Structural Studies of Mercury(II) Halide Pyridine Complexes $[HgX_2(py)_2]$, X = Cl, Br, or I

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The structures of the three title compounds have been determined by single-crystal *X*-ray diffraction methods at 295(1) K. For $[HgCl_2(py)_2]$, (1), a redetermination, the cell is Monoclinic, space group $P2_1/n$, with a = 17.726(7), b = 8.572(3), c = 3.910(2) Å, β = 92.00(4)°, and Z = 2. The structure is a chloride-bridged polymeric lattice of $HgCl_4$ square-planar entities [Hg–Cl 2.754(2) and 2.765(2) Å] with pyridine ligands filling the *trans*-octahedral sites about the mercury atom [Hg–N 2.266(6) Å]. For $[HgBr_2(py)_2]$, (2), the cell is Orthorhombic, space group $Pca2_1$, with a = 18.023(5), b = 8.754(3), c = 8.592(3) Å, and Z = 4; the basic structural unit is the $[HgBr_2(py)_2]$ molecule [Hg–Br 2.478(3) and 2.483(3) Å, Br–Hg–Br 141.2(1)°; Hg–N 2.38(2) and 2.39(2) Å, N–Hg–N 90.7(7)°, N–Hg–Br 102.5(5)—104.3(4)°]. For $[HgI_2(py)_2]$, (3), the cell is also Orthorhombic, space group *Pnma*, with a = 14.545(7), b = 11.396(6), c = 8.510(5) Å, and Z = 4, the stuctural unit also being the $[HgI_2(py)_2]$ molecule with similar geometry to that of (2); in particular, Hg–I 2.70(1) and 2.65(1) Å, I–Hg–I 141.7(4)°.

COMPLEXES of mercury(II) halides with pyridine (py) have been studied extensively by vibrational spectroscopy;[1-5] only one complex, $[HgCl_2(py)_2]$, (1), has been the subject of a single-crystal *X*-ray study,[6] and is reputedly polymeric with octahedrally co-ordinated mercury and isomorphous with $[CuCl_2(py)_2]$.[7] The more recent vibrational studies suggest the bromide[3,4] (2) and iodide[3] (3) analogues to be monomeric with four-co-ordinate mercury.[3,4] As the earlier structure determination of $[HgCl_2(py)_2]$ is old, and reputedly different to that of the bromide and iodide analogues, it was decided to undertake determinations of all three complexes to clarify the situation. While good specimens of (1) and (2) were readily obtained by well established methods, (3) would not crystallize readily and a poor specimen was only fortuitously obtained from a solution of $[Hg(SEt)_2]$ and HgI_2 in pyridine.

EXPERIMENTAL

Preparation of Complexes and Preliminary Crystallographic Studies.—Crystals of $[HgX_2(py)_2]$ (X = Cl, Br, or I) were grown from solutions of the parent mercury(II) halides in pyridine. The crystals readily lose pyridine and were enclosed in capillaries for oscillation and Weissenberg photography. Preliminary results for $[HgCl_2(py)_2]$ were in agreement with cell dimensions reported earlier.[6] Suitable crystals of $[HgI_2(py)_2]$ could not be obtained in this way, and a better crystal was accidentally obtained (during a separate study) from a pyridine solution containing equimolar quantities of $[Hg(SEt)_2]$ and HgI_2. A powdered sample of $[HgI_2(py)_2]$, obtained from crystals grown from HgI_2 in pyridine and enclosed in a capillary, gave a Debye–Scherrer *X*-ray powder-diffraction pattern that could be indexed satisfactorily with the cell dimensions obtained from the crystal used for data collection. For iron-filtered Co-K_α radiation (λ = 1.7902 Å) results are recorded in the form of d spacings (Å) as $d_{\text{meas.}}[d_{\text{calc.}}(\text{index})]$ with abbreviations s (strong), m (medium), w (weak), br (broad): 6.95s,br [7.27 (200)], 5.64m [5.70 (020)], 4.45s [4.49 (220)], 3.94s [3.97 (221), 3.95 (311)], 3.44m [3.46 (410)], 2.75w [2.75 (013), 2.76 (402)], 2.69w [2.71 (113), 2.69 (412)], 2.57w [2.57 (213)], 2.48w [2.49 (422)], 2.34w [2.34 (142)], 2.28w [2.27 (033)], 1.98m [1.98 (124, 442)], and 1.84w [1.84 (134, 324, 404)].

Crystallography.—General. For each compound a unique data set was measured at 295 K within a given 2θ range determined by the extent of the data using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode and equipped with monochromatic Mo-K_α radiation (λ = 0.710 69 Å); n independent reflections were measured, n_o of these with $I > 3\sigma(I)$ being considered ' observed ' and used in the structure determination and refinement after correction for absorption. Full-matrix least-squares refinement was used in each case, anisotropic thermal parameters being used for the non-hydrogen atoms in each structure, except in the case of (3), where these could not validly be refined because of the limited data available. In all cases hydrogen atoms were included with positional parameters invariant at estimated trigonal values and U_H set at 1.25 $\langle U_{ii}(\text{parent C})\rangle$. Final residuals quoted are R, R', reflection weights being set at $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were used throughout, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[8] Computation was carried out using the ' *X*-RAY '76 ' program system[9] implemented on a Perkin-Elmer 8/32 computer. Tables of structure-factor amplitudes, hydrogen-atom parameters, thermal parameters, pyridine ring planes and geometries are listed in Supplementary Publication No. SUP 23182 (21 pp.).†

TABLE 1

Non-hydrogen atomic co-ordinates of $[HgCl_2(py)_2]$, (1)

Atom	x	y	z
Hg	0	0	0
Cl	0.081 5(1)	0.152 5(2)	0.510 9(5)
N	0.086 9(4)	−0.193 8(7)	0.028 8(15)
C(2)	0.158 5(5)	−0.164 2(10)	−0.051 4(22)
C(3)	0.213 4(6)	−0.274 7(13)	−0.040 2(28)
C(4)	0.195 8(7)	−0.425 4(12)	0.058 8(21)
C(5)	0.122 4(8)	−0.456 2(13)	0.137 1(35)
C(6)	0.069 5(5)	−0.338 2(10)	0.117 3(22)

Crystal data. (1), $C_{10}H_{10}Cl_2HgN_2$, M = 429.7, Monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, no. 14), a = 17.726(7), b = 8.572(3), c = 3.910(2) Å, β = 92.00(4)°,

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2

Non-hydrogen atomic co-ordinates of $[HgBr_2(py)_2]$, (2)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Hg	0.891 86(4)	0.791 71(10)	$\frac{3}{4}$			
Br	0.998 1(1)	0.630 5(3)	0.830 7(4)	0.817 6(1)	1.014 6(3)	0.837 5(5)
N	0.922 7(11)	0.855 0(24)	0.488 5(24)	0.801 4(9)	0.611 2(24)	0.661 4(27)
C(2)	0.884 2(13)	0.957 6(33)	0.411 1(37)	0.729 6(14)	0.646 4(30)	0.671 1(37)
C(3)	0.897 6(22)	0.989 7(37)	0.241 6(50)	0.675 8(17)	0.545 1(43)	0.616 7(45)
C(4)	0.952 2(18)	0.912 7(46)	0.176 7(52)	0.697 1(17)	0.409 7(40)	0.553 5(34)
C(5)	0.990 5(14)	0.805 3(37)	0.267 4(66)	0.769 7(19)	0.374 6(39)	0.542 9(55)
C(6)	0.972 3(15)	0.776 8(32)	0.418 2(32)	0.819 2(14)	0.479 9(36)	0.594 9(40)

$U = 593.7(4)$ Å^3, $Z = 2$, $D_c = 2.40$ g cm^{-3}, $F(000) = 396$, $2\theta_{max.} = 60°$, $n = 1\ 650$, $n_o = 1\ 292$. $R,R' = 0.033, 0.061$. Specimen size 0.14 × 0.21 × 0.60 mm (enclosed in capillary), $\mu_{Mo} = 129$ cm^{-1}. The cell setting follows that used previously.[6]

(2), $C_{10}H_{10}Br_2HgN_2$, $M = 518.6$, Orthorhombic, space group *Pca*2$_1$ (C_{2v}^5, no. 29), $a = 18.023(5)$, $b = 8.754(3)$, $c = 8.592(3)$ Å, $U = 1\ 356(1)$ Å^3, $Z = 4$, $D_c = 2.54$ g cm^{-3}, $F(000) = 936$, $2\theta_{max.} = 45°$, $n = 971$, $n_o = 708$, $R,R' = 0.030, 0.036$. Specimen size 0.19 × 0.16 × 0.45 mm (enclosed in capillary), $\mu_{Mo} = 167$ cm^{-1}.

(3), $C_{10}H_{10}HgI_2N_2$, $M = 612.7$, Orthorhombic, space group *Pnma* (D_{2h}^{16}, no. 62), $a = 14.545(7)$, $b = 11.396(6)$, $c = 8.510(5)$ Å, $U = 1\ 411(1)$ Å^3, $Z = 4$, $D_c = 2.89$ g cm^{-3},

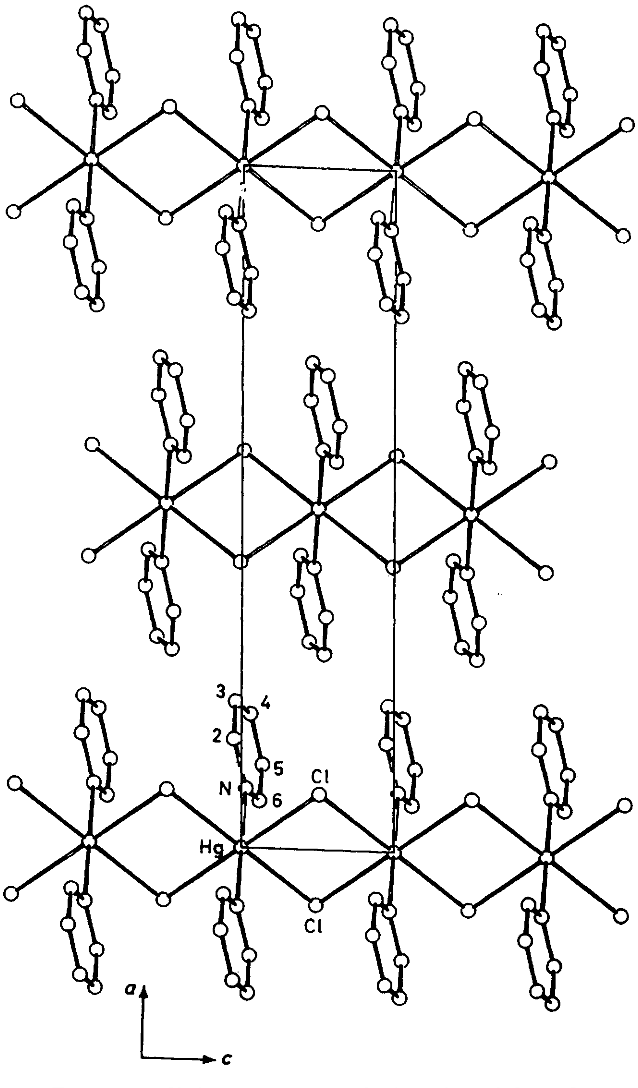


FIGURE 1 Unit-cell contents of (1) projected down *b*

TABLE 3

Non-hydrogen atom co-ordinates of $[HgI_2(py)_2]$, (3)

Atom	*x*	*y*	*z*
Hg	0.003 0(5)	$\frac{1}{4}$	0.065 8(5)
I(A)	0.165 5(6)	$\frac{1}{4}$	0.219 3(9)
I(B)	−0.067 7(7)	$\frac{1}{4}$	−0.221 4(9)
N	−0.069(4)	0.401(6)	0.197(7)
C(2)	−0.132(7)	0.484(7)	0.119(9)
C(3)	−0.184(5)	0.571(6)	0.184(8)
C(4)	−0.181(5)	0.579(8)	0.357(10)
C(5)	−0.130(7)	0.492(8)	0.431(9)
C(6)	−0.073(5)	0.406(7)	0.350(9)

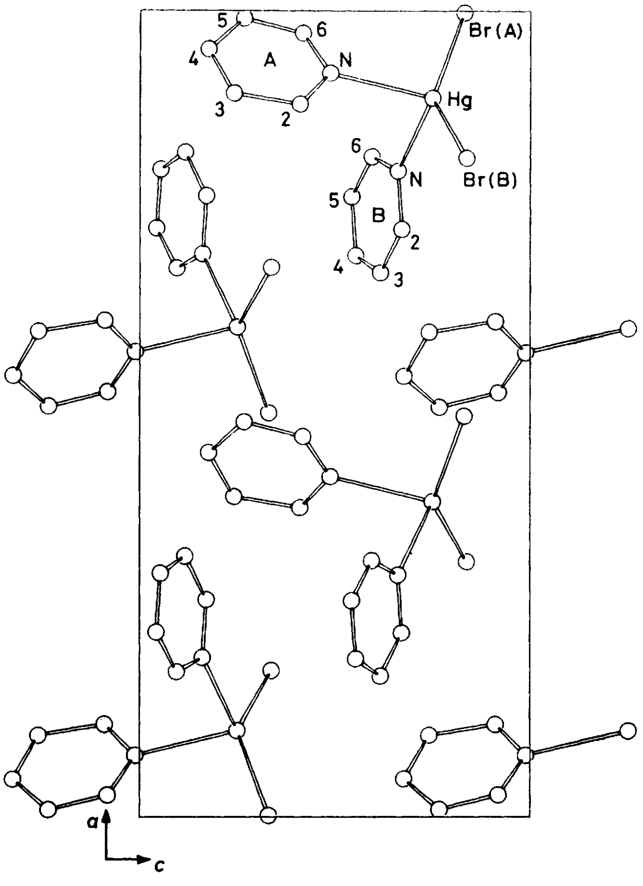


FIGURE 2 Unit-cell contents of (2) projected down *b*

$F(000) = 1\,080$, $2\theta_{max.} = 40°$, $n = 700$, $n_o = 317$, R,R', 0.095, 0.117. Specimen size: 0.10 × 0.15 × 0.25 mm (coated), $\mu_{Mo} = 146$ cm^{-1}.

Abnormal Features.—All samples lose pyridine in air. Compounds (1) and (2) were enclosed in capillaries, but for (3) only a small amount of material was available and a coated specimen was used yielding data of poor quality; the material was difficult to obtain suitably crystalline and no better sample presented itself.

Atomic numbering for the pyridine ring is as shown in Figures 1—3; the code for hydrogen atoms follows that for the carbon atoms.

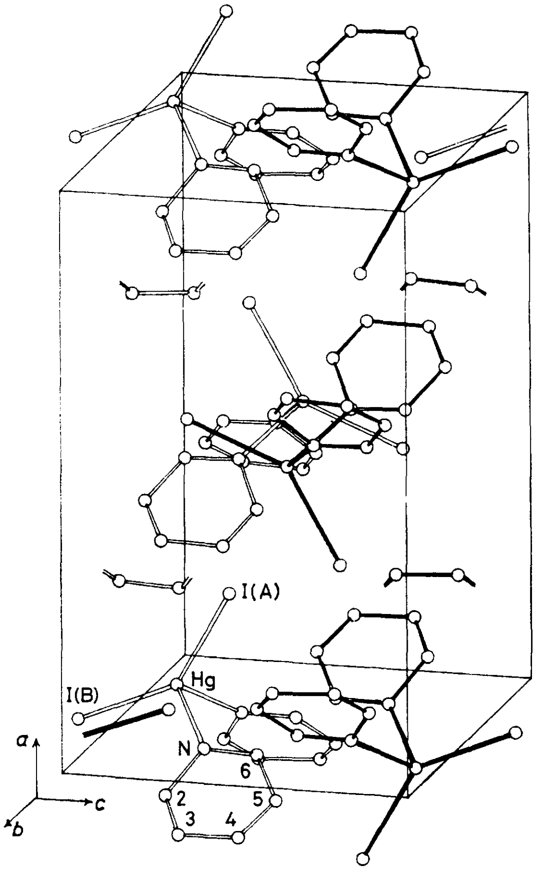
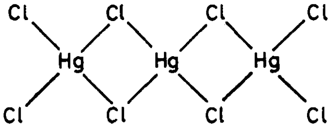


FIGURE 3 Unit-cell contents of (3)

RESULTS AND DISCUSSION

The stoicheiometry of all three complexes is shown to be $[HgX_2(py)_2]$ as expected.

Compound (1) comprises an infinite one-dimensional polymeric array of $[HgCl_2(py)_2]$ units running parallel to *c*; successive mercury atoms are separated by the *c* cell spacing, 3.910(2) Å, and bridged by pairs of chlorine atoms. The two independent Hg–Cl distances are almost identical, 2.754(2) and 2.765(2) Å, and the disposition of the four symmetry-related chlorines about the mercury is almost a perfect square (see below). The angle at the chlorine atoms is 90.21(7)°. In mercury(II) chloride the mean Hg–Cl distance is reported to be 2.291(9) Å,[10] and thus in spite of the increased co-ordination number for mercury in the present compound it is apparent that the Hg–Cl bonds are quite weak. By contrast, the mercury–nitrogen bonds, 2.266(6) Å, which make up a pseudo-octahedral co-ordination environment about the mercury are quite strong, and similar to those in the related complex $[Hg(O_2CCF_3)_2(py)_2]$ which has *trans*-pyridine ligands [N–Hg–N 170.2(6)°, Hg–N 2.11(2), 2.13(2) Å] and five weaker bonds to oxygen atoms in an equatorial plane [2.56(1)—2.87(2) Å].[11]



The complex $[HgBr_2(py)_2]$, (2), has a structure quite different from that of (1), with each mercury atom clearly four-co-ordinated by two bromine and two pyridine ligands with no suggestion of polymer formation. The Hg–N bonds are appreciably longer than in (1) in spite of the reduced co-ordination number, the two independent values being 2.38(2) and 2.39(2) Å, while the two (equal) Hg–Br distances are very much shorter than the Hg–Cl distances in (1), being 2.478(3) and 2.483(3) Å, suggesting that in (2) relative to (1) Hg–X bond order has been increased at the expense of Hg–N bond order. This is supported by the observation that in the mercury environment of (2), which is a very good approximation to *mm* point symmetry, Br–Hg–Br [141.2(1)°] is very much larger than N–Hg–N [90.7(7)°].

TABLE 4

Mercury halide environments of $[HgCl_2(py)_2]$, (1) (independent values only)

(*a*) Distances (Å)	
Hg–Cl	2.754(2)
Hg–N	2.266(6)
Hg–Cl^{I}	2.765(2)
(*b*) Angles (°)	
Cl–Hg–N	88.5(2)
Cl–Hg–Cl^{I}	90.21(6)
Cl–Hg–Cl^{II}	180(—)
N–Hg–Cl^{I}	90.6(2)
Hg–Cl–Hg^{III}	90.21(7)

Transformations of the asymmetric unit: I $x, y, z - 1$; II $\bar{x}, \bar{y}, \bar{z}$; III $x, y, 1 + z$.

The structure of $[HgI_2(py)_2]$, (3), although less precise than the other two, contains basic units of single pseudo-tetrahedral molecules with internal pseudo-*mm* symmetry resembling the structure of (2) rather than (1) [(2) and (3) are not isomorphous, however]. Although the precision of the Hg–N distance determination is very poor, the angular geometry, in particular I–Hg–I, strongly suggests a close similarity in relative bond strengths of Hg–X and Hg–N for (2) and (3) (Table 5). The most closely related iodomercury(II) complex reported previously is the 1,2-diaminoethane complex $[Hg_3I_6(en)_2]$ which contains the species $[HgI(en)]^+$, $[HgI_3]^-$, and $[HgI_2(en)]$ in equal proportions.[12] The neutral complex, like $[HgI_2(py)_2]$, contains the moiety 'HgI_2N_2' with Hg–I 2.673(3) and 2.702(3) and Hg–N

TABLE 5

Mercury halide environments of $[HgBr_2(py)_2]$, (2), and $[HgI_2(py)_2]$, (3)

Atoms	$[HgBr_2(py)_2]$	$[HgI_2(py)_2]$
(*a*) Distance (Å)		
Hg–X(A)	2.478(3)	2.70(1)
Hg–X(B)	2.483(3)	2.65(1)
Hg–N(A)	2.38(2)	2.30(6)
Hg–N(B)	2.39(2)	
(*b*) Angles (°)		
X(A)–Hg–X(B)	141.2(1)	141.7(4)
X(A)–Hg–N(A)	102.5(5)	99(2)
X(A)–Hg–N(B)	103.9(5)	
X(B)–Hg–N(A)	103.2(5)	106(2)
X(B)–Hg–N(B)	104.3(4)	
N(A)–Hg–N(B)	90.7(7)	97(2)

2.32(3) and 2.37(3) Å, similar to those in $[HgI_2(py)_2]$ [2.65(1), 2.70(1), and 2.30(6) Å, respectively].

The structural studies reported here confirm that $[HgCl_2(py)_2]$ has a polymeric structure, and confirm the more recent vibrational studies which suggested that $[HgX_2(py)_2]$ (X = Br [3,4] and I [3]) are monomeric.

We gratefully acknowledge receipt of a grant from the Australian Research Grants Committee in support of this work.

[1/565 *Received, 9th April*, 1981]

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