Preparation and Structural Characterization of Methylmercury(II) Complexes of 8-Azaadenine and 9-Methyl-8-azaadenine

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Abstract

Methylmercury(II) complexes of 8-azaadenine (AadH) and 9-methyl-8-azaadenine (Maad) have been isolated from aqueous solution in the pH range 1–10 and structurally characterized by ^{1}H NMR spectroscopy and X-ray structural analysis. No N7- or N8-coordinated complexes could be isolated. If N9 is blocked then either N1 or N3 of the pyrimidine ring is the chosen secondary binding site. Coordination of N6 by CH_3Hg^+ leads to an enhancement of N1 as a metal binding site relative to N3. Dismutation of N6-monosubstituted complexes in d_6-DMSO solution is characteristic. In the complex $[(CH_3Hg)Maad]NO_3$ prepared in the pH range 2–3, N6 is coordinated by CH_3Hg^+ and N1 is protonated.

Introduction

Replacement of the 8-CH function in purines by an aza nitrogen leads to pronounced alterations in the chemical and biological properties of the resultant bases. For instance various 8-azapurine nucleosides have been demonstrated to display effective antineoplastic properties [1]. It has been postulated that characteristic conformational changes at the glycosidic bond N9–C1′ may be mainly responsible for the mode of action of the 8-azapurines, but it is manifest that changes in the pattern of hydrogen bonding and in the charge distribution within the heterocyclic base may also play a significant role [2]. Molecular orbital calculations have revealed that N7 and N8 in H9-tautomers of 8-azapurines carry virtually no residual charge [2, 3].

Interaction of base nitrogen atoms of these modified purines with metal cations in biological systems may be expected to lead to further alterations in the charge distribution within the heterocycles and could also influence the nature of hydrogen bonding interactions between base pairs. On account of its ability to function as a uniligating Lewis acid with minimal steric effects the CH_3Hg^+ ion has proved to be a suitable cation for the characterization of binding sites for 8-azapurines in the pH range 1–10 [4–6]. As for the parent base adenine, we have established N9 as the primary binding site for both the methylmercury(II) and copper(II) cations with neutral 8-azaadenine (AadH) in their respective complexes $[(CH_3Hg)AadH]NO_3$ (**1i**) [4] and $[Cu(H_2O)_4(AadH)_2](NO_3)_2$ [7]. This coordination position has also been established by X-ray structural analysis for the 8-azaadeninate anion in $[(CH_3Hg)Aad]\cdot 4H_2O$ (**1n**·$4H_2O$) [4]. Our studies on 8-azaadenine have also demonstrated that the pyrimidine nitrogens N1 and N3 are potential metal binding sites. For instance, N3 and N9 were identified as Hg coordination sites in $[(CH_3Hg)_2Aad]NO_3\cdot H_2O$ (**2i**·H_2O), N1, N6 and N9 in $[(CH_3Hg)_3AadH_{-1}]NO_3$ (**3i**) [4]. For the N9-substituted bases 8-aza-9-methyladenine (Maad) and 8-aza-9-benzyladenine (Baad), N1 and N3 are the rhodium coordination sites in their respective complexes $[RhCl(CO)_2(Maad)]$ and $[RhCl(CO)_2(Baad)]$ [8].

These findings indicate that, in contrast to the parent base adenine, only one nitrogen atom in the triazole ring of 8-azaadenine is available for either protonation or metal binding. They, furthermore, suggest that with N9 blocked in 8-azaadenine nucleosides, N7 or N8 of the triazole ring may not be competitive as a site for metal binding in biological systems. In order to investigate this hypothesis we have now extended our studies to cover CH_3Hg^+ complexes of 8-aza-9-methyladenine. We report an analytical investigation for the pH range 1–10. The following complexes were isolated: $[(CH_3Hg)Maad]NO_3$ (**M1i**), $[(CH_3Hg)_2MaadH_{-1}]X^-$ ($X^- = NO_3^-$, ClO_4^-) (**M2i**), $[(CH_3Hg)MaadH_{-1}]$ (**M1n**) and $[(CH_3Hg)_2MaadH_{-2}]$ (**M2n**). The structures of **M1i** and **M2i** ($X^- = ClO_4^-$) were established by X-ray diffraction for the solid state. A full analytical study of the interaction of CH_3Hg^+ with 8-azaadenine in the same pH range allows the isolation of five complexes: **1i**, **1n**, **2i**·H_2O, **3i** and $[(CH_3Hg)_2AadH_{-1}]$ (**2n**). The crystal structures of the first four derivatives were reported previously (**1n** as tetrahydrate) [4]. We now present ^{1}H NMR spectroscopic data for these 8-azaadenine complexes, in addition to those of 8-aza-9-methyladenine.

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Experimental

Methylmercury(II) hydroxide (Alfa) and 8-azaadenine (Sigma) were used as received. 9-Methyl-8-azaadenine was prepared as described previously [9]. IR spectra were recorded as 1% KBr discs on a Perkin-Elmer 297 spectrometer; ^{1}H NMR spectra were measured on a Bruker WP 200 for 5% solutions in d_6-DMSO with the DMSO signal as reference; δ values are in ppm. The analytical and ^{1}H NMR data for the methylmercury(II) complexes are presented in Tables 1 and 2.

Preparation

All preparations were carried out in a well ventilated fume hood. In a typical preparation 0.27 mmol (0.061 g) methylmercury(II) hydroxide was added to an appropriate suspension of the base in 5 ml H_2O to yield the required metal-to-ligand ratio. It was necessary to heat to 50–60 °C for 1–3 h to achieve reaction. The pH was adjusted to a predetermined value (Figs. 1 and 3) by addition of 1 M HNO_3 or NaOH. Products were obtained by cooling or by slow evaporation of the solvent and after filtration were washed with ethanol and ether.

X-ray Structural Analysis

Crystal and refinement data for **M1i** and **M2i** ($X^- = ClO_4^-$) are summarized in Table 3. Unit cell constants were obtained from a least-squares fit to the settings for 25 reflections centred on an Enraf-Nonius CAD4 diffractometer. Intensities were collected on the diffractometer at variable scan rates with graphite-monochromated Mo Kα radiation (λ =

TABLE 1. Analytical data for methylmercury(II) complexes of 8-azaadenine and 9-methyl-8-azaadenine[a]

Compound		Found(calc.) (%)		
		C	H	N
$[(CH_3Ag)AadH]NO_3$	**1i**	14.5(14.51)	1.73(1.71)	23.7(23.70)
$[(CH_3Hg)Aad]$	**1n**	16.4(16.69)	1.95(1.96)	23.2(23.36)
$[(CH_3Hg)_2Aad]NO_3 \cdot H_2O$	**2i**·H_2O	11.1(11.15)	1.69(1.72)	15.4(15.17)
$[(CH_3Hg)_2AadH_{-1}]$	**2n**	12.8(12.75)	1.47(1.43)	14.8(14.87)
$[(CH_3Hg)_3AadH_{-1}]NO_3$	**3i**	10.1(9.97)	1.29(1.32)	11.5(11.63)
$[(CH_3Hg)Maad]NO_3$	**M1i**	16.7(16.85)	2.05(2.12)	22.7(22.92)
$[(CH_3Hg)_2MaadH_{-1}]NO_3$	**M2i**	13.0(13.09)	1.68(1.73)	15.4(15.26)
$[(CH_3Hg)_2MaadH_{-1}]ClO_4$	**M2i**	12.3(12.37)	1.59(1.63)	12.5(12.36)
$[(CH_3Hg)MaadH_{-1}]$	**M1n**	18.9(19.76)	2.27(2.21)	22.1(23.04)
$[(CH_3Hg)_2MaadH_{-2}]$	**M2n**	14.4(14.51)	1.68(1.74)	14.6(14.51)

[a]Microanalyses were performed on a Perkin-Elmer 240.

TABLE 2. ^{1}H NMR data for methylmercury(II) complexes of 8-azaadenine and 9-methyl-8-azaadenine (d_6-DMSO, 293 K)

Compound	δ (NH)	δ (H6)	T_c (K)[a]	δ (H2)	δ (N–CH_3)	(Hg–CH_3)	$^2J(^{199}Hg-^1H)$ (Hz)
AadH	15.9(H9)	8.27, 8.02(2H)	295	8.26			
1i	10.5(H1)	9.57, 9.10(2H)	315	8.52		0.91	227
1n		7.79(2H)		8.17		0.86	211
2i		9.22, 8.95(2H)	297	8.45		0.89	223
2n[b]		6.94(1H)		8.03		0.77[c]	197[c]
3i[b]		8.0(1H)		8.29		0.84[c]	210[c]
3n				7.92			
4i				8.15			
Maad		8.39, 8.04(2H)	315	8.29	4.11		
M1i		9.19, 8.81(2H)	308	8.47	4.18	0.88	244
M2i/N3 (83%)[d]		8.3(1H)	293	8.42	4.17	0.85[c]	215[c]
M2i/N1 (17%)[d]		9.03, 8.61(1H)	305	8.35	4.14		
M1n (66%)[b, d]		7.30(1H)		8.16	4.06	0.69	188
M1n (34%)[b, d]		7.04(1H)		8.13	4.07	0.75	192
M2n				8.00	4.00	0.65	178
						0.59	174

[a]Coalescence temperature of the amino protons. [b]Dismutates in solution. [c]Average value for all species in solution. [d]Present in equilibrium.

TABLE 3. Crystal and refinement data for **M1i** and **M2i** ($X^- = ClO_4^-$)

Compound	**M1i**	**M2i** ($X^- = ClO_4^-$)
Space group	*Pc*	$P2_1/c$
a (Å)	10.894(1)	11.363(3)
b (Å)	7.460(1)	16.190(4)
c (Å)	6.876(1)	7.860(2)
α (°)	90.57(1)	99.45(3)
Z	2	4
D_c (g cm^{-3})	2.54	3.17
Radiation	Mo Kα	Mo Kα
μ (cm^{-1})	137.8	217.1
Scan method	ω	ω–2θ
$2\theta_{max}$ (°)	45°	45°
Reflections measured	801	1927
Reflections observed	756	1126
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.038	0.059
R_w	0.032	0.052
P	0.005	0.013

0.71073 Å). Empirical absorption corrections were applied to the reflection intensities. The structures were solved by Patterson and difference syntheses and refined by full-matrix least-squares. Hydrogen atoms were not included in the refinement. The mercury and anion atoms were assigned anisotropic temperature factors. The terminal reliability indices are listed in Table 3, where $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$, with weights given by the expression $w = (\sigma^2(F_o) + p^2F_o^2)^{-1}$. Atom positional parameters with isotropic temperature factors have been listed in Table 4, the coordination geometries of the mercury atoms in Table 5.

Discussion

The reaction of the methylmercury(II) cation with 8-azaadenine is summarized in the interaction scheme presented in Fig. 1. Crystal structures for **1i**, **1n**·$4H_2O$, **2i**·H_2O and **3i** were reported previously [4]. The ^1H NMR spectroscopic data indicate N6,N9-coordination for the neutral complex **2n**. As for the free base AadH, restricted rotation of the amino group is observed for the cationic species **1i** at 293 K. Coalescence of the amino proton signals occurs at 315 K; the free activation enthalpy for rotation $\Delta G^{\ddagger}$ is estimated to be 63.5 kJ mol^{-1}. A similar phenomenon is found for the N3,N9-coordinated species **2i**, with a coalescence temperature of 297 K. Protonation at N1 as in **1i** or CH_3Hg^+-coordination at N3 as in **2i** lead to a formal positive charge being localized in the pyrimidine ring. As a result, the amino nitrogen N6 might be expected to release more charge density into the heterocyclic ring system. Inspection of resonance structures indicates that this should lead to an increased double bond character for C6–N6 and, thereby, to an increase in the energy barrier to rotation about this bond.

Protonation at N1 produces marked downfield shifts for both the H2 and, in particular, the H6 signals of **1i** in comparison to AadH (Fig. 2). The effect of N3-coordination in **2i** is less pronounced. Substitution of amino protons is reflected in upfield shifts for H2 and H6. The strength of metal binding in CH_3Hg^+ complexes may be gauged from the magnitude of the $^2J(^{199}Hg-^1H)$ coupling constants. Lower values are associated with an increased stabil-

TABLE 4. Atom positional parameters with equivalent isotropic temperature factors (Å^2 × 10^3)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
M1i				
Hg6	0.0000	0.2220(1)	0.000	40(1)*
N1	−0.2787(16)	0.4102(24)	−0.1146(27)	47(5)
N3	−0.4783(16)	0.4451(21)	−0.2421(31)	44(5)
N6	−0.1767(14)	0.1409(23)	−0.0906(25)	34(5)
N7	−0.4171(14)	−0.0228(26)	−0.2414(28)	45(5)
N8	−0.5297(14)	−0.0191(26)	−0.3160(27)	50(6)
N9	−0.5685(16)	0.1543(23)	−0.3249(28)	50(5)
C2	−0.3737(18)	0.5098(32)	−0.1755(34)	44(6)
C4	−0.4774(15)	0.2586(26)	−0.2497(29)	32(5)
C5	−0.3860(17)	0.1529(29)	−0.2062(31)	36(6)
C6	−0.2719(16)	0.2210(27)	−0.1343(28)	30(5)
C9	−0.6865(21)	0.1998(36)	−0.4118(38)	63(8)
C61	0.1752(23)	0.3091(39)	0.0847(41)	78(9)
N10	−0.0625(12)	−0.2788(23)	0.0108(24)	37(5)*
O11	0.0171(17)	−0.1645(20)	0.0332(46)	95(7)*
O12	−0.1433(13)	−0.2497(22)	−0.1127(23)	61(5)*
O13	−0.0616(14)	−0.4221(20)	0.1039(24)	61(6)*
M2i ($X^- = ClO_4^-$)				
Hg1	0.4726(1)	0.1788(1)	0.3298(2)	56(1)*
Hg6	0.2117(1)	0.4378(1)	0.4080(2)	53(1)*
Cl10	0.4589(7)	−0.0573(6)	0.2384(11)	75(3)*
O11	0.4069(19)	0.0207(15)	0.1794(34)	100(10)*
O12	0.4466(24)	−0.1142(18)	0.1100(37)	120(11)*
O13	0.4121(26)	−0.0826(20)	0.3859(34)	159(13)*
O14	0.5871(22)	−0.0474(25)	0.2887(35)	154(14)*
N1	0.2997(17)	0.1775(15)	0.3987(28)	45(7)
N3	0.1430(20)	0.0923(16)	0.4829(33)	61(8)
N6	0.2969(20)	0.3232(18)	0.4109(34)	70(8)
N7	0.0550(18)	0.2990(16)	0.5206(29)	53(7)
N8	−0.0348(20)	0.2614(16)	0.5570(33)	59(8)
N9	−0.0130(18)	0.1803(17)	0.5572(3)	57(7)
C2	0.2451(27)	0.1030(23)	0.4254(46)	75(12)
C4	0.0973(22)	0.1677(19)	0.5038(37)	46(8)
C5	0.1320(21)	0.2448(17)	0.4832(34)	37(8)
C6	0.2489(23)	0.2502(19)	0.4278(38)	49(9)
C9	−0.1000(26)	0.1155(22)	0.6056(44)	67(11)
C11	0.6452(22)	0.1913(20)	0.2560(37)	48(8)
C61	0.1244(27)	0.5534(25)	0.3936(46)	79(11)

[a]Starred atoms were refined anisotropically.

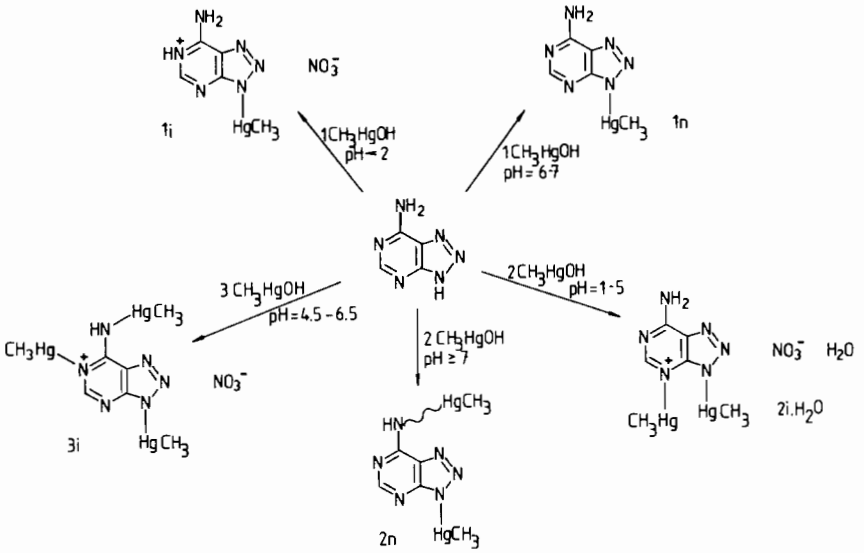


Fig. 1. Reaction of 8-azaadenine with the CH_3Hg^+ cation.

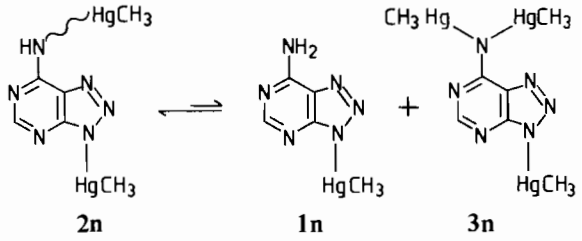
TABLE 5. Bond lengths (Å) and angles (°) to the mercury atoms

M1i			
Hg6–N6	2.11(1)	Hg6–C61	2.09(3)
Gh6–O1ŧ	2.90(2)	Hg6–O12[a]	3.11(2)
Hg6–O13[b]	2.83(2)		
N6–Hg6–C61	178.4(9)	N6–Hg6–O11	78.2(6)
N6–Hg6–O12[a]	78.9(7)	N6–Hg6–O13[b]	97.2(6)
C61–Hg6–O11	103.2(9)	C61–Hg6–O12[a]	101.9(9)
C61–Hg6–O13[b]	81.8(8)	O11–Hg6–O12[a]	91.8(7)
O11–Hg6–O13[b]	158.1(7)	O12[a]–Hg6–O13[b]	66.4(8)
M2i ($X^- = ClO_4^-$)			
Hg1–N1	2.12(2)	Hg1–C11	2.14(2)
Hg1–O11	2.87(2)	Hg1–O13[c]	2.86(3)
Hg6–N6	2.09(2)	Hg6–C61	2.11(3)
Hg6–N7	3.08(2)	Hg6–O11[d]	2.89(2)
Hg6–O14[e]	2.97(3)		
N6–Hg6–C61	177.6(11)	N6–Hg6–N7	68.9(8)
N6–Hg6–O11[d]	84.3(7)	N6–Hg6–O14	71.5(9)
C61–Hg6–N7	111.9(11)	C61–Hg6–O11[d]	97.5(9)
C61–Hg6–O14[e]	107.2(10)	N7–Hg6–O11[d]	111.5(7)
N7–Hg6–O14[e]	137.5(9)	O11[d]–Hg6–O14[e]	78.6(6)

[a]Denotes $x, -y, 0.5 + z$; [b]$x, 1 + y, z$; [c]$1 - x, -y, 1 - z$; [d]$x, 0.5 - y, 0.5 + z$; [e]$1 - x, 0.5 + y, 0.5 - z$.

ity of the complexes [10]. Introduction of a positive charge into the pyrimidine ring leads to a marked reduction in the formation constant for binding at a given sites. The $^2J(^{199}Hg-^1H)$ values of 227 and 211 Hz for **1i** and **1n**, respectively indicate that N9 metal binding is much stronger in the neutral complex.

Two rotamers are possible for **2n**, with N6–Hg in a position either *syn* or *anti* to C6–N1. As an X-ray structural determination was not possible for **2n**, it is not known which rotamer is present in the solid state. Both **2n** and **3i** dismutate in d_6-DMSO solution; **2n** lies in equilibrium with **1n** and **3n**. Addition of authentic **1n** confirms the presence of this species; **3n** is indicated by the H2 resonance at



2n **1n** **3n**

7.92 ppm. The equilibrium constant is estimated to be 0.11. A value of 0.10 was determined for the analogous dismutation of $[(CH_3Hg)_2AdH_{-1}]$ (AdH = adenine) [11]. The presence of **2i** in a d_6-DMSO

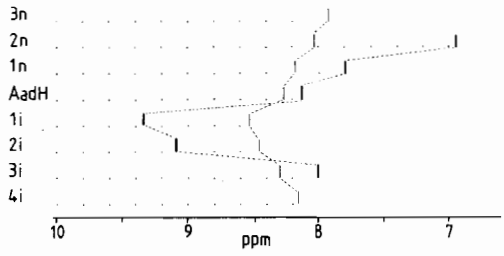


Fig. 2. Chemical shifts for H2 and H6 in CH_3Hg^+ complexes of 8-azaadenine (thin lines H2, thick lines average values for H6).

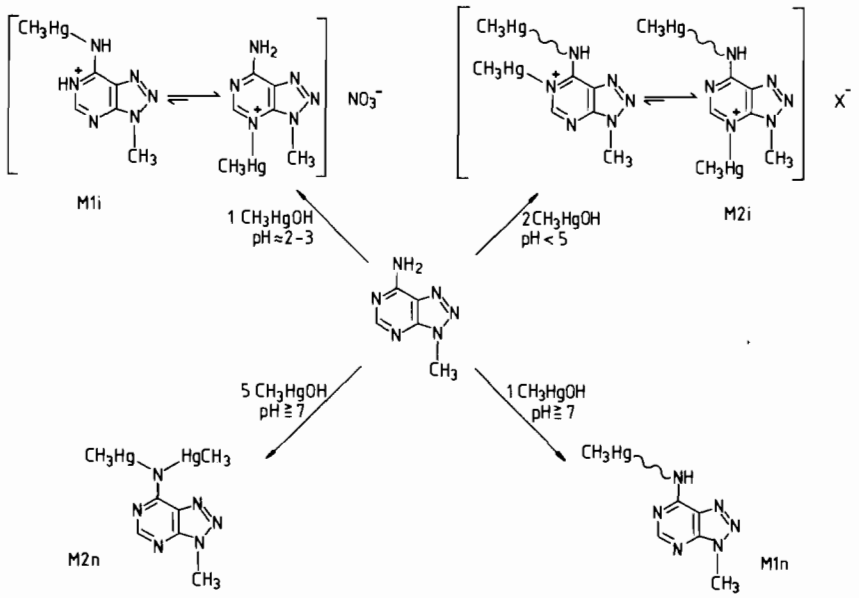
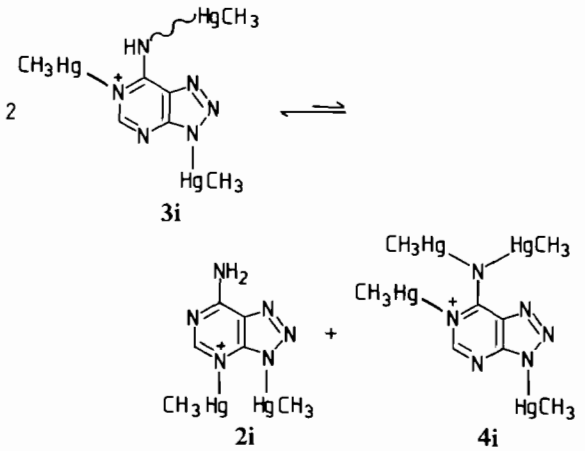


Fig. 3. Reaction of 9-methyl-8-azaadenine with the CH_3Hg^+ cation.

solution of **3i** was confirmed by addition of an authentic sample of the former. The H2 resonance at 8.15 in the ^1H NMR spectrum of this solution was assigned to the second dismutation product, presumably **4i** (Fig. 2). The dismutation constant



was determined as 0.16. In addition to N6 (twice) and N9, either N1 or N3 may be a potential metal binding site in this species. As N1 is the observed coordination position in **3i** in the solid state, it seems reasonable to assume that this is also the case for **4i**. Substitution of an amino proton by CH_3Hg^+ will lead to an increase in ring electron density; the basicity of the closer nitrogen N1 will be enhanced relative to the more distant N3. As a result, N1 coordination is observed in **3i** as opposed to N3 coordination in **2i**. The replacement of both amino protons in **4i** should further enhance N1 as the preferred binding site in the pyrimidine ring.

The reaction of the methylmercury(II) cation with 9-methyl-8-azaadenine is summarized in the interaction scheme depicted in Fig. 3. Respectively N6- and N1,N6-coordination were established for CH_3-Hg^+ in the complexes **M1i** and **M2i** ($X^- = ClO_4^-$) in the solid state (Fig. 4). The structure of **M1i** with N1-protonation is remarkable, as this complex was prepared at a low pH value (2–3). Whereas the N6–Hg bond adopts the *syn* position in **M1i**, the *anti* position is preferred in **M2i**, allowing a weak Hg6...N7 interaction of length 3.08(2) Å.

In contrast to the solid state, the amino group in **M1i** is not substituted in d_6-DMSO solution. The integral for the two H6 resonances at 8.81 and 9.19 ppm is in accordance with two amino protons (Fig. 5). Coalescence of the H6 signals occurs at 308 K indicating restricted rotation of the amino group about C6–N6, as is also found for the free base Maad. On the basis of the following observations for **M2i** it is suggested that N3 rather than N1 is the metal binding site in **M1i**. The temperature dependence of the lowfield range (7.7–9.2 ppm) of the ^1H NMR spectrum of **M2i** is displayed in Fig. 6. Identical spectra are obtained for the nitrate and perchlorate. Two isomers are present for **M2i** at 320 K in an approximate ratio 5:1. Respective H2 resonances are observed at 8.39 and 8.35 ppm with broad signals for H6 at 8.08 and 8.52 ppm. The signals for the isomers coalesce upon heating the solution from 320 to 370 K. Upon cooling from 320 to 290 K the resonances for the amino proton broaden and coalescence temperatures of *c.* 305 and 293 K may

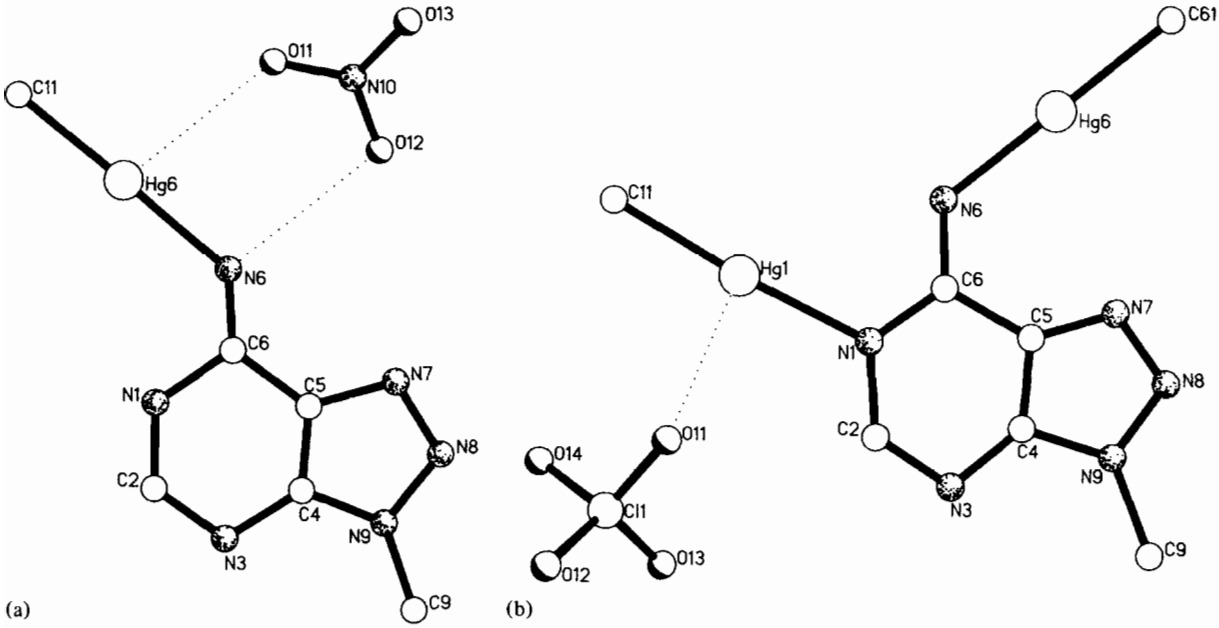


Fig. 4. Molecular structures of (a) **M1i** and (b) **M2i** ($X^- = ClO_4^-$).

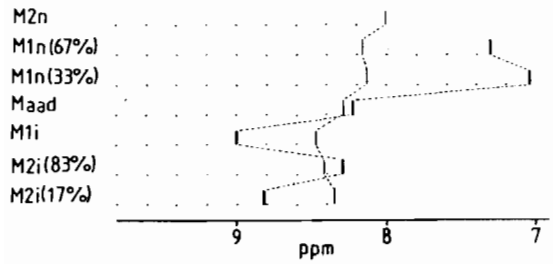


Fig. 5. Chemical shifts for H2 and H6 in CH_3Hg^+ complexes of 9-methyl-8-azaadenine (thin lines H2, thick lines average values for H6).

be established for the 17% and 83% isomers respectively (individual H6 signals for the latter isomer are masked by the H2 signals at 290 K). An average resonance is found for the NCH_3 group at 320 K, which splits into two signals in a 5:1 ratio upon cooling. As CH_3Hg^+-coordination of N1 would be predicted to lead to a more pronounced downfield shift for the amino proton H6 in comparison to the alternative binding site N3, it is reasonable to assume N1,N6-coordination for the 17% isomer (average δ(H6) = 8.82 ppm), as was found in the solid state, and N3,N6-coordination for the 83% isomer (δ(H6) = 8.3 ppm). Above 310 K rotation about the C6–N6 bond is fast for both isomers on the NMR time scale. At 290 K rotamers with N6–Hg6 in both the *syn* and *anti* position with respect to C6–N1 are present for both **M2i** isomers.

Restricted rotation about C6–N6 is also observed for **M1n**; the rotamers are present in an approximately 2:1 ratio. As was also observed for the N6-coordinated complexes of 8-azaadenine **2n** and **3i**, **M1n** dismutates in d_6-DMSO. The presence of Maad and **M2n** in solution may be verified by addition of authentic samples.

Our studies on Cu^{2+}, CH_3Hg^+ and Rh(I) complexes of 8-azaadenine and 9-methyl-8-azaadenine now allow the following conclusions to be drawn, concerning the coordination behaviour of these modified purine bases.

1. N9 is the preferred binding site for neutral 8-azaadenine and the 8-azaadeninate anion.

2. If N9 is bonded to either an alkyl group, a proton or a metal atom, then either N1 or N3 of the pyrimidine ring is the chosen secondary binding site. No N7- or N8-coordinated complexes could be isolated from solution for the studied cations.

3. If N6 is not coordinated, then N3 appears to be the preferred coordination site in the pyrimidine ring for the CH_3Hg^+ cation, e.g. **2i** in the solid state.

4. Coordination of N6 by CH_3Hg^+ leads to an enhancement of the basicity of N1 relative to N3 so that the former nitrogen is now competitive as a secondary binding site, e.g. **3i** and **M2i** in the solid state, the equilibrium between N1,N6- and N3,N6-coordinated isomers for **M2i** in d_6-DMSO solution.

5. Dismutation of N6-monosubstituted CH_3Hg^+ complexes in d_6-DMSO solution is characteristic.

Our results suggest that with N9 blocked, N7 or N8 of 8-azaadenine may not be competitive as a site for metal binding in the DNA in which the base may act. Coordination of pyrimidine nitrogens instead of N7 can, of course, have a profound effect

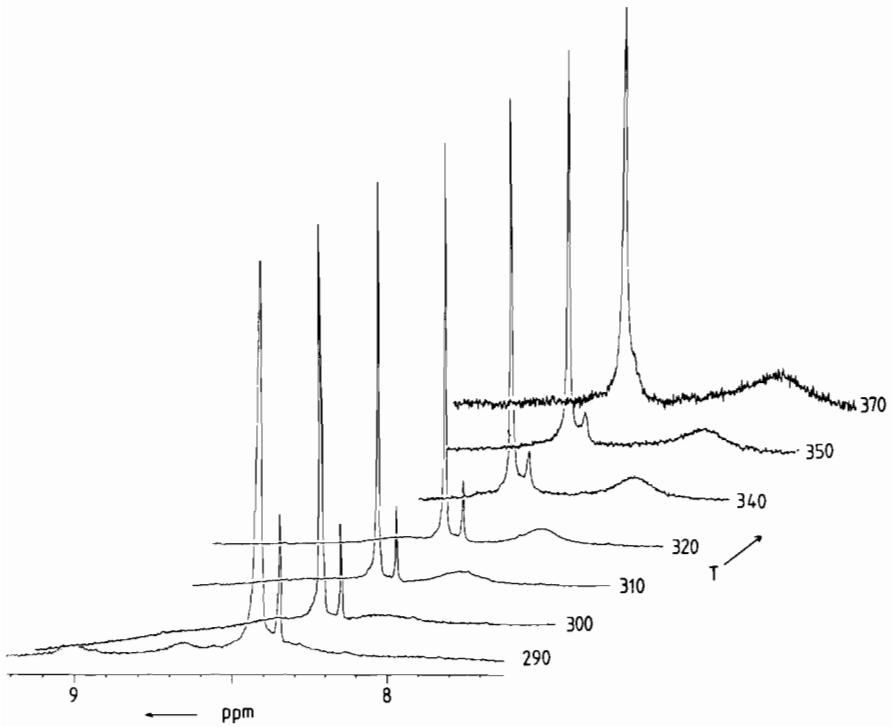


Fig. 6. Temperature dependence of the lowfield range of the ^{1}H NMR spectrum of **M2i** ($X^- = NO_3^-$).

on the base hydrogen bonding pattern (for N1) or on the conformation at the glycosidic bond N9–C1′ (for N3).

Supplementary Material

Tables of anisotropic temperature factors, observed and calculated structure factors and IR data are available from the authors on request.

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