

Structure of the 1:1 Complex of Mercury(II) Trifluoroacetate and 1,4-Dioxane

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Abstract. $[\text{Hg}(\text{CF}_3\text{CO}_2)_2] \cdot \text{C}_4\text{H}_8\text{O}_2$, $M_r = 514.7$, triclinic, $P\bar{1}$, $a = 9.31$ (1), $b = 8.06$ (1), $c = 4.783$ (5) Å, $\alpha = 83.8$ (1), $\beta = 100.1$ (1), $\gamma = 115.2$ (1)°, $U = 319$ Å³, $D_m = 2.703$, $D_x = 2.680$ Mg m⁻³, $Z = 1$. The structure, determined from 627 observed intensities ($R = 0.037$), shows Hg on site $\bar{1}$ with Hg–O 2.08 (1) and 2.75 (1) Å to trifluoroacetate; 1,4-dioxane molecules which also lie on $\bar{1}$ sites bridge Hg atoms parallel to b with Hg–O 2.64 (1) Å.

Introduction. The title compound was obtained from a dichloromethane solution of mercury(II) trifluoroacetate and 1,4-dioxane as acicular crystals elongated parallel to c with principal forms $\{100\}$, $\{010\}$, $\{110\}$. Crystal data were obtained from $hk0$, $h0l$ and $0kl$ Weissenberg photographs with Cu $K\alpha$ ($\lambda = 1.542$ Å) radiation. Intensities for the layers $l = 0-4$ were measured with graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation using a crystal $0.3 \times 0.12 \times 0.60$ mm on a Stoe STADI-2 automatic two-circle diffractometer. Corrections for absorption ($\mu = 11.68$ mm⁻¹) were made with *SHELX* (Sheldrick, 1976) which was used for all calculations. All 629 unique reflexions measured had $I > 3\sigma(I)$ and were used in the initial structure determination. The structure was solved by placing Hg at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and computing the $(F_o - F_c)$ map which revealed the positions of all atoms other than Hg. Anisotropic U_{ij} for Hg, isotropic U for

C, O and F and coordinates of all non-H atoms were refined by full-matrix least squares. For the reflexions $\bar{1}10$ and $\bar{1}20$ F_c was considerably greater than F_o ; this was assumed to be due to extinction and these reflexions were suppressed from the refinement. At a later stage H atoms were included, but not refined, at calculated positions (C–H 1.08 Å, U equal to that of the attached atom). In the last cycle shifts were $\leq 0.02\sigma$ and R was 0.037. Atomic scattering factors for Hg were from Cromer & Mann (1968) and Cromer & Liberman (1970) and those for all other atoms were from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and temperature factors are listed in Table 1.*

Discussion. The structure (Fig. 1) shows an Hg atom on a centre of symmetry, bound, at a typical covalent distance, to two centrosymmetrically related O(1) atoms of the trifluoroacetate groups. O(2) is not bound to this Hg atom but to one translated by c , the distance

* Lists of structure factors and bond lengths involving non-Hg atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36952 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z	U (Å ²)
Hg	500	500	500	*
C(1)	241 (2)	343 (2)	55 (3)	30 (4)
C(2)	73 (2)	284 (2)	-91 (4)	35 (4)
O(1)	266 (1)	420 (2)	291 (2)	41 (3)
O(2)	339 (1)	319 (2)	-52 (3)	47 (3)
F(1)	-38 (1)	223 (2)	84 (2)	62 (3)
F(2)	33 (1)	150 (2)	-271 (3)	70 (3)
F(3)	52 (1)	418 (2)	-247 (3)	68 (3)
C(3)	355 (2)	14 (2)	502 (4)	43 (5)
C(4)	624 (2)	152 (3)	401 (4)	48 (5)
O(3)	508 (1)	174 (2)	546 (2)	42 (3)

* Anisotropic thermal parameters for Hg (Å² $\times 10^4$)

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
262 (6)	249 (6)	348 (7)	96 (4)	-24 (4)	-95 (4)

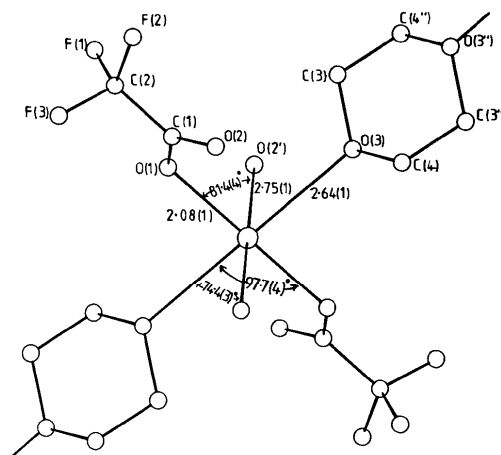


Fig. 1. View of $[\text{Hg}(\text{CF}_3\text{CO}_2)_2] \cdot \text{C}_4\text{H}_8\text{O}_2$ showing coordination around Hg. Distances are in Å. Symmetry code: (') $x, y, 1+z$; (')' $1-x, -y, 1-z$.

involved being intermediate between the covalent and van der Waals values. 1,4-Dioxane molecules, which lie on centres of symmetry displaced by $b/2$ relative to Hg, bridge the Hg atoms. The structure consists of layers of Hg atoms linked parallel to c by the trifluoroacetate groups and parallel to b by the 1,4-dioxane molecules. There are no other close contacts to Hg, the overall coordination thus being six.

Two other structures involving 1,4-dioxane complexed to Hg have been reported: in the 1:1 complex of 1,4-dioxane and mercury(II) chloride (Groth & Hassel, 1964) the dioxane molecules have a bridging role with Hg—O 2.66 Å in a closely similar structure also in space group $P\bar{1}$ ($Z = 1$). In the case of the 1:2 compound of mercury(II) bromide and 1,4-dioxane (Frey & Monier, 1971) Hg occupies a fourfold special position in a tetragonal structure with four Hg—O contacts of 2.83 Å. The present structure may be compared with the complexes of mercury(II) trifluoroacetate and pyridine (Halfpenny, Small & Thorpe, 1978; Halfpenny & Small, 1978) in which the pyridine molecules are more closely coordinated to Hg than are the trifluoroacetate groups. The close coordination of the trifluoroacetate groups to Hg in the present compound indicates that 1,4-dioxane is a weaker base than trifluoroacetate.

In the trifluoroacetate groups the significantly different C—O distances, C(1)—O(2) 1.21 (2) and

C(1)—O(1) 1.28 (2) Å, reflect the unequal coordination distances of these two O atoms to Hg. In this structure the U values of the F atoms have fairly normal values; this is in contrast with most other mercury(II) trifluoroacetate complexes where large values of U_{ij} or U for these atoms are observed (Halfpenny & Small, 1981).

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Tetraphenylarsonium Bis(fluorosulfonyl)amide at 290 and 112 K

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Abstract. $C_{24}H_{20}As^+ \cdot N(SO_2F)_2^-$, $M_r = 563.46$, monoclinic, $P2_1/n$, $Z = 4$, $a = 17.447$ (5), $b = 7.325$ (2), $c = 19.494$ (6) Å, $\beta = 94.20$ (2)°, $U = 2484.6$ Å³, $D_x = 1.506$, $D_m = 1.46$ (3) Mg m⁻³, $\mu(Mo K\alpha) = 1.57$ mm⁻¹ at 290 (1) K, and $a = 17.16$ (2), $b = 7.53$ (1), $c = 18.40$ (2) Å, $\beta = 94.2$ (1)°, $U = 2371.2$ Å³, $D_x = 1.578$ Mg m⁻³, $\mu(Mo K\alpha) = 1.64$ mm⁻¹ at 112 (2) K. The structure refined to $R = 0.076$ for 1946 unique observed data at 290 K and to $R = 0.047$ for 3332 data at 112 K. The thermal motion of the anion and hence the effect of libration and torsion on the observed dimensions are substantially reduced on cooling. The geometry and thermal motion of the cation are normal at both temperatures. The anion adopts

a staggered conformation of approximately 2 (C_2) symmetry at 112 K, with S—N—S 121.4 (2)°, S—N (mean) 1.568 (4), S—O (mean) 1.415 (7), S—F (mean) 1.574 (3) Å. The apparently quite different geometry observed for the anion at 290 K may be accounted for by two superimposed conformers subject to considerable thermal smearing; an attempt to determine the structure by room-temperature measurements alone would have led to chemically fallacious results.

Introduction. $Ph_4As^+ \cdot N(SO_2F)_2^-$ was prepared for us by Professor R. Mews by the reaction of $Ph_4As^+ \cdot Cl^-$ with $HN(SO_2F)_2$. Physical and spectroscopic measurements agreed with those reported by Roesky & Babb