

Crystal Structure and Infrared Spectra of Anhydrous (Adeninato)methylmercury(II)*

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Received November 28, 1983

The title compound, $C_6H_7HgN_5$, belongs to the orthorhombic space group $Pbcn$, $a = 14.658(8)$, $b = 8.407(5)$, $c = 13.006(9)$ Å, $D_{cal} = 2.898$ g cm $^{-3}$, $Z = 8$ molecules per cell. The structure was refined on 1132 unique nonzero reflections to $R = 0.026$. The crystal contains the same type of 1:1 monomeric molecule as the monohydrate, in which the CH_3Hg group is bonded to the N(9) position of deprotonated adenine. These molecules are associated into infinite ribbons by means of two pairs of complementary N—H...N bonds involving both amino protons and the lone pairs on N(1) and N(7) of each molecule. The infrared spectra of this material and of the monohydrate differ almost exclusively in the regions related to NH_2 vibrations. This simply results from differences in hydrogen-bonding patterns and no direct metal-amino interaction is taking place in any case. The spectral changes already identified as characteristic of N(9)-complexation for the monohydrate are also observed for the anhydrous compound.

INTRODUCTION

As part of our continuing interest for heavy-metal complexes with adenine (HAd) and other nucleic bases, we described in a previous report¹ the crystal structure of $CH_3HgAd \cdot H_2O$. The CH_3Hg^+ ion in this 1:1 complex was found to be bound to the deprotonated N(9) site of adenine. A detailed study of the vibrational spectra of this and related compounds was also carried out.² Under slightly different conditions, the compound of 1:1 stoichiometry was isolated in anhydrous form. The infrared spectra of the two varieties differed mainly in the regions assigned to vibrations of the 6- NH_2 group. In order to explain these spectral changes, the crystal structure of the anhydrous material was undertaken. The crystallographic results and the infrared spectra are discussed in the present paper.

EXPERIMENTAL

Reactants.

Adenine (Terochem), $[(CH_3Hg)_3O]OH$ (Alfa) and 1 M aqueous CH_3HgOH (Alfa) were used without further purification. Adenine was deuterated by refluxing in D_2O under N_2 atmosphere for 2 h. Filtration and drying *in vacuo* yielded a sample

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

fully deuterated at C(8). Deuteration was only partial at N(9) and the N(6) amino group.

Preparation of CH_3HgAd

Adenine (135 mg, 1 mmol) was mixed with 1 mL of 1 M aqueous CH_3HgOH in 19 mL of hot absolute ethanol. The colorless crystals precipitated upon cooling. Anal. Calcd. for $\text{C}_6\text{H}_7\text{HgN}_5$: C, 20.60; H, 2.02; Hg, 57.35; N, 20.02. Found: C, 20.16; H, 2.34; Hg, 57.13; N, 19.43. All attempts to recrystallize the compound from water resulted in the precipitation of the monohydrate.

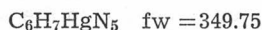
Preparation of $\text{CH}_3\text{HgAd}-(6,6,8)\text{d}_3$

Deuterated adenine (70 mg, 0.5 mmol) was mixed with $[(\text{CH}_3\text{Hg})_3\text{O}]\text{OH}$ (220 mg, 1 mmol) in 10 mL of hot D_2O under N_2 atmosphere. A white powder precipitated overnight. It was filtered and dried *in vacuo*. The compound remain fully deuterated at C(8), but only $\sim 80\%$ deuterated at the amino group. This solid sample was identified as the anhydrous material without detectable amount of monohydrate, from the weak infrared band at 1673 cm^{-1} for the minor undeuterated fraction.

Infrared Spectroscopy

The infrared spectra ($4000\text{--}350\text{ cm}^{-1}$) were recorded as KBr pellets with a Beckman IR4520 spectrophotometer.

Crystal data



Orthorhombic, $Pbcn$, $a = 14.658(8)$, $b = 8.407(5)$, $c = 13.006(9)\text{ \AA}$, $V = 1602.7\text{ \AA}^3$, $D_{\text{obs}} = 2.87(3)\text{ g cm}^{-3}$ (flotation in $\text{CH}_2\text{I}_2\text{--CHBr}_3$), $D_{\text{cal}} = 2.898\text{ g cm}^{-3}$, $Z = 8$, $\mu(\text{CuK}\alpha) = 1.54178\text{ \AA}$ (graphite monochromator), $T = 296\text{ K}$, $\mu(\text{CuK}\alpha) = 366.1\text{ cm}^{-1}$.

Crystallographic Measurements and Structure Determination

A colorless crystal of dimensions 0.07 mm ($110\text{--}\bar{1}\bar{1}0$) \times 0.12 mm ($\bar{1}10\text{--}\bar{1}\bar{1}0$) \times 0.16 mm ($001\text{--}001$) was used for X-ray work. A set of precession and cone-axis photographs showed mmm Laue symmetry and the space group was uniquely determined from its systematic absences ($0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h+k \neq 2n$). Accurate cell parameters and intensity data were obtained with an Enraf-Nonius CAD4 diffractometer, following procedure described elsewhere.³ The fluctuations of three standard reflections remained within $\pm 2\%$ during data collection. A total of 1892 hkl reflections within a sphere limited by $2\theta = 140^\circ$ was measured. After rejection of 375 systematic absences, the data set consisted of 1517 independent reflections, of which 1132 were used to interpret the structure ($I > 2.5\sigma(I)$). The data were corrected for absorption (Gaussian intergration, grid $8 \times 8 \times 8$, transmission range $0.032\text{--}0.223$), polarization and the Lorentz effect.

The structure was solved by the conventional heavy-atom method and refined on $|F_o|$. The Hg atom was located from a Patterson map and the remaining non-hydrogen atoms were found in the difference Fourier (ΔF) map phased on Hg. These atoms were first refined isotropically by full-matrix least squares, then anisotropically by block-diagonal least squares. A subsequent ΔF map revealed the positions of the hydrogens attached to C(2), N(6) and C(8), and of two of those of the C(9) methyl group. They were included in structure factor calculations and isotropically refined. The third methyl hydrogen was fixed at the ideal position ($\text{C--H} = 0.95\text{ \AA}$, $B = 5.0\text{ \AA}^2$) and not refined. The final residuals were $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.026$ and $R_w = [\Sigma (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.033$. The goodness-of-fit ratio was 1.24. The final ΔF map showed a general background below $\pm 0.50\text{ e \AA}^{-3}$ and a few ripples lower than $\pm 1.0\text{ e \AA}^{-3}$ within 1.5 \AA from Hg.

The scattering curves and anomalous dispersion coefficients of Hg were from standard sources.⁴ The programs used are listed elsewhere.⁵ The refined coordinates are listed in Table I. The temperature factors and structure-factor amplitudes are available from the authors upon request.

TABLE I
 Refined Coordinates of (Adeninato)methylmercury(II)
 ($\times 10^4$, Hg $\times 10^5$, H $\times 10^3$)

Atom	X	Y	Z
Hg(9)	18318(2)	22063(4)	14688(2)
N(1)	-1455(4)	-851(7)	939(6)
N(3)	138(5)	-253(7)	1254(5)
N(6)	-2580(4)	1062(8)	726(6)
N(7)	-998(4)	3498(8)	1056(6)
N(9)	441(5)	2556(7)	1307(5)
C(2)	-578(6)	-1207(9)	1125(7)
C(4)	-133(5)	1288(8)	1212(6)
C(5)	-1007(5)	1853(8)	1068(6)
C(6)	-1696(5)	720(8)	923(6)
C(8)	-129(6)	3840(10)	1215(7)
C(9)	3212(6)	1706(15)	1623(8)
H(2)	-64(9)	-263(13)	133(8)
H(8)	23(5)	492(10)	130(6)
H(61)	-315(5)	30(10)	77(6)
H(62)	-283(6)	199(11)	82(7)
H(91)	355(7)	107(14)	231(9)
H(92)*	335	279	174
H(93)	348(6)	114(12)	99(7)

* Not refined

DESCRIPTION OF THE CRYSTAL STRUCTURE

The CH_3HgAd molecule and the numbering scheme used to describe it are given in Figure 1. The present anhydrous form contains the same molecule as the monohydrate¹: the CH_3Hg^+ group is bound to the N(9) position of the deprotonated adenine anion. Thus, the perturbations noted on the NH_2 bands in infrared do not result from direct coordination of mercury to the amino group.

The Hg—N and Hg—C bonds, both roughly equal to 2.07 Å (Table II), are of the same length as observed for the monohydrate and a variety of CH_3Hg complexes.¹ The departure from linearity is highly significant ($\text{C}(9)\text{—Hg}(9)\text{—N}(9) = 176.5(3)^\circ$), but not unusual. The CH_3Hg group does not lie exactly along the expected direction of the N(9) lone pair. Appreciable displacement toward N(3) introduces a difference of 15.7° between the Hg(9)—N(9)—C angles. Large differences are usually associated with intramolecular steric hindrance,⁶ but it is not the case here. As N(3) is not involved in hydrogen bonding or intermolecular Hg—N contacts, space is available for the CH_3Hg group to be displaced toward N(3) and the distortion undoubtedly results from packing constraints. Bond strength does not seem to suffer appreciably from these distortions.

The geometry of the adenine moieties in this structure and in the monohydrate¹ shows no significant differences, although as usual, high esd's in both cases would mask any fine structural change. The two-ring system is best described as two individual planar cycles, with a slight bent of 1.4° about the C(4)—C(5) bond. The largest departure of a ring atom from its own plane is within 2σ (0.019(9) Å for C(2)). However, the amino N(6) atom deviates to

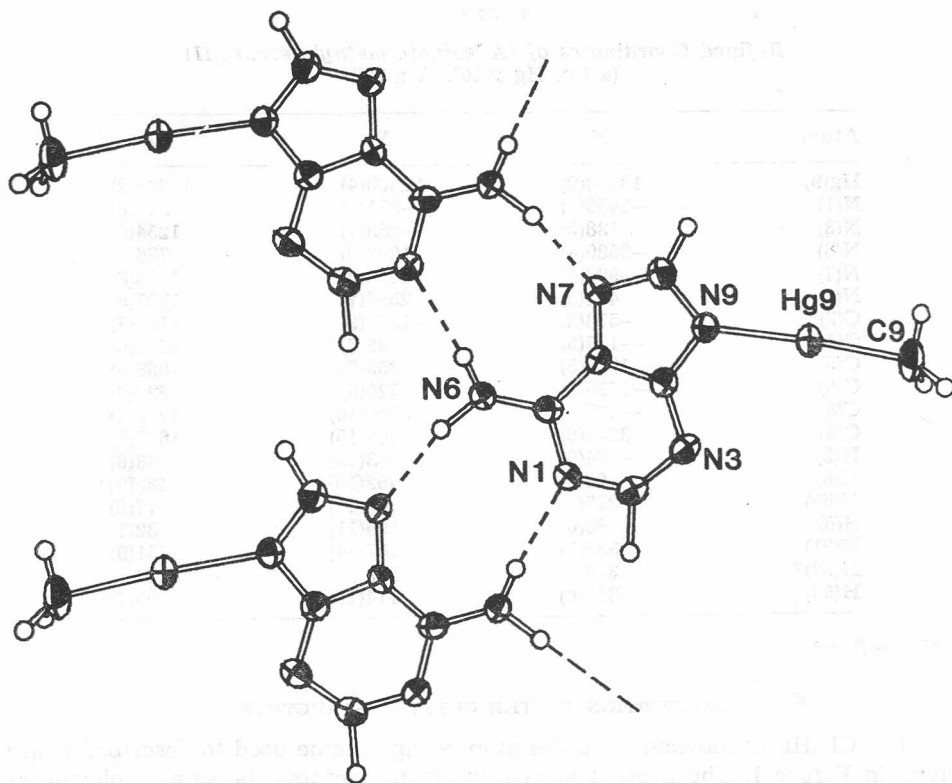


Figure 1. Portion of a ribbon of hydrogen-bonded (adeninato)methylmercury(II) molecules. The ellipsoids correspond to 50% probability. Hydrogens are shown as spheres of arbitrary sizes. Dashed lines represent hydrogen bonds

TABLE II
Interatomic Distances and Bond Angles in (Adeninato)methylmercury(II)

Distances (Å)

Hg(9) — N(9)	2.070(7)	C(5) — C(6)	1.401(10)
Hg(9) — C(9)	2.076(9)	C(6) — N(6)	1.352(10)
N(1) — C(2)	1.342(11)	C(5) — N(7)	1.383(9)
N(1) — C(6)	1.367(9)	N(7) — C(8)	1.322(10)
C(2) — N(3)	1.331(10)	C(8) — N(9)	1.370(10)
N(3) — C(4)	1.356(9)	N(9) — C(4)	1.364(10)
C(4) — C(5)	1.379(10)		

Angles (deg)

C(9) — Hg(9) — N(9)	176.5(3)	C(6) — C(5) — N(7)	133.2(7)
C(2) — N(1) — C(6)	117.7(7)	C(5) — C(6) — N(6)	124.9(7)
N(1) — C(2) — N(3)	130.0(8)	N(1) — C(6) — N(6)	117.1(7)
C(2) — N(3) — C(4)	109.8(7)	C(5) — N(7) — C(8)	103.0(6)
N(3) — C(4) — C(5)	127.3(7)	N(7) — C(8) — N(9)	115.4(7)
N(3) — C(4) — N(9)	124.2(7)	C(8) — N(9) — C(4)	103.4(6)
N(9) — C(4) — C(5)	108.4(6)	C(8) — N(9) — Hg(9)	136.1(6)
C(4) — C(5) — C(6)	117.0(7)	C(4) — N(9) — Hg(9)	120.4(5)
C(4) — C(5) — N(7)	109.7(7)		

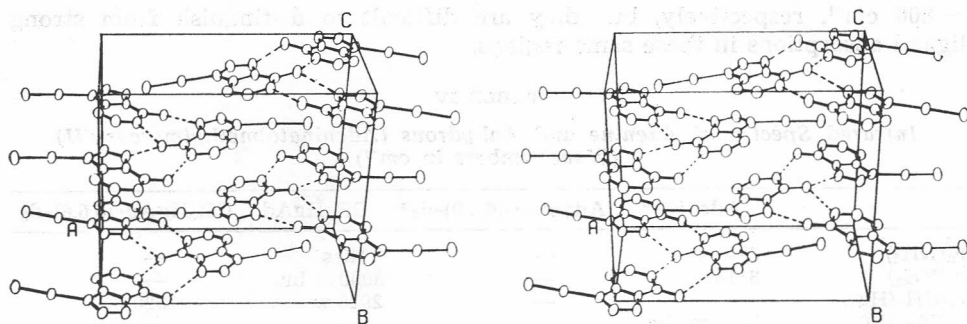


Figure 2. Stereoview of the unit cell down the c axis. The atoms are represented by spheres of arbitrary sizes, the larger ones corresponding to Hg atoms. Dashed lines correspond to hydrogen bonds.

a greater extent (0.040(8) Å) and the CH_3Hg^+ group as a whole is tipped out of the plane by 0.1000(3) Å at Hg(9) and 0.206(10) Å at C(9).

A view of the unit cell is given in Figure 2. Molecules linked by pairs of hydrogen bonds define puckered ribbons parallel to the ab plane and oriented along the b direction. A similar ribbon-like pattern is found in 9-methyladenine.⁷ Successive molecules along the ribbon are related by the b glide plane and associated by means of two pairs of complementary hydrogen bonds involving both amino N—H bonds as donors, and N(1) and N(7) as acceptors. The geometry of these H-Bonds is summarized in Table III. The N...N distances compare well those of 9-methyladenine (3.074(2) and 2.969(2) Å)⁷ and the angles are quite favorable. Thus, the present CH_3HgAd complex can be envisioned as an N(9)-substituted derivative similar to 9-methyladenine, with a bulkier substituent at N(9). This analogy holds not only to the molecule itself, but for the general packing arrangement as well.

TABLE III

Geometry of the Hydrogen Bonds in (Adeninato)methylmercury(II)

Distances (Å)

N(1) — N(6) ^a	2.969(9)	N(7) — N(6) ^b	3.029(9)
N(6) — N(1) ^b	2.969(9)	N(6) — N(7) ^a	3.029(9)

Angles (deg)

C(6) — N(6) — N(1) ^b	128.7(5)	C(6) — N(6) — N(7) ^a	118.8(5)
C(2) — N(1) — N(6) ^a	106.2(5)	C(5) — N(7) — N(6) ^b	135.0(5)
C(6) — N(1) — N(6) ^a	136.0(5)	C(8) — N(7) — N(6) ^b	122.0(5)

^a $-1/2 - x, -1/2 + y, z$; ^b $-1/2 - x, 1/2 + y, z$

INFRARED SPECTROSCOPY

The CH_3Hg^+ ion usually produces four well recognizable features in infrared.^{1,2,8} A sharp peak at 2920 cm^{-1} is due to the $\nu_s(\text{CH}_3)$ mode and the weak peak at 569 cm^{-1} originates in Hg—C stretching motion (Table IV). Bands arising from the $\delta_s(\text{CH}_3)$ and $\rho(\text{CH}_3)$ vibrations should appear at ~ 1200 and

$\sim 800 \text{ cm}^{-1}$, respectively, but they are difficult to distinguish from strong ligand absorptions in these same regions.

TABLE IV
Infrared Spectra of Adenine and Anhydrous (Adeninato)methylmercury(II)
(Wavenumbers in cm^{-1})

	Adenine*	Adenine-(6,6,9)- d_3 *	CH_3HgAd	$\text{CH}_3\text{HgAd}-(6,6,8)-\text{d}_3$
$\nu_a(\text{NH}_2)$	3294 s	—	3240 s	—
$\nu_s(\text{NH}_2)$	3118 s	—	3090 s, br	—
$\nu_s(\text{CH}_3(\text{Hg}))$	—	—	2920 w	2920 w
$\nu(\text{N9—H9})$	2800 m, br	—	—	—
$\nu_a(\text{ND}_2)$	—	2480 m	—	2445 m
$\nu_s(\text{ND}_2)$	—	2302 s	—	2275 s
$\nu_s(\text{N9—D9})$	—	$\sim 2150 \text{ m, br}$	—	—
$\delta(\text{NH}_2)$	1673 vs	—	1673 vs	—
	1604 vs	1602 vs	1599 vs	1597 s
	1570 sh	1572 vs	1559 m	1552 m
	1507 w	1513 m	1480 w	1483 m
	1449 m	1463 m	1459 s	1440 s
	1420 s	1422 s	1397 s	1378 s
	1367 m	1367 w	1357 m	1358 m
	1334 s	1333 s	1322 m	1320 s
	1308 vs	1304 vs	1312 m	1311 s
	1250 s	1255 vw	1268 w	1247 m
$\delta(\text{C}(8)—\text{H}(8))$	1235 sh	1225 s	1235 m	—
$\delta(\text{ND}_2)$	—	1200 w	—	1174 m
$\delta(\text{CH}_3(\text{Hg}))$	—	—	1211 w	1205 m
	1156 w	1175 m	1192 s	1193 m
	1125 m	1094 w	1140 m	1123 w
$\rho(\text{NH}_2)$	1023 m	—	1042 m	—
	—	—	980 w	—
$\delta(\text{N—D})$	—	949 m	—	[940 s
	939 s	931 s	937 w	940 s
	912 s	895 vs	902 w	—
	871 m]	860 m	854 w	875 s
$\gamma(\text{N}(9)—\text{H}(9))$	871 m]	—	—	—
$\rho(\text{ND}_2)$	—	860 sh	—	867 sh
$\gamma(\text{C}(8)—\text{H}(8))$	847 m	850 m	828 w	—
$\delta(\text{C}(8)—\text{D}(8))$	—	—	—	830 w
	796 m	796 s	798 m	798 s
$\rho(\text{CH}_3(\text{Hg}))$	—	—	798 m	798 s
	723 s	708 s	724 s	715 w
$\omega(\text{NH}_2)$	645 m	—	[697 m, br	683 m
	639 s	647 s	667 m	650 m
	621 m	605 m	659 w	623 w
$\gamma(\text{N—D})$	—	621 m	—	—
$\gamma(\text{C}(8)—\text{D}(8))$	—	—	—	600 s
$\nu(\text{Hg—C})$	—	—	569 m	565 w
	542 m	534 m	540 m	535 m
	530 sh	519 w	—	—
$\omega(\text{ND}_2)$	—	470 w	—	510 sh, br
	337 m	312 m	342 s	340 m

* From ref. 9.

The infrared and Raman spectra of adenine and adenine-(6,6,9)-d₃ were discussed by Lautié and Novak.⁹ Normal coordinate calculations on the planar vibrations of 9-methyladenine were carried out by Tsuboi, Takahashi and Harada.¹⁰ Our assignments are based on these studies.

The 6-amino group gives rise to five relatively pure vibrations: 3294 (ν_a), 3118 (ν_s), 1673 (δ_s), 1023 (ρ) and 645 cm⁻¹ (ω). In the anhydrous form of the CH₃HgAd complex, these bands are observed at 3240, 3090, 1673, 1042 and ~ 685 cm⁻¹, respectively. They were identified from their counterparts at 2445 (ν_a), 2275 (ν_s), 1174 (δ_s), 867 (ρ) and 510 cm⁻¹ (ω) in the spectrum of the deuterated compound. In the monohydrate, these same modes were found at 3295, 3100, 1654, 1042 and 630 cm⁻¹, respectively.

Displacement of the H(9) proton of adenine by CH₃Hg⁺ is accompanied by the disappearance of the broad absorption at 2800 (ν (N—H)) and at ~ 870 cm⁻¹ (δ (N—H)). A band at 1250 cm⁻¹ has been assigned to the δ (N—H) mode,⁹ but this interpretation should probably be reexamined, as both components of the adenine spectrum can still be found in the CH₃HgAd spectrum, in spite of the disappearance of H(9). The N—H motion is probably highly coupled with ring vibrations and the effect of substitution of the spectrum is not restricted to a single absorption, but spread over several bands. In addition, it would be difficult to distinguish these effects from those arising from changes in bond orders in the ring caused by H(9) substitution.

The numerous spectral differences between adenine and CH₃HgAd·H₂O have been discussed in detail.^{1,2} These changes are also observed here for the anhydrous material. The disappearance of the band at 621 cm⁻¹ and the shifts (within parentheses) of the following adenine bands can be considered as a characteristic for H(9) substitution: 1449 (+10), 1125 (+15), 1023 (+19) cm⁻¹. Other shifts are observed for H(9) substitution, but only if N(7) is not simultaneously coordinated: 1604 (—5), 1570 (—11), 1507 (—27) cm⁻¹. Finally, for other bands, the position is sensitive both to N(9) substitution and the pattern of occupancy of the remaining ring sites: 1334 (—12), 1308 (+4), 1250 (+18), 1156 (+36) cm⁻¹. Thus the four last bands can be used to identify the present complex.

In the deuterated derivative of CH₃HgAd studied here, both amino protons and the hydrogen attached to C(8) have been substituted by deuterium. A band at 1235 cm⁻¹ in the undeuterated complex is believed to have a high content of δ (C(8)—H(8)) motion.^{9,10} It is indeed removed at deuteration. The δ (C(8)—D(8)) counterpart is expected to appear around 850 cm⁻¹,¹¹ and a weak band at 830 cm⁻¹ is tentatively assigned to this vibration. The out-of-plane C(8)—H(8) bending probably occurs at 828 cm⁻¹, since it disappears at deuteration. A strong band at 600 cm⁻¹ is assigned to the corresponding γ (C(8)—D(8)) mode, as a similar band was invariably found in C(8)—D(8) derivatives of purines.¹² Deuteration at C(8) is probably responsible for a shift of —19 cm⁻¹ on the band at 1459 cm⁻¹, which probably involves appreciable contribution from δ (C(8)—H(8)) motion.

In addition to clear effects on the various modes of the NH₂ group, deuteration at this position also produces other less marked, but significant, changes. For instance, the shift from 1397 (undeuterated) to 1378 cm⁻¹ (deuterated) involves a vibration mainly located in the N(1)—C(6)—N(6) region of adenine.¹⁶ The displacement from 1140 to 1123 cm⁻¹ is probably due to loss of coupling

with the $\rho(\text{NH}_2)$ motion, since a similar shift from 1125 to 1094 cm^{-1} is observed between free adenine and its N-deuterated derivative.⁹

A modification in the 1250 cm^{-1} region is difficult to explain. The $\delta(\text{C}(8)\text{—H}(8))$ band at 1235 cm^{-1} and the weak absorption at 1268 cm^{-1} , are replaced by a single band at 1247 cm^{-1} in the $\text{CH}_3\text{HgAd-d}_3$ complex. Coupling with the $\delta(\text{ND}_2)$ motion in the deuterated derivative could provide an explanation, but it does not explain that a similar effect is not observed for free adenine upon deuteration.

CONCLUSION

The present work provides further support to our previous conclusion¹ that N(9) is the site first occupied by the CH_3Hg^+ ion in deprotonated adenine. It also stresses the fact that changes in infrared spectra have to be interpreted with care in systems like this, where extensive hydrogen bonding is present. The high wavenumber of the $\delta(\text{NH}_2)$ mode, which could have been misinterpreted as an effect of complexation appears to be related to differences in hydrogen bonding between the anhydrous form and the monohydrate. In a number of adenine complexes studied so far,² this band appears at $\sim 1650 \text{ cm}^{-1}$ and in none of these compounds, is the pattern of hydrogen bonds of Figure 1 present. On the other hand, 9-methyladenine, which contains this pattern, absorbs at 1670 cm^{-1} .¹³ Therefore, this high wavenumber seems to be characteristic of an adenine amino group involved in two pairs of complementary hydrogen bonds.

Acknowledgments. — We wish to thank M. J. Olivier who collected the X-ray intensity data. The financial supports of the Natural Science and Engineering Council of Canada and the Ministère de l'Éducation du Québec are gratefully acknowledged.

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SAŽETAK

Kristalna struktura i infracrveni spektri bezvodne (adeninato)metilžive(II)

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Kristali spoja u naslovu, $C_6H_7HgN_5$; jesu rompski, prostorna grupa $Pbcn$, i imaju elementarnu ćeliju dimenzija $a = 14,658(8)$, $b = 8,407(5)$, $c = 13,006(9)$ Å, izračunana gustoća $D = 2,898$ g cm⁻³, $Z = 8$. Struktura je riješena na osnovi 1132 refleksa i utočnjena do $R = 0,026$. Kristal sadržava istu vrstu 1 : 1 monomernih molekula kao i monohidrat u kojemu je skupina CH_3Hg vezana na atom dušika N(9) deprotoniranog adenina. Molekule su povezane u beskonačnu vrpcu s pomoću dva para N—H...N veza u koje su uključena oba protona iz amino-skupine i nepodijeljeni elektronski parovi na atomima N(1) i N(7) svake molekule. Infracrveni spektri tog spoja i monohidrata razlikuju se jedino u području vibracija NH_2 . To jednostavno proizlazi iz razlike u povezivanju preko vodikovih veza, a ne iz direktne interakcije metala i amino-skupine. Kao što je već utvrđeno u slučaju monohidrata, spektralne promjene karakteristične za kompleksiranje preko N(9) opažene su i u bezvodnom spoju.