Weak Intramolecular π Coordination to Methylmercury(II). Structure of (2-Benzylpyridine)methylmercury(II) Nitrate

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Abstract

$[Hg(CH_3)(C_{12}H_{11}N)]NO_3, C_{13}H_{14}HgN^+.NO_3^-$, is monoclinic, $a = 14.887$ (4), $b = 11.159$ (3), $c = 8.745$ (3) Å, $\beta = 90.60$ (3)°, $Z = 4$, space group $P2_1/n$. The structure was refined for 1082 counter-measured observed reflections to $R = 0.062$. The complex has a linear C(1)–Hg–N(1) group with Hg–C(1) 2.07 (3) and Hg–N(1) 2.10 (2) Å; there is a weak intramolecular π interaction between Hg and a C≡C bond of the phenyl ring with Hg–C distances of 3.23 (2) and 3.33 (3) Å.

Introduction

Weak interaction between Hg and aromatic rings in organomercury compounds was first demonstrated by conformational analysis using ^1H NMR spectroscopy for 3-arylpropylmercurials and confirmed by a crystal structure of one of these, $[ClHgCH_2C(Me)(OMe)CH_2$ (p-OMePh)], which has the Hg atom 3.05 Å above one of the phenyl bonds (Kiefer, Waters & Carlson, 1968). The ^1H resonances of MeHg^{II} in $[MeHg\overset{+}{N}H_2CH(CO_2^-)$ $CH_2Ph]$ (Rabenstein, Ozubko, Libich, Evans, Fairhurst & Suvanprakorn, 1974), $[MeHg\overset{+}{N}H_2CH(CO_2^-)$ $CH_2(p$-OHPh)] (Brown, Howarth & Moore, 1976), $[MeHg\overset{+}{N}H_2CH(CO_2^-)CH_2R]$ and $[MeHg\overset{+}{N}H_2CH_2$-$CH_2R]$ [R = indole substituted at C(3); Svejda, Maki & Anderson, 1978] are shifted upfield about 0.5–0.75 p.p.m. from that of $[MeHg\overset{+}{N}H_2CH_2CO_2^-]$ suggesting that the methyl group is shielded by the presence of a nearby aromatic ring. This shielding could result either from an interaction between the ring and the methyl group, or from the presence of a weak π interaction between the ring and Hg constraining the ring to lie close to the methyl group. A similar effect occurs in $[MeHgSCH_2Ph]$ which has the MeHg^{II} ^1H resonance 0.4 p.p.m. upfield from that of $[MeHgSMe]$

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(Bach & Weibel, 1976), and in $[MeHg(2$-Bzlpy)]NO$_3$ (2-Bzlpy = 2-benzylpyridine) and $[MeHg(3,3'$-dmbpy)]NO$_3$ (3,3'-dmbpy = 3,3'-dimethyl-2,2'-bipyridyl) which have the ^1H resonance 0.2–0.4 p.p.m. upfield from other pyridine and 2,2'-bipyridyl complexes (Canty & Marker, 1976). The 3-substituted propylmercurials also show this effect, *e.g.* $[ClHgCH_2C(Me)(OMe)CH_2(p$-OMePh)] has the HgCH$_2$ proton resonance upfield of that for $[ClHgCH_2C(Me)(OMe)CMe_3]$ (Kiefer, Waters & Carlson, 1968).

Crystallographic studies indicate that a phenyl ring in $[PhCH_2HgSCPh_3]$ (Bach, Weibel, Schmonsees & Glick, 1974) and $[MeHg\overset{+}{N}H_2CH(CO_2^-)(p$-OHPh)] (Alcock, Lampe & Moore, 1978), and the uncoordinated pyridyl ring in $[MeHg(3,3'$-dmbpy)]NO$_3$ (Canty, Chaichit, Gatehouse & Marker, 1978) are in an orientation consistent with the presence of a weak π interaction between Hg and a C≡C bond of a phenyl ring or the C(2')≡N(1') bond of the pyridyl ring. Thus, the three *solid-state* structures to date suggest that the observed upfield shift in ^1H NMR spectra of MeHg^{II} complexes also results from a weak π interaction in *solution*, and to further test this we have determined the structure of $[MeHg(2$-Bzlpy)]NO$_3$.

Experimental

Crystals of $[MeHg(2$-Bzlpy)]NO$_3$ were available from the initial preparation used for microanalysis and spectroscopic examination (Canty & Marker, 1976).

Crystal data

equipped with a graphite monochromator (Gatehouse & Miskin, 1974).

Intensity measurements

Intensities were collected on the diffractometer from a light-brown crystal $0.05 \times 0.10 \times 0.13$ mm (optimum size 0.18 mm) that had been checked for cracking or twinning with a polarizing microscope. The crystal was mounted on a silica capillary with Resiweld epoxy cement and centred on the goniometer with high-angle reflections selected from an initial rapid data collection. Three standard reflections monitored at 90 min intervals showed no significant variation in intensity.

Data were collected by the ω-scan technique with a symmetric scan width of $\pm 0.6°$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0.05°$ s^{-1}. The Mo $K\alpha$ radiation was monochromatized with a flat graphite crystal and no reflection was sufficiently intense to warrant the insertion of an attenuation filter. The data were processed with a program written for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). The background-corrected intensities were assigned e.s.d.'s $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$ where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 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 $(10,0,0)$, $(\bar{1}0,0,0)$, (055), $(0\bar{5}\bar{5})$, $(0\bar{5}5)$, and (055), and direction cosines calculated for the PW 1100 data. Maximum and minimum values of the transmission factors were 0.6296 and 0.4680, respectively. The total number of reflections measured to 2θ(Mo $K\alpha$) $= 60°$ was 4687; of these, 216 were rejected as being systematically absent and 248 were multiple observations [the measure of agreement between these, R, was 0.048 where $R = (\sum\{N\sum[w(F_{av} - F)^2]\}/\sum[(N - 1)\sum(wF^2)])^{1/2}$; the inner summations are over the N equivalent reflections averaged to give F_{av}, the outer summations are over all unique reflections (Sheldrick, 1976)]. This left 4223 unique reflections of which 1103 obeyed the condition $I \geq 3\sigma(I)$; 21 of these were considered suspect and were omitted during the refinement, leaving 1082 reflections in the final refinement.

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 synthesis. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| -$

Table 1. *Final fractional coordinates* $(\times 10^4)$ *and thermal parameters* $(\times 10^4)$ *for non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z	U (Å^2)
Hg	2691 (1)	4610 (1)	3014 (1)	*
C(1)	3790 (19)	5194 (27)	1786 (36)	812 (100)
C(2)	1591 (16)	3772 (20)	5826 (27)	367 (64)
C(3)	851 (17)	3320 (22)	6531 (32)	558 (79)
C(4)	18 (18)	3193 (22)	5774 (32)	524 (75)
C(5)	−14 (18)	3424 (22)	4219 (33)	580 (81)
C(6)	764 (17)	3835 (23)	3549 (31)	535 (78)
C(7)	2453 (17)	3954 (24)	6624 (30)	548 (79)
C(8)	3219 (15)	3174 (21)	6100 (26)	368 (64)
C(9)	4056 (18)	3636 (26)	5786 (30)	598 (81)
C(10)	4703 (17)	2883 (24)	5231 (29)	524 (75)
C(11)	4583 (19)	1650 (26)	5054 (32)	692 (88)
C(12)	3724 (17)	1180 (25)	5349 (28)	551 (76)
C(13)	3053 (18)	1900 (25)	5919 (30)	597 (82)
N(1)	1569 (14)	4026 (18)	4251 (24)	537 (62)
N(2)	2352 (16)	2406 (22)	532 (29)	672 (72)
O(1)	2809 (13)	2209 (17)	1657 (24)	802 (64)
O(2)	1848 (11)	3382 (15)	482 (19)	533 (49)
O(3)	2052 (16)	1699 (23)	−461 (30)	1197 (87)

* Mercury refined anisotropically: $U_{11} = 534$ (7), $U_{22} = 442$ (6), $U_{33} = 467$ (6), $U_{12} = -35$ (9), $U_{13} = 51$ (5), $U_{23} = -11$ (9). Thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

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

	x	y	z	U (Å^2)
H(1A)	4038	5959	2416	13 (6)
H(1B)	4307	4516	1738	13 (6)
H(1C)	3607	5465	639	13 (6)
H(3)	907	3049	7714	9 (3)
H(4)	−576	2926	6385	9 (3)
H(5)	−622	3288	3557	9 (3)
H(6)	728	4023	2339	9 (3)
H(7A)	2649	4877	6468	11 (7)
H(7B)	2352	3782	7825	11 (7)
H(9)	4199	4573	5975	9 (3)
H(10)	5341	3266	4912	9 (3)
H(11)	5129	1078	4705	9 (3)
H(12)	3589	245	5126	9 (3)
H(13)	2413	1521	6226	9 (3)

$|F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Several cycles, with the Hg atom refined anisotropically and other non-hydrogen atoms isotropically, resulted in $R = 0.085$, where $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. Absorption corrections were applied and refinement led to $R = 0.072$. Although a difference synthesis revealed some H atom positions the coordinates of all H atoms bonded to C were calculated geometrically with C—H $= 1.08$ Å. Finally, full-matrix least-squares refinement was carried out with anisotropic thermal parameters for Hg and

Table 3. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

(a) Mercury environment

Hg–C(1)	2·07 (3)	Hg–C(8)	3·23 (2)
Hg–N(1)	2·10 (2)	Hg–C(9)	3·33 (3)
Hg–O(1)	2·94 (2)	Hg–C(10)	4·04 (3)
Hg–O(2)	2·88 (2)	Hg–C(11)	4·68 (3)
Hg–O(1^i)	3·01 (2)	Hg–C(12)	4·59 (3)
Hg–O(3^i)	3·18 (3)	Hg–C(13)	3·98 (3)
C(1)–Hg–N(1)	180 (1)		

(b) Pyridyl ring

C(2)–N(1)	1·41 (3)	C(4)–C(5)	1·38 (4)
C(2)–C(3)	1·36 (3)	C(5)–C(6)	1·38 (4)
C(3)–C(4)	1·41 (4)	C(6)–N(1)	1·36 (3)
C(2)–N(1)–Hg	124 (2)	C(3)–C(2)–C(7)	123 (2)
C(6)–N(1)–Hg	121 (2)	C(2)–C(3)–C(4)	122 (2)
C(2)–N(1)–C(6)	115 (2)	C(3)–C(4)–C(5)	118 (2)
C(3)–C(2)–N(1)	120 (2)	C(4)–C(5)–C(6)	117 (3)
C(7)–C(2)–N(1)	117 (2)	C(5)–C(6)–N(1)	127 (3)

(c) Benzyl group

C(2)–C(7)	1·47 (3)	C(10)–C(11)	1·40 (4)
C(7)–C(8)	1·51 (3)	C(11)–C(12)	1·41 (4)
C(8)–C(9)	1·38 (3)	C(12)–C(13)	1·38 (4)
C(9)–C(10)	1·37 (4)	C(8)–C(13)	1·45 (4)
C(2)–C(7)–C(8)	116 (2)	C(9)–C(10)–C(11)	124 (3)
C(7)–C(8)–C(9)	122 (2)	C(10)–C(11)–C(12)	118 (3)
C(7)–C(8)–C(13)	118 (2)	C(11)–C(12)–C(13)	121 (3)
C(9)–C(8)–C(13)	120 (2)	C(8)–C(13)–C(12)	119 (2)
C(8)–C(9)–C(10)	119 (2)		

(d) Nitrate ion

N(2)–O(1)	1·21 (3)	O(1)–N(2)–O(2)	119 (2)
N(2)–O(2)	1·32 (3)	O(1)–N(2)–O(3)	130 (3)
N(2)–O(3)	1·25 (4)	O(2)–N(2)–O(3)	107 (2)

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

isotropic thermal parameters for other non-hydrogen atoms with the H atoms riding on their respective atoms, resulting in $R = 0.062$ and $R^1 = 0.056$ (for observed reflections), where $R^1 = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.* the final difference synthesis had no major characteristic >2.23 e Å^{-3}, this being in the vicinity of the Hg atom. The largest shift-to-e.s.d. ratio for the non-hydrogen atoms in the final refinement was -0.112 for the x parameter of C(1).

Final fractional coordinates, thermal parameters, interatomic distances and angles, and equations of mean planes are given in Tables 1–4. Scattering factors, corrected for anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970).

All calculations were carried out on the Monash University B6700 computer; the major programs used

Table 4. *Equations of mean planes and deviations (Å) 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:

$$\begin{pmatrix} 14·88700 & 0·000000 & -0·092186 \\ 0·000000 & 11·159000 & 0·000000 \\ 0·000000 & 0·000000 & 8·744514 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

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

$(0·2671)X + (-0·9408)Y + (-0·2085)Z - (-4·3862) = 0$

C(2)	-0·02 (2)	N(1)	-0·00 (2)
C(3)	0·03 (3)	C(1)	0·11 (3)
C(4)	-0·03 (3)	C(7)	-0·01 (3)
C(5)	0·01 (3)	C(8)	1·21 (2)
C(6)	0·01 (3)	Hg	0·060 (1)

Plane II: C(8), C(9), C(10), C(11), C(12), C(13)

$(-0·2934)X + (0·1721)Y + (-0·9404)Z - (-5·8051) = 0$

C(8)	0·01 (2)	C(1)	3·68 (3)
C(9)	-0·01 (3)	C(2)	1·06 (2)
C(10)	0·02 (3)	C(7)	0·06 (3)
C(11)	-0·02 (3)	N(1)	2·41 (2)
C(12)	0·02 (3)	Hg	3·044 (1)
C(13)	-0·02 (3)		

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

$(0·7405)X + (0·3720)Y + (-0·5598)Z - (3·2290) = 0$

O(1)	-0·04 (2)	O(3)	-0·03 (2)
O(2)	-0·03 (2)	N(2)	0·10 (3)
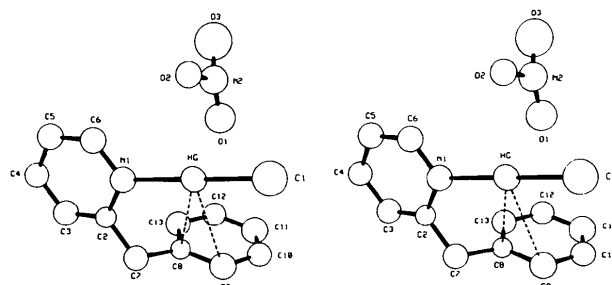
Fig. 1. A stereoscopic view of the structure of [MeHg(2-Bzlpy)]NO₃.

were *SHELX* 76 (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964), *MEANPL* (Blow, 1960), and *ORTEP* (Johnson, 1965).

Discussion of the structure

Aspects of the molecular geometry are given in Tables 3–5, and two different views of the structure in Figs. 1 and 2.

The geometry at Hg in the [MeHg(2-Bzlpy)]$^+$ cation is linear, and the Hg–C(1) length, 2·07 (3) Å, is similar to that found in other MeHg^{11} complexes of aromatic N-donor ligands [MeHgL]NO₃ [L = py, 2·04 (3) Å (Brownlee, Canty & Mackay, 1978); L = 3,3′-dmbpy, 2·01 (1) Å (Canty, Chaichit, Gatehouse & Marker, 1978); and L = 2,2′-bipyridyl, 2·07 (5) Å (Canty &

Table 5. Hg···C(or N) contacts in organomercury compounds

Complex	Hg···C(or N) (Å)	Reference
[ClHgCH₂C(Me)(OMe)CH₂(p-OMePh)]	3·05*	(1)
[PhCH₂HgSCPh₃]	3·30	(2)
[MeHg(3,3'-dmbpy)]NO₃	3·11 (1), 3·29 (1) [N(1')]	(3)
[MeHgN̄H₂CH(CO₂⁻)CH₂(p-OHPh)]	3·19 (2), 3·33 (2)	(4)
[MeHg(2-Bzlpy)]NO₃	3·23 (2), 3·33 (3)	(5)

References: (1) Kiefer, Waters & Carlson (1968). (2) Bach, Weibel, Schmonsees & Glick (1974). (3) Canty, Chaichit, Gatehouse & Marker (1978). (4) Alcock, Lampe & Moore (1978). (5) This work.
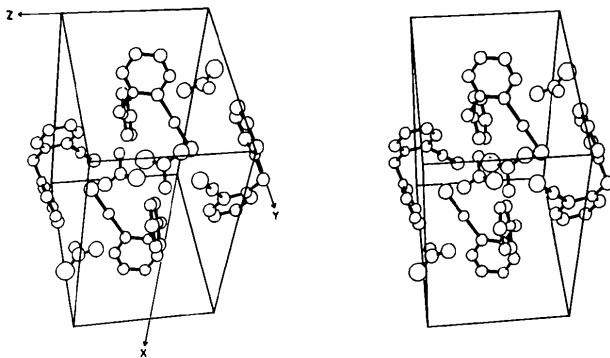
* Hg is '3·05 Å above one of the benzene π bonds'.

Fig. 2. A packing diagram for [MeHg(2-Bzlpy)]NO₃.

Gatehouse, 1976)]. The Hg—N length, 2·10 (2) Å, is also similar to those in the other analogues [py, 2·12 (2), and 3,3'-dmbpy, 2·11 (1) Å], except for bidentate 2,2'-bipyridyl which has longer Hg—N bonds [2·24 (3) and 2·43 (3) Å]. The shorter Hg—O distances, 2·88 (2) [O(2)], 2·94 (2) [O(1)], and 3·01 (2) Å [O(1¹)], are close to the sum of the van der Waals radii, 2·90 or 3·13 Å [where the van der Waals radius of O is taken as 1·40 Å (Pauling, 1960) and Grdenić's (1965) values of 1·50 and 1·73 Å are used for Hg, respectively]. The upper value is used by Grdenić to assess the presence of weak interactions. Thus, interaction with the nitrate ion is very weak, although the nitrate ion is distorted from D_{3h} symmetry (Table 3).

Two of the C atoms of the phenyl ring [C(8), C(9)] are much closer to Hg than the other four (Table 3), and the distances from Hg to the closer C atoms are very similar to those found in the 3,3'-dmbpy complex and the tyrosine complex, [MeHgN̄H₂CH(CO₂⁻)CH₂(p-OHPh)] (Table 5). The spatial relationship between MeHg[II] and the phenyl ring is closely related to that in the tyrosine complex, and the cation in Fig. 1 is presented in an orientation that illustrates this similarity (Alcock, Lampe & Moore, 1978). Interaction between Hg and the C(8)=C(9) bond must be very weak as the geometry of Hg is linear, as it is also in [PhCH₂HgSCPh₃] (Bach, Weibel, Schmonsees & Glick, 1974). Also, distortions from linearity in [MeHg(3,3'-

dmbpy)]NO₃ [172·7 (5)°] and [MeHgN̄H₂CH(CO₂⁻)CH₂(p-OHPh)] [169 (1)°] do not result from intramolecular π interactions, but from the weak interaction of Hg with nitrate ions and with the carboxylate group, respectively (Canty, Chaichit, Gatehouse & Marker, 1978; Alcock, Lampe & Moore, 1978). The C—Hg—Cl angle is apparently bent slightly from 180° in [ClHgCH₂C(Me)(OMe)CH₂(p-OMePh)] (Kiefer, Waters & Carlson, 1968), but insufficient details of the structure are available to determine whether this results from intramolecular π coordination.

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