)** have demonstrated that the N9 deprotonated adeninate anion is successively coordinated at N9 [5, 6], N7 [7] and N3 [8] upon increasing the metal-to-adenine ratio from 1:1 to 3:1. Crystal structures of compounds prepared under mild basic conditions have shown that the CH_3Hg^+ ion can substitute both N6 amino hydrogens [9, 10].

Only two methylmercury complexes of adenine ligands bearing monosubstituted amino groups have been structurally characterized by X-ray diffraction [11, 12]. Their coordination is identical, excluding N9 substituents: CH_3Hg groups are bonded to N1 and deprotonated N6 amino sites. The monosubstituted amino groups have the less sterically hindered anti orientation, *i.e.* the amino-bonded CH_3Hg group lies in the molecular plane with the N6–Hg6 bond *trans* to C6–N1. It would seem that, in the solid state, the monosubstituted amino group in CH_3Hg complexes of adenine derivatives having N1 coordination, prefers the anti orientation. But, a recent NMR investigation of solutions of mono-aminosubstituted methylmercury derivatives of 9-methyladenine and 9-(methylmercury)adenine, lacking N1 complexation, showed that they exist as two geometrical isomers, *anti* (Hg above N7) and *syn* (Hg above N1) (Scheme 1)



Scheme 1.

*Contribution NRC 26679.

**Abbreviations used for adenine: HAd = neutral molecule, Ad^- = monoanion without imidazole proton, $(Ad\text{-}H)^{-2}$ = dianion having lost the imidazole and one amino proton, and $(Ad\text{-}2H)^{-3}$ = trianion having lost the imidazole and two amino protons.

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[13]. It is therefore of interest to characterize such compounds by X-ray diffraction in order to find the orientation of the monomercurated amino group in the absence of N1 coordination in the solid state.

The crystal structure of the adenine complex $[(CH_3Hg)_2(Ad\text{-}H)]\cdot CH_3CH_2OH$ is reported, allowing comparisons to be made between structures found in the solid state and in solution. Relative affinities of the ring nitrogen donors of adenine and their modification upon metal binding at N9 and N6 amino, are also discussed.

Experimental

Preparation

$[(CH_3Hg)_2(Ad\text{-}H)]\cdot CH_3CH_2OH$

The title compound was prepared as described elsewhere [10]. Colorless plates were obtained from the cooled mixture. These crystals were collected and dried *in vacuo*.

Crystal Data

$C_9H_{15}Hg_2N_5O$, formula weight = 610.2, monoclinic, $P2_1/c$, a = 7.999(3), b = 24.056(8), c = 14.625(2) Å, β = 90.56(2)°, V = 2814.1 Å^3, Z = 8, D_c = 2.825 Mg M^{-3}, λ(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite-monochromatized), μ(Mo Kα) = 21.79 mm^{-1}, T = 295 K, crystal dimensions: 0.06 × 0.30 × 0.30 mm^3.

Crystallographic Measurements and Structure Solution

Accurate cell parameters and intensity data were obtained with an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. 3878 reflections ($2\theta \leqq 44°$) were collected. Three standard reflections monitored during the experiment indicated that the crystal slowly decomposed in the X-ray beam. Their intensities had decreased by the following percentages at the end of the data collection: $\bar{1}51$ (15%), $12\bar{3}$ (9%), 0100 (10%). This decay was taken into account during data reduction. After eliminating the systematically absent reflections, the data set consisted of 3582 unique reflections of which 2203 were retained as significantly above background ($I_{net} \geqq 2.5\ \sigma\ (I_{net})$) for structure determination. These data were corrected for the Lorentz effect, measured direct-beam polarization [14] and absorption (Gaussian integration grid 8 × 8 × 8, transmission range: 0.018–0.276). The cell parameters were obtained by least-squares refinement of the setting angles of 43 reflections ($40° \leqq 2\theta \leqq 44°$) [$\lambda$(Mo K$\alpha_1$) = 0.70932 Å].

The positions of the four Hg atoms were determined by direct methods using MULTAN [15]. The remaining non-hydrogen atoms, except the C atoms of the ethanol molecules, were located from a difference map. In the next Fourier map, it was clear that the missing C atoms of each ethanol molecule were disordered. At this point, the structure was refined isotropically and another map revealed several peaks linked to the oxygen atom of each solvent molecule. Refinement showed that each carbon atom of the ethanol molecules is disordered over two locations in a 1:1 ratio. H atoms on C2, C8 and N6 of each adenine of the asymmetric unit were included at their calculated positions but not refined (C(N)–H = 0.95 Å, sp^2 hybridization) with isotropic temperature factors related to the thermal motions of the atoms to which they are attached. The H atoms of the methyl groups and of the ethanol molecules could not be located. Counting statistics were used during refinement. Anisotropic refinement (full matrix least-squares) of all non-hydrogen atoms, except the disordered ethanol C atoms which were refined isotropically, converged to R_f = 0.053 and R_w = 0.026 (observed reflections only) with a goodness-of-fit ratio of 3.95. The maximum shift-to-error ratio in the last cycle was 0.24. The final difference map showed peaks in the range (±1.0–2.1 e/Å^3) near Hg, and the general background was below ±0.8 e/Å^3. All computations were performed with the NRCVAX system of programs [16].

Although the β angle value is very close to 90°, cell symmetry was checked with the program MISSYM which finds all metric symmetry elements from the fractional coordinates of any crystal structure and builds the symmetry generators located in the unit cell [17]. In the structure of the title compound, only symmetry elements of the space group $P2_1/c$ could be found. An inspection of the packing diagram (Fig. 4, supplementary material) revealed that the actual monoclinic cell ($P2_1/c$) is in fact a distorted orthorhombic cell (*Pbca*).

Results and Discussion

Description of the Structure

The final atomic coordinates and B_{eq} values are listed in Table I. The asymmetric unit consists of two independent molecules in which H atoms attached to N9† and N6 amino have been substituted by CH_3Hg^+ ions (Fig. 1). The mean interatomic distances and bond angles are schematically represented in Fig. 2. The Hg–N (ave. 2.06 Å σ = 0.02 Å) and Hg–C (2.05 Å σ = 0.02 Å) bond lengths are in good agreement with those reported for similar compounds [3, 5–12]. The four independent Hg atoms exhibit the linear

†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.

TABLE I. Atomic Parameters x, y, z and B_{iso}

Atom	x	y	z	B_{iso} [a]
HG61	0.81633(15)	0.09400(5)	0.53610(6)	5.91(7)
HG62	0.68485(15)	0.90444(6)	0.31993(6)	6.59(7)
HG91	0.40726(13)	0.31980(5)	0.75151(5)	4.92(6)
HG92	1.09383(14)	0.67893(5)	0.53507(5)	5.09(6)
O11	0.2320(20)	0.3742(7)	0.4875(7)	7.1(11)
O12	1.2725(18)	0.6288(7)	0.2731(7)	6.6(10)
N11	0.5423(22)	0.2343(7)	0.4105(8)	4.8(11)
N12	0.9572(22)	0.7692(7)	0.1886(8)	4.5(11)
N31	0.4375(21)	0.2917(9)	0.5205(8)	7.2(15)
N32	1.0670(23)	0.7076(8)	0.2978(9)	6.8(13)
N61	0.6990(24)	0.1506(7)	0.4500(9)	5.6(13)
N62	0.7912(21)	0.8516(8)	0.2280(8)	4.8(11)
N71	0.6604(22)	0.1786(8)	0.6413(8)	5.9(12)
N72	0.8512(24)	0.8219(8)	0.4220(9)	6.7(13)
N91	0.5152(21)	0.2563(8)	0.6761(8)	5.9(12)
N92	0.9884(23)	0.7402(8)	0.4560(8)	6.5(13)
C11A	0.351(7)	0.419(3)	0.510(3)	11.4(18)
C11B	0.205(6)	0.4324(23)	0.5343(24)	7.4(15)
C12A	1.162(6)	0.5923(24)	0.2806(24)	8.1(14)
C12B	1.299(7)	0.570(3)	0.288(3)	10.4(18)
C21	0.468(3)	0.2790(11)	0.4458(11)	9.2(20)
C22	1.040(3)	0.7252(10)	0.2217(10)	6.7(17)
C31A	0.283(7)	0.463(3)	0.487(3)	10.2(18)
C31B	0.316(7)	0.4603(24)	0.572(3)	8.9(17)
C32A	1.178(6)	0.5465(23)	0.2793(24)	7.7(15)
C32B	1.237(6)	0.5490(21)	0.3386(23)	6.4(13)
C41	0.511(3)	0.2533(9)	0.5794(10)	4.4(13)
C42	0.991(3)	0.7479(10)	0.3609(11)	5.6(14)
C51	0.610(3)	0.2125(11)	0.5614(10)	8.2(16)
C52	0.9007(24)	0.7908(9)	0.3470(10)	3.0(11)
C61	0.622(3)	0.1961(11)	0.4690(11)	6.8(16)
C61	0.919(4)	0.0328(9)	0.6262(12)	5.2(17)
C62	0.886(3)	0.8045(9)	0.2530(11)	4.3(13)
C62	0.591(3)	0.9576(10)	0.4187(12)	6.4(15)
C81	0.591(3)	0.2170(10)	0.7018(10)	5.2(15)
C82	0.916(3)	0.7841(9)	0.4835(10)	4.9(15)
C91	0.297(3)	0.3801(10)	0.8079(12)	6.4(15)
C92	1.211(3)	0.6119(10)	0.5990(12)	7.1(17)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

two-coordination usually encountered for this element. Departure from linearity of each type of CH_3Hg group (N6 amino and N9 bound) is significant (ave. H_3C–Hg6–N6 176.3° $\sigma = 0.8°$; ave. H_3C–Hg9–N9 173.0° $\sigma = 0.7°$) but such deviations are often caused by packing forces. The angles about the N6 amino atoms (ave. Hg6–N6–C6 127° $\sigma = 1°$) indicate a trigonal planar geometry. Therefore, the N6 atoms retain sp^2 hybridization, as in free adenine derivatives and their complexes having methylmercury substitution of amino hydrogens [9–12, 18, 19]. As shown in Fig. 1, the CH_3Hg^+ ion on the monosubstituted amino group is located on the five-membered ring side of adenine, 2.83(2) Å away from N7. That *anti* conformation was also found, as mentioned before, in crystal structures of CH_3Hg^+ complexes of 9-methyladenine and 8-azadenine [11, 12].

The two non equivalent ligands have the same geometry within experimental error. Light-atom positions cannot be determined with high accuracy. The high esd's on bond lengths and angles make it difficult to draw firm conclusions about changes in ligand geometry resulting from complexation or substitution. The individual rings in both molecules are planar within 2σ (0.06 Å). Each adenine moiety is best described as two individually planar rings, slightly bent about the C4–C5 bond, with dihedral angle valued of 1.9(9)° and 2.3(8)° found between the five- and six-membered rings in molecules 1 and 2 respectively.

A projection of the unit cell along the b axis (Fig. 3) shows successive chains of molecule 1, parallel to c, stacked on chains of molecule 2, with the usual stacking separation of ~3.5 Å (along the a

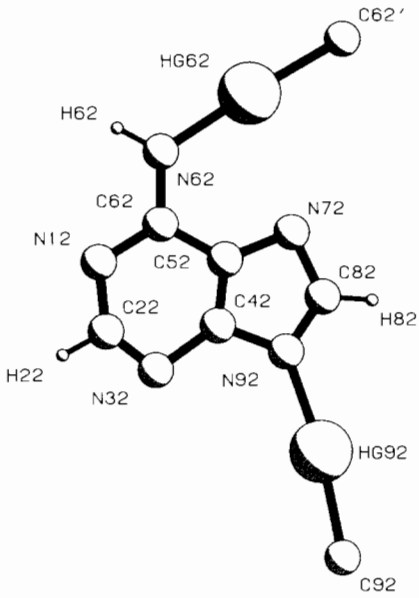

Fig. 1. PLUTO drawing [16] of the $[(CH_3Hg)_2(Ad\text{-}H)]$ molecule (molecule 2).

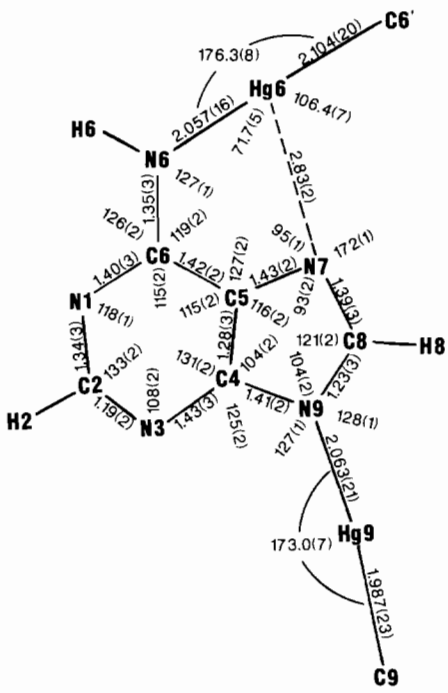

Fig.2. Interatomic distances (Å) and bond angles (°). The values averaged over the two independent molecules are given. Individual values have been deposited.

axis) found for such structure [8, 10, 20], between molecules 1 and 2. In each chain, adjacent molecules are oriented ~65° apart, about the *c* direction. Glide planes parallel to the *ac* plane, $y = 1/4$ and 3/4, produce intermolecular N1···Hg9 contacts (N11···Hg91 = 2.87(1) Å; N12···Hg92 = 2.80(1) Å) with

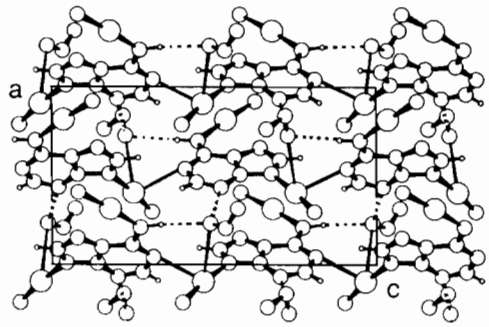

Fig. 3. [010] projection showing one half of the packing diagram (Fig. 4, deposited) for $[(CH_3Hg)_2(Ad\text{-}H)]$. *a* and *c* are parallel to the side and the bottom of the page, respectively. The atoms are of arbitrary size with Hg larger than the others. Ethanol molecules are showed in one of the disordered orientations. Hg···O and Hg···N contacts are illustrated with thin lines and H-bonds with dashed lines.

reasonable geometry at N1 (ave. C2–N1–Hg9 119° $\sigma = 1°$; ave. C6–N1–Hg9 114° $\sigma = 1°$), although Hg9 atoms are far from their respective molecular plane (ave. −1.54(3) Å) where best Hg-bonding is expected. Such N1···Hg intermolecular contact has not so far been encountered in crystal structures of methylmercury complexes with adenine. The lattice is further stabilized by N···O hydrogen bonds involving N3 and N6 amino and Hg···O contacts (Table VI, deposited) between molecules of stacked chains and ethanol molecules acting as three-way links. Crystal packing, along the *b* axis, is mainly determined by Van der Waals interactions between sheet arrangements like the one shown in Fig. 3 (Fig. 4, deposited).

Solid vs. Solution Structure

Recently, multinuclear NMR spectroscopy was used to investigate the solution behavior of amino-substituted methylmercury derivatives of adenine and 9-methyladenine [13]. It was reported that compounds with monomercurated amino groups exist in solution as a mixutre of *syn* and *anti* isomers. The anti isomer of $[(CH_3Hg_2)(Ad\text{-}H)]$ was found in the present structure. It would seem that any kind of interaction of N1 with Hg, whether it is a true bond or an intermolecular contact, as found here, dictates the *anti* orientation of the monomercurated amino group. Opposite *syn* orientation would result in either two side-by-side CH_3Hg^+ groups, as in adenine derivatives coordinated at N1 and N6, or two Hg atoms in close proximity, as in the present structure. Some angular deformations might then be required to accommodate these arrangements showing Hg–Hg distances of 3.0 Å, which correspond to the sum of their Van der Waals radii [21]. Such structures are not unrealistic since Hg–Hg separations of ~3.05 Å were found in crystal structures of 1-methylcytosine compounds with the side-by-side arrangement [22].

The intramolecular Hg6–N7 distance (2.83(2) Å) is shorter than the sum of the relevant Van der Waals radii (3.05 Å) [21]. Although, it could indicate a weak Hg–N secondary bond, the geometry at N7 is not favorable to such interaction as Hg6 is far from the ideal N7 lone pair direction (Table VI, deposited).

$[(CH_3Hg)_2(Ad\text{-}H)]$ was also shown to disproportionate to some extent in solution, into $[(CH_3Hg)_3(Ad\text{-}2H)]$ and $[(CH_3Hg)(Ad)]$, compounds with, respectively, disubstituted ($-N(HgCH_3)_2$) and unsubstituted ($-NH_2$) amino groups [13]. The latter two compounds were structurally characterized in the solid state by X-ray diffraction [5, 6, 10]. Although, the IR spectrum of the title compound suggested hydrogen substitution by CH_3Hg^+ groups at N9 and N6 [10], still it left some doubt as to its structure in the solid state, since the analogous 9-methyladenine complex does not exist in the solid state [13]. The single crystal X-ray work reported here does confirm the existence of the mono-aminosubstituted $[(CH_3Hg)_2(Ad\text{-}H)]$ species in the solid state as well as in solution.

Affinities of Adenine Donor Sites

Beauchamp *et al.* [5–8] have concluded from crystal structures of methylmercury complexes of adenine that initial substitution of the imidazolic N9 proton leads to an enhancement of the donor abilities of the remaining ring nitrogens in the order N7 > N3 > N1. On the other end, replacement of an amino hydrogen would be expected to induce enhancement of donor basicities in the opposite direction, N1 > N3 > N7. Hence, it is interesting to speculate on the relative importance of those opposite effects and the resulting modification of remote nitrogen donor basicities as the present structure shows simultaneous metal coordination at N6 amino and N9.

The intramolecular Hg6–N7 contact should not be considered as a true secondary bond for geometric reasons. The present structure seems to indicate some pyrimidine ring activation, since Hg9–N1 intermolecular contacts and O1–N3 H-bonds are found. N7 might be activated by N9 metallation but the *anti* orientation of CH_3Hg^+ at N6 shields it from any type of interaction. Whether the enhancement effect of N6 substitution is different or not from N9 substitution, one might therefore consider that new additional steric factor. So, as no adenine compound with side-by-side metal coordination at N1 and N6 amino exists, the orientation of the monosubstituted amino group will affect nearby nitrogen donors, N1 and N7, to different extents and, presumably, the location of the next metal coordination in the solid state as well as in solution.

As there are no known CH_3Hg^+ compounds with adenine having coordination at N1, one may need only to consider the relative affinities of the N3 and N7 donor sites. One way to estimate the ring charge distribution in $[(CH_3Hg)_2(Ad\text{-}H)]$ would be to look at its ring addition compound, $[(CH_3Hg)_3(Ad\text{-}H)]X$ ($X = NO_3$ or ClO_4). Beauchamp *et al.* reported its preparation and, based on IR and Raman spectra of the solid, concluded that N7 was the ring coordination site in addition to N9 and N6 amino [5, 23]. So, solid state spectroscopic data indicated that H9 substitution releases more electron density in the ring than amino proton displacement, that the monosubstituted amino group must have the *syn* orientation and that N7 is more basic than N3. However, ^{13}C NMR shifts of the ring carbons of $[(CH_3Hg)_3(Ad\text{-}H)]NO_3$ in DMSO-d_6 suggested N3 coordination as well as N7 and that the N3, N6, N9 tautomer is the major component in solution [10]. Thus, solution NMR data would rather indicate that N3 is more basic than N7 as amino proton displacement should activate N3 more than N7 and H9 substitution seems to barely activate N7 more than N3 which is possible since N3 is roughly as close to N9 as N7. The resulting net charges at N3 and N7 in the title compound should then be similar. As $[(CH_3Hg)_2(Ad\text{-}H)]$ exists in solution as an equal mixture of *syn* and *anti* isomers, N3 will become a better coordination site than N7 as it is unaffected by that isomerism. On the contrary, *anti* orientation will prevent CH_3Hg^+ from binding at N7 and that might explain the predominance of the N3, N6, N9 tautomer over N6, N7, N9.

Conclusion

The present report does confirm that $[(CH_3Hg)_2(Ad\text{-}H)]$ is coordinated at N6 and N9 as suggested earlier by its infrared spectrum. The X-ray structure showed that the monomercurated amino group has the *anti* orientation and that, for the first time, N1 is involved in an intermolecular contact with Hg. There is no structural evidence which might explain the presence of the *anti* over the *syn* oriented amino group. From solution and solid state data published earlier and describing $[(CH_3Hg)_3(Ad\text{-}H)]X$, it would seem that the charge distribution in the ring of the title compound is such that the basicities of N3 and N7 are similar. Further ring addition would be sterically dependent on the orientation of the monosubstituted amino group, either *syn* or *anti*.

Supplementary Material

Refined anisotropic temperature factors, calculated coordinates of hydrogen atoms, interatomic distances and angles, mean-plane calculations, list of structure factors and a packing diagram (Fig. 4) are available from the author on request.

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