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Adducts from Mercury(I) and Mercury(II) Compounds with Bispyrazolylalkanes. X-Ray Crystal Structure of Bis(3,5-dimethylpyrazol-1-yl)methane(dicyano)-mercury(II)

AUGUSTO CINGOLANI, ADRIANA LORENZOTTI, GIANCARLO GIOIA LOBBIA, DANTE LEONESI, FLAVIO BONATI
Dipartimento di Scienze Chimiche dell'Universitá, via S. Agostino 1, 62032 Camerino, Italy
and BRUNA BOVIO
Dipartimento di Chimica Generale, viale Taramelli 12, 27100 Pavia, Italy

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Abstract

The 1:1 adducts between the bis(3,5-dimethylpyrazol-1-yl)methane (L′–L′) or 2,2′-bis(pyrazol-1-yl)propane (L″–L″) ligand and HgX_2 (with X = Cl, CN or CO_2CF_3) have been obtained as well as $[(L'-L')_2]Hg(ClO_4)_2$ and the mercury(I) derivative $(ligand)_2Hg_2(ClO_4)_2$. The adducts have been characterized from analytical and spectral data (IR, proton and ^{13}C NMR). Four-coordinated mercury is present in $(L'-L')Hg(CN)_2$, in which the metal–$(N-N)_2C$ ring adopts an asymmetric boat form. The molecular parameters are significantly different for the two independent molecules, the C–Hg–C angles and the two Hg–N distances being 163.1(9)° and 2.55(1) plus 2.70(1) Å in the one case, and 148.2(8)° and 2.40(1) plus 2.51(1) Å, in the other; correspondingly the N–Hg–N angle, the 'bite' of the ligand, ranges from 79.0(5)° to 71.7(4)°, a value outside the range previously reported.

Introduction

We have previously described the preparation of mercury(II) adducts with bis(pyrazol-1-yl)methane (L–L) [1]. We now report studies of the use of bis(pyrazol-1-yl)alkanes as ligands, namely bis(3,5-dimethylpyrazol-1-yl)methane (L′–L′) (chosen because it provides more steric hindrance and is more basic than (L–L)) and 2,2-bis(pyrazol-1-yl)propane (L″–L″); the latter was chosen initially because the Me–C–Me moiety was expected to improve the solubilities of the complexes without being much different from (L–L) in steric requirements or basic character. The preparations of some mercury(I) derivatives are also reported.

Results and Discussion

The mercury(I) compounds **I**–**III** (Table I) were obtained in high yield from each of the ligands and mercury(I) perchlorate. The colourless solids are 1:1 adducts and are soluble only in dimethylsulphoxide; the proton NMR spectra showed that the compounds are diamagnetic in this solvent, and that the ligand has not undergone any structural change. The IR spectra show bands due to the organic ligands and ionic perchlorato groups (Table II), suggesting a formula such as $[(ligand)Hg-Hg(ligand)](ClO_4)_2$, in which both ligands may be bidentate and there is a Hg–Hg bond, typical of mercury(I) [2]. The formation of stable Hg(I) derivatives, showing no tendency

TABLE I. Mercury(I) Derivatives: Analytical and Other Data

Compound	Melting point (°C)	Yield (%)	Elemental analyses (%)[a]		
			C	H	N
$(C_7H_8N_4)HgClO_4$ (**I**)	224–8	95	18.70 (18.75)	1.85 (1.80)	12.47 (12.50)
$(C_{11}H_{16}N_4)HgClO_4$ (**II**)	260–5	80	26.28 (26.20)	3.25 (3.20)	11.20 (11.11)
$(C_9H_{12}N_4)HgClO_4$ (**III**)	150–2	70	21.65 (22.70)	2.46 (2.52)	11.50 (11.75)

[a]Calculated values are in parentheses.

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TABLE II. Mercury(I) Derivatives: Infrared and NMR Data

Compound	IR data[a] (cm^{-1})				δ (^{1}H)[b]		
	ν(C–H) azole	1500–1600	500	ν(ClO_4)	CH_2	C(4)–H	C(3)–, C(5)–H
I	3130w	1520w	420m	1090vs,br	6.60s	6.43t	7.68d, 8.10d (1.6) (2.2)
II	3140w	1540sh 1560m	490w	1110vs,br 1060vs,br[d] 620s	6.53s	6.22s	2.48s, 2.30s[c]
III	3180w 3140w	1540w	370m	1100vs,br 1070vs,br[d]	2.20s[c]	6.30s	7.53d, 7.72d (2.4) (1.4)

[a] Nujol mull. [b] δ in ppm for internal TMS; DMSO solvent; s = singlet, d = doublet, t = triplet. J values in parentheses in Hz.
[c] H = Me. [d] A strong band at 1060–1070 due to the ligand is also observed in the same region.

TABLE III. Mercury(II) Derivatives: Analytical and Other Data

Compound	Melting point (°C)	Yield (%)	Elemental analyses (%)[a]		
			C	H	N
($C_{11}H_{16}N_4$)[b] (L′–L′)	102–3	85	64.64 (64.68)	7.92 (7.90)	27.44 (27.42)
(L′–L′)$HgCl_2$ (IV)	210	70	27.80 (27.76)	3.42 (3.39)	11.80 (11.78)
(L′–L′)$HgCN_2$[c] (V)	183–5	30	34.12 (34.17)	3.58 (3.53)	18.42 (18.39)
(L′–L′)$Hg(C_2F_3O_2)_2$ (VI)	145–8	85	28.50 (28.56)	2.60 (2.56)	9.05 (8.88)
(L′–L′)$Hg(ClO_4)_2$[d] (VII)	205	70	32.80 (32.70)	4.10 (4.00)	13.75 (13.86)
($C_9H_{12}N_4$)[b] (L″–L″)	85	40	61.35 (61.34)	6.87 (6.86)	31.78 (31.80)
L″–L″)$HgCl_2$ (VIII)	114–5	65	24.00 (24.14)	2.72 (2.70)	12.58 (12.51)
(L″–L″)$Hg(C_2F_3O_2)_2$ (IX)	104–5	50	26.10 (25.90)	2.10 (2.00)	9.25 (9.29)

[a] Calculated values are in parentheses. [b] Prepared according to ref. 24. [c] Molecular weight by osmometry: Calc.: 456.9. Found: 279, 268, 308 at 1.10, 1.09 and 1.60 respectively (10^2 w/w) (see text). [d] Oxygen: 15.90, (15.84); Λ = 270 ohm^{-1} cm^2 mol^{-1} in acetone solution (1.04 × 10^{-3} M).

to disproportionate into Hg(0) and Hg(II) species, is consistent with the previously recognized [1] moderate donor character of the ligands employed.

Except for X = acetate, the mercury(II) derivatives HgX_2 reacted with L′–L′ and L″–L″ according to the equation:

$$HgX_2 + n\text{ligand} = (\text{ligand})_n HgX_2$$

	IV	V	VI	VII	VIII	IX
Ligand	L′–L′	L′–L′	L′–L′	L′–L′	L″–L″	L″–L″
X	Cl	CN	CF_3–CO_2	ClO_4	Cl	CF_3–CO_2
n	1	1	1	2	1	1

The products are colourless solids and were identified from the analytical and conductivity data (Table III).

The IR spectra support the formulae proposed since they contain absorptions due to the nitrogen ligand and the X anions, as shown in Table IV. The presence of weak C–H stretching vibrations due to the heterocyclic ring can always be detected, even in the compounds containing the 3,5-dimethylpyrazolyl group. On the other hand, the C≡N stretching vibration found as a medium intensity band at 2193 cm^{-1} for mercury(II) cyanide could not be detected for compound V, (L′–L′)$Hg(CN)_2$, whose structure was established by an X-ray crystal structure deter-

TABLE IV. Mercury(II) Derivatives: Infrared Data[a] (cm^{-1})

Compound	ν(C–H) azole	1500–1600	<500	Others
(L′–L′)	3140vw 3100vw	1560vs	475s 360m 310m 280m	
IV		1560m	490w 470w 360w 310m^b	
V	3120w 3140w	1560m	490w 470w 420m 360w^c 290w	
VI	3140w	1560m 1520w	380w 350w 280w	ν(C=O) 1685sh 1665vs 1425s ν(C–F) 1200vs,br 1130s
VII	3140w	1560m	480w	ν(ClO_4) 1100vs,br 625s
(L″–L″)	3140w 3120w	1540w 1510m	370m	
VIII	3160w 3140w	1510w	460w 360w 310m^b	
IX	3170w 3160w 3130w	1520w	460w 370w 280w	ν(C=O) 1680vs 1660 1650s 1420s ν(C–F) 1200vs 1140vs

[a] Nujol mull. [b] ν(Hg–Cl). [c] ν(Hg–CN).

mination. The absence of the C≡N stretching vibration is in line with its low intensity for some other adducts of mercury cyanide, *e.g.* those with *N*-methyl- [3] or *N*-benzylimidazole, and an explanation has been offered [4].

The compounds III–IX are insoluble in ether, hydrocarbons, or chlorinated hydrocarbons, but are soluble in acetone (L′–L′ derivatives) or methanol (L″–L″ derivatives). The NMR spectra (Table V) were therefore recorded in these solvents rather than in dimethylsulphoxide because the latter is likely to displace the other ligands from the coordination sphere. The spectra of the compounds show that the ligands have not undergone any structural change upon coordination. In acetone solution, all the proton signals shift to lower field upon coordination, whereas of the ^{13}C signals only those from the protons of the pyrazole ring follow this same trend, the signals from the methyl and bridging methylene groups moving in the opposite direction, in keeping with known behaviour [1].

While the ^{13}C NMR spectrum of compound VI, (L′–L′)$Hg(O_2C{-}CF_3)_2$, was not unusual in any way, although the fluorine-coupled signals could not be detected, the proton NMR spectrum in acetone shows a singlet for the 4-CH and for the bridging methylene, plus four singlets for the methyl groups, instead of either one or one plus two singlets as is usually found. For VI in solution several coordination modes are possible for the mercury(II) atom; *e.g.*, pseudotetrahedral with chelating L′–L′, pseudooctahedral if all the ligands are chelating, or a five-coordination if only one of the ligands is monodentate. In any of these cases, however, the two pyrazole rings and the two protons of the methylene groups would no longer be magnetically equivalent as they are in the ligands or in other symmetric complexes. Moreover, these protons do not become equivalent because of fluxionality in the ^1H NMR spectrum, run at 90 MHz, although they become equivalent in the ^{13}C spectrum run at 20 MHz. Additional support comes from the spectrum in acetone at higher temperature (50 °C), or in another solvent (DMSO) at room temperature, only one set of signals being observed. The unique behaviour of mercury(II) trifluoroacetate among the other mercury(II) derivatives employed is not without precedent: in the solid state its adduct with dipyridyl has been shown to contain only chelating ligands and both six- and seven-coordinated mercury atoms [5].

Mercury acetate reacts in a quite different way with L′–L′ or L″–L″, no simple adduct being formed.

X-ray Crystal Structure Determination of V

The crystal structure of compound V consists of discrete molecules. The interatomic distances and bond angles of two independent molecules are listed in Table VI; the average values with their standard deviation are given in Table VII. An ORTEP [7] representation of the molecules with the numbering scheme is shown in Fig. 1. The molecules have virtual C_s, symmetry but they exhibit no real crystallographic symmetry and all the atoms occupy general positions. The packing in the crystal is given in Fig. 2. The shortest intermolecular approaches between the molecule A (x,y,z) and the molecules B (x,y,z; $x,y,z-1$; $-x+1,y+\frac{1}{2},-z+1$; $-x+\frac{1}{2},y+\frac{1}{2},z$; $-x+\frac{1}{2},y+\frac{1}{2},z-1$) are normal van der Waals contacts, whereas those between the molecule A and its equivalents and between the molecule B and its equivalents are greater than 3.60 Å.

TABLE V. Mercury(II) Derivatives: Nuclear Magnetic Resonance Data[a]

Compound		$\delta(^1H)$			$\delta(^{13}C)$					
		CH_2	C(4)–H	C(3)–, C(5)–Me	C(3)	C(4)	C(5)	CH_2	Me(3)	Me(5)
(L′–L′)	(1)	6.03s	5.75s	2.06s, 2.44s	147.7	105.8	140.3	59.5	13.0	10.5
	(2)	6.01s	5.73s	2.13s, 2.38s	148.3	106.4	140.5	60.5	13.5	11.2
IV	(1)	6.48s	6.10s	2.33s, 2.57s	150.6	107.1	142.2	57.3	12.7	10.4
V	(1)	6.27s	5.97s	2.24s, 2.53s	149.4	106.6	142.3	58.3	12.9	10.4
VI	(1)	6.66s 6.51s	6.13s 6.06s	2.18s, 2.24s 2.58s, 2.71s	150.4		142.3	57.9	12.8	10.5
VII	(1)	6.82s	6.38s	*ca.* 2.30br,s 2.69s	152.2	108.4	144.8	58.2	12.7	10.7
		$C(Me)_2$	C(4)–H	C(3)–, C(5)–H	C(3)	C(4)	C(5)	Me	C(quat.)	
(L″–L″)	(1)	2.24s	6.23t (2.0)	7.55d, 7.46d (2.5), (1.4)	140.9	107.5	129.0	29.2	77.8	
	(3)	2.24s	6.30t (1.8)	7.58d, 7.48d (2.3), (1.2)	140.8	106.9	128.9	28.2	76.7	
VIII	(3)	2.22s	6.32t (1.8)	7.55d, 7.65d (2.5), (1.2)	140.8	106.9	128.9	28.2	76.5	
IX	(3)	2.32s	6.42t (2.0)	8.0–7.6m	138.9	106.1	127.3	32.6		

[a] δ in ppm from internal TMS; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. *J* values in parentheses in Hz. For the ligands, *cf.* ref. 24. (1) In acetone. (2) In chloroform. (3) In methanol.

There is a considerable difference between several of the corresponding molecular parameters in A and in B, although not enough to suggest a different coordination at the metal atoms. (Such a difference in coordination is found [8] in tris(ethylenediamine)-chromium(III)pentacyanonickelate(II) sesquihydrate, which contains two crystallographically independent $[Ni(CN)_5]^{-3}$ anions, one square-pyramidal and the other trigonal-bipyramidal.) Since hydrogen bonding cannot be operating with our compound, the differences may arise from a very shallow minimum of the potential energy function for the mercury complex, and/or the contribution of the packing forces to the stability, a contribution which may be different for each molecule. In the absence of any satisfactory explanation one might surprisingly conclude that interaction between the same donor, L′–L′, and the same acceptor, $Hg(CN)_2$, can give two complexes, A and B, the first weaker than the other. Thus the NC–Hg–CN angle and the Hg–N distances in A are larger and the N–Hg–N and NC–Hg–N angles smaller than those in B.

Whichever molecule of the two is considered, some features can be seen:

(1) The six-membered $C(NN)_2Hg$ ring adopts the boat form, as is usual [9], e.g. for the molecules listed in Table VIII; the Hg atom forms the bow (displacements from the plane of the nitrogen atoms: 1.003(1) and 0.980(1) Å for the molecules A and B, respectively) and the C(8) atom the stern (displacements from the plane of the nitrogen atoms: 0.748(21) and 0.702(18) Å for the molecules A and B, respectively); the Hg...C(8) fold angles are 120.3° and 122.3° respectively. However, the boat does not, as expected, contain a plane of symmetry passing through the metal and the carbon atom, as is found for most of the compounds listed in Table VIII; both molecules of our compound have to be asymmetric in order to fit the coordination requirements. Such asymmetry is not common, but it has been observed in a nickel derivative (Table VIII) or, in the case of three-coordination, even in a methylmercury(II) adduct [9a]. The puckering parameters calculated according to Cremer and Pople [10] are:

$Q = 0.970 \quad \theta = 85.0° \quad \phi = 359.3°$ in molecule A

$Q = 0.934 \quad \theta = 84.2° \quad \phi = 0.5°$ in molecule B

The pure boat conformation corresponds to $\theta = 90°$ and $\phi = 0°$ (360°), whereas the inverted boat conformation corresponds to $\theta = 90°$ and $\phi = 180°$; in contrast, a pure chair conformation has $\theta = 0°$. For

TABLE VI. Bond Lengths (Å) and Angles (°) (with e.s.d.s in parentheses)

Molecule A			
In the coordination sphere			
Hg–N(2)	2.55(1)	N(2)–Hg–C(9)	96.6(7)
Hg–N(2′)	2.70(1)	N(2)–Hg–C(11)	98.1(6)
Hg–C(9)	2.09(2)	N(2′)–Hg–C(9)	95.8(7)
Hg–C(11)	2.03(2)	N(2′)–Hg–C(11)	96.6(6)
N(2)–Hg–N(2′)	71.7(4)	C(9)–Hg–C(11)	163.1(9)
In the cyanide groups			
C(9)–N(10)	1.10(2)	Hg–C(9)–N(10)	176(2)
C(11)–N(12)	1.10(3)	Hg–C(11)–N(12)	171(2)
In the bis(3,5-dimethyl-1-pyrazolyl)methane ligand			
N(1)–N(2)	1.39(2)	N(1′)–N(2′)	1.37(2)
N(1)–C(8)	1.52(3)	N(1′)–C(8)	1.48(2)
N(2)–C(3)	1.32(3)	N(2′)–C(3′)	1.32(2)
C(3)–C(4)	1.37(3)	C(3′)–C(4′)	1.39(4)
C(3)–C(6)	1.45(3)	C(3′)–C(6′)	1.48(3)
C(4)–C(5)	1.34(3)	C(4′)–C(5′)	1.36(4)
C(5)–N(1)	1.33(3)	C(5′)–N(1′)	1.36(3)
C(5)–C(7)	1.46(3)	C(5′)–C(7′)	1.46(3)
N(2)–N(1)–C(5)	112(2)	N(2′)–N(1′)–C(5′)	113(2)
N(2)–N(1)–C(8)	114(1)	N(2′)–N(1′)–C(8)	117(1)
C(5)–N(1)–C(8)	133(2)	C(5′)–N(1′)–C(8)	130(2)
N(1)–N(2)–C(3)	102(2)	N(1′)–N(2′)–C(3′)	109(2)
Hg–N(2)–N(1)	127(1)	Hg–N(2′)–N(1′)	122(1)
Hg–N(2)–C(3)	130(1)	Hg–N(2′)–C(3′)	128(1)
N(2)–C(3)–C(4)	113(2)	N(2′)–C(3′)–C(4′)	104(2)
N(2)–C(3)–C(6)	122(2)	N(2′)–C(3′)–C(6′)	124(2)
C(4)–C(3)–C(6)	125(2)	C(4′)–C(3′)–C(6′)	130(2)
C(3)–C(4)–C(5)	106(2)	C(3′)–C(4′)–C(5′)	114(2)
C(4)–C(5)–N(1)	107(2)	C(4′)–C(5′)–N(1′)	100(2)
C(4)–C(5)–C(7)	131(2)	C(4′)–C(5′)–C(7′)	132(2)
N(1)–C(5)–C(7)	122(2)	N(1′)–C(5′)–C(7′)	124(2)
N(1)–C(8)–N(1′)	112(2)		
Molecule B			
In the coordination sphere			
Hg–N(2)	2.40(1)	N(2)–Hg–C(9)	102.0(7)
Hg–N(2′)	2.51(1)	N(2)–Hg–C(11)	103.5(6)
Hg–C(9)	2.06(2)	N(2′)–Hg–C(9)	102.0(7)
Hg–C(11)	2.13(2)	N(2′)–Hg–C(11)	101.2(6)
N(2)–Hg–N(2′)	79.0(5)	C(9)–Hg–C(11)	148.2(8)
In the cyanide groups			
C(9)–N(10)	1.11(2)	Hg–C(9)–N(10)	170(2)
C(11)–N(12)	1.14(3)	Hg–C(11)–N(12)	176(2)
In the bis(3,5-dimethyl-1-pyrazolyl)methane ligand			
N(1)–N(2)	1.40(2)	N(1′)–N(2′)	1.35(2)
N(1)–C(8)	1.49(2)	N(1′)–C(8)	1.43(2)
N(2)–C(3)	1.38(2)	N(2′)–C(3′)	1.28(2)
C(3)–C(4)	1.43(3)	C(3′)–C(4′)	1.38(3)
C(3)–C(6)	1.45(3)	C(3′)–C(6′)	1.54(3)
C(4)–C(5)	1.33(3)	C(4′)–C(5′)	1.35(3)
C(5)–N(1)	1.35(3)	C(5′)–N(1′)	1.38(2)
C(5)–C(7)	1.51(3)	C(5′)–C(7′)	1.49(3)
N(2)–N(1)–C(5)	108(2)	N(2′)–N(1′)–C(5′)	110(1)
N(2)–N(1)–C(8)	121(1)	N(2′)–N(1′)–C(8)	120(1)
C(5)–N(1)–C(8)	130(2)	C(5′)–N(1′)–C(8)	130(1)
N(1)–N(2)–C(3)	107(1)	N(1′)–N(2′)–C(3′)	107(1)
Hg–N(2)–N(1)	118(1)	Hg–N(2′)–N(1′)	118(1)
Hg–N(2)–C(3)	134(1)	Hg–N(2′)–C(3′)	135(1)
N(2)–C(3)–C(4)	108(2)	N(2′)–C(3′)–C(4′)	111(2)
N(2)–C(3)–C(6)	119(2)	N(2′)–C(3′)–C(6′)	121(2)
C(4)–C(3)–C(6)	133(2)	C(4′)–C(3′)–C(6′)	128(2)
C(3)–C(4)–C(5)	107(2)	C(3′)–C(4′)–C(5′)	106(2)
C(4)–C(5)–N(1)	111(2)	C(4′)–C(5′)–N(1′)	106(2)
C(4)–C(5)–C(7)	127(2)	C(4′)–C(5′)–C(7′)	133(2)
N(1)–C(5)–C(7)	122(2)	N(1′)–C(5′)–C(7′)	121(2)
N(1)–C(8)–N(1′)	110(1)		

TABLE VII. Average Bond Distances (Å) and Angles (°) with their Standard Errors[a]

	N	x_m	σ_m	σ'_m
Hg–N	4	2.545	0.063	0.007
Hg–C	4	2.074	0.021	0.009
C–N	4	1.110	0.010	0.012
N(1)–N(2)	4	1.374	0.012	0.010
N(1)–C(8)	4	1.479	0.018	0.012
N(2)–C(3)	4	1.325	0.020	0.012
C(3)–C(4)	4	1.390	0.014	0.016
C(3)–C(6)	4	1.486	0.024	0.014
C(4)–C(5)	4	1.347	0.006	0.016
C(5)–N(1)	4	1.356	0.011	0.013
C(5)–C(7)	4	1.482	0.014	0.015
N–Hg–N	2	75.3	3.7	0.3
N–Hg–C	8	99.6	1.1	0.2
C–Hg–C	2	155.2	7.4	0.6
Hg–C–N	4	172.9	1.6	0.9
N(2)–N(1)–C(5)	4	110.5	1.0	0.8
N(2)–N(1)–C(8)	4	118.5	1.6	0.7
C(5)–N(1)–C(8)	4	130.8	0.7	0.8
N(1)–N(2)–C(3)	4	106.1	1.3	0.8
Hg–N–N	4	121.2	2.1	0.5
Hg–N–C	4	132.1	1.5	0.6
N(2)–C(3)–C(4)	4	109.1	1.9	0.9
N(2)–C(3)–C(6)	4	121.4	1.0	0.9
C(4)–C(3)–C(6)	4	129.2	1.7	0.9
C(3)–C(4)–C(5)	4	107.9	1.8	0.9
C(4)–C(5)–N(1)	4	106.0	2.0	0.9
C(4)–C(5)–C(7)	4	131.1	1.3	1.0
N(1)–C(5)–C(7)	4	121.9	0.7	1.0
N–C(8)–N	2	110.9	0.6	1.1

[a] All values were calculated from ref. 6.

both molecules A and B the distortion from the pure boat is very small (5–6°), and ϕ corresponds to a normal boat conformation; thus the ring is distorted from the pure boat in the direction of a half-boat and is flattened at the C(8) apex (the stern).

(2) The 'bite' of the ligand, *i.e.* the N–M–N angle (Table VIII), lies in the range 84–89° for all the compounds for which X-ray single crystal structure determinations have been carried out except for the two

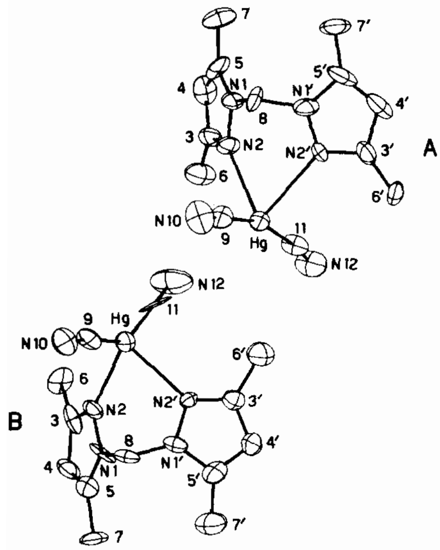

Fig. 1. ORTEP plot and numbering scheme of atoms down the *a* axis of the cell. Thermal ellipsoids enclose 30% of the electron density. Carbon atoms are indicated only by numbers and hydrogen atoms are omitted for clarity.

mercury compounds, which alone are neither square-planar nor octahedral.

(3) The four donor atoms are arranged around the mercury atom in a pattern which can hardly be regarded as tetrahedral since the C–Hg–N angles are smaller and the NC–Hg–CN (163.1(9)° or 148.2(8)°) significantly larger than 109°. The angles should be compared with the still larger C–Hg–C values (165–167°) reported for a series of adducts between 1.10-phenanthroline and R_2Hg (165.6(4)° or 165(1)° and 168(1)° when RH is phenylacetylene [11], 3-chloropropyne [12] respectively), or phenylmercury cyanide (167.5(4)°) [13] or between 3,4,7,8-tetramethyl-1,10-phenanthroline and $(Cl_2C{=}CCl)_2Hg$ (164.8(3)°) [18]. Clearly mercury cyanide is a better Lewis acid than most organomercury compounds, even those bearing other electronegative substituents.

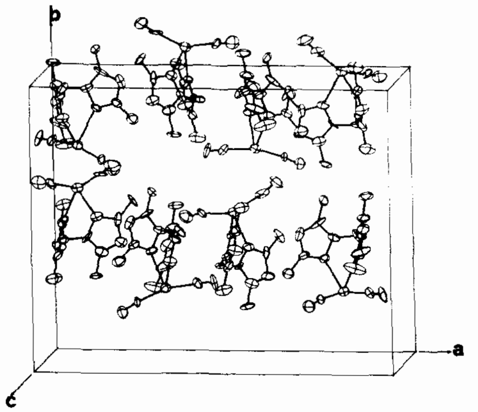

Fig. 2. Molecular packing in the unit cell viewed along the *c* axis.

(4) The Hg–CN bond distances range between 2.03(2), 2.06(2), 2.09(2) and 2.13(2) Å, but are not very different from the values reported for the same distance in the adduct between phenylmercury cyanide and phenanthroline (2.063(14) Å [13]), a

TABLE VIII. Parameters of the $LM(N{-}N)_2C$ Ring (N–N is Pyrazolato)

LM	M–N (A)	M–N–N	N–N–C	N–C–N	N–M–N	Reference
$Hg(CN)_2$ [a] (Mol. A)	2.55(1) 2.70(1)	127(1) 122(1)	114(1) 117(1)	112(2)	71.7(4)	this work
$Hg(CN)_2$ [a] (Mol. B)	2.40(1) 2.51(1)	118(1) 118(1)	121(1) 120(1)	110(1)	79.0(5)	this work
$MeHg^+$	2.16(1) 2.96(2)	123(1) 107(1)	122(1) 119(2)	113(1)	78.6(5)	9a
Me_3PtI [a]	2.236(4)	119.3(3)	119.3(4)	110.7(5)	84.7(2)	9b
$NiCl(\mu\text{-}Cl)$ [a]	2.099(3) 2.033(3)	116.8(2) 118.8(2)	118.6(3) 117.9(3)	110.6(3)	87.6(1)	9c
$(COD)Rh^+$	2.111(8) 2.097(7)	119.9(6) 120.2(5)	120.5(7) 119.7(7)	110.4(8)	88.4(3)	9d
Me_2PtI_2	2.183(7)	123.4(6)	119.8(8)	112.4(11)	84.4(4)	9e
Me_2PtI_2 [a]	2.236(4)	119.1(3)	120.5(5)	113.9(6)	85.8(2)	9e
$PdCl_2$	2.018(3) 2.030(3)	122.6(1) 123.8(1)	120.6(2) 119.9(2)	106.4(2)	87.8(1)	9f
PdI_2	2.004(3) 2.003(2)	120.8(2) 120.6(2)	118.8(3) 119.0(3)	109.4(3)	89.0(2)	9f

[a] N–N is 3,5-dimethylpyrazolato.

comparison more appropriate than that with mercury cyanide (2.015(3) [14]), or methylmercury cyanide (2.05(1) Å [15]), where the metal is linearly coordinated.

(5) The C≡N bond distances are comparable with those reported for mercury cyanide, methylmercury cyanide, and even $Ba[Hg(CN)]_4 \cdot 4$-pyridine (1.137(3) [14], 1.14(1) [15] or 1.124(9) Å [16], respectively).

(6) There are three long and one very long Hg–N bonds at 2.40(1), 2.51(1), 2.55(1) and at 2.70(1) Å, respectively; these values are in between the covalent length (2.1-2.2 Å) and the van der Waals distance (estimated to be 3.1 [14] or 2.85-2.90 Å [17]). For four-coordinated compounds we find the Hg–N bond distances are consistent with the suggestion made by Graddon [17] that in several adducts between HgX_2 and chelating bases such as dipyridyl there is steric misfit between the disposition of the two chelated donor atoms and the preferred stereochemistry at the mercury atom, thus leading to a weakening of the Hg–N bonds. Such a weakening may account for the observed dissociation in acetone solution; thus the apparent molecular weight in acetone solution has a value which is only *ca.* 60% of the formula weight.

The least-squares planes of the pyrazole rings, the deviations of atoms from them, and the values χ^2 ($n = 2$) with the corresponding probability P that the rings are non-planar are shown in Table IX.

X-ray Analysis

The crystal used for X-ray studies measured approximately 0.1 × 0.08 × 0.5 mm. Unit cell dimensions were derived from 25 measurements on a single crystal Philips PW1100 computer-controlled diffractometer with graphite-monochromated Mo Kα radiation at the Department of Organic Chemistry, University of Padua (Italy) and by least-squares refinement of 2θ values. The intensities were measured at room temperature with the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.02° s^{-1}) within the angular range $2 \leqslant \theta \leqslant 25°$. The intensities of two standard reflections were monitored every 180 min and showed no significant variation. Of the 2965 reflections collected, 1873 with $I \geqslant 3\sigma(I)$ were regarded as observed and used in the structure analysis. The usual Lorentz and polarization factors and an empirical absorption correction [19] with minimum and maximum absorption factors of 0.9909 and 1.6312 were applied. An approximate absolute scale factor and a mean thermal parameter of 6.39 Å^2 were determined by Wilson's method [20].

Crystal Data

$C_{13}H_{16}N_6Hg$: $M_r = 456.9$; orthorhombic; $a = 22.224(7)$, $b = 17.746(7)$, $c = 8.243(5)$ Å; $V = 3251(3)$ Å^3; $Z = 8$; $D_c = 1.87$ g cm^{-3}; $F(000) = 1728$; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 96.7 cm^{-1}. Systematic absences $hk0$, h odd and $0kl$, k odd; space group $Pb2_1a$ (nonstandard setting of C_{2v}, No 29). The statistical distribution of the normalized structure factors $|E|$ ($\langle E \rangle = 0.862$, $\langle E^2 - 1 \rangle = 0.769$, $\langle E^3 \rangle = 1.360$, $\langle E^4 \rangle = 2.086$) agrees with an acentric space group.

Structure Determination and Refinement

The asymmetric unit in the crystal is composed of two independent molecules. The structure was solved by direct methods, using 310 reflections ($|E| \geqslant 1.54$) with the program MULTAN-80 [21]. In the phase determination 8000 Σ_2 relationships were used and for the PSI(zero) figure of merit the phases of 100 reflections ($|E| \leqslant 0.06$) were taken into account. The E-map computed from the phase set with the best combined FOM = 2.4000 (ABS FOM = 1.1536, PSI(zero) = 3.480 and RESID = 5.99) correctly revealed two top peaks corresponding to the mercury atoms, which were confirmed by the three-dimensional Patterson map.

The positions of the mercury atoms were refined to $R = 0.145$ in three cycles of full-matrix least-squares refinement. A subsequent three-dimensional difference Fourier map revealed all the remaining non-hydrogen atoms. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters reduced R to 0.056. The hydrogen atoms were located on a difference Fourier map and were not refined, but were included in the calculations with same isotropic thermal parameters as their bonded atoms. Refinement was terminated at $R = 0.046$ ($R_w = 0.034$), when the maximum shift/error was 0.69. The maximum and minimum $\Delta\rho$ values on the final difference Fourier map were 0.54 and −0.86 e Å^{-3}, both close to a Hg atom. Unit weights were used in the early stages, and in the last two cycles a weight $w = \sigma^{-2}(|F_0|)$. Scattering factors for non-hydrogen atoms were taken from ref. 22 and those for hydrogen atoms from ref. 23, and anomalous dispersion effects were taken into account. The enantiomorphic structure was checked by reversing the sign of the y-coordinates of all atoms and a final R value of 0.080 was thereby obtained, indicating that the original model was correct. The final set of atomic coordinates is given in Table X.

Experimental

The samples were pumped to constant weight (20°, *ca.* 0.1 torr). Carbon, hydrogen and nitrogen analyses were carried out in our department or by Mr A. Canu at the University of Sassari. The molecular weight determinations were performed at the Pascher's Mikroanalitisches Laboratorium, Remagen, F.R.G.

TABLE IX. Least-squares Planes[a]

Equation, χ^2, P	Atoms	Displacements (Å)
Molecule A		
$-0.3660X + 0.0580Y - 0.9288Z + 3.2210 = 0$	N(1)*	−0.003(15)
	N(2)*	0.007(14)
	C(3)*	−0.017(21)
	C(4)*	0.011(19)
	C(5)*	−0.004(22)
	C(6)	−0.011(22)
	C(7)	0.004(19)
	C(8)	0.083(18)
	Hg	0.309(1)
$\chi^2 = 1.30$ $(n = 2), P = 47.5\%$		
$-0.9873X - 0.1428Y - 0.0695Z - 7.8007 = 0$	N(1′)*	0.009(17)
	N(2′)*	−0.010(16)
	C(3′)*	0.019(25)
	C(4′)*	−0.008(26)
	C(5′)*	−0.007(24)
	C(6′)	−0.251(32)
	C(7′)	−0.415(24)
	C(8)	−0.066(23)
	Hg	−0.459(1)
$\chi^2 = 1.47$ $(n = 2), P = 51.7\%$		
Molecule B		
$-0.4305X - 0.0384Y - 0.9018Z + 7.9459 = 0$	N(1)*	0.008(15)
	N(2)*	−0.009(13)
	C(3)*	0.014(17)
	C(4)*	−0.011(20)
	C(5)*	0.002(20)
	C(6)	0.023(18)
	C(7)	0.062(20)
	C(8)	0.075(19)
	Hg	0.317(1)
$\chi^2 = 1.69$ $(n = 2), P = 55.9\%$		
$0.9844X + 0.1628Y - 0.0675Z - 9.2108 = 0$	N(1′)*	0.004(15)
	N(2′)*	−0.008(15)
	C(3′)*	0.014(18)
	C(4′)*	−0.017(25)
	C(5′)*	0.002(19)
	C(6′)	0.036(26)
	C(7′)	0.049(23)
	C(8)	0.000(18)
$\chi^2 = 1.44$ $(n = 2), P = 51.1\%$		

[a] Starred atoms are included in the plane calculations.

Infrared spectra from 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 instrument.

^{1}H and ^{13}C NMR spectra were recorded on Varian EM-390 and FT80A instruments operating at room temperature (90 and 20 MHz).

No attempts were made to reduce the reaction times.

[Bis(1-pyrazolyl)methane]perchloratemercury(I)

An ethanol solution (20 ml) of the ligand (2.0 mmol) was added to a stirred ethanol solution of mercury(I) perchlorate (20 ml; 1.05 mmol). A white precipitate was obtained immediately and the compound **I** was filtered, and washed. Compounds **II**, **III**, **IV**, **V** (from the refrigerated ethanol solution

TABLE X. Coordinates and Equivalent Isotropic Thermal Parameters of Non-hydrogen Atoms (with e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	*B* (Å^2)
Molecule A				
Hg	0.36936(3)	0.29470	0.02751(8)	4.99(2)
N(1)	0.3485(8)	0.4897(9)	0.1167(17)	5.8(6)
N(2)	0.3243(7)	0.4176(8)	0.1315(16)	5.7(6)
C(3)	0.2705(10)	0.4317(13)	0.1937(25)	5.6(8)
C(4)	0.2598(9)	0.5070(13)	0.2115(23)	4.7(8)
C(5)	0.3101(13)	0.5426(11)	0.1646(25)	6.6(8)
C(6)	0.2277(11)	0.3724(13)	0.2303(26)	9.8(9)
C(7)	0.3254(8)	0.6223(13)	0.1581(23)	6.5(7)
C(8)	0.4104(10)	0.4922(11)	0.0400(21)	7.8(8)
N(1′)	0.4076(8)	0.4782(9)	−0.1372(19)	7.2(7)
N(2′)	0.3970(7)	0.4054(8)	−0.1851(15)	6.9(6)
C(3′)	0.3940(11)	0.4036(14)	−0.3449(24)	10.3(1.0)
C(4′)	0.4002(12)	0.4786(15)	−0.3898(28)	9.1(9)
C(5′)	0.4092(11)	0.5270(12)	−0.2636(32)	9.9(1.0)
C(6′)	0.3717(15)	0.3385(10)	−0.4391(19)	12.1(1.1)
C(7′)	0.4004(11)	0.6084(13)	−0.2484(25)	9.1(9)
C(9)	0.4496(7)	0.3012(15)	0.1583(19)	5.1(6)
N(10)	0.4908(7)	0.3018(16)	0.2323(18)	8.4(8)
C(11)	0.2961(8)	0.2555(9)	−0.0923(22)	6.0(6)
N(12)	0.2585(9)	0.2255(10)	−0.1494(21)	7.6(7)
Molecule B				
Hg	0.40462(4)	0.10509(5)	0.49593(11)	5.24(2)
N(1)	0.3850(7)	−0.0746(8)	0.5792(18)	4.7(5)
N(2)	0.3582(7)	−0.0049(9)	0.6096(15)	4.3(5)
C(3)	0.3031(7)	−0.0195(13)	0.6788(20)	4.5(7)
C(4)	0.2978(10)	−0.0996(13)	0.6963(23)	8.0(9)
C(5)	0.3477(11)	−0.1292(11)	0.6335(23)	6.4(9)
C(6)	0.2644(8)	0.0431(12)	0.7217(21)	5.8(7)
C(7)	0.3626(11)	−0.2119(9)	0.6133(22)	8.5(8)
C(8)	0.4442(8)	−0.0803(8)	0.4945(24)	5.0(6)
N(1′)	0.4377(7)	−0.0620(8)	0.3265(18)	4.8(6)
N(2′)	0.4265(7)	0.0093(7)	0.2800(17)	4.3(5)
C(3′)	0.4236(8)	0.0091(10)	0.1245(20)	4.7(7)
C(4′)	0.4301(11)	−0.0627(11)	0.0630(21)	7.9(9)
C(5′)	0.4403(8)	−0.1081(10)	0.1917(24)	5.0(7)
C(6′)	0.4125(12)	0.0827(9)	0.0294(26)	7.6(8)
C(7′)	0.4536(10)	−0.1898(15)	0.2081(26)	11.6(1.0)
C(9)	0.4849(8)	0.1092(13)	0.6200(20)	6.9(8)
N(10)	0.5240(7)	0.1058(12)	0.7035(19)	7.4(7)
C(11)	0.3312(8)	0.1644(9)	0.3902(26)	7.1(8)
N(12)	0.2940(10)	0.2000(11)	0.3325(27)	15.8(1.1)

this compound was obtained in crystalline form), and **VII** were obtained in a similar way. Compounds **VI**, **VIII** and **IX** were obtained from ethereal solution.

Supplementary Material

Thermal parameters, hydrogen coordinates, and a list of structure factors can be obtained from one of the authors (B. Bovio) on request.

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References

1 A. Lorenzotti, A. Cingolani, D. Leonesi and F. Bonati, *Gazz. Chim. Ital., 115,* 619 (1985).
2 K. Brodersen, R. Doellig and G. Liehr, *Z. Anorg. Allg. Chem., 464,* 17 (1981) and refs. therein.
3 A. Cingolani, A. Lorenzotti, D. Leonesi and F. Bonati, *Inorg. Chim. Acta, 81,* 127 (1984).
4 A. Cingolani, A. Lorenzotti, D. Leonesi and F. Bonati, *Gazz. Chim. Ital., 111,* 243 (1981).
5 J. Halfpenny, *Acta Crystallogr., Sect. B, 38,* 2049 (1982).
6 A. Domenicano, A. Vaciago and C. A. Coulson, *Acta Crystallogr., Sect. B, 31,* 221 (1975).
7 C. K. Johnson, 'ORTEP', *Report ORNL-3794,* Oak Ridge National Laboratory, Tenn., U.S.A., 1965.
8 K. N. Raymond, P. W. R. Corfield and J. A. Ibers, *Inorg. Chem., 7,* 1362 (1968); J. H. Hueehey, 'Inorganic Chemistry', 2nd edn., Harper and Row, New York, 1977, p. 345.
9 (a) A. J. Canty, C. V. Lee, N. Chaichit and B. M. Gatehouse, *Acta Crystallogr., Sect. B, 38,* 743 (1982); (b) H. C. Clark, G. Ferguson, V. K. Jain and M. Parvez, *J. Organomet. Chem., 270,* 365 (1984); (c) J. C. Jansen, H. van Koningsveld, J. A. C. van Ooijen and J. Reedijk, *Inorg. Chem., 19,* 170 (1980); (d) L. A. Oro, M. Esteban, R. M. Claramunt, J. Elguero, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem., 276,* 79 (1984); (e) H. C. Clark, G. Ferguson, V. K. Jain and M. Parvez, *Organometallics, 2,* 806 (1983); (f) G. Minghetti, M. Cinellu, A. L. Bandini, G. Banditelli and F. Demartin, *J. Organomet. Chem., 315,* 387 (1986).
10 D. Cremer and J. A. Pople, *J. Am. Chem. Soc., 97,* 1354 (1975).
11 E. Gutierrez-Puebla, A. Vegas and S. Garcia-Blanco, *Acta Crystallogr., Sect. B, 34,* 3382 (1978).
12 E. Gutierrez-Puebla, A. Vegas and S. Garcia-Blanco, *Cryst. Struct. Commun., 8,* 861 (1979).
13 A. Ruiz-Amil, S. Martinez-Carrera and S. Garcia-Blanco, *Acta Crystallogr., Sect. B, 34* 2711 (1978).
14 R. C. Seccombe and C. H. L. Kennard, *J. Organomet. Chem., 18,* 243 (1969).
15 J. C. Mills, H. S. Preston and C. H. L. Kennard, *J. Organomet. Chem., 14,* 33 (1968).
16 K. Brodersen, I. Beck, R. Beck, H. U. Hummel and G. Liehr, *Z. Anorg. Allg. Chem., 516,* 30 (1984).
17 D. P. Graddon, *Rev. Inorg. Chem., 4,* 211 (1982).
18 N. A. Bell and I. S. Nowell, *Acta Crystallogr., Sect. B, 36,* 447 (1980).
19 A. C. T. North, D. C. Phillips and F. C. Mathews, *Acta Crystallogr., Sect. A, 24,* 351 (1968).
20 A. J. C. Wilson, *Nature (London), 150,* 152 (1942).
21 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, 'MULTAN-80', Univer-

sity of York, U.K., and Louvain-la-Neuve, Belgium, 1980.

22 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

23 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, *42*, 3175 (1965).

24 (a) S. Trofimenko, *J. Am. Chem. Soc.*, *92*, 5118 (1970); (b) C. Ochoa, J. Elguero, J. P. Fayet and M. C. Vertut, *J. Heterocyclic Chem.*, *19*, 1141 (1982); (c) R. M. Claramunt, H. Hernandez, J. Elguero and S. Julia, *Bull. Soc. Chim. Fr.*, 5 (1983).