Structure of an Unusual 5:2 Methylmercury:Adenine Complex

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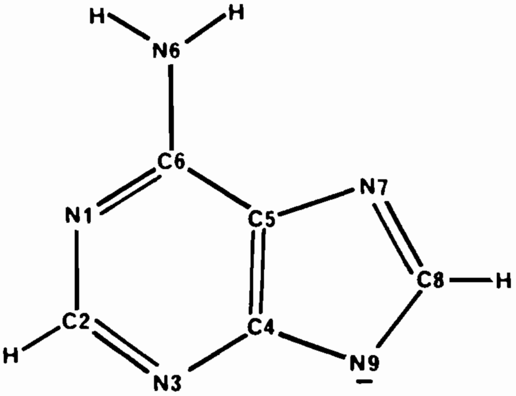
Abstract

The $[(CH_3Hg)_5Ad_2](NO_3)_3 \cdot 3H_2O$ compound is monoclinic, $P2_1/c$, $a = 10.717(7)$, $b = 26.680(8)$, $c = 11.778(2)$ Å, $\beta = 102.59(4)°$, $Z = 4$. The structure was solved on 2841 observed reflections to $R = 0.045$. The crystal contains an equal number of N7, N9-bonded $[(CH_3Hg)_2Ad]^+$ ions and N3,N7,N9-bonded $[(CH_3Hg)_3Ad]^{2+}$ ions joined into dimers via pairs of complementary N6–H···N1 hydrogen bonds. The $[(CH_3Hg)_3Ad]^{2+}$ ion is also found in crystals of $[(CH_3Hg)_3Ad](NO_3)_2 \cdot H_2O$: triclinic, $P\bar{1}$, $a = 7.017(3)$, $b = 11.345(6)$, $c = 12.722(3)$ Å, $\alpha = 64.91(3)$, $\beta = 87.50(3)$, $\gamma = 89.59(4)°$, $Z = 2$, $R = 0.057$, 1960 observed reflections. The ^1H and ^{13}C NMR spectra of the 5:2 complex in DMSO-d_6 contain only one set of proton signals for the adenine ring and the CH_3Hg^+ ions. This indicates that the complexes exchange their stoichiometries rapidly on the NMR time scale. In addition, the CH_3Hg^+ cations are shuffled among the five unequivalent coordination sites.

Introduction

Complexes of purine and pyrimidine bases, nucleosides, and nucleotides have been extensively studied as model compounds for metal–nucleic acid interactions. We are currently investigating the interaction of the CH_3Hg^+ ion with various nucleobase derivatives. This labile cation, with only one coordination site available for binding to a nitrogen site of the ligand, has been shown to form a series of complexes with the adeninate ion, Ad^-. At a 1:1 metal to adenine (HAd) ratio, the N9** complex is formed [1, 2]. Increasing the ratio to 2:1 gives an N7, N9 complex [3, 4]. For the 3:1 ratio, the N3, N7, N9 complex was observed for both the perchlorate [5] and the nitrate [6] salts. Under mildly basic conditions mono- or disubstitution at N6 is observed [7, 8].



While examining by NMR the equilibria and exchange processes involving CH_3Hg^+–adenine complexes of various stoichiometries, a crystalline material (**I**) precipitated from a 1:1 mixture of $[(CH_3Hg)_2Ad]NO_3$ and $[(CH_3Hg)_3Ad](NO_3)_2$ in water. Its composition corresponded to the average CH_3Hg^+:adenine ratio in the system (2.5:1), but the crystals were different from those of either of the starting materials. The molecular and crystal structure of compound **I** presented in this report provides the first example of two differently coordinated adenine ligands simultaneously present in a complex.

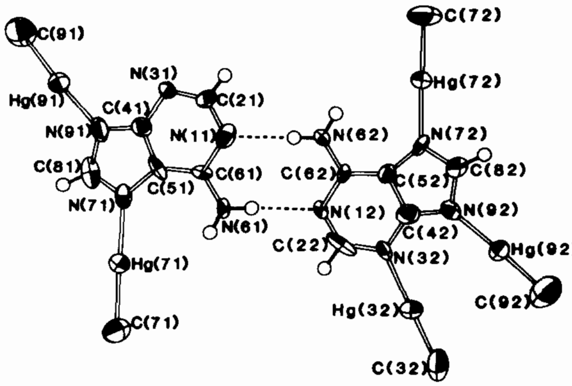


Fig. 1. The cation–dication pair found in $[(CH_3Hg)_2Ad] \cdot [(CH_3Ag)_3Ad]NO_3 \cdot 3H_2O$ (I).

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**Unparenthesized symbols are used to identify the atoms of the adenine ring in a general way, whereas specific atoms in the crystal structures are designated with parenthesized symbols defined in Figs. 1 and 2.

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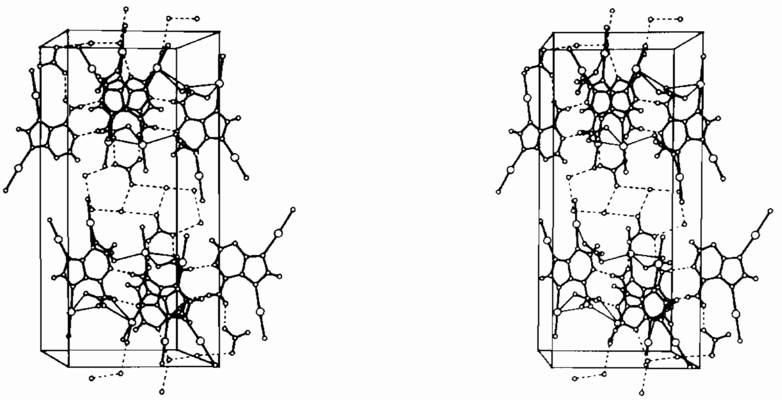

Fig. 2. Packing diagram for I. c and b are parallel to the bottom and side of the page, respectively. The atoms are of abritrary size, with Hg larger than the others. Hg•••O contacts are illustrated with thin lines and H-bonds with dashed lines.

The paper also reports on a new monohydrate variety, **II**, of the $[(CH_3Hg)_3Ad](NO_3)_2$ complex, which was isolated as a minor component when attempting to prepare CH_3Hg^+ complexes of adenosine under acidic conditions.

Experimental

$[(CH_3Hg)_5Ad_2](NO_3)_3 \cdot 3H_2O$, I

Preparation

$[(CH_3Hg)_2Ad]NO_3 \cdot 2H_2O$ (0.33 g; 0.5 mmol) and $[(CH_3Hg)_3Ad](NO_3)_2$ (0.45 g; 0.5 mmol), prepared as described earlier [1], were dissolved in 20 ml of hot water. Colorless crystals were obtained from the cooled mixture. All crystals had the same shape, which was different from those of either of the starting materials. These crystals were collected and dried *in vacuo* (0.69 g; 88% yield).

Crystal data

$C_{15}H_{29}Hg_5N_{13}O_{12}$, formula weight = 1586.4, monoclinic, $P2_1/c$, $a = 10.717(7)$, $b = 26.680(8)$, $c = 11.778(2)$ Å, $\beta = 102.59(4)°$, $V = 3286.7$ Å^3, $Z = 4$, $D_c = 3.205$ g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 233.4 cm^{-1}, $T = 293$ K, crystal dimensions: $0.10 \times 0.16 \times 0.20$ mm^3.

Crystallographic measurements and structure resolution

The cell and space group determinations and the data collection procedure on the Enraf-Nonius CAD4 diffractometer have been described elsewhere [9]. Three standard reflections fluctuated within ±2.9%. A total of 4038 *hkl* and $hk\bar{l}$ reflections ($2\theta \leq 44°$) were collected. A set of 2841 reflections with $I/\sigma > 3.0$ was retained for structure resolution. The data were corrected for Lorentz and polarization effects. An absorption correction (Gaussian integration, grid $8 \times 8 \times 8$) was applied. The transmission factor ranged from 0.021 to 0.147.

The positions of the five Hg atoms were determined by direct methods using MULTAN [10]. The remaining non-hydrogen atoms were located from a subsequent difference Fourier (ΔF) map, using programs described elsewhere [5, 6]. All atoms were refined isotropically, and the adenine hydrogens were added to the model using calculated positions and a fixed isotropic temperature factor ($B = 5.0$ Å^2). After anisotropic refinement of the non-hydrogen atoms, convergence was reached at $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o| = 0.045$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.058$, with $w = 1/\sigma_{F^2}$. The goodness-of-fit ratio was 1.993. The final ΔF map showed peaks in the range ±(3.2–1.0) e/Å^3 near the Hg atoms, and a general background <1 e/Å^3. The scattering curves were taken from Cromer and Waber [11], except for that of hydrogen [12]. The anomalous dispersion corrections for Hg were from Cromer [13].

$[(CH_3Hg)_3Ad](NO_3)_2 \cdot H_2O$, II

Preparation

Adenosine (2.67 g, 10 mmol; Aldrich) was stirred in 10 ml H_2O at room temperature, and 30.0 ml of aqueous 1.00 M CH_3HgNO_3, prepared as described previously [1], was slowly added. After several days, clear plates of **II** formed (final pH = 1.94).

Crystal data

$C_8H_{15}Hg_3N_7O_7$, formula weight = 923.02, triclinc, $P\bar{1}$, $a = 7.017(3)$, $b = 11.345(6)$, $c = 12.722(3)$ Å, $\alpha = 64.91(3)$, $\beta = 87.50(3)$, $\gamma = 89.59(4)°$, $V = 916.26$ Å^3, $Z = 2$, $D_c = 3.34$ g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.71069 Å, μ(Mo Kα) = 251.1 cm^{-1}, $T = 293$ K, crystal dimensions (approximate): $0.11 \times 0.14 \times 0.21$ mm.

Crystallographic measurements and structure resolution

Cell and space group determination and data collection procedures [9] have been described. The

TABLE I. Atomic Coordinates

Atom	x	y	z
[($CH_3Hg)_5Ad_2$] ($NO_3)_3$•$3H_2O$, **I**, (×10^3, Hg × 10^5)			
Hg(32)	14476(11)	42966(4)	17666(11)
Hg(71)	−37702(10)	32073(4)	64540(9)
Hg(72)	17980(10)	16083(4)	5435(9)
Hg(91)	−38840(10)	9607(4)	75931(10)
Hg(92)	30589(11)	37763(4)	−510(10)
O(1)	−43(2)	36(1)	840(2)
O(2)	−83(2)	−70(1)	595(3)
O(3)	−157(5)	29(1)	620(4)
O(10)	464(2)	193(1)	378(2)
O(11)	273(1)	176(1)	296(1)
O(12)	406(2)	209(1)	202(2)
O(20)	−47(3)	395(1)	676(2)
O(21)	−110(2)	454(1)	554(2)
O(22)	−128(2)	379(1)	496(2)
O(30)	375(2)	366(1)	264(2)
O(31)	312(3)	312(1)	374(2)
O(32)	509(2)	334(1)	403(1)
N(10)	383(2)	193(1)	294(2)
N(20)	−95(2)	409(1)	577(2)
N(30)	398(2)	338(1)	351(2)
N(11)	−175(2)	191(1)	416(2)
N(12)	−31(2)	295(1)	270(1)
N(31)	−244(2)	127(1)	527(2)
N(32)	77(2)	355(1)	178(2)
N(61)	−198(2)	276(1)	439(1)
N(62)	−26(2)	210(1)	235(2)
N(71)	−349(2)	244(1)	625(2)
N(72)	140(2)	238(1)	59(1)
N(91)	−356(2)	160(1)	671(2)
N(92)	191(2)	321(1)	39(1)
C(21)	−193(2)	144(1)	448(2)
C(22)	6(3)	340(1)	253(2)
C(32)	217(4)	502(1)	176(3)
C(41)	−296(2)	165(1)	582(2)
C(42)	120(2)	317(1)	118(2)
C(51)	−285(2)	217(1)	559(2)
C(52)	81(2)	266(1)	134(2)
C(61)	−222(2)	230(1)	471(2)
C(62)	11(2)	257(1)	214(2)
C(71)	−398(3)	397(1)	667(2)
C(72)	228(4)	84(1)	46(4)
C(81)	−385(2)	210(1)	694(2)
C(82)	203(3)	271(1)	8(2)
C(91)	−416(3)	27(1)	844(3)
C(92)	425(4)	437(1)	−41(4)
H(21)	−161	120	403
H(22)	−20	365	298
H(81)	−427	219	754
H(82)	253	261	−46
H(611)	−224	302	473
H(621)	−156	281	384
H(612)	−3	185	198
H(622)	−73	206	285
[($CH_3Hg)_3Ad$] ($NO_3)_2$•H_2O, **II**, (×10^3, Hg × 10^4)			
Hg(3)	1158(1)	4368(1)	3531(1)
Hg(7)	7434(1)	8745(1)	−1361(1)
Hg(9)	5268(1)	3630(1)	2632(1)
N(1)	81(2)	837(2)	88(2)
C(2)	54(3)	717(2)	177(3)
N(3)	179(2)	619(2)	211(2)
C(3)	80(4)	266(3)	496(3)
C(4)	339(3)	644(2)	140(2)
C(5)	377(3)	763(2)	47(2)
C(6)	243(3)	859(2)	26(2)
N(6)	259(3)	983(2)	−63(2)
N(7)	554(2)	755(2)	0(2)
C(7)	922(7)	985(3)	−272(3)
C(8)	607(3)	632(2)	64(2)
N(9)	482(2)	558(2)	149(2)
C(9)	558(5)	166(3)	370(4)
N(10)	−10(3)	371(2)	136(2)
O(10)	−111(2)	422(2)	189(2)
O(11)	160(2)	354(2)	160(2)
O(12)	−78(4)	344(2)	63(2)
N(20)	486(3)	211(3)	689(2)
O(20)	364(3)	250(2)	731(2)
O(21)	575(6)	282(5)	609(3)
O(22)	499(6)	98(3)	724(3)
O(1)	705(4)	486(2)	392(2)
H(2)	−81	700	227
H(8)	739	594	45
H(61)	364	1007	−113
H(62)	170	1043	−79

three standard reflections fluctuated with 3.1%. A total of 3515 reflections with $2\theta \leqslant 50.0°$ (hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$) were measured. A set of 1960 unique reflections with $I > 3\sigma(I)$ were used for structure refinement. Lorentz, polarization and absorption corrections were applied. The transmission coefficient ranged from 0.024 to 0.134.

The three Hg atoms were located using automated direct methods in the SHELX package [14]. The non-hydrogen atoms were found on a ΔF map and refined anisotropically. The adenine hydrogens were placed in calculated positions with isotropic temperature factors, and allowed to refine. Secondary extinction (0.0000(2)) and weighting parameters were varied, and the final refinement cycle (with H atoms fixed) gave $R = 0.057$ and $R_w = 0.072$, with $w = I/(\sigma_{F^2} + 0.00764\ F^2)$. The goodness-of-fit ratio was 0.786. The final difference map showed six peaks <4 e/Å^3 all within 1 Å of a Hg atom. The scattering curves and anomalous dispersion terms were supplied by the program, except for those of Hg [15].

The refined coordinates for both compounds are listed in Table I*.

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*See also 'Supplementary Material'.

NMR measurements

The samples were made by dissolving ~100 mg of material in 1.0 ml (^{1}H) or 1.5 ml (^{13}C) of DMSO-d$_6$ (Merck, Sharp & Dohme Canada). TMS was used as an internal standard. The spectra were recorded at ambient probe temperature with a Bruker WH-90 (90 MHz) spectrometer for the ^{1}H spectra and a WH-80 instrument operating at 20.17 MHz for the ^{13}C spectra.

Results

Description of the Structures

The 5 2 compound **I** should be formulated as $[(CH_3Hg)_3Ad][(CH_3Hg)_2Ad](NO_3)_3 \cdot 3H_2O$. The cations with the appropriate labelling are shown in Fig. 1. One cation is comprised of an adeninate moiety bridging two CH_3Hg^+ ions via N(71) and N(91), while the other contains three CH_3Hg^+ units, occupying the N(32), N(72), and N(92) sites of the Ad$^-$. The two cations form a dimeric unit via complementary N(61)–H$\cdots$N(12) and N(62)–H$\cdots$N(11) hydrogen bonds of moderate strength (average N$\cdots$N separation = 2.99(3) Å). This is the first example of a structure containing two differently coordinated adenine ligands.

The interatomic distances and bond angles are listed in Table II The primary coordination about Hg is linear within experimental errors. The Hg–N and Hg–C distances (means 2.10(2) and 2.09(4), respectively) are normal [1–7]. The Hg(3)$\cdots$Hg(9) separation is 3.332(2) Å. The geometries of the nucleobase [1–7] and the nitrate ions [16] are in good agreement with previous results.

The packing arrangement is illustrated in Fig 2 The cations form relatively flat dimers, separated from parallel dimers by 3.5 Å. They are complemented by three independent nitrate ions. The lattice is further stabilized by various hydrogen bonds and Hg$\cdots$O contacts (see Table II). Nitrate N(20) interacts via two of its oxygens with open amino protons belonging to adjacent complex cations. The other two nitrates take part in multidentate interactions with Hg atoms. All these interactions take place within layers parallel to the *ac* plane and of thickness ~$b/2$ The interlayer region at $y \sim 0$ and $\sim\frac{1}{2}$ is filled with water molecules forming many hydrogen bonds among themselves and with nitrate oxygens or the free N(31) site of the $[(CH_3Hg)_2Ad]^+$ cation.

The labelling for the dication of $[(CH_3Hg)_3Ad](NO_3)_2 \cdot H_2O$ (**II**) is defined in Fig. 3. The adeninate ligand bridges the CH_3Hg^+ groups via N3, N7 and N9. The coordination and internal geometry are insignificantly different from those of the same cation in the corresponding anhydrous nitrate salt [6], the per-

TABLE II. Selected Interatomic Distances (Å) and Bond Angles (deg) for **I** and **II**

	I			**II**
	N7, N9		N3, N7, N9	N3, N7, N9
Bonds				
Hg3–C3			2.08(4)	2.03(3)
Hg3–N3			2.12(2)	2.12(2)
Hg7–C7	2.07(3)		2.12(3)	2.04(4)
Hg7–N7	2.09(2)		2.10(2)	2.11(2)
Hg9–C9	2.14(4)		2.13(4)	2.08(4)
Hg9–N9	2.07(2)		2.09(2)	2.10(2)
N1–C2	1.32(3)		1.28(3)	1.36(4)
C2–N3	1.27(3)		1.34(3)	1.35(3)
N3–C4	1.39(3)		1.37(3)	1.36(3)
C4–C5	1.42(3)		1.46(3)	1.38(3)
C5–C6	1.39(3)		1.34(3)	1.38(3)
C6–N1	1.38(3)		1.35(3)	1.32(3)
C6–N6	1.33(3)		1.35(3)	1.39(3)
C5–N7	1.37(3)		1.40(3)	1.37(3)
N7–C8	1.33(3)		1.34(3)	1.34(3)
C8–N9	1.41(3)		1.38(3)	1.34(3)
N9–C4	1.34(3)		1.33(3)	1.37(3)
N10–O10		1.17(3)		1.25(3)
N10–O11		1.27(3)		1.24(3)
N10–O12		1.23(3)		1.21(4)
N20–O20		1.22(4)		1.17(4)
N20–O21		1.24(3)		1.15(5)
N20–O22		1.23(3)		1.17(5)
N30–O30		1.25(3)		
N30–O31		1.23(3)		
N30–O32		1.22(3)		
Angles				
N3–Hg3–C3			178(1)	174(1)
Hg3–N3–C2			122(2)	122(2)
Hg3–N3–C4			122(2)	124(2)
N7–Hg7–C7	178(1)		177(1)	177(1)
Hg7–N7–C5	134(2)		131(1)	138(2)
Hg7–N7–C8	122(2)		121(1)	117(2)
N9–Hg9–C9	177(1)		177(1)	176(1)
Hg9–N9–C4	129(2)		133(2)	133(2)
Hg9–N9–C8	128(2)		122(1)	124(2)
C6–N1–C2	120(2)		118(2)	117(2)
N1–C2–N3	131(2)		129(2)	126(2)
C2–N3–C4	111(2)		114(2)	114(2)
N3–C4–C5	124(2)		120(2)	123(2)
C4–C5–C6	118(2)		117(2)	117(2)
C5–C6–N1	116(2)		121(2)	122(2)
C5–C6–N6	127(2)		121(2)	124(2)
N1–C6–N6	117(2)		118(2)	114(2)
C4–C5–N7	109(2)		104(2)	107(2)
C6–C5–N7	132(2)		139(2)	136(2)
C5–N7–C8	104(2)		106(2)	104(2)
N7–C8–N9	115(2)		116(2)	116(2)
C8–N9–C4	103(2)		103(2)	102(2)
N9–C4–C5	109(2)		112(2)	111(2)
N9–C4–N3	127(2)		128(2)	126(2)
O10–N10–O11		120(2)		117(2)

(continued)

TABLE II. *(continued)*

	I		II
	N7, N9	N3, N7, N9	N3, N7, N9
O11–N10–O12	120(2)		123(3)
O12–N10–O10	120(2)		120(3)
O20–N2–O21	121(3)		120(4)
O21–N20–O22	117(2)		122(4)
O22–N20–O20	123(3)		117(3)
O30–N30–O31	120(2)		
O31–N30–O32	122(2)		
O32–N30–O30	118(2)		

Possible Hydrogen Bonds

I		II	
O(1)···O(3)	2.61(5)	O(1)···O(20)^{c}	2.78(4)
O(1)···O(21)^{a}	2.79(3)	O(1)···O(21)	2.87(5)
O(1)···O(21)^{b}	2.85(3)	O(22)···N(6)^{d}	2.92(5)
O(2)···O(3)	2.79(4)	N(1)···N(6)^{e}	3.07(3)
O(2)···O(20)^{b}	2.90(4)		
O(3)···N(31)	2.91(4)		
O(20)···N(62)^{a}	2.90(3)		
O(22)···N(61)	2.90(3)		
N(11)···N(62)	2.98(3)		
N(12)···N(61)	3.00(2)		

Hg Contacts (72° < N–Hg···O < 108°)

I		II	
Hg(32)···O(30)	2.99(2)	Hg(3)···O(10)	2.74(2)
Hg(32)···O(1)^{f}	3.20(3)	Hg(3)···O(11)	2.98(2)
Hg(32)···O(2)^{g}	3.13(3)	Hg(3)···O(1)^{i}	2.99(3)
Hg(71)···O(12)^{h}	2.67(2)	Hg(7)···O(11)^{k}	2.81(2)
Hg(71)···O(32)^{i}	2.87(2)	Hg(7)···O(22)^{k}	2.99(4)
Hg(72)···O(12)	2.94(2)	Hg(9)···O(11)	2.96(2)
Hg(72)···O(11)	2.83(2)	Hg(9)···O(1)	2.89(3)
Hg(72)···O(31)^{f}	2.89(3)	Hg(9)···Hg(10)^{l}	2.66(2)
Hg(91)···O(30)^{h}	2.74(2)	Hg(3)···Hg(9)	3.289(1)
Hg(91)···O(32)^{h}	2.90(2)		
Hg(92)···O(2)^{g}	2.78(3)		
Hg(92)···O(10)^{f}	3.06(2)		
Hg(92)···O(11)^{f}	2.70(2)		
Hg(32)···Hg(92)	3.332(2)		

Atom coordinates related to those in Table I by:
$^{a}x, \frac{1}{2} - y, \frac{1}{2} + z$. $^{b}-x, y - \frac{1}{2}, 1\frac{1}{2} - z$. $^{c}1 - x, 1 - y, 1 - z$. $^{d}x, y - 1, 1 + z$. $^{e}-x, 2 - y, -z$. $^{f}x, \frac{1}{2} - y, z - \frac{1}{2}$. $^{g}-x, \frac{1}{2} + y, \frac{1}{2} - z$. $^{h}x - 1, \frac{1}{2} - y, \frac{1}{2} + z$. $^{i}x - 1, y, z$. $^{j}1 - x, 1 - y, -z$. $^{k}x, y + 1, z - 1$. $^{l}x + 1, y, z$.

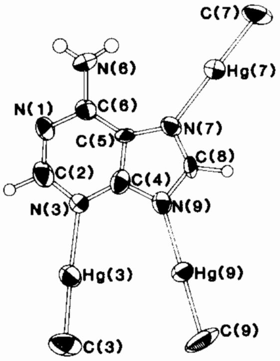

Fig. 3. The dication of [(CH$_3$Hg)$_3$Ad](NO$_3$)$_2$·H$_2$O (**II**).

chlorate salt [5], and the above 5:2 compound. The Hg(3)···Hg(9) distance is 3.289(1) Å.

The packing diagram (Fig. 4) shows that pairs of [(CH$_3$Hg)$_3$Ad]$^{2+}$ cation form N6–H···N1 hydrogen bonds about the inversion center at the origin, to give a dimer similar to that seen in the perchlorate salt and the monocation–dication pair of the 5:2 compound. Two independent nitrate ions balance the charge, and help stabilize the lattice. One of these

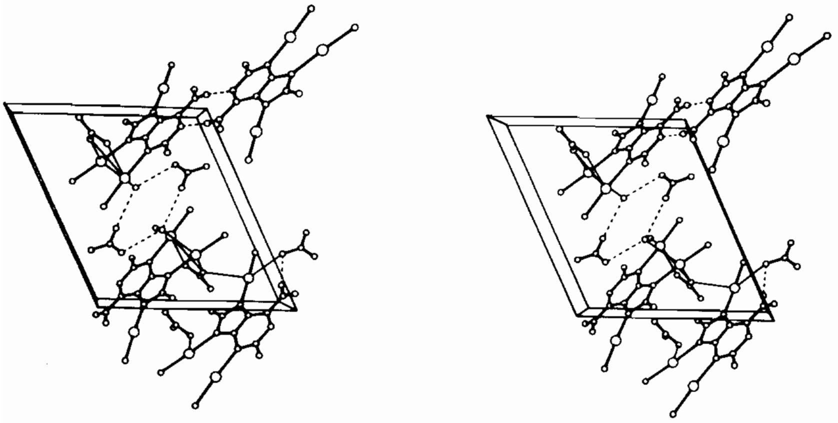

Fig. 4. Packing diagram for **II**. *b* is along the bottom of the page. The view is down *a**. The atoms are of arbitrary size, with Hg larger than the others. Hg···O contacts are illustrated with thin lines and H-bonds with dashed lines.

TABLE III. ^{1}H NMR Data[a]

	Binding sites[c]	H(2)	H(8)	NH_2	$CH_3(Hg)$	$^{2}J(^{199}Hg-^{1}H)$[b]
$[(CH_3Hg)_2Ad]NO_3$	N9, N7	8.30	8.24	7.71	0.86	218
$[(CH_3Hg)_3Ad](NO_3)_2$	N9, N7, N3	8.54	8.63	8.48	0.89	230
$[(CH_3Hg)_5Ad_2](NO_3)_3$	N9, N7 and N9, N7, N3	8.42	8.44	8.13	0.88	225

[a] In DMSO-d$_6$, 298 K, *vs.* TMS. [b] In Hz. [c] In the solid state.

TABLE IV. ^{13}C NMR Data[a]

	C(2)	C(4)	C(5)	C(6)	C(8)	$CH_3(Hg)$	$^{1}J(^{199}Hg-^{13}C)$[b]
$[(CH_3Hg)_2Ad]NO_3$	151.7	154.0	118.0	154.9	149.2	1.30	1726
$[(CH_3Hg)_3Ad](NO_3)_2$	152.3	151.7	116.9	154.4	151.2	1.60	1824
$[(CH_3Hg)_5Ad_2](NO_3)_3$	151.9	152.7	117.3	154.5	150.2	1.53	[c]

[a] In DMSO-d$_6$, 298 K *vs.* TMS. [b] In Hz. [c] Undetected.

anions (N(10)) form Hg···O contacts with the three independent Hg atoms. The other anion forms hydrogen bonds to the free amino hydrogen and to the water molecule. The water, in turn, bridges an Hg(3) to an Hg(9) in a different molecule (see Table II). No base stacking is observed in this case.

NMR Spectroscopy

The ^{1}H NMR signals for the 5:2 compound are compared in Table III with those of the parent $[(CH_3Hg)_3Ad]^{2+}$ and $[(CH_3Hg)_2Ad]^{+}$ cations. The H2 and H8 signals, which are close together in all cases, were identified by comparison with those obtained from the same compounds prepared from C8-deuterated adenine [2].

The H2 and H8 protons appear as singlets in DMSO solutions of the 5:2 compound despite the presence of two differently coordinated adeninate ligands. Furthermore, the chemical shifts are the means of those of the parent compounds. Single resonances were also observed at average positions in the ^{13}C spectra (Table IV). It must be concluded that the $[(CH_3Hg)_3Ad]^{2+}$ and $[(CH_3Hg)_2Ad]^{+}$ cations are in fast exchange on the NMR time scale. Slow exchange between CH_3Hg^+ complexes of different stoichiometries has been observed [17, 18], but the metal was bonded to sites much more basic than those of the present system. The exchange observed here could be explained if the N3-bound CH_3Hg^+ group, which is presumably the most loosely retained, can migrate readily to the free N3 site of a 2:1 cation, leading to interchange of stoichiometries. Although this process probably takes place, it is only part of a more complex exchange process of the CH_3Hg^+ groups between the five different coordination sites. Already in the parent 3:1 and 2:1 cations, only one averaged signal for the CH_3Hg^+ protons and one averaged $^{2}J(^{199}Hg-^{1}H)$ coupling constant were observed for all the CH_3Hg^+ groups in fast exchange between the various coordination sites. When these two cations are simultaneously present in a solution of the 5:2 compound, the chemical shift of the CH_3Hg^+ protons and the coupling constant are the weighted average of the values for the parent compounds (e.g. $(3 \times 230 + 2 \times 218)/5 = 225$ Hz). Therefore, on the NMR time scale, the CH_3Hg^+ groups are rapidly shuffled among the five unequivalent coordination sites.

Discussion

The structures presented in this report give further proof to the lack of affinity of N1 for mercury when N9 is coordinated. Metallation at N9 enhances the basicity of N3 and N7, to make them better binding sites than the sterically unhindered N1. There are now four different structures containing N3, N7, N9 coordinated adenine ions, found in five different packing environments, thus ruling out the possibility of packing effects determining coordination site preference.

To achieve optimum overlapping with the nitrogen lone pair, coordination should take place with equal Hg–N–C angles. This is rather uncommon and differences as large as 21° (for N(7)) are found in the present structures. For Hg7, opening of the Hg7–N7–C5 angle would be consistent with direct crowding of the Hg7–C7 unit by the amino group. For Hg9, the C4–N9–Hg9 angle tends to open away from Hg3, as seen in **I** (Hg(92)–N(92)–C(42) = 133(2)° and Hg(92)–N(92)–C(82) = 122(1)° *versus* Hg(91)–

N(91)--C(41) = 129(2)° and Hg(91)–N(91)–C(81) = 128(2)°). Repulsion from Hg3 probably contributes to the coordination angle asymmetry, but it was not strong enough to induce noticeable asymmetry in $[(CH_3Hg)_3Ad](ClO_4)_2$ [5]. Angular distortions of this type are probably not costly in energy and may result from small displacements of the CH_3Hg^+ group to favor Hg•••O contacts in the lattice. It is interesting that the Hg bound to N3 in the six-membered ring is geometrically more rigid and does not deviate appreciably from the bisecting position.

Base stacking is not an important factor in these chelating adenine complexes, although the complementary N6–H•••N1 centrosymmetric hydrogen bonding is frequently observed. This 'dimerization' is likely an important factor in concentrated solution. This dimer formation is the major packing difference between **II** and the anhydrous nitrate salt [6], which contained isolated dications. The water molecule in **II** provides the lattice with hydrogen bond donors, which were lost in the dimerization.

Supplementary Material

Temperature factors, structure factor amplitudes, and least-squares plane and hydrogen geometry calculations are available from the authors on request.

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References

1 L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *Can. J. Chem., 59,* 1311 (1981).

2 J.-P. Charland and A. L. Beauchamp, *Croat. Chem. Acta, 57,* 679 (1984).

3 A. L. Beauchamp, *J. Cryst. Mol. Struct, 10,* 149 (1980).

4 L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *J. Am. Chem. Soc., 101,* 2765 (1979).

5 J. Hubert and A. L. Beauchamp, *Can. J. Chem., 58,* 1439 (1980).

6 J. Hubert and A. L. Beauchamp, *Acta Crystallogr., Sect. B, 36,* 2613 (1980).

7 J.-P. Charland, M. Simard and A. L. Beauchamp, *Inorg. Chim. Acta, 80,* L57 (1983).

8 J.-P. Charland and A. L. Beauchamp, *Inorg. Chem.,* submitted for publication.

9 F. Bélanger-Gariépy and A. L. Beauchamp, *J. Am. Chem. Soc., 102,* 3461 (1980).

10 P. Main, M. M. Woolfson, L. Lessinger, G. Germain and J. P. Declercq, 'MULTAN', A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York (U.K.) and Louvain, Belgium, 1978.

11 D. T. Cromer and J. T. Waber, *Acta Crystallogr., 18,* 104 (1965).

12 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).

13 D. T. Cromer, *Acta Crystallogr., 18,* 17 (1965).

14 G. Sheldrick, 'SHELX', a program for crystal structure determination and refinement, University of Cambridge, 1976.

15 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography., Vol. IV, Kynoch Press, Birmingham, 1974, Table 2.2B, p. 99 ff.

16 C. S. Gibbons and J. Trotter, *J. Chem. Soc. A,* 2058 (1971).

17 F. Allaire, M. Simard and A. L. Beauchamp, *Can. J. Chem., 63,* 2054 (1985).

18 J. P. Charland, M. T. Phan Viet, M. St-Jacques and A. L. Beauchamp, *J. Am. Chem. Soc., 107,* 8202 (1985).