

We wish to acknowledge the support of the Phillips Petroleum Company for support in the form of a fellowship to WCD. The authors also wish to acknowledge helpful discussion with P. N. Swepston.

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Acta Cryst. (1981). **B37**, 2223–2225

The Structure of the Trifluoroacetate of the (3-Oxo-2-butyl)(pyridine)mercury(II) Cation

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(Received 20 March 1981; accepted 22 May 1981)

Abstract. $[\text{Hg}(\text{C}_3\text{H}_5\text{N})(\text{C}_4\text{H}_7\text{O})](\text{C}_2\text{F}_3\text{O}_2)_2$, $\text{C}_9\text{H}_{12}\text{HgNO}^+\cdot\text{C}_2\text{F}_3\text{O}_2^-$, triclinic, $P\bar{1}$, $a = 9.81(1)$, $b = 9.20(1)$, $c = 10.04(1)$ Å, $\alpha = 117.7(1)$, $\beta = 61.72(6)$, $\gamma = 110.7(1)^\circ$, $D_m = 2.245$, $D_c = 2.22$ Mg m^{-3} with $Z = 2$; $R = 0.049$ for 1741 diffractometer-measured intensities. Hg forms two covalent bonds: to the 3-oxo-2-butyl group, $\text{Hg}-\text{C} = 2.12(2)$ Å, and to pyridine, $\text{Hg}-\text{N} = 2.16(1)$ Å, with $\angle\text{C}-\text{Hg}-\text{N} = 174(1)^\circ$. In addition there are contacts from Hg to trifluoroacetate O, 2.77(2), 2.82(1), 2.85(2) Å, and to the 3-oxo-2-butyl O, 2.89(1) Å. The distances indicate an ionic structure.

Introduction. This compound is one of a series of complexes of nitrogen donor ligands with mercury(II) trifluoroacetate and its derivatives. Material supplied by Dr A. J. Bloodworth was recrystallized from dichloromethane to give oblique prisms showing the forms $\{011\}$, $\{100\}$ and $\{010\}$. With $\text{Cu } K\alpha$ radiation ($\lambda = 1.542$ Å), the Laue group and cell dimensions were obtained from Weissenberg photographs with crystals

mounted successively about **a**, **b** and **c**. Intensity data on 1944 unique reflections were collected with graphite-monochromatized $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107$ Å) on the Stoe STADI-2 automatic two-circle diffractometer, from a well developed crystal with dimensions $0.16 \times 0.06 \times 0.20$ mm. Data from the layers $l = 0-9$ within the range $20 \leq 40^\circ$ were processed with an initial data reduction program and all further calculations were performed with *SHELX* (Sheldrick, 1976). Absorption corrections ($\mu = 10.67 \text{ mm}^{-1}$) were applied and reflections with $F < 6\sigma(F)$ were eliminated, leaving 1741 values for the structure determination and refinement. Statistical tests indicated a centric intensity distribution. Assuming the space group $P\bar{1}$, the Patterson map was used to determine the position of Hg. These coordinates were used to phase an $(F_o - F_c)$ map to give the positions of the remaining non-H atoms. Refinement of atomic parameters proceeded with anisotropic U_{ij} for Hg and isotropic U for C, N and O. Scale factors for the data collection layers were also refined at an intermediate stage. When refinement was

Table 1. Atomic positions ($\times 10^3$, $\times 10^4$ for Hg) and temperature factors ($\text{\AA}^2 \times 10^3$, $\times 10^4$ for Hg)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> _{eq} *
C(1)	-136 (2)	127 (2)	317 (2)	57 (4)
C(2)	-84 (2)	-35 (2)	181 (2)	65 (4)
C(3)	61 (2)	-81 (2)	159 (2)	84 (6)
C(4)	-305 (2)	139 (2)	350 (2)	70 (5)
C(5)	229 (2)	536 (2)	37 (2)	52 (4)
C(6)	351 (2)	654 (2)	-25 (2)	68 (5)
C(7)	463 (2)	740 (2)	45 (2)	73 (5)
C(8)	453 (2)	708 (2)	170 (2)	72 (5)
C(9)	327 (2)	592 (2)	225 (2)	59 (4)
C(10)	-180 (2)	591 (2)	408 (2)	54 (4)
C(11)	-295 (3)	713 (3)	492 (3)	96 (7)
N	219 (1)	509 (1)	160 (1)	46 (3)
O(1)	-144 (1)	514 (2)	261 (2)	74 (3)
O(2)	-139 (1)	578 (1)	502 (2)	71 (3)
O(3)	-160 (1)	-125 (2)	95 (2)	73 (3)
F(1)	-353 (2)	710 (3)	403 (2)	170*
F(2)	-210 (3)	871 (2)	519 (3)	181*
F(3)	-395 (2)	714 (3)	627 (2)	212*
Hg	317 (1)	3243 (1)	2453 (1)	505*

* U_{eq} values from diagonalized matrix U_{ij} : $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

terminated at $R = 0.049$ the shifts on all parameters were less than 0.05 of the e.s.d. and there were no significant features on the ($F_o - F_c$) map. Atomic scattering factors for Hg, including anomalous scattering, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); those for all other atoms were from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and isotropic temperature factors are listed in Table 1.*

Discussion. Bond distances within one unit of structure are shown in Fig. 1 (bond angles for atoms other than Hg are included in the supplementary data). The pyridine ligand and the 3-oxo-2-butyl group are covalently bound to Hg and the trifluoroacetate, which has been displaced, is unusually distant from Hg. The Hg—O(1) and Hg—O(2) distances are considerably in excess of typical covalent values (normally within the range 2.0–2.3 Å) and must indicate that the structure is ionic. The ionic Hg—O distance has been previously estimated (Halfpenny & Small, 1978) at 2.54 Å. There is no obvious reason for the longer distances found in this structure; screening of Hg by attached ligands would not appear to be sufficient to prohibit a closer approach. It is of interest that the Hg—O(3)' contact (Table 2) between neighbouring cations is not significantly greater than Hg—O(1), Hg—O(2) between cation

* Lists of structure factors, anisotropic thermal parameters and bond angles around non-Hg atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36196 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

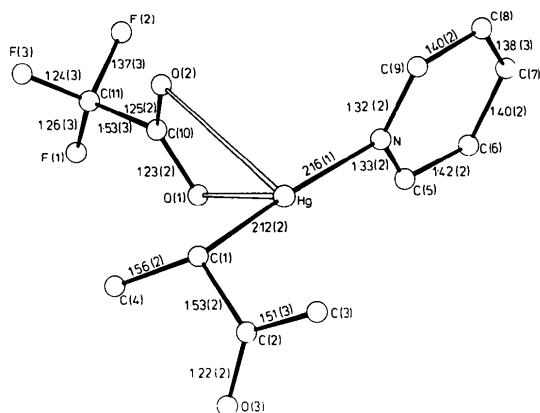


Fig. 1. View of one unit of structure of the trifluoroacetate of the (3-oxo-2-butyl)(pyridine)mercury(II) cation. (Distances in Å.)

Table 2. Coordination around Hg

Bond lengths (Å)			
Hg—N	2.16 (1)	Hg—O(1)	2.77 (2)
Hg—C(1)	2.12 (2)	Hg—O(2)	2.82 (1)
		Hg—O(3)'	2.89 (1)
		Hg—O(2)''	2.85 (2)
Angles (°)			
N—Hg—O(1)	80.6 (5)	C(1)—Hg—O(1)	104.6 (5)
N—Hg—O(2)	90.1 (4)	C(1)—Hg—O(2)	95.1 (5)
N—Hg—O(2)''	88.0 (5)	C(1)—Hg—O(2)''	91.1 (7)
N—Hg—O(3)'	80.5 (3)	C(1)—Hg—O(3)'	95.9 (5)
O(1)—Hg—O(2)	47.0 (5)	C(1)—Hg—N	174.4 (6)
O(2)—Hg—O(2)''	75.6 (4)	O(3)'—Hg—O(1)	104.5 (5)
O(2)''—Hg—O(3)'	130.4 (4)		

Symmetry code: (') $-x, -y, -z$; (') $-x, 1-y, 1-z$.

and anion. The coordination around Hg is summarized in Table 2. The effective sixfold coordination is completed by an additional Hg—O(2)'' contact; however, in terms of the definition of 'characteristic' coordination (Grdenić, 1965), in this structure Hg would be deemed to be linear two-covalent.

Within the cation, Hg is coplanar with the pyridine within the limits of error. The torsion angle Hg—C(1)—C(2)—O(3), $110(1)^\circ$, is larger than that in (chloromercurio)acetaldehyde (98°) (Halfpenny & Small, 1979), with no intramolecular Hg—O interaction. The group C(1)C(2)C(3)O(3) is planar to within the limits of error. The large U_{ij} values of F atoms (reflected in the large U_{eq} , Table 1) are a typical feature of all trifluoroacetate groups in Hg^{II} trifluoroacetate derivatives examined [e.g. in bis(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny, Small & Thorpe, 1978); tris(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny & Small, 1978); phenyl(pyridine)mercury(II) trifluoroacetate (Halfpenny & Small, 1980)] and appear to indicate some persistent disorder of the CF₃ group.

JH thanks Professor J. C. Bevington, Chemistry Department, University of Lancaster, for providing research facilities.

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Structure of Dichloro(1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane-*S,S'*)mercury(II)–Mercury Dichloride

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(Received 10 February 1981; accepted 27 May 1981)

Abstract. [Hg(C₁₂H₂₄O₄S₂)Cl₂].HgCl₂, $M_r = 839.3$, triclinic, $P\bar{1}$, $a = 8.410(2)$, $b = 11.351(9)$, $c = 12.347(6)$ Å, $\alpha = 92.48(5)$, $\beta = 94.52(3)$, $\gamma = 105.66(5)^\circ$, $V = 1128.8(11)$ Å³, $Z = 2$, $D_o = 2.43$, $D_c = 2.46$ Mg m⁻³, $R = 0.058$, $R_w = 0.063$ for 2113 independent data. The crystal structure consists of one HgCl₂ unit coordinated to a bidentate macrocyclic ligand and a second HgCl₂ unit which does not interact with an organic ligand. Only the S atoms of the organic ligand interact with the HgCl₂ unit resulting in a distorted tetrahedral geometry.

Introduction. The complex was prepared by mixing an aqueous solution of the ligand with a large excess of HgO dissolved in concentrated HCl. Chemical analysis of the resulting crystals indicated that there was more than one Hg for each ligand. The crystallographic study was initiated to determine the chemical composition, stoichiometry and coordination of the material. A small, nearly spherical crystal with an average diameter of 0.17 mm was mounted on a Syntex $P\bar{1}$ autodiffractometer. The lattice parameters given in the *Abstract* were determined by a least-squares refinement of 13 2θ values. Intensity statistics and the fact that $Z = 2$ suggested that the space group was $P\bar{1}$. This choice of space group was confirmed by the subsequent solution of the structure. Intensity data were collected using graphite-monochromated Mo $K\alpha$

radiation ($\lambda = 0.71073$ Å). The data were recorded with a scintillation counter. Five check reflections which were measured every 95 reflections showed no significant change. A total of 2113 independent data points were recorded for $2\theta \leq 40^\circ$ ($\sin \theta/\lambda = 0.482$ Å⁻¹). These data included 321 reflections which were considered unobserved as $I < 2\sigma_I$; σ_I was based on counting statistics. Absorption corrections for a spherical crystal were applied to the data ($\mu = 15.6$ mm⁻¹); the correction factor ranged from 1.04 to 1.10.

The trial structure was obtained by the heavy-atom technique. Positions for the H atoms were calculated from geometrical considerations; the C–H bond length was assumed to be 1.04 Å. The structure was refined using *ORFLS* (Busing, Martin & Levy, 1962), a full-matrix least-squares procedure. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. No attempt was made to refine H parameters. The refinement was considered complete when all change/error ratios were less than 0.05. At that point the R value was 0.058 and the weighted R value using unit weights was 0.063. The goodness-of-fit term was 2.5 with $m = 2113$ and $n = 217$. All data were included in the refinement. The final positional parameters are listed in Table 1.* Scattering-factor

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36199 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Contribution No. 247.