

related by the screw axis at  $(\frac{1}{2}, y, \frac{1}{4})$ . There are no unusually short distances between non-bonded atoms.

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## Structure of Tris(pyridine)mercury(II) Bis(trifluoroacetate)

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**Abstract.**  $\text{Hg}(\text{C}_5\text{H}_5\text{N})_3(\text{CO}_2\text{CF}_3)_2$ ,  $\text{C}_{19}\text{H}_{15}\text{F}_6\text{HgN}_3\text{O}_4$ , monoclinic,  $P2_1/c$ ,  $a = 13.31$  (1),  $b = 20.24$  (2),  $c = 8.97$  (1) Å,  $\beta = 110.2$  (1)°,  $Z = 4$ ,  $D_c = 1.94$  g cm<sup>-3</sup>. The structure has been determined from 1863 diffractometer intensities (Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å) to  $R = 0.068$ . There is sevenfold coordination around Hg (Hg–N, 2.28, 2.27 and 2.36 Å; Hg–O, 2.66, 2.72, 2.79 and 2.53 Å). The N–Hg–N angles are 161.0, 99.2 and 99.5°. A complex ion,  $\text{Hg}(\text{C}_5\text{H}_5\text{N})_3^{2+}$ , appears to be formed.

**Introduction.** Acicular crystals of the title compound occur as the initial product of the reaction between pyridine and mercury(II) trifluoroacetate. Crystals, removed from pyridine and dried, effloresced on exposure to the atmosphere, with a weight loss corresponding to one molecule of pyridine per formula unit. Powder photographs showed that the residue was bis(pyridine)mercury(II) bis(trifluoroacetate). Sealing the crystals in Lindemann-glass tubes prevented efflorescence, but nevertheless decomposition occurred on exposure to X-rays. With Cu  $K\alpha$  radiation ( $\lambda = 1.542$  Å) the cell dimensions and space group were obtained from Weissenberg photographs. It was not possible to measure the crystal density as it changed rapidly due to decomposition in all suspension liquids. Intensity measurements were made with one crystal of dimensions  $0.25 \times 0.25 \times 0.85$  mm using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å). The crystal was set about  $c$  on the Stoe STADI 2 automatic two-circle diffractometer. 2386 intensities in the range  $2\theta < 40^\circ$  were measured; 1863 for which  $I > 3\sigma(I)$  were used for the structure determination.

Absorption corrections ( $\mu = 70.2$  cm<sup>-1</sup>) and data reduction were carried out using the *SHELX* suite of programs (Sheldrick, 1976); the remainder of the calculations were performed with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Patterson maps were used to obtain the Hg coordinates and a Fourier  $F_o$  map phased on Hg revealed the rest of the non-H atoms. In the least-squares refinement, anisotropic  $U_{ij}$  for Hg, isotropic  $U$  for other non-H atoms and positions of all non-H atoms were refined alternately with scale factors for each layer of the reciprocal lattice measured on the diffractometer. Inclusion of H atoms at positions calculated with C–H = 1.00 Å and  $U = 0.05$  Å<sup>2</sup> was found to improve the agreement; the  $R$  value at which convergence was complete was 0.068. Final coordinates and temperature factors are given in Table 1.\* Atomic scattering factors for Hg atoms (including anomalous dispersion) were taken from Cromer & Mann (1968); those for all other atoms were from *International Tables for X-ray Crystallography* (1962).

**Discussion.** One unit of the structure is shown in Fig. 1, the bond distances and angles around Hg are given in Table 2.\*

\* Lists of structure factors and bond lengths and angles around non-Hg atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33857 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the sevenfold coordination about Hg (Fig. 1), the three Hg—N distances are much shorter than those to the four O atoms. Some appreciably shorter covalent Hg—N distances (2.03–2.10 Å) have been reported in two-covalent mercury compounds but bonds would be

Table 1. Fractional atomic coordinates ( $\times 10^3$ , for Hg  $\times 10^4$ ) and thermal parameters ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
N(1)	312 (2)	75 (1)	817 (3)	80 (7)
C(1)	328 (2)	17 (1)	157 (3)	59 (7)
C(2)	368 (2)	17 (1)	323 (4)	68 (8)
C(3)	394 (2)	74 (1)	404 (4)	74 (8)
C(4)	376 (2)	134 (1)	321 (4)	63 (7)
C(5)	337 (2)	135 (1)	158 (3)	55 (7)
N(2)	177 (1)	116 (1)	557 (2)	42 (5)
C(6)	179 (2)	180 (1)	530 (3)	48 (6)
C(7)	138 (2)	204 (1)	382 (4)	65 (8)
C(8)	102 (2)	161 (1)	249 (4)	65 (8)
C(9)	102 (2)	94 (1)	280 (3)	60 (7)
C(10)	137 (2)	71 (1)	434 (3)	53 (7)
N(3)	253 (1)	963 (1)	758 (2)	45 (5)
C(11)	344 (2)	940 (1)	757 (3)	59 (7)
C(12)	352 (2)	871 (1)	722 (4)	80 (9)
C(13)	265 (2)	832 (1)	697 (4)	71 (8)
C(14)	172 (2)	858 (1)	702 (3)	63 (7)
C(15)	169 (2)	926 (1)	732 (3)	54 (7)
O(1)	440 (1)	88 (1)	802 (2)	69 (5)
C(16)	439 (2)	149 (1)	825 (3)	43 (6)
O(2)	375 (1)	183 (1)	846 (2)	65 (5)
C(17)	537 (3)	182 (2)	799 (5)	88 (10)
F(1)	620 (2)	150 (1)	828 (3)	156 (8)
F(2)	516 (2)	219 (1)	683 (4)	176 (10)
F(3)	573 (1)	231 (1)	919 (3)	113 (6)
O(3)	28 (2)	46 (1)	752 (3)	102 (7)
C(18)	18 (2)	104 (1)	800 (3)	57 (7)
O(4)	91 (1)	142 (1)	850 (2)	65 (5)
C(19)	908 (4)	128 (3)	798 (7)	163 (19)
F(4)	831 (2)	95	692 (3)	129 (7)
F(5)	895 (3)	182 (2)	799 (4)	214 (14)
F(6)	889 (2)	103 (2)	923 (4)	208 (13)
Hg	2427 (1)	773 (0)	8100 (1)	*

\* Anisotropic thermal parameters for Hg ( $\times 10^4$ )

$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
602 (6)	365 (5)	368 (5)	-62 (5)	171 (5)	-29 (5)

Table 2. Bond lengths (Å) and angles (°) around the Hg atom

Hg—N(1)	2.28 (2)	Hg—O(1)	2.66 (2)
Hg—N(2)	2.27 (2)	Hg—O(2)	2.72 (2)
Hg—N(3)	2.38 (2)	Hg—O(3)	2.79 (2)
		Hg—O(4)	2.53 (2)
N(1)—Hg—N(2)	161.0 (.7)	N(2)—Hg—O(2)	81.8 (.6)
N(1)—Hg—N(3)	99.2 (.7)	N(2)—Hg—O(3)	82.9 (.7)
N(2)—Hg—N(3)	99.5 (.6)	N(2)—Hg—O(4)	85.1 (.6)
N(1)—Hg—O(1)	89.4 (.8)	N(3)—Hg—O(1)	86.8 (.6)
N(1)—Hg—O(2)	83.1 (.7)	O(1)—Hg—O(2)	46.5 (.5)
N(1)—Hg—O(3)	102.0 (.8)	O(2)—Hg—O(4)	95.1 (.5)
N(1)—Hg—O(4)	84.8 (.7)	O(4)—Hg—O(3)	47.9 (.5)
N(2)—Hg—O(1)	89.2 (.6)	O(3)—Hg—N(3)	82.5 (.6)

expected to lengthen with increased coordination number. Grdenić (1965) estimates an increase in the covalent radius of Hg from 1.30 to 1.48 Å for a change from two to four covalency and in bis(ethylene-diamine)mercury(II) diperchlorate (Duplancić, Grdenić, Kamenar, Matković & Sikirica, 1976) Hg forms four almost equal covalent Hg—N bonds of length 2.32 Å. The Hg—N bonds in the present compound are short enough to be regarded as covalent.

The Hg—O distances are markedly longer than the covalent value (2.03 Å) given by Sikirica & Grdenić (1974). With one exception they are also longer than the ionic distance (2.53 Å) which may be estimated from the Hg<sup>2+</sup> ionic radius (1.04 Å) (Grdenić, 1965) and the effective O radius in the trifluoroacetate ion (1.50 Å) (Golič & Speakman, 1965). In covalently bonded carboxylates, *e.g.* phenylmercury(II) acetate (Kamenar & Penavić, 1972), mercury(II) acetate (Allman, 1973), mercury(I) trifluoroacetate (Sikirica & Grdenić, 1974) and mercury(II) trifluoroacetate (Halfpenny & Small, 1978), the two Hg—O distances to one carboxylate group differ typically by 0.7 Å, the shorter being in the range 2.00–2.20 Å. The two carboxylate C—O distances also differ appreciably (by 0.3 Å), the one closest to Hg being the longer. In the title compound the Hg—O (Table 2) and C—O distances [C(16)—O(1) = 1.27 (3), C(16)—O(2) = 1.16 (3), C(18)—O(3) = 1.26 (3), C(18)—O(4) = 1.21 (3) Å] do not follow this pattern and provide evidence for Hg—O ionic bonding with Hg(py)<sub>3</sub><sup>2+</sup> as the cation. This ion may be compared with Hg(py)<sub>2</sub><sup>2+</sup> found in bis(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny, Small & Thorpe, 1978) in which the Hg—N distances are 2.11 and 2.13 Å, and the N—Hg—N angle is 170°. In that compound the coordination is completed by five equatorial O atoms, with Hg—O distances similar to those in the present compound. In Hg(py)<sub>3</sub><sup>2+</sup> the atoms of the two pyridine groups defined by N(1) and N(2) lie in one plane which also contains Hg and N(3) (Table 3). The atoms of the third pyridine lie in a plane inclined at 85° to the plane of the other two.

Although no ionic Hg<sup>2+</sup> oxyacid or carboxylate compounds are known, several involving complexed Hg<sup>II</sup> ions have been reported. Grdenić (1965) distinguishes between 'characteristic' coordination and 'effective' or overall coordination in Hg compounds. By

Table 3. Deviations of atoms from least-squares planes (Å  $\times 10^{-3}$ )

Plane A: Hg -37; N(1) -22; C(1) -29; C(2) 12; C(3) 17; C(4) 38; C(5) -11; N(2) -2; C(6) -38; C(7) 23; C(8) -15; C(9) 11; C(10) 53.
Plane B: Hg -6; N(3) -2; C(11) 14; C(12) -15; C(13) 4; C(14) 8; C(15) -9.
Plane C: Hg -29; N(1) 13; N(2) 13; N(3) 4.

this nomenclature the present compound, although having an effective coordination of seven, would have a characteristic coordination of three by virtue of three primarily covalently bonded N atoms. Examples of characteristic three coordination are uncommon; the present cation is the only recorded example of a complex with three monodentate ligands. In the case of the bidentate complex tris(1,8-naphthyridine)-mercury(II) bis(perchlorate) (Epstein, Dewan, Kepert & White, 1974) each naphthyridine forms one short and one long bond to Hg, giving a planar configuration of the three shorter bonds similar to that in the title compound. Planar three coordination is also present in (2,2'-bipyridyl)methylmercury (Carty & Gatehouse, 1976), arising from the unsymmetrical bidentate character of the ligand.

The CCOO groups of the trifluoroacetate ions are

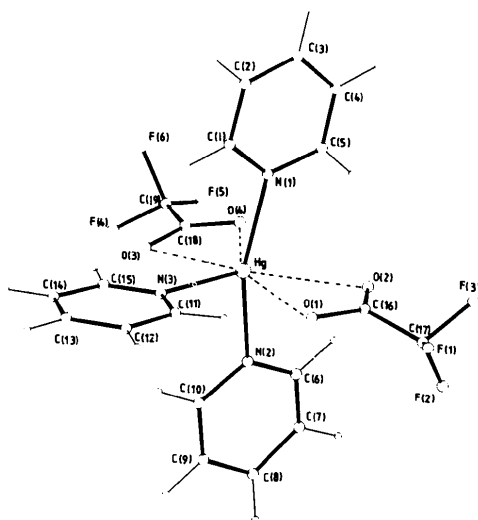


Fig. 1. A unit of the structure of tris(pyridine)mercury(II) bis(trifluoroacetate) showing the coordination around Hg.

planar as expected; O(1) and O(2) of one of these ions are coplanar with Hg and N(3) whilst those of the other are rotated  $15^\circ$  relative to this plane. Both trifluoroacetate ions have high  $U$  values for the F atoms, suggesting disorder. All the bonds from the anions are to the same Hg complex cation. There is no indication of any bonding between neighbouring structural units.

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### $\mu$ -(1-4- $\eta$ : 11-14- $\eta$ -1,3,11,13-Tetradecatetraene-5,10-diol)-bis(tricarbonyliron)

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**Abstract.**  $[(\text{CO})_3\text{Fe}(\text{C}_4\text{H}_5)\text{CHOHC}_2\text{H}_4]_2$ ,  $\text{C}_{20}\text{H}_{22}\text{Fe}_2\text{O}_8$ , monoclinic,  $P2_1/c$ ,  $a = 14.321(12)$ ,  $b = 6.114(3)$ ,  $c = 12.565(10)$  Å,  $\beta = 105.20(5)^\circ$  at  $-35^\circ\text{C}$ ,

$D_c(-35^\circ\text{C}) = 1.581$ ,  $D_m(21^\circ\text{C}) = 1.57$  g cm $^{-3}$ ,  $Z = 2$ . The molecule is composed of a fully extended 1,3,11,13-tetradecatetraene-5,10-diol ligand  $\pi$  bonded with two  $\text{Fe}(\text{CO})_3$  fragments in the customary butadiene-iron tricarbonyl fashion. Full-matrix least-

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