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## Interaction of Methylmercury(II) with Bidentate Ligands Containing Pyridine and Pyrazole Rings. Synthesis and Structure of Methyl[1-(2-pyridyl)pyrazole]mercury(II) Nitrate and [Di(1-pyrazolyl)methane]methylmercury(II) Nitrate

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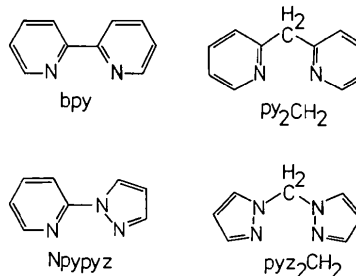
### Abstract

The complexes  $[\text{MeHg}L]\text{NO}_3$  [ $L = 1$ -(2-pyridyl)pyrazole or di(1-pyrazolyl)methane] have  $L$  present as bidentate ligands to give irregular three coordination for Hg in the  $\text{CHgN}_2$  moieties. The 1-(2-pyridyl)pyrazole complex,  $[\text{Hg}(\text{CH}_3)(\text{C}_8\text{H}_7\text{N}_3)]\text{NO}_3$ , is triclinic, with  $a = 10.201$  (9),  $b = 10.347$  (9),  $c = 7.650$  (7) Å,  $\alpha = 91.16$  (2),  $\beta = 106.89$  (3),  $\gamma = 127.07$  (2)°,  $U = 596.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.355$ ,  $D_m = 2.36$  (2) Mg m<sup>-3</sup>,  $F(000) = 392$ , and space group  $P\bar{1}$ . The structure was refined for 869 counter-measured observed reflections to  $R = 0.066$ . The complex has C(1)–Hg–N(1) 168 (2)° and Hg–N(1) 2.21 (3) Å [N(1) is the pyrazole donor atom], Hg–N(1') (pyridine ring) 2.61 (5) Å, and nitrate O atoms 2.97 (3), 3.07 (3), and 3.14 (3) Å from Hg. The di(1-pyrazolyl)methane complex,  $[\text{Hg}(\text{CH}_3)(\text{C}_7\text{H}_8\text{N}_4)]\text{NO}_3$ , is triclinic, with  $a = 8.457$  (9),  $b = 10.461$  (7),  $c = 8.455$  (5) Å,  $\alpha = 100.68$  (1),  $\beta = 107.73$  (2),  $\gamma = 114.39$  (2)°,  $U = 605.74$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.334$ ,  $D_m = 2.34$  (22) Mg m<sup>-3</sup>,  $F(000) = 396$ , and space group  $P\bar{1}$ ;  $R = 0.043$  for 1112 reflections; the cation has C(1)–Hg–N(1) 179 (1)°, Hg–N(1) 2.16 (1), Hg–N(1') 2.96 (2) Å, and nitrate O atoms 2.88 (2) and 2.90 (2) Å from Hg. In both structures the cations

and anions are grouped to form  $\{[\text{MeHg}L]\text{NO}_3\}_2$  dimeric units *via*  $\text{Hg}\cdots\text{O}$  interactions.

### Introduction

In studying the tendency of methylmercury(II) to form complexes with coordination numbers for Hg greater than two we have employed aromatic N donor ligands that can potentially act as either unidentate or polydentate donors. Thus, 2,2'-bipyridyl (bpy) and 4,4',4''-triethyl-2,2':6',2''-terpyridyl act as bidentate and tridentate ligands, respectively, towards  $\text{MeHg}^{\text{II}}$  in the solid state, although <sup>1</sup>H nuclear magnetic resonance spectra show that both these ligands act as bidentate in methanol; di(2-pyridyl)methane ( $\text{py}_2\text{CH}_2$ ) has a methylene bridge between the pyridyl rings and coordinates



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as a bidentate ligand to  $\text{MeHg}^{\text{II}}$  in both the solid state and solution (Canty & Gatehouse, 1976; Canty & Marker, 1976; Canty, Hayhurst, Chaichit & Gatehouse, 1980; Canty, Chaichit, Gatehouse, George & Hayhurst, 1981). We have extended this study to include 1-(2-pyridyl)pyrazole (Nppyz) and di(1-pyrazolyl)methane ( $\text{pyz}_2\text{CH}_2$ ) to explore the effect of the much lower basicity of pyrazole rings with retention of flexibility in the orientation of the rings, allowing the ligand to act as either a unidentate or a bidentate ligand.

### Experimental

1-(2-Pyridyl)pyrazole was synthesized as described by Khan & Polya (1970), and di(1-pyrazolyl)methane was obtained from Columbia Organic Chemicals Company, Inc. Crystals of  $[\text{MeHg}L]\text{NO}_3$  formed from acetone solutions containing equimolar quantities of methylmercury(II) nitrate and  $L$  ( $L = \text{Nppyz}$ : yield 47%; composition: found: C 25.6, H 2.5, Hg 47.2%; calculated for  $[\text{MeHg}(\text{Nppyz})]\text{NO}_3$ : C 25.6, H 2.4, Hg 47.4%.  $L = \text{pyz}_2\text{CH}_2$ : yield 20%; composition: found: C 22.4, H 2.7, Hg 47.0%; calculated for  $[\text{MeHg}(\text{pyz}_2\text{CH}_2)]\text{NO}_3$ : C 22.6, H 2.6, Hg 47.1%). Microanalyses were by the Australian Microanalytical Service, Melbourne.

#### Crystal data

Unit-cell parameters were determined with a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator as described previously (Gatehouse & Miskin, 1974).

For  $[\text{MeHg}(\text{Nppyz})]\text{NO}_3$  three standard reflections monitored at 2 h intervals showed a small systematic decrease in intensity; no systematic variation in intensity was observed for  $[\text{MeHg}(\text{pyz}_2\text{CH}_2)]\text{NO}_3$ .

Data were collected by the  $\omega/2\theta$ -scan technique with a symmetric scan width of  $\pm 0.65^\circ$  in  $\omega$  from the calculated Bragg angle, with an allowance for dispersion, at scan rates of  $0.1^\circ \text{ s}^{-1}$  (Nppyz complex) and  $0.05^\circ \text{ s}^{-1}$  ( $\text{pyz}_2\text{CH}_2$  complex). The Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) was monochromatized using a flat graphite crystal and no reflection was sufficiently intense to require attenuation. The data were processed with a program written specifically for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). Values of  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects.

$[\text{MeHg}(\text{Nppyz})]\text{NO}_3$ . An absorption correction ( $\mu = 12.43 \text{ mm}^{-1}$ ) was applied and maximum and minimum values of the transmission factors were 0.5923 and 0.3799. 3644 reflections were measured to  $2\theta = 60^\circ$  from a crystal  $0.05 \times 0.08 \times 0.09 \text{ mm}$  and, of these, 869 unique reflections [ $I \geq 3\sigma(I)$ ] were used in the analysis.

$[\text{MeHg}(\text{pyz}_2\text{CH}_2)]\text{NO}_3$ . An absorption correction ( $\mu = 12.24 \text{ mm}^{-1}$ ) was applied and maximum and minimum values of the transmission factors were 0.7592 and 0.4631. 3635 reflections were measured to  $2\theta = 60^\circ$  from a crystal  $0.03 \times 0.06 \times 0.13 \text{ mm}$  and, of these, 1112 unique reflections [ $I \geq 3\sigma(I)$ ] were used in the analysis.

For both complexes the Patterson synthesis enabled location of the Hg atom by standard methods; the Hg atom position was refined and all non-hydrogen atoms were located in the subsequent difference Fourier syntheses. The function minimized in full-matrix least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  is

Table 1. Final fractional coordinates and thermal parameters ( $\times 10^3$ , for Hg  $\times 10^4$ ) for  $[\text{MeHg}(\text{Nppyz})]\text{NO}_3$ , with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}$ ( $\text{\AA}^2$ )
Hg	2831 (2)	839 (2)	910 (2)	659 (10)
C(1)	411 (4)	313 (4)	228 (6)	83 (30)
C(3)	61 (5)	-400 (5)	-217 (5)	57 (10)
C(4)	-66 (4)	-386 (5)	-346 (5)	67 (27)
C(5)	-1 (4)	-228 (5)	-268 (6)	55 (26)
C(2')	338 (5)	-199 (6)	85 (6)	64 (28)
C(3')	367 (6)	-314 (6)	99 (6)	89 (36)
C(4')	518 (7)	-253 (6)	242 (7)	117 (41)
C(5')	632 (6)	-97 (6)	376 (6)	101 (35)
C(6')	581 (5)	-6 (5)	334 (5)	57 (33)
N(1)	139 (4)	-155 (3)	-115 (5)	73 (23)
N(2)	180 (4)	-257 (3)	-76 (4)	67 (21)
N(3)	-60 (4)	-220 (4)	227 (4)	68 (23)
N(1')	437 (4)	-47 (4)	196 (5)	63 (23)
O(1)	56 (4)	-230 (4)	241 (4)	131 (25)
O(2)	-16 (3)	-84 (3)	224 (4)	85 (20)
O(3)	-205 (3)	-345 (3)	218 (4)	106 (22)

Table 2. Final fractional coordinates and thermal parameters ( $\times 10^3$ , for Hg  $\times 10^4$ ) for  $[\text{MeHg}(\text{pyz}_2\text{CH}_2)]\text{NO}_3$ , with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}$ ( $\text{\AA}^2$ )
Hg	-986 (1)	6224 (1)	6532 (1)	501 (4)
C(1)	-305 (3)	613 (3)	445 (3)	94 (16)
C(2)	224 (2)	886 (2)	1055 (2)	66 (12)
C(3)	345 (2)	717 (2)	1146 (2)	45 (10)
C(4)	301 (2)	572 (2)	1060 (2)	63 (12)
C(5)	158 (2)	521 (2)	895 (2)	64 (12)
C(3')	74 (3)	935 (2)	1253 (3)	70 (14)
C(4')	-109 (4)	895 (2)	1222 (3)	93 (17)
C(5')	-217 (3)	812 (2)	1041 (4)	90 (17)
N(1)	119 (2)	627 (1)	873 (2)	39 (8)
N(2)	233 (2)	747 (1)	1028 (2)	47 (8)
N(3)	308 (2)	795 (2)	589 (2)	55 (10)
N(1')	-110 (2)	801 (1)	961 (2)	57 (9)
N(2')	67 (2)	875 (1)	1093 (2)	49 (9)
O(1)	301 (2)	883 (1)	699 (2)	89 (10)
O(2)	164 (2)	677 (2)	487 (2)	82 (10)
O(3)	453 (2)	826 (2)	572 (2)	146 (16)

the weight  $[1/\sigma^2(F_o)]$ . Several cycles, with the Hg atom refined anisotropically and other non-hydrogen atoms refined isotropically, resulted in  $R$  values of 0.074 (Npypy complex) and 0.070 ( $\text{pyz}_2\text{CH}_2$  complex), where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

Absorption corrections were applied and several cycles of full-matrix least-squares refinement led to  $R^1$  0.065, 0.050 (for observed reflections), where  $R^1 = \sum w^{1/2}(|F_o| - |F_c|) / \sum w^{1/2}|F_o|$ . All coordinates of H atoms were calculated according to the geometry of the C atom to which they are bonded ( $\text{C}-\text{H} = 1.08 \text{ \AA}$ ) and all H atoms were assigned isotropic thermal parameters.

Final refinements, with H atoms riding on their respective C atoms, and all non-hydrogen atoms refined anisotropically, involved 156 (Npypy complex) and 160 ( $\text{pyz}_2\text{CH}_2$  complex) variables and gave  $R$  0.066, 0.043, and  $R^1$  0.058, 0.036, respectively. Final difference syntheses had no major characteristic greater than  $2.19 \text{ e \AA}^{-3}$  (Npypy) and  $0.88 \text{ e \AA}^{-3}$

Table 3. *Interatomic distances (Å) and angles (°) in [MeHg(Npypy)]NO<sub>3</sub>, with e.s.d.'s in parentheses*

(a) Mercury environment			
Hg—C(1)	1.95 (4)	Hg...O(2)	2.97 (3)
Hg—N(1)	2.21 (3)	Hg...O(1)	3.14 (3)
Hg—N(1')	2.61 (5)	Hg...O(2')	3.07 (3)
		Hg...Hg <sup>1</sup>	4.632 (4)
C(1)—Hg—N(1)	168.4 (16)	N(1)—Hg—O(1)	67.2 (11)
C(1)—Hg—N(1')	117.0 (15)	N(1)—Hg—O(2)	78.7 (12)
C(1)—Hg—O(2)	97.8 (15)	N(1')—Hg—O(2)	106.2 (11)
C(1)—Hg—O(1)	123.5 (15)	N(1')—Hg—O(1)	69.0 (11)
C(1)—Hg—O(2')	92.9 (14)	N(1')—Hg—O(2')	147.6 (9)
N(1)—Hg—N(1')	69.8 (12)	O(1)—Hg—O(2)	38.5 (11)
N(1)—Hg—O(2)	88.8 (12)	O(1)—Hg—O(2')	105.9 (8)
Hg...O(2)...Hg <sup>1</sup>	100.1 (9)	O(2)—Hg—O(2')	79.9 (9)
(b) Npypy rings			
C(3)—C(4)	1.47 (7)	C(2')—N(1')	1.32 (6)
C(3)—N(2)	1.36 (4)	C(2')—C(3')	1.39 (10)
C(4)—C(5)	1.38 (7)	C(3')—C(4')	1.34 (7)
C(5)—N(1)	1.30 (4)	C(4')—C(5')	1.41 (6)
N(1)—N(2)	1.36 (6)	C(5')—C(6')	1.33 (9)
C(2')—N(2)	1.45 (5)	C(6')—N(1')	1.34 (6)
C(3)—C(4)—C(5)	103 (3)	C(2')—N(2)—N(1)	121 (3)
C(3)—N(2)—N(1)	107 (3)	C(2')—C(3')—C(4')	112 (5)
C(3)—N(2)—C(2')	132 (5)	C(2')—N(1')—C(6')	113 (5)
C(4)—C(5)—N(1)	111 (5)	C(2')—N(1')—Hg	109 (3)
C(4)—C(3)—N(2)	107 (4)	C(3')—C(2')—N(2)	114 (4)
C(5)—N(1)—N(2)	111 (3)	C(3')—C(2')—N(1')	128 (4)
C(5)—N(1)—Hg	128 (4)	C(3')—C(4')—C(5')	126 (7)
N(2)—N(1)—Hg	120 (2)	C(4')—C(5')—C(6')	112 (5)
N(2)—C(2')—N(1')	119 (5)	C(5')—C(6')—N(1')	129 (4)
		C(6')—N(1')—Hg	137 (3)
(c) Nitrate ion			
N(3)—O(1)	1.22 (7)	O(1)—N(3)—O(2)	114 (3)
N(3)—O(2)	1.19 (5)	O(1)—N(3)—O(3)	119 (4)
N(3)—O(3)	1.22 (4)	O(2)—N(3)—O(3)	127 (5)

Symmetry code: (i)  $-x, -y, -z$ .

Table 4. *Interatomic distances (Å) and angles (°) in [MeHg(py<sub>2</sub>CH<sub>2</sub>)]NO<sub>3</sub>, with e.s.d.'s in parentheses*

(a) Mercury environment			
Hg—C(1)	2.02 (2)	Hg...O(2)	2.90 (2)
Hg—N(1)	2.16 (1)	Hg...O(2')	2.88 (2)
Hg—N(1')	2.96 (2)	Hg...Hg <sup>1</sup>	4.445 (2)
C(1)—Hg—N(1)	178.5 (7)	N(1')—Hg—O(2)	135.2 (4)
C(1)—Hg—N(1')	102.4 (8)	C(1)—Hg—O(2')	98.6 (7)
N(1)—Hg—N(1')	78.6 (5)	N(1)—Hg—O(2')	79.9 (5)
C(1)—Hg—O(2)	93.4 (8)	N(1')—Hg—O(2')	137.1 (5)
N(1)—Hg—O(2)	86.7 (5)	O(2)—Hg—O(2')	79.5 (4)
Hg...O(2)...Hg <sup>1</sup>	100.5 (4)		
(b) Pyrazole rings			
N(1)—N(2)	1.36 (1)	N(1')—N(2')	1.34 (2)
C(5)—N(1)	1.31 (3)	C(5')—N(1')	1.31 (4)
C(3)—N(2)	1.33 (2)	C(3')—N(2')	1.35 (3)
C(3)—C(4)	1.38 (3)	C(3')—C(4')	1.35 (4)
C(4)—C(5)	1.36 (2)	C(4')—C(5')	1.39 (3)
C(2)—N(2)	1.47 (3)	C(2)—N(2')	1.42 (3)
C(5)—N(1)—Hg	130 (1)	C(5')—N(1')—Hg	146 (1)
N(2)—N(1)—Hg	123 (1)	N(2')—N(1')—Hg	107 (1)
C(5)—N(1)—N(2)	107 (1)	C(5')—N(1')—N(2')	104 (2)
C(2)—N(2)—C(3)	127 (1)	C(2)—N(2')—C(3')	127 (1)
C(2)—N(2)—N(1)	122 (1)	C(2)—N(2')—N(1')	119 (2)
C(3)—N(2)—N(1)	110 (1)	C(3')—N(2')—N(1')	114 (2)
C(4)—C(3)—N(2)	106 (1)	C(4')—C(3')—N(2')	105 (2)
C(3)—C(4)—C(5)	107 (2)	C(3')—C(4')—C(5')	106 (3)
C(4)—C(5)—N(1)	110 (2)	C(4')—C(5')—N(1')	112 (2)
N(2)—C(2)—N(2')	113 (1)		
(c) Nitrate ion			
N(3)—O(1)	1.22 (3)	O(1)—N(3)—O(2)	121 (2)
N(3)—O(2)	1.21 (2)	O(1)—N(3)—O(3)	121 (2)
N(3)—O(3)	1.20 (3)	O(2)—N(3)—O(3)	118 (2)

Symmetry code: (i)  $-x, 1 - y, 1 - z$ .

( $\text{pyz}_2\text{CH}_2$ ), these occurring in the vicinity of the Hg atom.

Refinements of the model for the Npypy complex were carried out using the data set corrected for the small amount of decomposition that occurred and the uncorrected data set. The correction for decomposition made no significant improvement to the final structure. Thus, the uncorrected data set was used in the final refinement.

Final fractional coordinates, thermal parameters, interatomic distances and angles, and equations of mean planes are given in Tables 1–6.\* Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). All calculations were carried out using the Monash University B6700 computer. The major programs used were *SHELX 76* (Sheldrick, 1976), *ORFFE* (Busing,

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36381 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. Equations of mean planes and deviations ( $\text{\AA}$ ) of individual atoms from planes in  $[\text{MeHg}(\text{Npypyzy})]\text{NO}_3$

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

$$\begin{pmatrix} 10.201000 & -6.236639 & -2.222083 \\ 0.000000 & 8.256194 & -1.872794 \\ 0.000000 & 0.000000 & 7.076545 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

Plane (I): Mean plane through C(1), Hg, N(1), N(1')

$$(0.5913)X + (0.5858)Y + (-0.5543)Z - (1.3384) = 0$$

C(1)	0.05 (4)	N(1)	0.05 (4)
Hg	-0.111 (2)	N(1')	0.01 (4)

Plane (II): Mean plane through C(3), C(4), C(5), N(1), N(2)

$$(0.6476)X + (0.5450)Y + (-0.5326)Z - (1.5551) = 0$$

C(3)	0.01 (4)	N(2)	-0.01 (4)
C(4)	-0.01 (5)	C(1)	-0.12 (5)
C(5)	0.00 (5)	Hg	-0.213 (2)
N(1)	0.01 (4)	C(2')	0.06 (5)

Plane (III): Mean plane through C(2'), C(3'), C(4'), C(5'), C(6'), N(1')

$$(0.5974)X + (0.5483)Y + (-0.5852)Z - (1.3559) = 0$$

C(2')	-0.00 (5)	C(6')	0.02 (5)
C(3')	-0.01 (6)	N(1')	0.00 (4)
C(4')	0.03 (7)	C(1)	-0.08 (4)
C(5')	-0.03 (6)	Hg	-0.155 (2)
		N(2)	0.03 (4)

Plane (IV): Mean plane through N(3), O(1), O(2), O(3)

$$(0.0822)X + (0.0085)Y + (-0.9966)Z - (-1.5979) = 0$$

N(3)	-0.00 (3)	O(2)	0.00 (3)
O(1)	0.00 (3)	O(3)	0.00 (3)

Table 6. Equations of mean planes and deviations ( $\text{\AA}$ ) of individual atoms from planes in  $[\text{MeHg}(\text{pyz}_2\text{CH}_2)]\text{NO}_3$

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

$$\begin{pmatrix} 8.457000 & -4.319324 & -2.575379 \\ 0.000000 & 9.527642 & -2.887791 \\ 0.000000 & 0.000000 & 7.517653 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}.$$

Plane (I): C(1), Hg, N(1), N(1')

$$(0.4306)X + (0.9024)Y + (-0.0147)Z - (1.3227) = 0$$

C(1)	-0.01 (3)	N(1)	-0.01 (1)
Hg	0.013 (1)	N(1')	0.00 (2)

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

$$(0.7911)X + (0.5060)Y + (-0.3437)Z - (-3.6447) = 0$$

C(3)	-0.01 (2)	N(2)	0.00 (2)
C(4)	0.01 (2)	C(1)	-0.24 (3)
C(5)	-0.01 (2)	C(2)	-0.03 (2)
N(1)	0.01 (2)	Hg	-0.115 (1)

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

$$(-0.1815)X + (0.9683)Y + (-0.1716)Z - (4.7020) = 0$$

C(3')	0.00 (2)	N(2')	-0.01 (1)
C(4')	0.00 (2)	C(1)	0.29 (3)
C(5')	-0.01 (2)	C(2)	0.01 (2)
N(1')	0.01 (1)	Hg	-0.684 (1)

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

$$(-0.2656)X + (0.7125)Y + (-0.6495)Z - (1.9512) = 0$$

N(3)	-0.02 (2)	O(2)	0.01 (2)
O(1)	0.01 (2)	O(3)	0.01 (2)

Martin & Levy, 1964) and *MEANPL* (Blow, 1960), and figures were drawn with *ORTEP* (Johnson, 1965).

### Discussion of the structures

Both structures are composed of  $[\text{MeHgL}]^+$  cations and nitrate anions (Figs. 1–4).

In each cation the geometry at Hg is based on a dominant C(1)–Hg–N(1) moiety  $|168(2)$  (Npypyzy),  $179(1)^\circ$  ( $\text{pyz}_2\text{CH}_2$ ) having Hg–N(1)  $2.21(3)$  ( $\text{pyz}$  ring of Npypyzy) and  $2.16(1)$   $\text{\AA}$  ( $\text{pyz}_2\text{CH}_2$ ), with weaker Hg–N(1') bonds  $[2.61(5)$  ( $\text{py}$  ring of Npypyzy),  $2.96(2)$   $\text{\AA}$  ( $\text{pyz}_2\text{CH}_2$ )]. The  $\text{CHgN}_2$  groups are approximately planar (Tables 5, 6), and the largest deviation from mean planes occurs for the Hg atom in the Npypyzy complex  $[-0.111(2)$   $\text{\AA}$ ]. The pyridyl ring is planar and the pyrazolyl rings are planar and identical (within 2 e.s.d.'s in bond lengths and angles).

The Hg atom is close to the planes of the coordinated rings in the Npypyzy complex

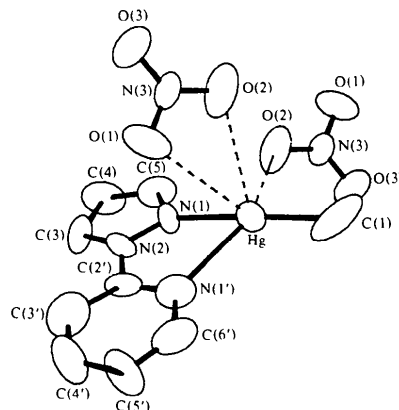


Fig. 1. View of the structure of  $[\text{MeHg}(\text{Npypyzy})]\text{NO}_3$  showing a centrosymmetrically related pair of neighbouring nitrate ions.

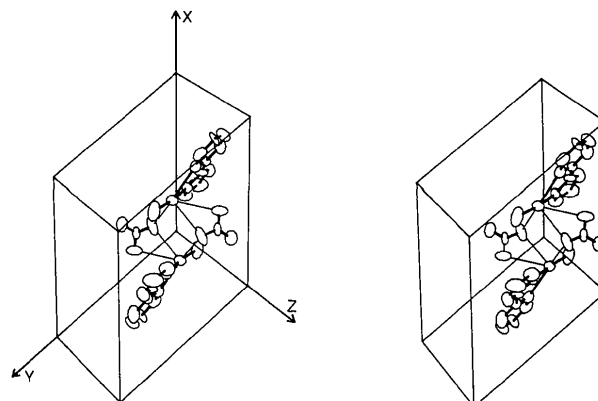


Fig. 2. Packing diagram for  $[\text{MeHg}(\text{Npypyzy})]\text{NO}_3$  illustrating the weakly bridging role of the nitrate ions to form dimeric units. Mercury–oxygen interactions are shown as faint lines, and only one dimeric unit is shown for clarity.

[ $-0.213(2)$  Å from the plane containing N(1),  $-0.155(2)$  Å from the plane containing N(1')], and, consistent with greater interaction with N(1) than N(1'), the angles Hg–N(1)–N(2), C(5) are similar [ $120(2)$ ,  $128(4)^\circ$  respectively] but

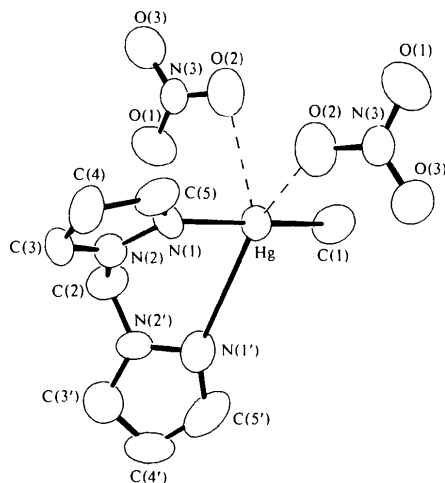


Fig. 3. View of the structure of  $[\text{MeHg}(\text{py}_2\text{CH}_2)]\text{NO}_3$  showing a centrosymmetrically related pair of neighbouring nitrate ions.

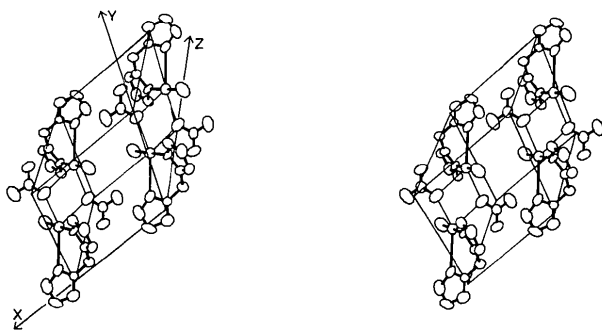


Fig. 4. Packing diagram for  $[\text{MeHg}(\text{py}_2\text{CH}_2)]\text{NO}_3$  illustrating the weakly bridging role of the nitrate ion to form dimeric units. Mercury–oxygen interactions are shown as faint lines.

Hg–N(1')–C(2'), C(6') are markedly different [ $109(3)$ ,  $137(3)^\circ$  respectively].

In the  $\text{py}_2\text{CH}_2$  complex the Hg atom is  $-0.115(1)$  Å from the plane containing N(1) but  $-0.684(1)$  Å from the plane containing the more weakly coordinated N(1'), and angles at N(1) and N(1') are also consistent with weaker interaction with N(1') [Hg–N(1)–N(2), C(5)  $123(1)$ ,  $130(1)^\circ$ ; Hg–N(1')–N(2'), C(5')  $107(1)$ ,  $146(1)^\circ$ ]. A similar result was found for the  $\text{py}_2\text{CH}_2$  complex which also has an approximately 'T-shaped' geometry for Hg (Table 7) [e.g. the Hg atom lies  $-0.076(1)$  Å from the plane containing N(1),  $0.469(1)$  Å from the plane containing N(1')].

Grdenić (1965) has suggested that a radius of  $1.73$  Å for Hg be used in assessing the presence of weak bonding. This has recently been suggested as a general value for the van der Waals radius of Hg, although some interactions at distances corresponding to a larger radius cannot be excluded (Canty & Deacon, 1980). Thus, using Pauling's (1960) value for the van der Waals radius of O ( $1.4$  Å), weak Hg...O interactions are evident in both structures (Tables 3, 4) and these are indicated in Figs. 1–4. In both structures the nitrate ion is present as a weakly interacting bridging ligand between neighbouring cations, *via* Hg...O(2) interactions of  $2.97(3)$ ,  $3.07(3)$  Å for the Npypy complex and  $2.90(2)$ ,  $2.88(2)$  Å for the  $\text{py}_2\text{CH}_2$  complex, to give  $[\text{MeHgL}]\text{NO}_3$  dimeric units having a centre of symmetry.

It is interesting that the closely related bidentate ligands bpy and Npypy form complexes with similar geometry, and that addition of a methylene bridge to give  $\text{py}_2\text{CH}_2$  and  $\text{py}_2\text{CH}_2$  results in  $\text{MeHg}^{\text{II}}$  complexes with similar geometry but different from bpy and Npypy (Table 7). The structural data in this table also indicate that as the Hg–N(1') distance increases from  $2.43(3)$  to  $2.96(2)$  Å the angle C(1)–Hg–N(1) approaches  $180^\circ$ , and the Hg–N(1) distance decreases from  $2.24(3)$  to  $2.16(1)$  Å, *cf.*  $2.12(2)$  Å in the linear complex of unidentate pyridine,  $[\text{MeHg}(\text{pyridine})]\text{NO}_3$  (Brownlee, Canty & Mackay, 1978).

Table 7. Selected structural data for complexes of  $\text{MeHg}^{\text{II}}$  with bidentate ligands containing pyridyl and/or pyrazolyl donors

Ligand	Hg–C(1) (Å)	Hg–N(1) (Å)	C(1)–Hg–N(1) ( $^\circ$ )	Hg–N(1') (Å)	Hg...O (Å)	Reference
bpy	2.07 (5)	2.24 (3)	164 (1)	2.43 (3)	2.99 (3), 2.99 (3)	(1)
Npypy	1.95 (4)	2.21 (3)*	168 (2)	2.61 (5)	2.97 (3), 3.07 (3), 3.14 (3)	(2)
$\text{py}_2\text{CH}_2$	2.10 (2)	2.16 (1)	172 (1)	2.75 (2)	2.76 (2)	(3)
$\text{py}_2\text{CH}_2$	2.02 (2)	2.16 (1)	179 (1)	2.96 (2)	2.88 (2), 2.90 (2)	(2)

References: (1) Canty & Gatehouse (1976). (2) This work. (3) Canty, Chaichit, Gatehouse, George & Hayhurst (1981).

\* Pyrazole nitrogen.

Although Hg–N(1') bonding is weak in complexes of py<sub>2</sub>CH<sub>2</sub> and pyz<sub>2</sub>CH<sub>2</sub>, <sup>1</sup>H NMR studies show that these ligands remain chelated to MeHg<sup>II</sup> on dissolution of the [MeHgL]NO<sub>3</sub> complexes in methanol (Canty, Chaichit, Gatehouse, George & Hayhurst, 1981; Canty, 1980).

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## The Structure of Bis(triethylphosphine)[ $\eta^2$ -bis(trimethylsilyl)diphosphene]nickel, [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Ni[PSi(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, at 175 K, a Complex Containing a P–Ni–P Ring System\*

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#### Abstract

The crystal structure of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Ni[PSi(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, C<sub>18</sub>H<sub>48</sub>NiP<sub>4</sub>Si<sub>2</sub>, has been determined by three-dimensional X-ray diffraction data collected at 175 K. The compound crystallizes in the monoclinic space group *P2<sub>1</sub>/c*, with *a* = 10.026 (5), *b* = 17.466 (9), *c* = 20.69 (1) Å,  $\beta$  = 127.45 (3)°, *Z* = 4. The structure was solved independently by *MULTAN* as well as by the heavy-atom method and refined by block-diagonal least-squares techniques. The final discrepancy factor *R* is 0.038 for 3719 symmetrical independent reflections

of the low-temperature measurement. In the complex the Ni atom is nearly planar coordinated by four P atoms. The Ni–P bond lengths to the P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> groups are about 0.07 Å shorter than the Ni–P bond distances to the PSi(CH<sub>3</sub>)<sub>3</sub> groups [2.236 (2) and 2.258 (2) Å]. The bond length between the P atoms of the PSi(CH<sub>3</sub>)<sub>3</sub> groups [2.149 (2) Å] is significantly shorter than is expected for a normal P–P single bond.

#### Introduction

During our investigations concerning the ligand properties of the P(SiMe<sub>3</sub>)<sub>2</sub> group towards transition metals (Schäfer, 1978, 1979*a, b*, 1980) we studied reactions of LiP(SiMe<sub>3</sub>)<sub>2</sub> with (R<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> complexes. It was found that definite compounds could be isolated only if *R* is

\* Parts of this work were presented as a poster contribution at the 19th Diskussionstagung der Arbeitsgemeinschaft Kristallographie at Aachen (Deppisch & Schäfer, 1979).