

twist (Berry, 1960) in these two stereochemistries. The more trigonal-distorted square-pyramidal stereochemistry of (II) may be related to the smaller bite angle of 77.0° of the bpy ligand (Johnson, Beineke & Jacobson, 1971) relative to that of 89.2° in the dpyam ligand (Stephens, 1972), but it is then difficult to see how the bite angle influences the smaller value of N(1)—Cu—N(3) in (I).

The pyridine rings of the dpyam and bpy ligands are reasonably planar in (I) and (II), respectively; in (I) they are inclined at an angle of 4.29° to each other while in (II) they are twisted about the C(11)—C(12) bond by an angle of 2.15° , both in reasonable agreement with previously observed values (Johnson, Beineke & Jacobson, 1971; Stephens, 1972).

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Crystal and Molecular Structure of (3,3'-Dimethyl-2,2'-bipyridyl)methylmercury(II) Nitrate; a Complex That May Have Weak Intramolecular π -Coordination

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$C_{13}H_{15}HgN_3O_3$ is monoclinic, $a = 10.521(5)$, $b = 9.310(5)$, $c = 16.570(8)$ Å, $\beta = 106.6(1)^\circ$, $Z = 4$, space group $P2_1/c$. The structure was solved by Patterson and Fourier techniques using 1560 counter-measured observed reflections and refined by the full-matrix least-squares method to $R = 0.061$. The complex has a bent C(1)—Hg—N(1) group [$172.7(5)^\circ$] with Hg—C(1) 2.01(1) and Hg—N(1) 2.11(1) Å, weak interaction between Hg and nitrate O atoms, and evidence suggesting the presence of a weak intramolecular π -interaction between Hg and the second pyridyl ring, with Hg—C(2') 3.11(1), Hg—N(1') 3.29(1) Å and an angle of 100.5° between the planes of the pyridyl rings.

Introduction

Methylmercury(II) forms complexes involving irregular three-coordination for Hg with 2,2'-bipyridyl (Canty, Marker & Gatehouse, 1975; Canty & Gatehouse, 1976) and methyl-substituted 2,2'-bipyridyls, except for 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) where steric interaction between 3,3'-dimethyl groups prevents

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coplanarity of the pyridyl rings required by chelation (Canty & Marker, 1976). Coordination of only one N to methylmercury(II) has been shown by ^1H NMR spectroscopy for $[\text{MeHg}(3,3'\text{-dmbpy})]\text{NO}_3$ (Canty & Marker, 1976), but ^{199}Hg NMR studies of MeHg^{11} complexes of pyridine, 2,2'-bipyridyl, and related substituted ligands suggest that there may be weak π -interaction between Hg and the second aromatic ring in this complex and also in the analogous 2-benzylpyridine complex (Canty, Marker, Barron & Healy, 1978). Chemical shifts for the Hg atom in these two complexes are approximately 90 ppm upfield from

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values for complexes with unidentate ligands of similar basicity, *e.g.* pyridine; a similar upfield shift for dimethylmercury in benzene (50.4 ppm upfield from neat Me₂Hg) has been attributed to weak π -interaction with benzene (Sens, Wilson, Ellis & Odom, 1975). A weak π -interaction does occur in some γ -substituted propylmercury complexes, *e.g.* ClHgCH₂C(Me)-(OMe)CH₂(*p*-OMePh) which has Hg...Ph 3.05 Å (Kiefer, Waters & Carlson, 1968), and in order to determine whether weak π -interactions occur in the chemistry of MeHg^{II} we have determined the crystal and molecular structure of [MeHg(3,3'-dmbpy)]NO₃.

Experimental

Crystals of [MeHg(3,3'-dmbpy)]NO₃ for this study were available from the initial preparation used for microanalysis and spectroscopic examination (Canty & Marker, 1976).

Crystal data

C₁₃H₁₅HgN₃O₃, *M_r* = 461.87, monoclinic, *a* = 10.521 (5), *b* = 9.310 (5), *c* = 16.570 (8) Å, β = 106.6 (1)°, *U* = 1555.39 Å³, *D_m* = 1.97 (2) (by flotation in a CCl₄/CH₂I mixture), *D_c* = 1.97 g cm⁻³, *Z* = 4, *F*(000) = 872. Data collected at 20°C, Mo *K* α radiation (λ = 0.7107 Å), μ (Mo *K* α) = 117.9 cm⁻¹. Space group *P*2₁/*c* (No. 14, *C*_{2h}⁵) from systematic absences: *h*0*l*, *l* odd, 0*k*0, *k* odd. Unit-cell parameters were determined using a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator by a method described previously (Gatehouse & Miskin, 1974).

Intensity measurements

Intensity data were collected using the diffractometer above and a colourless to white crystal of dimensions 0.05 × 0.11 × 0.11 mm that had been checked for cracking or twinning using a polarizing microscope. The crystal was mounted on a silica capillary using 'Resiweld' epoxy cement and centred on the goniometer using high-angle reflections selected from an initial rapid data collection. Three standard reflections monitored at 90 min intervals showed no significant systematic variation in intensity.

Data were collected by the ω -scan technique with a symmetric scan width of $\pm 0.5^\circ$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0.02° s⁻¹. No reflection was sufficiently intense to warrant the insertion of an attenuation filter. The data were processed with a program written specifically for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). The background-corrected intensities were assigned standard deviations

according to: $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$ where *CT* is the total integrated peak count obtained in scan time *t_c*; *B₁* and *B₂* are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$; *q* was 0.04 and is an allowance for 'machine errors'. Values of *I* and $\sigma(I)$ were then corrected for Lorentz and polarization effects. An absorption correction was applied based on the indexed crystal faces (100), ($\bar{1}00$), (010), (0 $\bar{1}0$), (10 $\bar{3}$) and (103), and direction cosines calculated for the PW 1100 data. Maximum and minimum transmission factors were 0.6393 and 0.3557 respectively. 4171 reflections were measured to 2θ (Mo *K* α) = 56°; of these, 614 were rejected as being systematically absent or having zero *F* or *I*. A further 141 were multiple observations and the measure of agreement between these, *R*, was 0.03 where *R* is given by $(\sum \{N \sum [w(F_{av} - F)^2]\} / \sum \{(N-1) \times \sum (wF^2)\})^{1/2}$. [The inner summations are over the *N* equivalent reflections averaged to give *F_{av}*, and the outer summations are over all unique reflections (Sheldrick, 1976).] This left 3416 unique reflections of which 1560 obeyed the condition $I \geq 3\sigma(I)$ and were used in the subsequent calculations.

Structure determination and refinement

The structure was solved by Patterson and Fourier techniques; the Hg atom position was refined and all non-hydrogen atoms were located in the subsequent difference Fourier synthesis. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where *w* is the weight $[1/\sigma^2(F_o)]$. All non-hydrogen atoms were refined anisotropically to give *R* = 0.071. Although a difference Fourier synthesis revealed some H atom positions, all coordinates were

Table 1. Final coordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Hg	1526 (1)	684 (1)	2510 (0)
C(1)	1303 (13)	1029 (17)	1280 (8)
C(6)	1355 (13)	-470 (18)	4177 (9)
C(5)	1635 (14)	-622 (19)	5033 (10)
C(4)	2630 (15)	170 (15)	5562 (9)
C(3)	3348 (14)	1143 (15)	5210 (9)
C(2)	2967 (14)	1265 (15)	4331 (9)
C(2')	3689 (14)	2243 (15)	3909 (8)
C(3')	3348 (14)	3667 (17)	3824 (9)
C(4')	4024 (13)	4535 (16)	3405 (9)
C(5')	4977 (13)	3892 (16)	3081 (8)
C(6')	5205 (15)	2496 (16)	3197 (10)
C(7)	4483 (14)	1972 (16)	5777 (9)
C(7')	2303 (12)	4367 (17)	4183 (9)
N(1)	2002 (10)	446 (13)	3828 (7)
N(1')	4555 (12)	1626 (13)	3571 (8)
N(2)	1290 (14)	-2809 (14)	2362 (9)
O(1)	2389 (10)	-2243 (13)	2659 (8)
O(2)	300 (11)	-2062 (13)	2351 (8)
O(3)	1154 (11)	-4006 (12)	2095 (7)

calculated according to the geometry of the C atom to which they are bonded, and with C—H = 1.08 Å. Final refinement with isotropic H atoms riding on their respective C atoms gave $R = 0.061$ and $R^1 = 0.042$, where $R^1 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. * The final difference synthesis had no major characteristic greater than that ($1.6 \text{ e } \text{Å}^{-3}$) in the vicinity of the Hg atom. The largest shift to e.s.d. ratio in the final cycle was 0.023 for the C(3) y parameter.

Final parameters for all atoms are listed in Tables 1 and 2. Atomic scattering factors, corrected for anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970).

All calculations were carried out using the Monash University B 6700 computer; the major programs used were *SHELX 76* (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964), *MEANPL* (Blow, 1960) and *ORTEP* (Johnson, 1965).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33731 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Calculated fractional coordinates ($\times 10^4$) and isotropic thermal parameters for hydrogen atoms, numbered according to the carbon atoms to which they are attached

	x	y	z	B (Å ²)
H(1A)	1721	2063	1200	6.4
H(1B)	261	1018	941	6.4
H(1C)	1807	195	1039	6.4
H(4)	2858	50	6237	5.4
H(5)	1070	-1368	5293	6.1
H(6)	579	-1119	3774	5.7
H(4')	3821	5672	3331	4.8
H(5')	5518	4523	2743	4.9
H(6')	5980	2035	2969	6.2
H(7A)	4913	2661	5400	6.9
H(7B)	5226	1233	6130	6.9
H(7C)	4125	2619	6207	6.9
H(7'A)	1866	3559	4488	6.4
H(7'B)	1540	4852	3677	6.4
H(7'C)	2769	5181	4635	6.4

Discussion of the structure

The structure consists of $[\text{MeHg}(3,3'\text{-dmbpy})]^+$ cations and nitrate anions as shown in Fig. 1 where the numbering scheme follows that used for the 2,2'-bipyridyl complex (Canty & Gatehouse, 1976). Interatomic distances for the anion and cation, together with other distances around the Hg atom, are given in Table 3. A packing diagram is given in Fig. 2. The planes of the two pyridyl rings are at an angle of 100.5° to one another, and at angles of 92.7 and 52.9° to the plane of the nitrate ion. Equations for the three planes are given in Table 4 together with the distances of relevant atoms from them. The torsion angle C(6)—N(1)—Hg—C(1) is $-162(4)^\circ$, and C(2)—N(1)—Hg—C(1) is $20(5)^\circ$, where the sign of the angle follows accepted convention (Klyne & Prelog, 1960). The angles at Hg are: C(1)—Hg—N(1) $172.7(5)$, C(1)—Hg—N(1') $108.3(5)$ and N(1)—Hg—N(1') $64.4(4)^\circ$. The nitrate ion angles are: O(1)—N(2)—O(2) $117(1)$, O(1)—N(2)—O(3) $123(1)$ and O(2)—N(2)—O(3) $120(1)^\circ$.

The nitrate bond lengths and angles suggest a small but real distortion away from the D_{3h} symmetry of an

Table 3. Interatomic distances (Å) with estimated standard deviations in parentheses

(a) Mercury environment		(b) 3,3'-dmbpy	
Hg—C(1)	2.01 (1)	C(2)—N(1)	1.35 (2)
Hg—N(1)	2.11 (1)	C(2)—C(3)	1.40 (2)
Hg—O(2)	2.84 (1)	C(2)—C(2')	1.48 (2)
Hg—O(1)	2.86 (1)	C(3)—C(4)	1.41 (2)
Hg—O(2')	2.90 (1)	C(3)—C(7)	1.50 (2)
Hg—O(3')	3.09 (1)	C(4)—C(5)	1.37 (2)
Hg—C(2')	3.11 (1)	C(5)—C(6)	1.37 (2)
Hg—N(2)	3.27 (1)	C(6)—N(1)	1.32 (2)
Hg—N(1')	3.29 (1)	C(2')—N(1')	1.33 (2)
Hg—N(2')	3.34 (2)	C(2')—C(3')	1.37 (2)
		C(3')—C(4')	1.39 (2)
		C(4')—C(5')	1.40 (2)
		C(5')—C(6')	1.33 (2)
		C(6')—N(1')	1.32 (2)
		C(7')—C(3')	1.54 (2)

(c) Nitrate group

N(2)—O(1)	1.24 (2)
N(2)—O(2)	1.25 (2)
N(2)—O(3)	1.19 (2)

Symmetry code: (i) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

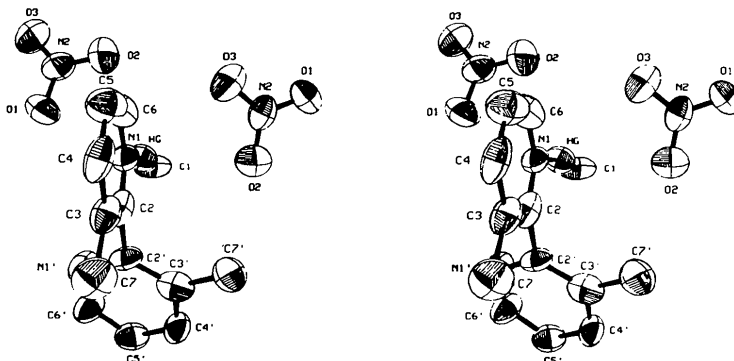
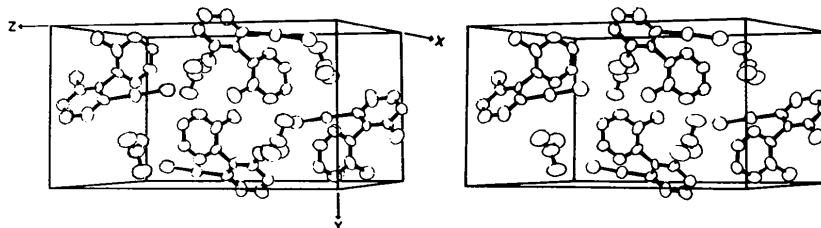


Fig. 1. A stereoscopic view of the structure of $[\text{MeHg}(3,3'\text{-dmbpy})]\text{NO}_3$, showing the relationship between Hg and the nearest nitrate ions.

Fig. 2. A packing diagram for $[\text{MeHg}(3,3'\text{-dmbpy})]\text{NO}_3$.Table 4. Equations of mean planes and deviations (\AA) of individual atoms from planes

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z in the crystal system by the matrix equation:

$$\begin{pmatrix} 10.521200 & 0.000000 & -4.732413 \\ 0.000000 & 9.309700 & 0.000000 \\ 0.000000 & 0.000000 & 15.879626 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Plane I: N(1), C(6), C(5), C(4), C(3), C(2)

$$(0.7000)X + (-0.7136)Y + (-0.0286)Z - (-0.2699) = 0$$

N(1)	0.006 (12)	Hg	-0.006 (1)
C(6)	0.007 (16)	C(7)	0.085 (15)
C(5)	-0.009 (16)	C(2')	0.025 (15)
C(4)	-0.001 (15)	C(1)	0.064 (15)
C(3)	0.014 (15)	C(6')	1.241 (15)
C(2)	-0.017 (15)	C(3')	-1.141 (16)
		N(1')	1.199 (13)

Plane II: C(2'), C(3'), C(4'), C(5'), C(6'), N(1')

$$(-0.4775)X + (-0.1775)Y + (-0.8605)Z - (-6.6580) = 0$$

C(2')	-0.024 (14)	C(7)	-2.508 (14)
C(3')	0.008 (14)	C(3)	-1.156 (14)
C(4')	0.004 (14)	N(1)	1.212 (11)
C(5')	0.001 (14)	Hg	2.915 (1)
C(6')	-0.016 (16)	C(1)	4.373 (13)
N(1')	0.028 (13)	C(4)	-1.035 (14)
C(2)	0.019 (14)	C(6)	1.291 (14)
C(7')	0.009 (14)	C(5)	0.199 (15)

Plane III: N(2), O(1), O(2), O(3)

$$(0.2438)X + (0.3417)Y + (-0.9076)Z - (-4.2392) = 0$$

N(2)	0.001 (14)	C(6)	-2.065 (14)
O(1)	0.000 (13)	N(1)	-1.065 (11)
O(2)	0.000 (13)	Hg	0.941 (1)
O(3)	0.000 (11)	C(1)	2.908 (13)

Plane	Direction cosines		
I	0.7000	-0.7136	-0.0286
II	-0.4775	-0.1775	-0.8605
III	0.2438	0.3417	-0.9076

Angles between normals to planes

I-II	100.5°
I-III	92.7
II-III	52.9

isolated NO_3^- ion. The shortest Hg—O distances involve O(1) and O(2) [$\text{O}(1)\text{—Hg—O}(2) = 43.6(3)^\circ$] and a small closing of the $\text{O}(1)\text{—N}(2)\text{—O}(2)$ angle is observed, together with a small lengthening of $\text{N}(2)\text{—O}(1)$ and $\text{N}(2)\text{—O}(2)$. O(3) is 3.09(1) \AA from Hg. Thus weak interaction is present between the Hg atom and the nitrate O atoms. Fig. 1 shows the relationship

Table 5. Selected structural data for complexes of MeHg^{II} with neutral nitrogen donor ligands

Complex	C—Hg—N ($^\circ$)	Hg—N (\AA)	Hg—C (\AA)	Reference
$[\text{MeHg}(\text{py})]\text{NO}_3$	179.7 (6)	2.12 (2)	2.04 (3)	1
$\text{MeHg}^+\text{—NH}_2\text{CH}(\text{CO}_2^-)\text{—CH}_2\text{CH}_2\text{SMe}$	173 (2)	2.06 (4)	2.11 (5)	2
$[\text{MeHg}(3,3'\text{-dmbpy})]\text{NO}_3$	172.7 (5)	2.11 (1)	2.01 (1)	3
$\text{MeHg}^+\text{—NH}_2\text{CH}(\text{CO}_2^-)\text{—CMe}_2\text{SHgMe}$	170 (1)	2.13 (3)	2.07 (4)	4
$[\text{MeHg}(\text{bpy})]\text{NO}_3$	164 (1)	2.43 (3)	2.07 (5)	5

References: (1) Brownlee, Canty & Mackay (1977). (2) Wong, Carty & Chieh (1977a). (3) This work. (4) Wong, Carty & Chieh (1977b). (5) Canty & Gatehouse (1976).

between Hg and the nearest nitrate ions. Grdeni \acute{c} (1965) considers the van der Waals radius of Hg to be 1.50 \AA , but suggests that if the radius is <1.73 \AA some form of bonding is present. Taking the van der Waals radius for O as 1.40 \AA (Pauling, 1960), the two Hg—O radii sums are 2.90 and 3.13 \AA ; these are *ca* 0.0–0.3 \AA greater than the observed Hg—O distances of 2.84 (1), 2.86 (1) and 2.90 (1) \AA . An additional O is 3.09 (1) \AA from Hg.

A value of 1.75 \AA for the radius of Hg^{II} has been suggested from close contacts between Hg atoms in $[\text{Et}_4\text{N}]_2\text{Hg}_3\text{MCl}_{10}$ ($M = \text{Pd}, \text{Pt}$) (Barr, Goldstein, Hairs, McPartlin & Markwell, 1974), and in the phenylmercury(II) creatinine complex



Hg atoms within the cation are 3.407(2) \AA apart (Canty, Fyfe & Gatehouse, 1978). From physical and crystallographic studies of organomercury(II) quinolin-8-olates it has been suggested that the van der Waals radius of Hg approaches 2.0 \AA (Bertino, Deacon & Müller, 1978).

The distances Hg—C(1) and Hg—N(1) are similar to those in other MeHg^{II} complexes involving neutral N donor ligands (Table 5). The distance from Hg to the midpoint of the C(2')—N(1') bond is 3.13 \AA and is longer than the 3.05 \AA found for the distance of Hg to the midpoint of a C...C bond in the phenyl ring in $\text{ClHgCH}_2\text{CH}(\text{Me})\text{OMeCH}_2(p\text{-OMePh})$ where the presence of a π -interaction has been shown from conformational analysis by ^1H NMR spectroscopy (Kiefer, Waters & Carlson, 1968). If a weak π -interaction is present in the solid state, it is apparently

weaker than the Hg...O interactions as the methyl group bonded to Hg is bent away from the nitrate O atoms towards the second pyridyl ring, whereas if appreciable Hg...pyridyl interaction were present the opposite would be expected.

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Structure Cristalline de l'Acide Ethanediyliidènetétrathiotétraacétique

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Ethanediyliidènetétrathiotétraacétique acid, $C_{10}H_{14}O_8S_4$, crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell of dimensions $a = 7.785$ (3), $b = 10.688$ (4), $c = 5.195$ (2) Å, $\alpha = 92.43$ (4), $\beta = 102.71$ (4), $\gamma = 114.52$ (4)°. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to a final R value of 0.047 for 1815 observed reflexions. Each molecule is hydrogen-bonded to four neighbouring molecules, whose centres lie in $(\bar{1}11)$ planes, by single OH...O bonds to form three types of rings. One of these connects four carboxyl groups together to form a cyclic hydrogen-bonded planar system.

Introduction

Dans le cadre d'une étude générale des structures d'acides polythiopolycarboxyliques, nous avons établi celles des acides méthylènedithiodipropionique et

méthylènedithiodiacétique (Canonne, Boivin, Nowogrocki & Thomas, 1977, 1978). L'acide éthanediyliidènetétrathiotétraacétique (ETTA) est un tétraacide dont les constantes d'acidité sont très proches (Nowogrocki, Canonne & Wozniak, 1976). Il possède