tively. If Cl(2″) and Cl(4) are considered to be within the coordination sphere of Hg(1), the resulting polyhedron about the metal resembles that of an elongated trigonal bipyramid with the equatorial Cl(1), Cl(2″), Hg(1), Cl(4) unit almost planar.

Within the $[(Me_2EtP)HgCl_3]^-$ anion, Hg(2) is surrounded by a distorted tetrahedral arrangement with the angles at Hg ranging from 98·2 to 132·9°. This angular distortion may again reflect the donor ability of the phosphine and certainly the largest deviation from a regular tetrahedral angle involves P and Cl(4), the two atoms closest to Hg.

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Polymeric Dibromo(2,4-dimethylpyridine)mercury(II)

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Abstract. $[HgBr_2(C_7H_9N)]$, $C_7H_9Br_2HgN$, $M_r = 467·55$, monoclinic, Cc, $a = 12·750$ (11), $b = 10·804$ (11), $c = 7·780$ (8) Å, $\beta = 94·00$ (5)°, $U = 1069·11$ Å^3, Mo $K\alpha$, $\lambda = 0·71069$ Å, $Z = 4$, $D_m = 2·91$ (3), $D_c = 2·90$ Mg m^{-3}, μ(Mo $K\alpha$) = 21·16 mm^{-1}, $F(000) = 832$. The final $R = 0·053$ for 684 observed reflections. The structure is polymeric, Hg being pentacoordinate within a distorted coordination polyhedron of a N and four Br atoms. Units of (2,4-dimethylpyridine)HgBr$_2$ are linked together by Br bridges to give single chains running parallel to **c**. Preliminary photographic evidence suggests that the analogous (2,4-dimethylpyridine)HgCl$_2$ has a similar structure.

Introduction. Hg^{II} halides are known to form 1:1 complexes with a wide range of neutral unidentate ligands (Dean, 1978). The types of structure adopted by these complexes in the solid state are numerous and contain Hg in a variety of coordination polyhedra. The coordination number of Hg ranges from four [e.g. (Ph$_3$PSe)HgCl$_2$, Cl-bridged dimer (Glasser, Ingram, King & McQuillan, 1969); (guanosine)HgCl$_2$, zigzag chain structure (Authier-Martin, Hubert, Rivest &

Beauchamp, 1978)] to five [e.g. (tetrahydrothiophene)HgCl$_2$, polymeric Cl-bridged structure (Brändén, 1964)] and to six [e.g. (tetrahydrofuran)HgBr$_2$, Br-bridged double-chain structure (Frey, 1970)]. However, few crystallographic studies of LHgX$_2$ complexes in which L functions as a unidentate N-donor ligand have been reported, and the available data appear to be limited to (guanosine)HgCl$_2$ (Authier-Martin et al., 1978) and (2,4,6-trimethyl-pyridine)HgCl$_2$ (Kulpe, 1967). To broaden the crystallographic base and hence facilitate establishment of vibrational spectra–structure correlations for such N-donor systems, we now report the X-ray study of (2,4-dimethylpyridine)HgX_2 (X = Cl, Br).

Addition of an ethanolic solution of 2,4-dimethyl-pyridine (0·005 mol) to a solution of either Hg^{II} chloride or bromide (0·005 mol) in ethanol gave complexes of composition (C$_7$H$_9$N)HgX_2 (X = Cl or Br). Great difficulty was encountered in obtaining crystals of a quality suitable for single-crystal X-ray analysis. Despite repeated recrystallization from a variety of solvents, the quality of the colourless crystals for both complexes was poor. Thus while unit-cell parameters were obtained from Weissenberg and precession photographs for both compounds (Table 1), only crystals of the Br complex were at all suitable for data collection.

Table 1. *Crystal data for* (2,4-*dimethylpyridine*)HgX₂

	$X = \text{Br}$	$X = \text{Cl}$
a (Å)	12·750 (11)	12·361 (21)
b (Å)	10·804 (11)	10·934 (18)
c (Å)	7·780 (8)	7·504 (12)
β (°)	94·00 (5)	95·33 (9)
D_m (Mg m⁻³)	2·91	2·47
D_c ($Z = 4$) (Mg m⁻³)	2·90	2·49
Space group*	Cc	Cc

* Although the observed systematic absences [hkl: $h + k = 2n + 1$; $h0l$: l (h) $= 2n + 1$] do not distinguish between the space groups Cc and $C2/c$, $Z = 4$ for $C2/c$ requires the molecule to have C_2 or $\bar{1}$ symmetry. The asymmetric nature of the methyl substituents in the pyridine ring precludes this and both complexes have been assigned to the space group Cc.

An irregular crystal of (2,4-dimethylpyridine)-HgBr₂, 0·17 × 0·18 × 0·28 mm, was selected and mounted with **c** coincident with the rotation (ω) axis of a Stoe Stadi 2 two-circle diffractometer. With monochromated Mo $K\alpha$ radiation and the background–ω-scan–background technique, 927 reflections were measured of which 684 had $I > 2\sigma(I)$ and were considered to be observed. [The net intensity $I = T - B$, where $T =$ scan count, $B =$ mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$, where $c =$ scan time, $t =$ time for background measurements at each end of the scan.] Corrections for Lorentz and polarization effects were made. Attempts were made to apply corrections for absorption, but the irregular shape of the crystal prevented a satisfactory treatment. The large errors of the positional parameters (particularly for the ligand atoms) and the associated bond distances and angles can be attributed in part to the poor quality of the crystal and the lack of a successful absorption correction. The y coordinate of the Hg atom (the x and z values being fixed at 0·00 and 0·25 respectively) and the Br positions were determined from the Patterson function. The remaining non-H atoms were located from successive electron-density maps.

Scattering factors were calculated with an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme was $w = 0·5262/[\sigma^2(F_o) + 0·0043(F_o)^2]$. Full-matrix refinement with anisotropic temperature factors for Hg and Br and isotropic for the remaining non-H atoms gave the final $R = 0·053$ and $R' = 0·054$. Atomic parameters are given in Table 2.*

Discussion. Bond lengths and angles are given in Table 3 and mean planes in Table 4. The complex adopts a polymeric Br-bridged structure in which Hg is tetracoordinate (Fig. 1). N, Br(1) and Br(2) form a distorted trigonal arrangement about Hg with bond angles at the central atom varying from 106 to 129 (1)°. The

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

Symmetry code: superscript: none x,y,z; (') x, $-y$, 0·5 + z; ('') $x, -y, -0·5 + z$.

Hg–Br(1)	2·621 (3)	C(1)–C(2)	1·37 (5)
Hg–Br(1')	2·911 (3)	C(1)–C(7)	1·54 (5)
Hg–Br(2)	2·486 (4)	C(2)–C(3)	1·34 (5)
Hg–Br(2'')	3·548 (4)	C(3)–C(4)	1·49 (5)
Hg–N	2·21 (2)	C(3)–C(6)	1·47 (6)
N–C(1)	1·30 (5)	C(4)–C(5)	1·40 (5)
N–C(5)	1·38 (5)		

Br(1)–Hg–Br(1')	92·4 (2)	Hg–N–C(1)	128 (3)
Br(1)–Hg–Br(2)	122·2 (2)	Hg–N–C(5)	115 (2)
Br(1)–Hg–Br(2'')	83·5 (2)	C(1)–N–C(5)	117 (3)
Br(1)–Hg–N	106 (1)	N–C(1)–C(2)	125 (3)
Br(1')–Hg–Br(2)	100·8 (2)	N–C(1)–C(7)	114 (3)
Br(1')–Hg–Br(2'')	164·9 (3)	C(2)–C(1)–C(7)	121 (3)
Br(1')–Hg–N	90 (1)	C(1)–C(2)–C(3)	123 (4)
Br(2)–Hg–Br(2'')	93·6 (2)	C(2)–C(3)–C(4)	115 (3)
Br(2)–Hg–N	129 (1)	C(2)–C(3)–C(6)	126 (4)
Br(2'')–Hg–N	77 (1)	C(4)–C(3)–C(6)	119 (3)
Hg–Br(1)–Hg''	91·6 (2)	C(3)–C(4)–C(5)	118 (3)
Hg–Br(2)–Hg'	80·3 (2)	N–C(5)–C(4)	123 (3)

Table 2. *Fractional positional parameters* (×10⁴) *with e.s.d.'s in parentheses*

	x	y	z
Hg	0	372 (1)	2500
Br(1)	1455 (3)	−425 (4)	4779 (5)
Br(2)	−1396 (3)	−1007 (5)	1189 (7)
N	40 (33)	2414 (21)	2656 (60)
C(1)	−738 (25)	3187 (33)	2384 (50)
C(2)	−651 (30)	4444 (36)	2524 (55)
C(3)	241 (25)	5015 (29)	3063 (46)
C(4)	1144 (28)	4175 (34)	3541 (52)
C(5)	1002 (26)	2912 (30)	3228 (48)
C(6)	405 (46)	6362 (53)	3215 (85)
C(7)	−1787 (33)	2567 (41)	1758 (64)

Table 4. *Equations of least-squares planes referred to orthogonal axes with distances* (Å) *of relevant atoms from the planes in square brackets*

Plane *A*: Hg, Br(1), Br(2), N

$$0·6376X - 0·0655Y - 0·7675Z + 1·7657 = 0·0000$$

[Hg, 0·155 (0); Br(1), −0·043 (4); Br(2), −0·056 (5); N, −0·056 (45)]

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

$$0·3213X + 0·0827Y - 0·9433Z + 1·7724 = 0·0000$$

[N, 0·014 (46); C(1), −0·032 (38); C(2), 0·011 (42); C(3), 0·024 (37); C(4), −0·040 (40); C(5), 0·024 (35); C(6), 0·097 (65); C(7), −0·048 (49)]
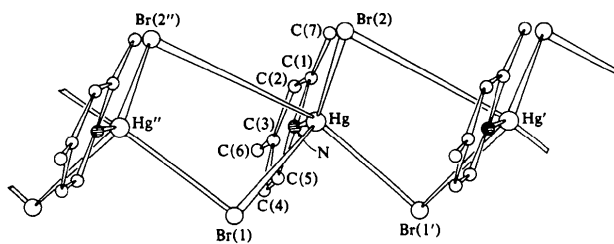
Fig. 1. Single chain running parallel to the c direction.

NHgBr$_2$ unit is distinctly non-planar, Hg lying out of the best least-squares plane by 0·155 Å. The Hg—Br distance for Br(1) is significantly longer than that involving Br(2) and appears preferentially to reflect the influence of the heterocyclic ligand upon Hg. Thus, while the Hg—Br(2) distance of 2·486 (4) Å is similar to that found in HgBr$_2$ itself (2·48 Å; Verweel & Bijvoet, 1931), the longer Hg—Br(1) distance of 2·621 (3) Å is comparable to the values [2·554, 2·615 (5) Å] found in the strongly coordinated [tris(σ-diphenylarsinophenyl)arsine]HgBr$_2$ complex, which is monomeric with Hg tetrahedrally coordinated (Dyer, Goodall, Mais, Powell & Venanzi, 1966). The coordination about Hg in the present complex is completed by two further Br atoms at 2·911 (3) and 3·548 (4) Å from the metal. The resulting coordination polyhedron is considerably distorted and its description as an elongated trigonal bipyramid seems inappropriate. This is best seen by considering the Br(1')—Hg—Br(2") angle of only 164·9 (3)° and the (axial Br)—Hg—(equatorial atom) angles which vary from 77 to 101°. Additionally, the Br(2")···Hg interaction must be extremely weak, because the interatomic distance of 3·548 Å is significantly longer than the Hg—Br bridging distances [2·605, 3·142 (1) Å] found in the dimeric (2,2'-bipyridine)HgBr$_2$ complex (Craig, Farhangi, Graddon & Stephenson, 1973) and is only just within the sum of the van der Waals radii for Br (1·95 Å; Pauling, 1960) and Hg [1·73 Å; the upper limit suggested by Grdenić (1965)].

The chain structure in the present complex is comparable to that in (2,4,6-trimethylpyridine)HgCl$_2$, except that in the latter the Hg$_2$Cl$_2$ bridges contain

centres of symmetry and the trigonal NHgCl$_2$ unit is effectively planar and less distorted [Hg—Cl, 2·455, 2·542 (18) Å; N—Hg—Cl, 122·5, 128·4° (Kulpe, 1967)]. Bond distances and angles within the 2,4-dimethylpyridine ligand are as expected and fall into the range of values observed for methyl-substituted pyridines (e.g. Kulpe, 1967; Stahlin & Oswald, 1971). The heterocyclic ring is effectively planar and twisted relative to the NHgBr$_2$ mean plane by 22·6°. A similar arrangement is found in (2,4,6-trimethylpyridine)-HgCl$_2$, for which the angle of twist of the heterocyclic ring from the NHgCl$_2$ plane is calculated to be 30·9°.

The similarity in unit-cell constants, and close correspondence of the Weissenberg and precession photographs, suggests that (2,4-dimethylpyridine)-HgCl$_2$ has a similar polymeric structure to that found for the Br analogue.

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