

would be difficult to reconcile with metal to ligand back-bonding. The mean N—C and C—S distances in $\text{Na}_3[\text{V}(\text{NCS})_6] \cdot 12\text{H}_2\text{O}$, 1.152 (3) and 1.631 (2) Å, agree well with N—C and C—S distances found in N-bonded thiocyanato complexes (Norbury, 1975).

The water molecules appear to be loosely bound in the structure, the only short O...O contacts being those between O(2) and O(4), *i.e.* 2.951 (8) and 2.989 (8) Å. The positions of the H atoms bonded to O(4) are also consistent with hydrogen bonding. All other O...O contacts are greater than 3.10 Å. As is seen in Fig. 1, the thermal parameters of some of the O atoms are rather large. This could be due either to partial loss of water or to disorder in the positions of the loosely bound water molecules. It was not, however, considered to be in the interest of computer economy to investigate these points further, as it seemed unlikely that the geometry of the $[\text{V}(\text{NCS})_6]^{3-}$ ion would be affected. Both Na ions are surrounded by a distorted octahedron of water molecules, the Na—O contacts ranging from 2.364 (4) to 2.462 (5) Å for Na(1) and from 2.279 (7) to 2.661 (7) Å for Na(2).

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Bis(pyridine)mercury(II) Bis(trifluoroacetate)

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Abstract. $\text{Hg}(\text{C}_5\text{H}_5\text{N})_2(\text{CO}_2\text{CF}_3)_2$, monoclinic, $P2_1/c$, $a = 9.83$ (1), $b = 9.85$ (1), $c = 20.57$ (2) Å, $\beta = 115.8$ (1)°, $D_m = 2.13$, $D_c = 2.13$ g cm⁻³ with $Z = 4$. The structure has been determined from 1620 diffractometer-measured intensities (Mo $K\alpha$, $\lambda = 0.7107$ Å) and refined to $R = 0.067$. There is sevenfold coordination around Hg with two Hg—N bonds of 2.11 (2) and 2.13 (2) Å, the N—Hg—N angle is 170.2 (6)°. Five equatorial Hg—O bonds of 2.73 (2), 2.56 (2), 2.87 (2), 2.59 (1) and 2.64 (2) Å are formed to the trifluoroacetate anions, the cation being $\text{Hg}(\text{C}_5\text{H}_5\text{N})_2^{2+}$.

Introduction. The title compound was obtained as the stable end-product of the reaction of pyridine with mercuric trifluoroacetate. Evaporation of excess pyridine yielded prismatic crystals which were stable in air but decomposed slowly on exposure to X-rays.

Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) were used to obtain the cell dimensions and space group. Intensity measurements were made on a Stoe STADI-2 automatic two-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A crystal of dimensions 0.4 × 0.3 × 0.2 mm, set about a , was used; the limiting 2θ angle was 40°. Of the 2086 intensities measured, 1620 with $I > 3\sigma(I)$ were used for the structure determination. Absorption corrections and data reduction were carried out using the *SHELX* suite of programs (Sheldrick, 1976), the remainder of the calculations were done with the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Patterson maps were used to obtain the Hg position and a Fourier map phased on Hg gave the remainder of the non-H atoms. Least-squares refinement of all atomic positions, aniso-

tropic U_{ij} for Hg and isotropic U values for other atoms was alternated with refinement of the interlayer scale factors of the intensity data sets, until convergence was reached at $R = 0.067$; no improvement was found on inclusion of H atoms at their expected positions.

Atomic scattering factors for Hg were those of Cromer & Mann (1968); values for other atoms were

Table 1. Fractional atomic coordinates ($\times 10^3$, $\times 10^4$ for Hg) and temperature factors (\AA^2 , $U \times 10^3$, $U_{ij} \times 10^4$)

	x	y	z	U
N(1)	861 (2)	527 (2)	606 (1)	59 (5)
C(5)	969 (3)	560 (3)	674 (1)	80 (8)
C(6)	943 (3)	658 (3)	717 (2)	89 (8)
C(7)	802 (3)	725 (3)	688 (2)	90 (8)
C(8)	694 (3)	687 (3)	619 (1)	81 (8)
C(9)	730 (3)	591 (3)	580 (1)	70 (7)
N(2)	910 (2)	224 (2)	472 (1)	65 (5)
C(10)	44 (3)	186 (3)	471 (2)	85 (8)
C(11)	55 (3)	84 (3)	428 (1)	72 (7)
C(12)	917 (3)	23 (3)	379 (2)	106 (10)
C(13)	781 (3)	58 (3)	376 (2)	103 (10)
C(14)	776 (3)	162 (3)	424 (2)	95 (9)
O(1)	618 (2)	279 (1)	524 (1)	83 (5)
C(1)	680 (3)	208 (3)	575 (1)	73 (7)
O(2)	815 (2)	191 (2)	613 (1)	84 (5)
C(2)	578 (6)	123 (6)	601 (3)	167 (16)
F(1)	612 (3)	139 (4)	666 (2)	221 (12)
F(2)	436 (3)	166 (3)	570 (1)	166 (8)
F(3)	584 (3)	-1 (4)	590 (2)	209 (12)
O(3)	188 (2)	461 (2)	562 (1)	114 (7)
C(3)	238 (3)	412 (3)	624 (2)	78 (7)
O(4)	173 (2)	334 (2)	647 (1)	89 (5)
C(4)	413 (5)	463 (6)	673 (3)	150 (15)
F(4)	490 (3)	452 (3)	642 (1)	180 (10)
F(5)	460 (3)	375 (3)	728 (2)	191 (10)
F(6)	403 (3)	578 (4)	696 (2)	219 (13)
Hg	8996 (1)	3661 (1)	5468 (1)	

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	782 (39)	674 (7)	538 (7)	36 (5)	257 (5)	15 (8)

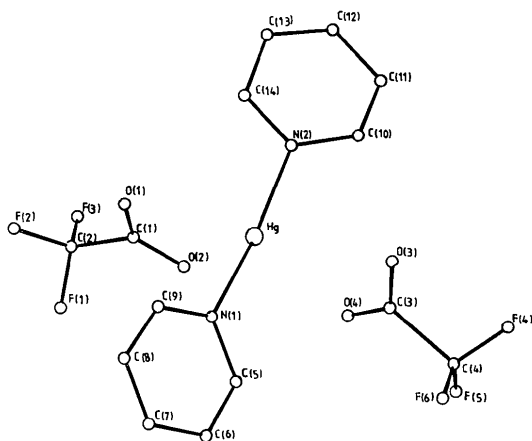


Fig. 1. Perspective view of the asymmetric unit of bis(pyridine)mercury(II) bis(trifluoroacetate).

taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and temperature factors are listed in Table 1.*

Discussion. The unit of the structure is in Fig. 1 and bond distances and angles are listed in Table 2 and Fig. 2. The coordination around the Hg atom is also shown in Fig. 2.

The Hg atom is primarily bonded to the two pyridine N atoms at distances which are in the typical covalent

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33671 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA) and angles ($^\circ$)

(a) Distances not involving Hg		(c) Other angles	
N(1)—C(5)	1.38 (3)	Hg—N(1)—C(5)	121 (2)
C(5)—C(6)	1.39 (4)	Hg—N(1)—C(9)	121 (1)
C(6)—C(7)	1.41 (4)	C(5)—N(1)—C(9)	119 (2)
C(7)—C(8)	1.40 (3)	N(1)—C(5)—C(6)	122 (2)
C(8)—C(9)	1.37 (4)	C(5)—C(6)—C(7)	119 (2)
C(9)—N(1)	1.33 (3)	C(6)—C(7)—C(8)	118 (3)
N(2)—C(10)	1.39 (4)	C(7)—C(8)—C(9)	120 (2)
C(10)—C(11)	1.36 (4)	C(8)—C(9)—N(1)	123 (2)
C(11)—C(12)	1.42 (3)	Hg—N(2)—C(10)	123 (1)
C(12)—C(13)	1.36 (5)	Hg—N(2)—C(14)	117 (2)
C(13)—C(14)	1.46 (5)	C(10)—N(2)—C(14)	119 (2)
C(14)—N(2)	1.39 (3)	N(2)—C(10)—C(11)	124 (2)
O(1)—C(1)	1.20 (3)	C(10)—C(11)—C(12)	117 (3)
O(2)—C(1)	1.22 (3)	C(11)—C(12)—C(13)	123 (3)
C(2)—C(1)	1.56 (7)	C(12)—C(13)—C(14)	118 (3)
C(2)—F(1)	1.26 (7)	C(13)—C(14)—N(2)	119 (3)
C(2)—F(2)	1.33 (6)	O(1)—C(1)—O(2)	130 (3)
C(2)—F(3)	1.25 (7)	O(1)—C(1)—C(2)	117 (3)
O(3)—C(3)	1.25 (4)	O(2)—C(1)—C(2)	113 (3)
O(4)—C(3)	1.21 (4)	C(1)—C(2)—F(1)	113 (4)
C(4)—C(3)	1.68 (5)	C(1)—C(2)—F(2)	112 (4)
C(4)—F(4)	1.29 (7)	C(1)—C(2)—F(3)	113 (5)
C(4)—F(5)	1.26 (6)	F(1)—C(2)—F(2)	102 (5)
C(4)—F(6)	1.20 (7)	F(1)—C(2)—F(3)	107 (5)
		F(2)—C(2)—F(3)	110 (4)
		O(3)—C(3)—O(4)	127 (2)
		O(3)—C(3)—C(4)	114 (3)
		O(4)—C(3)—C(4)	119 (3)
		C(3)—C(4)—F(4)	106 (3)
		C(3)—C(4)—F(5)	104 (4)
		C(3)—C(4)—F(6)	107 (4)
		F(4)—C(4)—F(5)	108 (4)
		F(4)—C(4)—F(6)	113 (5)
		F(5)—C(4)—F(6)	119 (5)

(b) Angles around Hg	
N(1)—Hg—N(2)	170.2 (0.6)
N(1)—Hg—O(1)	85.1 (0.6)
N(1)—Hg—O(2)	90.9 (0.7)
N(1)—Hg—O(3)	96.3 (0.7)
N(1)—Hg—O(4)	90.8 (0.6)
N(1)—Hg—O(3 ¹)	86.0 (0.8)
N(2)—Hg—O(1)	91.9 (0.7)
N(2)—Hg—O(2)	94.1 (0.7)
N(2)—Hg—O(3)	86.2 (0.7)
N(2)—Hg—O(4)	97.8 (0.6)
N(2)—Hg—O(3 ¹)	85.1 (0.8)
O(1)—Hg—O(2)	48.8 (0.8)
O(2)—Hg—O(4)	87.6 (0.6)
O(4)—Hg—O(3)	47.3 (0.7)
O(3)—Hg—O(3 ¹)	80.0 (0.7)
O(3)—Hg—O(1)	96.8 (0.6)

Torsion angle defined by atoms C(5)N(1)N(2)C(10) = $-31 (3)^\circ$

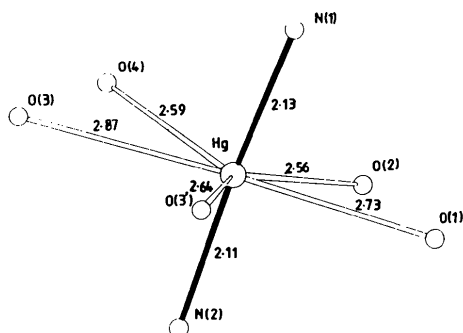


Fig. 2. Coordination around Hg. All e.s.d.'s 0.02 Å. O(3') is at $1-x, 1-y, 1-z$.

range (Grdenić, 1965), the direction of the bonds is slightly but significantly non-linear. Similar small departures from linearity are observed in most Hg compounds which are primarily two-coordinated. Two O atoms from each trifluoroacetate residue, O(1), O(2), O(3), O(4), and one, O(3'), from a centrosymmetrically related trifluoroacetate, complete the coordination (Fig. 2). The distances of these atoms from the best least-squares plane through them and the Hg are respectively 0.021, -0.083, -0.142, 0.163, 0.059 and (for Hg) -0.019 Å. The angles between this plane and Hg-N(1), Hg-N(2) are respectively 80.1 and 90.0°. O(3) is bound to two Hg atoms. The Hg-O distances are considerably longer than the typical covalent distance (Grdenić, 1965) and must be regarded as being secondary in character. The disposition of the trifluoroacetate groups and the lengths of the C-O bonds (all within the range 1.20 to 1.25 Å) suggest that these groups are ionic with the group $\text{Hg}(\text{py})_2^{2+}$ acting as the cation. The presence of trifluoroacetate ions was confirmed by the IR spectrum of the solid material.

The pyridine residues are planar to within the limits of error and the distances and angles are those normally found. The two pyridine rings are twisted about the N-N vector and make an angle of 31.1° to

each other. The $\text{Hg}(\text{py})_2^{2+}$ ion is similar to that reported in bis(pyridine)mercury(II) nitrate dihydrate (Kamenar, Hergold-Brundić & Sikirica, 1976), where the Hg-N distances are 2.129 (8) and 2.135 (8) Å, the angle N-Hg-N is 176.8 (3)° and the overall coordination is described as distorted octahedral with only four O atoms in the equatorial plane. Seven-coordinated Hg, similar to that found in the title compound, has been observed in tetraethyleneglycol(dimethyl ether) mercury(II) chloride (Iwamoto, 1973) in which there are two axial Cl atoms at 2.31 and 2.29 Å and five equatorial O atoms at 2.96, 2.78, 2.79, 2.82 and 2.86 Å. In the trifluoroacetate ions of the present compound, the atoms O, O, C, C are coplanar within the limits of error and there is evidence of considerable thermal vibration of the CF_3 groups of both ions. Apart from the Hg-O bond referred to above, there is no evidence of intermolecular bonding between adjacent units of the structure.

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2-*exo*-(Chloromercurio)-3-*exo*-acetoxybicyclo[2.2.1]heptane

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Abstract. $\text{C}_9\text{H}_{13}\text{ClHgO}_2$, monoclinic, $P2_1/c$, $a = 14.10$ (1), $b = 10.48$ (1), $c = 7.218$ (7) Å, $\beta = 96.33$ (7)°, with $Z = 4$, $D_c = 2.44$, $D_m = 2.38$ g cm $^{-3}$. Crystals were invariably twinned about c . The structure

was determined from 423 diffractometer-measured intensities (Mo $K\alpha$, $\lambda = 0.7107$ Å) which were free from twinning overlap, $R = 0.080$. The distances Hg-Cl and Hg-C are 2.32 (2) and 2.10 (6) Å, the