

Structure of μ_3 -(Adeninato- N^3, N^7, N^9)-tris[methylmercury(II)] Nitrate

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Abstract

$C_8H_{13}Hg_3N_7O_6$, $M_r = 905.01$, monoclinic, space group $C2/c$, $a = 20.939$ (7), $b = 23.976$ (3), $c = 7.073$ (6) Å, $\beta = 94.29$ (4)°, $Z = 8$, $d_c = 3.394$ Mg m⁻³. The structure was refined on 1603 independent nonzero reflections to an R factor of 0.045. Ring sites N(3), N(7) and N(9) of a deprotonated adenine ligand are occupied by linearly coordinated methylmercury groups as observed in the corresponding perchlorate salt. Layers parallel to the ac plane contain parallel [adeninato(CH₃Hg)₃]²⁺ cations bridged by nitrate ions interacting with the metal atoms. The remaining nitrate ions form strong hydrogen bonds with amino groups in the interlayer region.

Introduction

We have previously reported that CH₃Hg⁺ ions bind to N(3), N(7) and N(9) of deprotonated adenine in [adeninato(CH₃Hg)₃](ClO₄)₂ (Hubert & Beauchamp, 1980). Although CH₃Hg binding at N(7) and N(9) was anticipated from crystallographic work on a 2:1 complex (Prizant, Olivier, Rivest & Beauchamp, 1979), the fact that the third CH₃Hg group was bonded to N(3) instead of N(1) was rather surprising, since N(1) had been found to be the first acceptor site with respect to protons (Hodgson, 1977) and some metal ions (Olivier & Beauchamp, 1980; McCall & Taylor, 1975) in N(9)-substituted adenine ligands. Stabilization of that particular pattern of substitution by crystal-packing forces could not be ruled out. This prompted us to examine the structure of a similar complex with a counter ion of different geometry. The nitrate salt was prepared according to a method described elsewhere (Prizant, Rivest & Beauchamp, 1981) and its crystal structure is reported here.

Experimental

Intensity measurements

Crystals suitable for X-ray work were obtained from the initial preparation used for microanalysis (Prizant

et al., 1981). A specimen of dimensions 0.09 × 0.21 × 0.45 mm was used. The data were collected at 295 K, using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The unit-cell parameters were determined from 25 reflections centered on an Enraf–Nonius CAD-4 diffractometer.

Space groups Cc and $C2/c$ were consistent with the monoclinic Laue symmetry and the systematic absences (hkl , $h + k \neq 2n$ and $h0l$, $l \neq 2n$) noted on a set of precession photographs. Intensity data were collected by the $\omega/2\theta$ scan technique. A fixed slit of 2.0 mm was used and the scan range was $\omega = (0.80 + 0.35 \times \tan \theta)^\circ$ extended 25% on each side for background. Preliminary intensities I were obtained from a prescan at 6.7° min⁻¹ and all reflections having $I/\sigma(I) < 1$ were labeled 'weak' and not remeasured. For the final measurement, a scan rate S between 6.7 and 0.60° min⁻¹ was automatically selected to make $I/\sigma(I) = 100$, but a maximum scan time of 120 s was imposed. Three standard reflections were measured every hour as a check on instrument and crystal stability. They showed random fluctuations within $\pm 4\%$ about their respective means. Crystal orientation was checked every 100 reflections by recentering three reflections. The actual position of the scattering vectors and the directions deduced from the orientation matrix always differed by $< 0.1^\circ$ and no crystal reorientation was necessary during data collection.

A set of 2303 independent reflections of the type $h + k = 2n$ in octants hkl and $h\bar{k}l$ ($2\theta \leq 45^\circ$) were collected using the Enraf–Nonius option *FLAT*, a procedure to measure intensity at the ψ angle where absorption is minimum for a plate-like crystal. The net intensity I was obtained from $I = (P - 2B)S$, where P is the total scan count and B is the total background count (measured during one half of the scan time). The standard deviation was calculated from $\sigma^2(I) = (P + 4B)S^2 + (0.02I)^2$. A total of 1603 reflections with $I/\sigma(I) \geq 3$ were retained for structure determination. An absorption correction [$\mu(\text{Mo } K\alpha) = 25.98$ mm⁻¹] was applied using the Gaussian integration method (grid 8 × 8 × 8). The transmission factor ranged from 0.055 to 0.110. The data were finally corrected for Lorentz and polarization effects.

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Structure determination and refinement

The structure was solved by the heavy-atom method and refined by full-matrix least squares in the early stages. The centrosymmetric space group $C2/c$ was clearly indicated by the E statistics. Thus, the asymmetric unit includes three independent Hg atoms, one adenine ligand and two nitrate ions. Two Hg atoms were located from a three-dimensional Patterson synthesis. The third Hg, the adenine ligand and one nitrate group 1 were then positioned from a Fourier map. In the next Fourier map, it was clear that nitrate ions 2 occupied special position 4(e) on a twofold axis, but there were no unassigned peaks of comparable height that might be assigned to the remaining set of four nitrate groups in the cell. At this point, the structure was isotropically refined and a new electron-density map showed that the missing nitrate groups 3 were also located on a twofold axis. However, their nitrogens were the only atoms to be on this position, the O atoms being involved in a twofold disorder. With N(30) on position 4(e) surrounded by six half-oxygens [O(30), O(31), O(32)] distributed on three general positions, isotropic refinement was continued and converged to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.105$ (nonzero reflections only). H atoms on C(2), C(8) and the N(6) amino group were fixed at their calculated coordinates [C(N)—H = 0.95 Å, sp^2 hybridization] with isotropic temperature factors B of 5.5 Å². The H parameters were not refined, but the coordinates were recalculated after each cycle. The H atoms on the methyl groups were not located. In the last cycles of refinement, individual weights $w = 1/\sigma^2(F)$ based on counting statistics were applied to each reflection. Anisotropic refinement (block-diagonal least squares) of all nonhydrogen atoms converged to $R = 0.045$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.059$ (nonzero reflections only). The goodness-of-fit ratio was 2.14. The shift-to-error ratios in the last cycle were all < 0.1 .

Although the disorder of nitrate ion 3 could in principle indicate that the space group might be Cc instead of $C2/c$, the lack of any other disorder or dissymmetric electron density elsewhere in the structure and the distribution of the normalized structure factors were taken as evidence that the crystal belongs to the centrosymmetric space group $C2/c$. The final ΔF map showed a general background lower than $\pm 0.6 \text{ e } \text{Å}^{-3}$, except for some peaks ($< \pm 1.4 \text{ e } \text{Å}^{-3}$) within 1.2 Å from Hg.

The scattering curves were those of Cromer & Waber (1965) except for H (Stewart, Davidson & Simpson, 1965). Anomalous-scattering terms for Hg were taken from Cromer (1965). All calculations were carried out with a CYBER 173 computer. The major programs used were: *NRC-3* (absorption correction) by Ahmed & Singh (1973), *NUCLS* (least-squares refinement) by R. J. Doedens & J. A. Ibers (unpublished),

with a block-diagonal procedure introduced by J. Sygusch, *FORDAP* (Fourier synthesis) by A. Zalkin (unpublished) and *ORTEP* (drawings) by Johnson (1965).

The final coordinates of the nonhydrogen atoms are listed in Table 1.*

Description of the structure

The main purpose of this study was to identify the nitrogen donors of adenine occupied by CH_3Hg groups. Mercury is found to bind to the same set of sites, *i.e.* N(9), N(7) and N(3), as in the corresponding perchlorate (Hubert & Beauchamp, 1980), thus confirming that N(3) is used in preference to N(1) to accept the third CH_3Hg group.

Interatomic distances and bond angles are schematically represented in Fig. 1. The Hg—N (ave. 2.11

* A table of observed and calculated structure factors, lists of anisotropic temperature factors, of hydrogen coordinates and angles involving Hg—O contacts, and the equations of the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35488 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Refined fractional coordinates* ($\times 10^3$, Hg $\times 10^5$) *and equivalent isotropic temperature factors* ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq.}}$ (Å ²)
Hg(3)	41256 (5)	15257 (5)	17573 (15)	576
Hg(7)	34914 (5)	39453 (4)	77893 (13)	457
Hg(9)	33478 (5)	15101 (5)	56183 (14)	568
N(1)	433 (1)	332 (1)	134 (2)	441
C(2)	429 (1)	281 (1)	110 (3)	507
N(3)	411 (1)	240 (1)	230 (3)	406
C(3)	415 (2)	65 (1)	150 (5)	935
C(4)	389 (1)	262 (1)	394 (3)	364
C(5)	395 (1)	316 (1)	439 (3)	334
C(6)	417 (1)	355 (1)	304 (3)	447
N(6)	423 (1)	410 (1)	329 (2)	445
N(7)	367 (1)	326 (1)	609 (3)	430
C(7)	320 (1)	462 (1)	933 (4)	553
C(8)	349 (1)	274 (1)	651 (3)	474
N(9)	360 (1)	235 (1)	531 (3)	491
C(9)	309 (2)	67 (1)	583 (5)	1117
N(10)	267 (1)	177 (1)	8 (3)	584
O(10)	317 (1)	182 (1)	-84 (3)	675
O(11)	269 (1)	165 (1)	174 (2)	700
O(12)	213 (1)	186 (1)	-82 (3)	1029
N(20)	0	44 (1)	250	426
O(20)	44 (1)	19 (1)	337 (2)	569
O(21)	0	95 (1)	250	636
N(30)	0	338 (2)	250	853
O(30)*	-11 (2)	332 (2)	69 (6)	1067
O(31)*	-44 (3)	322 (2)	337 (7)	1141
O(32)*	47 (3)	375 (3)	324 (10)	1727

* Occupancy factor 0.50.

Å) and Hg—C (ave. 2.09 Å) bond lengths do not differ significantly from those reported for similar compounds (Prizant *et al.*, 1979; Olivier & Beauchamp, 1980; Hubert & Beauchamp, 1980; Canty, Chaichit, Gatehouse & Marker, 1978; Wong, Carty & Chieh, 1977). Departure from linearity is significant for Hg(7) with a C(7)—Hg(7)—N(7) angle of 173 (1)°, as a result of packing effects. The Hg(3)···Hg(9) separation, 3.283 (2) Å, is similar to those observed in the corresponding perchlorate (Hubert & Beauchamp, 1980) and the absence of appreciable repulsion is suggested by the nearly equal Hg—N—C angles about both N(9) and N(3).

Within the experimental errors, which are large because light atoms make only a small contribution to the total electron density, the geometry of the adenine moiety corresponds to the typical values reported by Voet & Rich (1970) and to our results on the perchlorate salt (Hubert & Beauchamp, 1980). Individual weighted least-squares planes have been calculated through the five-membered and the six-membered rings respectively.* The maximum atom-to-plane displacement for a ring atom is 0.05 (2) Å for C(4), and the 7° bend along the common C(4)—C(5) bond is somewhat larger than commonly found. The amino group N(6) is essentially within the plane of the six-membered ring [distance = -0.05 (2) Å], but the CH₃Hg groups are tilted out of the molecular plane, with the following distances: Hg(3), -0.167 (1), C(3), -0.38 (4) Å; Hg(7), 0.092 (1), C(7), 0.42 (3) Å; Hg(9), 0.011 (1), C(9), 0.06 (4) Å. Hg(7) is obviously

* See previous footnote.

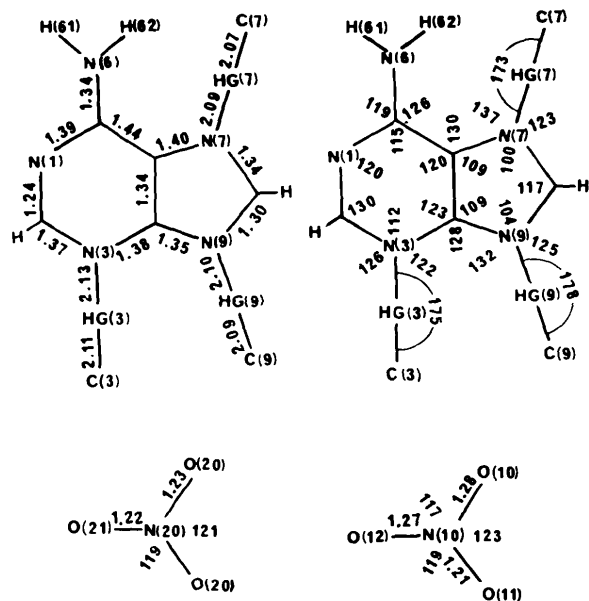


Fig. 1. Interatomic distances (Å) and bond angles (°). Standard deviations are 0.02–0.04 Å on distances and 2° on angles (except N—Hg—C, 1°).

the most strained group, due to packing, as seen by the larger difference between the two Hg(7)—N(7)—C angles (14°) and the C(7)—Hg(7)—N(7) of 173 (1)°.

Nitrate ions 1 and 2 show the expected trigonal planar structure (Fig. 1). Nitrate 3 (Fig. 2) seems to be more distorted, but this could be the result of our positioning of N(30) on equipoint 4(e), if the nitrogens of the two disordered individuals actually occupy two unresolved positions slightly off the twofold axis.

A packing diagram is shown in Fig. 3. The structure can be described as consisting of flat [adeninato(CH₃Hg)₃]²⁺ cations stacked in layers parallel to the *ac* plane. The cations are held together by an intricate network of Hg···O contacts with nitrate oxygens, without direct contacts between aromatic rings. The amino groups at the layer surface form strong hydrogen bonds with type 2 nitrate ions acting as inter-layer bridging groups. Both symmetry-related O(20) atoms in each ion act as acceptors for two hydrogen bonds: O(20)···N(6) ($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$) = 2.95 (3) Å, O(20)···N(6) ($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$) = 2.97 (3) Å and the corresponding O—N(6)—C(6) angles are 134 (2) and 147 (2)°, respectively.

All Hg···O contacts shorter than 3.05 Å have been shown as continuous lines in Fig. 3. This limit has been

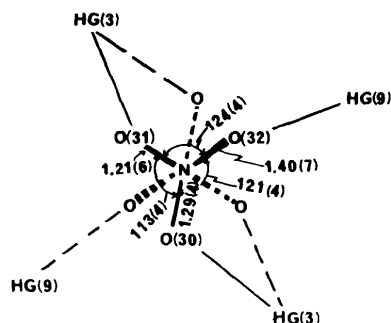


Fig. 2. Projection down the twofold axis showing the two disordered orientations of nitrate ion 3 and the interactions with nearby Hg atoms.

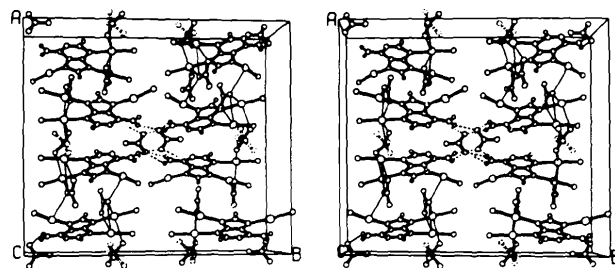


Fig. 3. Molecular packing in the unit cell of [adeninato(CH₃Hg)₃](NO₃)₂. Atoms in the complex cations can be identified by reference to Fig. 1. Nitrate ions 3 can be recognized from the two overlapping disordered components, one of which is shown dashed. Nitrate 2 lies on the twofold axes, whereas nitrate 1 is on a general position. Dashed bonds represent hydrogen bonds and thin lines correspond to Hg···O contacts shorter than 3.05 Å.

Table 2. Intermolecular contacts (Å) involving nitrate 1

O(10)—Hg(3)	2.71 (2)	O(11)—Hg(7) ⁱⁱ	2.90 (2)
O(10)—Hg(9) ⁱ	2.66 (2)	O(11)—Hg(9)	2.99 (2)
O(11)—Hg(3)	3.02 (2)		

Symmetry code

- (i) $x, y, -1 + z$
(ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$

selected assuming the usual value (1.40 Å) for the van der Waals radius of oxygen (Cotton & Wilkinson, 1972) and using one half of the Hg—Hg separation observed here as the van der Waals radius of mercury (1.65 Å). This is intermediate between the two values proposed by Grdenić (1965), that is 1.50 Å, which undoubtedly correspond to an appreciable Hg...O bonding effect, and 1.76 Å, which probably indicates a vanishingly weak interaction. Only nitrate ions 1 and 3 take part in Hg...O contacts. Interatomic distances are given in Table 2 and Fig. 2; a detailed list of angles has been deposited.* All contacts are within $\pm 15^\circ$ from the mercury equatorial plane (perpendicular to the C—Hg—N bonds) and Fig. 3 shows that each mercury is efficiently surrounded by another mercury and/or a nitrate O atom. While the Hg...O interactions in the corresponding perchlorate salt are weak, the shortest Hg...O distance being 2.85 Å (Hubert & Beauchamp, 1980), shorter contacts 2.62–2.71 Å are found in the present nitrate compound, indicating greater basicity of the nitrate ions. Fig. 2 shows how the disordered nitrate ion interacts with neighboring Hg atoms. In either orientation, two relatively short contacts remain.

The present structure reinforces our previous conclusion that once the imidazole ring has been saturated

* See deposition footnote.

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X-ray Structure of Bis(benzyltriphenylphosphonium) Hexachlorodidcadmate

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Abstract

The molecular and crystal structure of the title compound was determined by X-ray diffractometry. The structure was solved by direct and Fourier methods and refined by least-squares techniques to $R =$

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by mercury coordination to N(7) and N(9), the first site attacked by the metal on the pyrimidine ring is N(3) instead of N(1). Since the packing patterns in the nitrate and in the perchlorate salts are totally different, we conclude that the preference for N(3) rather than N(1) cannot result from solid-state effects, but should be ascribed to electronic distribution in the purine ring.

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0.055 for 2655 non-zero independent reflections. Crystals are triclinic, space group $P\bar{1}$ with two $[P(C_6H_5)_3(C_7H_7)]_2[Cl_2Cd_6]$ formula units in a unit cell of dimensions $a = 20.593$ (20), $b = 12.832$ (15), $c = 12.730$ (18) Å, $\alpha = 120.84$ (5), $\beta = 117.84$ (6), $\gamma = 83.97$ (5)°. The structure is built up of well separated ions. The hexachlorodidcadmate anion geometry consists of two distorted tetrahedra joined by a double