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Role of the Carbonyl Groups in the N3-coordinated Thymine Ring. Crystal Structure of (1-Methylthyminato)methylmercury(II) Hemihydrate and its Mixed Compound with Sodium Nitrate

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The crystal structures of two compounds containing the (1-methylthyminato)methylmercury(II) molecule are reported. The hydrated compound $CH_3Hg(C_6H_7N_2O_2)\cdot\frac{1}{2}H_2O$ *belongs to the tetragonal space group* $P4_122$, $a = b = 8.118$ Å *and* $c = 30.084$ Å. *The structure was refined on 1107 reflections to an* R *factor of 0.058. The same molecule formed a mixed compound of the formula* $CH_3Hg(C_6H_7N_2O_2)\frac{1}{2}NaNO_3$, *belonging to the orthorhombic space group Pnma,* $a = 11.088$ Å, $b = 6.785$ Å, *and* $c = 27.31$ Å. *The structure was refined on 2128 reflections to* R $= 0.027$. *In both compounds, the* CH_3Hg *group is linearly coordinated to N3 of deprotonated 1-methylthymine. In the hemihydrate, carbonyl oxygen O4 forms a secondary Hg···O bond of 2.88 Å with an adjacent molecule and it acts as the acceptor in a strong hydrogen bond (O···O = 2.75 Å) with water. The other carbonyl group is not involved in any strong interactions. In the* $NaNO_3$ *compound, the two independent* $CH_3Hg(C_6H_7N_2O_2)$ *molecules lie on crystallographic mirror planes and the* CH_3Hg *groups are slightly displaced in the plane to make contacts of 2.919 Å with O4 in one molecule and of 2.995 Å with O2 in the other.* Na^+ *ions occupying inversion centers are surrounded by approximate octahedra consisting of two O4 oxygens at 2.324 Å from one type of molecules, two O2 atoms at 2.436 Å from the other type, and two nitrate oxygens at 2.406 Å.* NaO_6 *octahedral sharing edges form infinite chains along the c axis, surrounded by two infinite stacks of parallel* $CH_3Hg(C_6H_7N_2O_2)$ *molecules and two rows of nitrate ions.*

Introduction

Thymine and uracil contain no unprotonated nitrogen atoms at neutral pH and for this reason, their interactions with metals were not as extensively studied as those of the remaining DNA constituents [1, 2]. In the neutral form, these ligands have only carbonyl groups as potential coordination sites. Although oxygens are likely to act as suitable targets for hard metal ions, strong interactions with soft metals were apparently found only for $HgCl_2\cdot$uracil, in which short Hg···O4 contacts of 2.70 Å were observed, but no discrete molecular species were detected [3]. Reaction more commonly occurs by substitution of H3. Displacement of H3 by CH_3Hg^+ in uridine was found to take place even at pH 2–3 [4, 5], in spite of the high pK_a value (9.8) for H3 [1]. The recent interest in 'Platinum blues' as potential antitumor agents stimulated research on thymine platinum complexes. Compounds in which N1-blocked thymine is unidentate through N3 or bridging bidentate through N3 and a carbonyl oxygen have been studied [6, 7].

Substitution of H3 by the less electron-attracting metal ion is expected to release electron density into the ring, thus increasing the basic character of the adjacent carbonyl groups. This assumption is clearly supported by the crystal structure of the 1:1 silver compound with 1-methylthymine [8]. Indeed, one half of the Ag^+ ions is linearly coordinated by two N3 atoms from deprotonated ligands, whereas the other half is tetrahedrally surrounded by carbonyl oxygens. The Ag–O interactions, especially those with O4 at 2.333 Å, are moderately strong, even though no silver–carbonyl interactions had been detected with the neutral form of uridine [8]. The same ligands, when coordinated to platinum, also showed enhanced affinity of their carbonyl groups for cations such as H^+ [9], Ag^+ [10] and Mn^{2+} [11].

The present paper reports on two crystal structures containing the CH_3HgMT molecule*. From the known structure of $Hg(MT)_2$ [12], coordination to N3 of the deprotonated ligand was anticipated. However, we were interested in the extent of partici-

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*Neutral 1-methylthymine is represented by HMT and the N3-deprotonated anion, by MT^-.

pation of the carbonyl groups in either intermolecular associations in the solid or intramolecular Hg···O contacts such as those observed in complexes of cytosine ligands with Hg [13] and other metals [14].

Experimental

Preparation

$CH_3HgMT\cdot½H_2O$

HMT (Vega, 0.14 g, 1 mmol) was dissolved in 30 ml of warm water and 1.0 ml of CH_3HgOH 1.0 *M* (Alfa) was added. Quantitative yields of the compound were obtained as colorless crystals from the cooled mixture after removal of the solvent.

$CH_3HgMT\cdot½NaNO_3$

HMT was dissolved in warm water as above and 1.0 ml of CH_3HgNO_3 1.0 *M* was added, followed by 1.0 ml of NaOH 1.0 *M*. Crystals of the compound were obtained when the mixture was very slowly evaporated to near dryness. It has not been possible so far to obtain a product absolutely free of excess $NaNO_3$. Attempts to prepare the compound by mixing $CH_3HgMT\cdot½H_2O$ and $NaNO_3$ in stoichiometric amounts yielded mostly the unaltered starting materials.

Crystal Data

$CH_3HgMT\cdot½H_2O$

Formula: $C_7H_{10}HgN_2O_2\cdot½H_2O$ fw = 363.8. Tetragonal, space group $P4_122$ (or $P4_322$), $a = b = 8.118(1)$ Å, $c = 30.084(5)$ Å, $V = 1982.6$ Å^3, $D_o = 2.37(2)$ g cm^{-3} (flotation in bromobenzene-bromoform), $D_c = 2.429$ g cm^{-3}, $Z = 8$. $\mu(MoK\alpha) = 154.3$ cm^{-1}, $\lambda(MoK\bar{\alpha}) = 0.71069$ Å (graphite monochromator), T = 20 °C.

$CH_3HgMT\cdot½NaNO_3$

Formula. $C_7H_{10}HgN_2O_2\cdot½NaNO_3$ fw = 397.3. Orthorhombic, space group Pnma, $a = 11.088(3)$ Å, $b = 6.785(2)$ Å, $c = 27.31(2)$ Å, $V = 2054.6$ Å^3, $D_o = 2.51(2)$ g cm^{-3} (flotation in bromoform–bromobenzene), $D_c = 2.567$ g cm^{-3}, $Z = 8$. $\mu(CuK\alpha) = 290.4$ cm^{-3}, $\lambda(CuK\bar{\alpha}) = 1.54178$ Å (graphite monochromator) T = 20 °C.

Crystallographic measurements and resolution of the structure

The space groups and approximate cell dimensions were deduced from precession and cone-axis photographs. The accurate cell parameters given above were determined by least-squares refinement on the setting angles for 25 random reflections centered in the counter of an Enraf-Nonius CAD4 diffractometer.

The intensity data were collected by using the $\omega/2\theta$ scan technique. A fixed slit of 4.0 mm was used and the scan range ($\omega = 1.00 + 0.15 \tan\theta$ for $CuK\bar{\alpha}$, $= 0.80 + 0.35 \tan\theta$ for $MoK\bar{\alpha}$) was extended 25% on each side for backgrounds. Fast prescans were run at 6–10° min^{-1} and all weak reflections ($I < \sigma(I)$) were not remeasured at slower speed. The accepted reflections were measured at scan speeds S between 10.0 and 0.4° min^{-1}, selected to make the $I/\sigma(I)$ ratio equal to 100, but a maximum scan time was imposed (90 s for $CuK\bar{\alpha}$, 180 s for $MoK\bar{\alpha}$). Three standard reflections were measured every hour as a check on crystal and instrument stability. They showed random fluctuations within ±2.5%. Crystal orientation was also checked every 100 measurement by centering three reflections. No crystal recentering was made during data collection.

Net intensity I was obtained from $I = (P - 2B)S$, where P is the scan count and B is the total background, counted during one half of the scanning time. Variance was calculated from $\sigma(I)^2 = (P + 4B)S^2 + (0.04\,I)^2$.

$CH_3HgMT\cdot½H_2O$

The crystals of $CH_3HgMT\cdot½H_2O$ were of a rather poor quality. A total of 2259 hkl reflections in the sphere bounded by $2\theta \leqslant 50°$ was measured using the $MoK\bar{\alpha}$ radiation. After averaging the hkl and khl reflections, a set of 1107 independent reflections was obtained, of which 504 were retained for structure determination on the basis of the criterion $I \geqslant 2.5\,\sigma(I)$. They were corrected for the Lorentz and polarization effects, and also for absorption (Gaussian integration, grid 10 × 10 × 10, crystal dimensions 0.06 × 0.24 × 0.20 mm^3, transmission coefficient 0.08–0.35).

The structure was solved by the heavy-atom method and refined by full-matrix least squares. The Hg atom was located from a three-dimensional Patterson map and the light atoms were found in subsequent difference Fourier (ΔF) maps. The usual difficulties inherent to the presence of a pseudo 2-fold axis through N3 and C6 in the ligand were encountered and they were solved as previously [8]. Of the two possible models in which N1A and C2A would be interchanged with C5A and C6A, respectively, the model retained is the one leading to a C4A–C5A bond length (1.41(5) Å) greater than N1A–C2A (1.31(6) Å). Indeed, the same bonds also differ in free HMT (1.379(4) Å for N1–C2 and 1.432(4) Å for C4–C5 [16]) and their order is not expected to be reversed on complexation. In addition, the retained model refined marginally better (*R* is 0.001 lower) than the other.

The nonhydrogen atoms were refined isotropically, except for mercury, which was anisotropically refined. Individual weights based on counting statistics were also applied. The H atom on C6A was fixed at the calculated position with an isotropic B of 5.0 Å^2. The hydrogens on the water molecule and methyl groups were not located. The final R value ($\Sigma \| Fo | - | Fc \| / \Sigma | Fo |$) was 0.058 and $R_w = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w |Fo|^2]^{1/2}$ was 0.060. The goodness-of-fit ratio was 1.89.

The final ΔF map contained a residual peak of 1.3–1.6 e/Å^3 at 1.3 Å from Hg and the general background was $<\pm 1.0$ e/Å^3. Attempts to refine in the enantiomorph space group $P4_322$ led to the same R factor and the parameters refined in $P4_122$ are reported.

$CH_3HgMT \cdot ½NaNO_3$

A set of 2458 hkl reflections were collected ($2\theta \leqslant 140°$) using CuK$\bar{\alpha}$ radiation. Of them, 1638 were retained on the basis of the criterion $I \geqslant 2.5\sigma(I)$. These data were corrected for absorption (crystal dimensions 0.03 × 0.04 × 0.54 mm^3, transmission coefficient 0.09–0.48).

From the Patterson map, the Hg atoms were found to be distributed on two 4c special positions of space group Pnma, whereas the Na atom was found on position 4a. From subsequent ΔF maps, all the nonhydrogen atoms, but O12, were found to occupy 4c positions on the mirror planes. Distinction between the two halves of the ligands was made as above, by comparing the C4–C5 and N1–C2 bond lengths. The retained model also refined slightly better (R is 0.001 smaller) and led to more reasonable temperature factors for C5 and N1 than the alternate model in which the two sides would be exchanged.

All nonhydrogen atoms were anisotropically refined. The hydrogens on C6 were fixed at their calculated positions (B = 6.0 Å^2). Most of the methyl hydrogens were visible in the ΔF map. They were fixed at their ideal positions, assuming that they conformed to the mirror symmetry of the space group, with B = 8.0 Å^2. The final agreement factors were $R = 0.027$ and $R_w = 0.035$. The goodness-of-fit ratio was 1.28. The final ΔF map showed a residual of 0.96 e/Å^3 close to Hg, a few peak of 0.5–0.7 e/Å^3 near the methyl carbons, and a general background $<\pm 0.5$ e/Å^3.

The refined coordinates for both structures are listed in Table I. The programs used in this study have been listed elsewhere [13]. The forms factors were those of Cromer and Waber [17], except for hydrogen [18]. The f′ and f″ contributions to anomalous dispersion were taken into account for Hg and Na [19].

The refined temperature factors, as well as tables of observed and calculated structure factors, are included in the supplementary material available upon request.

TABLE I Refined Fractional Coordinates

$CH_3HgMT \cdot ½H_2O$ (10^3, Hg × 10^4)

Atom	X	Y	Z
HG3A	1287(2)	1530(2)	–511(1)
O1A	500	46(9)	0
O2A	263(4)	–111(4)	–114(1)
O4A	–189(4)	–32(4)	–29(1)
N1A	71(4)	–312(4)	–111(1)
N3A	29(5)	–67(4)	–71(1)
C1A	174(6)	–422(6)	–142(1)
C2A	125(6)	–165(6)	–101(1)
C3A	233(6)	360(7)	–31(1)
C4A	–115(4)	–126(4)	–56(1)
C5A	–178(5)	–280(5)	–69(1)
C6A	–81(6)	–377(6)	–98(1)
C7A	–341(5)	–338(6)	–57(1)
H6A	–117	–482	–108
$CH_3HgMT \cdot ½NaNO_3$ (10^4, Hg, Na × 10^5)			
HG3B	3544(3)	25000	14694(1)
HG3C	–20546(3)	25000	–11815(1)
NA	0	0	0
O11	3391(6)	2500	533(3)
O12	1726(5)	4082(9)	483(2)
O2B	–1128(6)	2500	447(2)
O4B	–1789(8)	2500	2090(3)
O2C	–779(8)	2500	–2148(3)
O4C	361(6)	2500	–563(2)
N	2294(8)	2500	499(3)
N1B	–3073(7)	2500	714(3)
N3B	–1471(6)	2500	1275(3)
N1C	1232(8)	2500	–1982(3)
N3C	–211(7)	2500	–1357(3)
C1B	–3521(9)	2500	218(4)
C2B	–1837(8)	2500	792(3)
C3B	2112(9)	2500	1712(4)
C4B	–2238(9)	2500	1678(4)
C5B	–3519(8)	2500	1575(3)
C6B	–3847(8)	2500	1112(4)
C7B	–4372(11)	2500	2003(4)
C1C	1506(13)	2500	–2522(5)
C2C	43(9)	2500	–1852(3)
C3C	–3907(9)	2500	–1081(5)
C4C	654(8)	2500	–1007(3)
C5C	1906(8)	2500	–1150(3)
C6C	2103(8)	2500	–1644(4)
C7C	2855(9)	2500	–769(5)

Description of the Structures and Discussion

The CH_3Hg group is bound to the deprotonated N3 site of 1-methylthymine (HMT) in the three independent CH_3HgMT molecules (one in $CH_3HgMT \cdot ½H_2O$ and two in $CH_3HgMT \cdot ½NaNO_3$). The interatomic distances and bond angles are collected in Fig. 1.

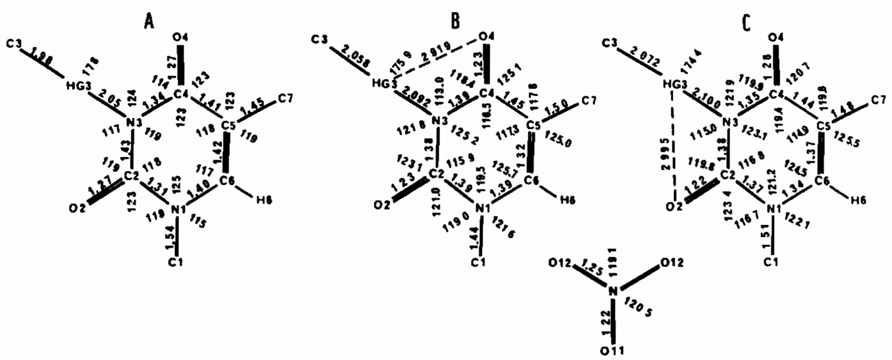


Fig. 1 Interatomic distances and bond angles in the three nonequivalent CH_3HgMT molecules. Molecule A belongs to CH_3-$HgMT \cdot ½H_2O$. Molecules B and C are crystallographically independent molecules in $CH_3HgMT \cdot ½NaNO_3$ The esd's for A are 0.05–0 06 Å and 3–4°, except for Hg3A–N3A, 0.03 Å and C3A–Hg3A–N3A, 2°. For B and C, they are 0.01 Å and 0.6–0.8°, except for Hg–N(O), 0.008 Å, Hg–C, 0 010 Å, C–Hg–N, 0 3°, and the Hg–N–C angles, 0.5°.

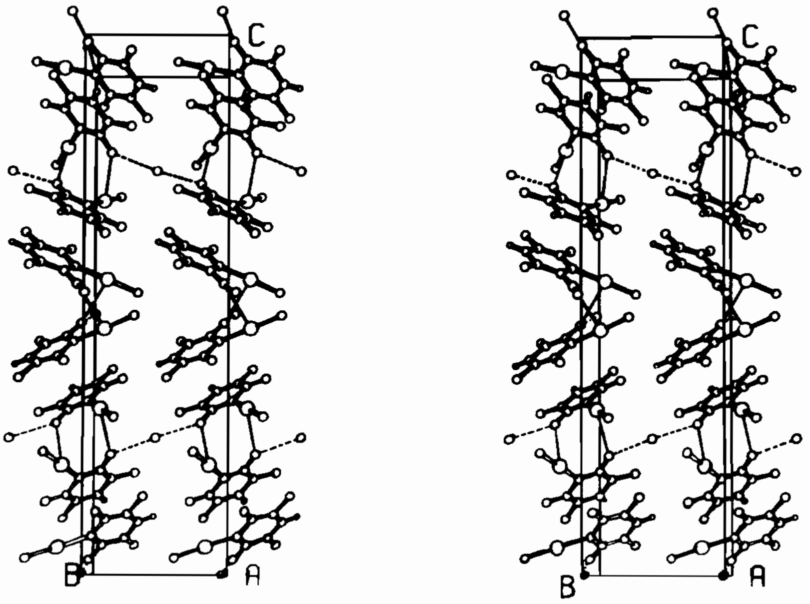


Fig 2 Stereo view of the unit cell of $CH_3HgMT \cdot ½H_2O$ Mercury and hydrogen are shown as large and small spheres, respectively. The remaining atoms can be identified by reference to Fig 1 The Hg···O(2) secondary bonds are shown as thin lines, whereas the hydrogen bonds involving water are dashed

Mercury exhibits the usual roughly linear coordination, the departure from linearity being significant, but not unusual, in the $NaNO_3$ compound. The Hg–N3 distances (av. 2.08 Å) compare well with those observed in $Hg(MT)_2$ (2.04(2) Å) [12] and in similar compounds [13, 15, 20]. The Hg–CH_3 distances (av. 2.03 Å) are normal as well [13, 15, 20]. Coordination exactly along the lone pair of N3 would produce equal Hg–N3–C angles with the adjacent N–C bonds. These angles differ by 7–9° in our molecules, although the difference is barely significant in $CH_3HgMT \cdot ½H_2O$. This displacement carries the CH_3Hg group within a distance from a carbonyl oxygen that might correspond to some Hg···O interaction (Hg3B–O4B, 2.919(8) Å, Hg3C–O2C, 2.995(8) Å). Interestingly, the external angles involving the above carbonyl oxygens are significantly different, with the smaller angle on the same side as the CH_3Hg group, as though the carbonyl oxygens were attracted by mercury. It is premature, however, to conclude that this does result from Hg···O bonding effect, since packing forces may well produce distortions of this magnitude. At any rate, intramolecular Hg···O contacts in thymine are much longer than in cytosine ligands, where distances as short as 2.84 Å were found with the adjacent carbonyl group [13].

TABLE II. Intermolecular Interactions.

Distances (A)		Angles (deg)	
$CH_3HgMT\cdot\frac{1}{2}H_2O$			
Hg···O contacts			
Hg3A–O4A[a]	2 88(3)	N3A–Hg3A–O4A[a]	82(1)
H-bonds		C3A–Hg3A–O4A[a]	97(2)
O1A–O4A[a,b]	2 75(3)	O1A–O4A[b]–C4A[b]	141(3)
		O4A[a]–O1A–O4A[b]	153(2)
$CH_3HgMT\cdot\frac{1}{2}NaNO_3$			
Hg···O contacts			
Hg3C–O12[c,d]	3.025(5)	C3C–Hg3C–O12[c,d]	92.1(3)
		N3C–Hg3C–O12[c,d]	91.5(2)
		O12[c]–Hg3C–O12[d]	100.1(1)

[a] −x, y, −z, [b] 1 + x, y, z, [c] −x, −½ + y, −z, [d] −x, 1 − y, −z

Due to the presence of mercury, the light atoms are positioned with limited accuracy, especially in the case of $CH_3HgMT\cdot\frac{1}{2}H_2O$. The large esd's preclude any detailed discussion on bond length differences between the molecules of Fig. 1, as well as comparisons with the free ligand or complexes with other metals. Similarly, most of the differences in bond angles are not significant, except for angles around the carbonyl groups, as discussed above. The six-membered ring including C1A, O2A and O4A is planar within 2.3 σ(0.07 Å) in the hemihydrate. The CH_3Hg and C-bonded methyl groups deviate appreciably from the plane. C7A, 0.14(4) Å; Hg3A, –0.103(2) Å, C3A, –0.28(5) Å). In the mixed compound with $NaNO_3$, both molecules including their substituents have to be perfectly planar, being coincident with crystallographic mirror planes.

The NO_3^- ions show the usual trigonal geometry, with normal N–O distances of 1.22–1.25 Å and angles close to 120° (Fig. 1) [21]. The ion is planar within 0.3σ (0.002 Å).

A packing diagram of $CH_3HgMT\cdot\frac{1}{2}H_2O$ is shown in Fig. 2. The crystal consists of infinite columns of CH_3HgMT molecules extending along the 4_1 axis coincident with the c edge of the cell. Successive molecules are joined into dimeric units by a pair of symmetry-equivalent Hg···O secondary bonds of 2.88(3) Å involving carbonyl oxygen O4A (Table II). The molecules are so oriented as to allow the interaction to take place along a direction expected to provide appreciable charge density around O4A (*i.e.* C4A–O4A–Hg3A = 140(2)°) [22]. Stacking interaction between the flat rings provide van der Waals contacts between the dimeric units.

The columns are cross-linked by water molecules forming strong H-bonds (O1A··O4A = 2.75(3) Å). Water molecules at z ~¼ and ~¾ join adjacent columns in the bc plane, whereas those at z ~0 and ~½ join the columns in the symmetry equivalent ac plane of the tetragonal cell.

It is noteworthy that O4A is the only carbonyl oxygen involved in H-bonding and Hg···O secondary bonds. The shortest intermolecular contact of O2A occurs with a Hg atom at 3.33 Å, which is much beyond the 3.0 Å limit usually accepted for such interations. O2A directly faces the H6A atom on a molecule in the adjacent chain, with possible C–H···O interaction: H6A···O2A = 2.24 Å, C6A–H6A–O2A = 161°, C2A–O2A–H6A, 158°.

A view of the unit cell of $CH_3HgMT\cdot\frac{1}{2}NaNO_3$ down the b axis is given in Fig. 3. This time, the CH_3HgMT molecules are stacked in a rigorously parallel arrangement because they lie in crystallographic mirror planes. No intermolecular Hg···O contacts shorter than 3.0 Å are found with either carbonyl or nitrate oxygens (Table II). Obviously, molecular packing is controlled to a large extent by the Na^+ ions aligned along the b edge of the cell and the parallel direction running through the middle of the ac face. A different view, perpendicular to the chain direction, is provided in Fig. 4. Each Na^+ ion is surrounded by an approximate octahedron consisting of three pairs of oxygens, that is O12 nitrate atoms, O2B from molecule B and O4C from molecule C. The Na···O12 distance to the nitrate oxygen (2.406(5) Å) (Fig. 5) is of the same magnitude as the short contacts in $NaNO_3$ itself [21]. The Na–O (carbonyl) distances are in the range observed with similar oxygen groups [23], the Na–O4C distance (2.324(4) Å) being much shorter than Na–O2B (2.436(4) Å). Chain propagation is achieved by the sharing of opposite equatorial edges, which contain only carbonyl oxygens, while the axial sites of successive octahedra are bridged, alternatively above and below the chain, by the bidentate nitrate groups.

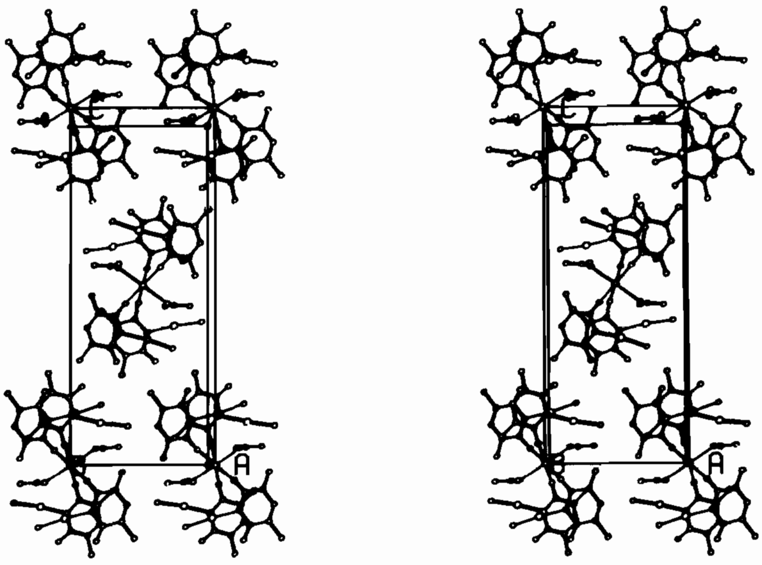


Fig 3 Stereo view of the unit cell of $CH_3HgMT \cdot \frac{1}{2}NaNO_3$ down the b axis. The Na^+ ions can be recognized by their octahedral environment on the center and corners of the drawing.

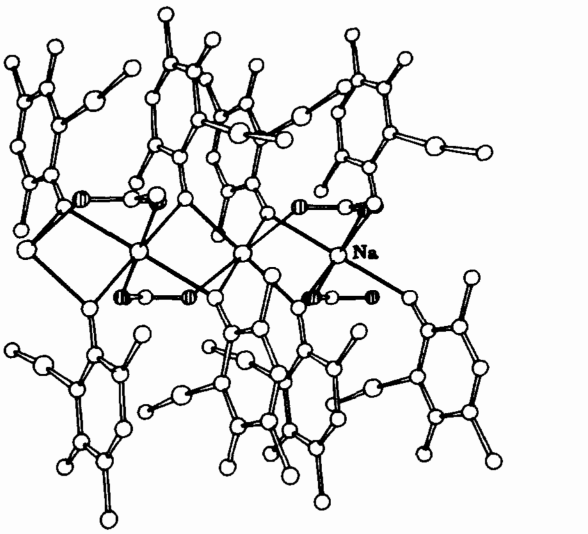


Fig. 4. Chain of octahedrally coordinated Na^+ ions along the b axis. The carbonyl groups occupy equatorial positions and are involved in the sharing of edges producing chain propagation Pairs of axial sites are bridged by bidentate nitrate ions

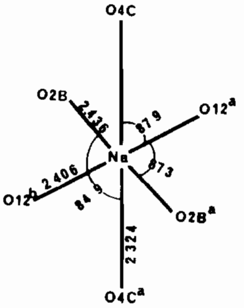
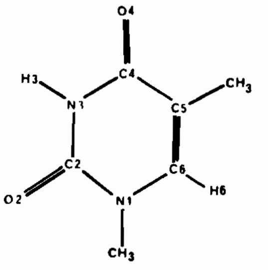


Fig 5 Coordination of the Na^+ cation in the chain. The Na^+ ion sits on a crystallographic inversion center a = −x, ½ + y, −z, b = x, ½ − y, z

Discussion

The very existence of the mixed $NaNO_3$ compound with CH_3HgMT is one of the most interesting aspects of this work. Indeed, to our knowledge, there is no evidence for appreciable interaction of cations like Na^+ with the carbonyl groups in free N1-substituted thymine or uracil rings. Nevertheless, total exclusion of $NaNO_3$ was required to isolate clean samples of $CH_3HgMT \cdot \frac{1}{2}H_2O$, some mixed $NaNO_3$ compound inevitably precipitating during the attempts to prepare the simple complex by neutralization of CH_3HgNO_3 and HMT mixtures by NaOH.

Greater basicity for the carbonyl groups in the complexes is not unexpected, since the electron distribution should be intermediate between those of HMT (formula I) and MT^- (formula II), respectively. More electron density should build up on the already electron-rich CO groups in the resonance forms for the anion(II). This effect manifests itself in $CH_3HgMT \cdot \frac{1}{2}H_2O$ by O4A forming strong H-bonds with water and an intramolecular secondary bond to mercury. At the same time, the closest neighbor to O2 is the C6–H6 bond of the next chain, with which the extent of interaction is uncertain. On the other hand, in the $NaNO_3$ compound, both carbonyl groups interact more efficiently with their surroundings



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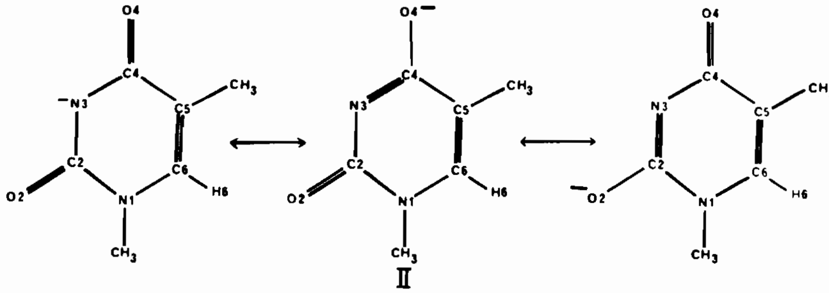

II

In both independent CH$_3$HgMT molecules, one C=O group is coordinated to Na$^+$ and the other is displaced toward Hg with which an intramolecular contact is established. Analogous interactions are, however, more efficient for O4 than for O2. For instance, the Na–O4C distance is 0.11 Å shofter than Na–O2B, while the intramolecular Hg3B–O4B contact is 0.08 Å shorter than Hg3C–O2C. This would be consistent with lesser basicity for O2, but more information should be gathered before it can be concluded that interaction with O4 always predominate. For instance, it is not clear why the Na$^+$ ions are not surrounded only by O4 groups and Hg by O2, or *vice versa,* since this would apparently affect the packing very little. In systems with bulky groups on N1 of a thymine or uracil ring, the relative availability of O2 and O4 could be a sensitive function of both basicity and steric hindrance.

The clustering effect of Na$^+$ ions is striking in the structure of the NaNO$_3$ compound (Fig. 3). In achieving its octahedral coordination of oxygens, the cation brings the complex molecules together in an arrangement completely different form the one observed in the hemihydrate. Although this is not unexpected in the solid state, it emphasizes the fact that hard cations may be involved in interactions, not only with phosphate groups [24], but also directly with the bases of DNA. Both Hg^{2+} and CH$_3$Hg$^+$ ions are known to show a marked preference for the thymine residue of DNA or polynucleotides [24, 25] and the influence of Na$^+$ on DNA denaturation by CH$_3$Hg$^+$ has been examined [26]. The presence of hard cations, such as alkaline or alkaline-earth ions, should not be overlooked in the general picture of the heavy-metal interactions with DNA constituents, since the binding of the soft metal to one site is likely to activate residual sites for which the hard cations already show a preference. Thus, there may result interesting synergistic effects, which could stabilize unusual base pairs or ring orientations in polynucleotides or nucleic acids.

References

1 L. G. Marzilli, *Progr. Inorg Chem., 23,* 255 (1977).
2 D. J. Hodgson, *Progr Inorg Chem , 23,* 211 (1977); L. G. Marzilli, T. Kistenmacher and G. L. Eichhorn, 'Nucleic Acid–Metal Ion Interactions', T. G. Spiro, Editor, Vol. 1, p. 179 (1980).
3 J. A. Carrabine and M. Sundaralingam, *Biochemistry, 10,* 292 (1971).
4 R. B. Simpson, *J. Am. Chem Soc., 86,* 2059 (1964).
5 S. Mansy, T. E. Wood, J. C. Sprowles and R. S. Tobias, *J Am. Chem. Soc , 96,* 1762 (1974).
6 C. J. L. Lock, H. J. Peresie, B. Rosenberg and G. Turner, *J Am Chem Soc., 100,* 3371 (1978)
7 B. Lippert, D. Neugebauer and U. Schubert, *Inorg Chim. Acta, 46,* L11 (1980)
8 F. Guay and A. L. Beauchamp, *J. Am. Chem. Soc , 101,* 6260 (1979).
9 B. Lippert and D. Neugebauer, *Inorg Chim Acta, 46,* 171 (1980).
10 B. Lippert, *Inorg. Chim. Acta, 55,* 5 (1981).
11 B. Lippert and U Schubert, *Inorg. Chim Acta,* (in the press)
12 L D. Kosturko, C. Folzer and R. F. Stewart, *Biochemistry, 13,* 3949 (1974).
13 M Authier-Martin and A L Beauchamp, *Can. J. Chem., 55,* 1213 (1977),
M. Simard and A. L. Beauchamp, (in preparation).
14 C Gagnon, A L. Beauchamp, D. Tranqui, *Can. J. Chem., 57,* 1372 (1979) and references therein.
15 L. Prizant, R Rivest and A. L Beauchamp, *Can J. Chem., 59,* 2290 (1981).
16 K Hoogsteen, *Acta Cryst , 16,* 28 (1963).
17 D. T. Cromer and J. T. Waber, *Acta Cryst., 18,* 104 (1965)
18 R F. Stewart, E R Davidson and W. T. Simpson, *J. Chem Phys., 42,* 3175 (1965).
19 D. T. Cromer, *Acta Cryst., 18,* 17 (1965).
20 J Hubert and A. L. Beauchamp, *Can J. Chem , 58,* 1439 (1980),
Acta Cryst , B36, 2613 (1980),
L. Prizant, M. J Olivier, R. Rivest and A. L Beauchamp, *J. Am Chem. Soc, 101,* 2765 (1979),
M. J. Olivier and A L. Beauchamp, *Inorg Chem , 9,* 1064 (1980).
21 K. O. Stromme, *Acta Chem Scand , 23,* 1616 (1969).
22 R. Bonaccorsi, A. Pullman, E. Scrocco and J. Tomasi, *Theor Chem Acta, 24,* 51 (1972).
23 J. R. Knox and C. K Prout, *Acta Cryst , B25,* 1857 (1969);
J. Albertsson, *Acta Chem Scand , 26,* 985 (1972),
J. J. Stezowski, R. Countryman and J. L. Hoard, *Inorg. Chem , 12,* 1749 (1973),
P. de Messter. D J Hodgson, H. C Freeman and C. J Moore, *Inorg Chem , 16,* 1494 (1977)
24 G. L. Eichhorn, 'Inorganic Biochemistry', Elsevier, Amsterdam, Vol. 2, Chap 34 (1973).
25 T. A. Beerman and J. Lebowitz, *J Mol Biol , 79,* 451 (1973);
A Walter and G. Luck, *Stud Biophys , 68,* 1 (1978)
26 M. S Clegg and D. W. Gruenwedel, *Z Naturforsch , 34C,* 259 (1979).