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**The Crystal Structure of Phenylmercury(II)
Trifluoroacetate and the Refinement of the
Crystal Structure of Phenylmercury(II) Acetate**

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The crystal structure of phenylmercury(II) trifluoroacetate (A) has been determined by the heavy-atom method using diffractometer X-ray diffraction data and refined by the least-squares procedure to the conventional *R* index of 0.051. The structure of phenylmercury(II) acetate (B) has also been redetermined and refined also with diffractometer data in order to obtain better values for bond lengths and angles and to compare them with those of (A). For (B) the refinement converged at an *R* index of 0.069. Both compounds, (A) and (B), have essentially the same molecular structure: characteristic coordination of mercury is digonal with almost collinear C-Hg-O bonds. In both structures the angles at the Hg atoms are identical and amount to 176.6°. The Hg-C and Hg-O bond lengths are 205.1 and 212.1 pm in (A), and 203.8 and 208.4 pm in (B), respectively. The effective coordination number of mercury in both structures is four: the mercury atoms, apart from being bonded to the phenyl-carbon and trifluoroacetato or acetato-oxygen atoms, are additionally surrounded in (A) by two trifluoroacetato-oxygen atoms, in (B) by two acetato-oxygen atoms. The Hg...O distances vary from 281.9 to 295.2 pm.

INTRODUCTION

It would be reasonable to suppose that the Hg-C bond length in asymmetric organomercurials of the R-Hg-X type depends upon the nature of R as well as upon the electronegativity of X. However, according to the published structural examples there is no definite proof that the Hg-C bond length differs appreciably when R is either an aliphatic or an aromatic part of the organomercury molecule. On the other hand, it has been noted that the Hg-C bond length increases very little with the decrease in electronegativity of X.¹ In order to extend this investigation to organomercury compounds in which X are carboxylate ions, we decided to determine the structure of phenylmercury(II) trifluoroacetate (A) and to redetermine the structure of phenylmercury(II) acetate (B). The

structure of (B) was solved more than ten years ago using film technique and refined to $R = 0.11$ so that the available data are not accurate enough for any comparison.² For example, the Hg-C bond length in this structure was determined to be 192(6) pm, which cannot be considered as a reliable value for such a bond.¹

EXPERIMENTAL

Preparation

The crystals of (A), prepared by dissolving mercury(II) trifluoroacetate in warm benzene,³ as well as those of (B) were obtained from benzene solution.

*Crystal Data, Structure Determinations and Refinement**

The crystal and experimental data are given in Table I. Lattice parameters were obtained by least-squares from the settings of 22 reflections (A) and 16 reflections (B) measured on a Philips PW 1100 automated diffractometer. For collecting the data for compound (A) graphite-monochromated MoK α was employed, while for (B) CuK α radiation was used. Three reference reflections were monitored every 90 minutes to check crystal stability. The data were corrected for Lorentz-polarization and absorption effects.

TABLE I

Crystal Data, Experimental and Refinement Parameters for Phenylmercury(II) Trifluoroacetate, (A) and Phenylmercury(II) Acetate (B)

<i>Crystal Data</i>	(A)	(B)
Molecular formula	C ₆ H ₅ HgOCOCF ₃	C ₆ H ₅ HgOCOCH ₃
<i>M</i>	390.7	336.7
Space group	P2 ₁ /c	P2 ₁ /c
<i>a</i>	1.0240(6) nm	0.5185(3) nm
<i>b</i>	0.5159(1)	2.4104(10)
<i>c</i>	1.7960(12)	0.7462(1)
β	104.24(4)°	113.80(1)°
<i>V</i>	0.9196 nm ³	0.8533 nm ³
<i>Z</i>	4	4
<i>D</i> _{obs}	2.82 Mg.m ⁻³	2.58 Mg.m ⁻³
<i>D</i> _{calc}	2.82	2.62
μ (CuK α)	325.5 cm ⁻¹	
μ (MoK α)		218.1 cm ⁻¹
λ	154.18 pm	71.07 pm
<i>F</i> (000)	704	608
Specimen dimensions	0.29 × 0.05 × 0.03 mm ³	0.34 × 0.11 × 0.06 mm ³
<i>Data collection</i>		
Scan mode	ω -2 θ	ω -2 θ
Scan width	1.60 °	1.60 °
Scan speed	0.04 ° θ s ⁻¹	0.04 ° θ s ⁻¹
Range scanned (sin θ / λ)	0.05 — 0.65	0.10 — 0.70
No. of reflections collected	1032	1691
No. of reflections used in the refinement	1014	1508
		[I _{rel.} > 2 σ I _{rel.}]
<i>Final refinement</i>		
$R = \Sigma[F_o - F_c] / \Sigma F_o $	0.051	0.069
$R_w = \Sigma w^{1/2}[F_o - F_c] / \Sigma w^{1/2} F_o $	0.065	0.077
Weighting scheme, <i>w</i>	1/ $\sigma^2(F_o)$	1/ $\sigma^2(F_o)$

* The lists of observed and calculated structure factors are obtainable from the authors on request.

The structure of (A) was solved by locating the mercury atom in a Patterson map and then all non-hydrogen atoms in the subsequent Fourier and difference maps. The atomic coordinates were refined by the full-matrix least-squares procedure assuming anisotropic thermal parameters for all atoms. The structure of (B) was refined by the same procedure using atomic coordinates from the previous structure determination.² Neutral-atom scattering factors for mercury, fluorine, carbon and oxygen atoms, and anomalous dispersion for mercury were taken from International Tables for X-Ray Crystallography.⁴ All calculations were performed on the UNIVAC 1110 computer of the Zagreb University Computing Centre (SRCE) using the programmes developed by Domenicano et al.⁵ Final atomic coordinates and equivalent temperature factors with their standard deviations are given in Table II.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

As can be seen from interatomic distances and angles given in Table III and from Figure 1, the molecular structures of both compounds are essentially identical. They show that the carboxylate ions do not form chelate structures with mercury so that the characteristic coordination of the mercury atom is digonal with nearly collinear C—Hg—O bonds. In both compounds the angles at the Hg atom are exactly equal and amount to 176.6°. Similarly, the angles between the least-squares best planes through the carbon atoms of the benzene rings and through the four non-fluorine and non-hydrogen atoms of the trifluoroacetate or acetate ions are almost the same: in (A) and (B) they are 59.4 and 60.1°, respectively. The Hg—C [205.1 in (A) and 203.8 pm in (B)] and Hg—O bond lengths [212.1 in (A) and 208.4 pm in (B)] are not equal, although taking into account their estimated standard deviations they are very close to each other. The difference between the Hg—C bond lengths is not significant

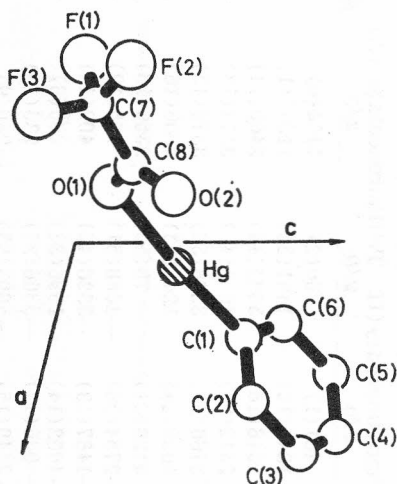


Figure 1. The molecular structure of phenylmercury(II) trifluoroacetate (A) viewed along the *b* axis. Since the structure of phenylmercury(II) acetate (B) is essentially the same as that of (A), for comparison the analogous atom-labelling scheme has been used for both structures.

TABLE III

Interatomic Distances and Angles with Estimated Standard Deviations in Parentheses

<i>Distances (pm)</i>	<i>Compound (A)</i>	<i>Compound (B)</i>
Hg—C(1)	205.1(17)	203.8(19)
Hg—O(1)	212.1(13)	208.4(13)
C(1)—C(2)	136(3)	138(2)
C(2)—C(3)	143(3)	140(4)
C(3)—C(4)	143(3)	136(4)
C(4)—C(5)	131(4)	128(4)
C(5)—C(6)	142(3)	142(4)
C(6)—C(1)	147(3)	139(3)
C(7)—C(8)	152(3)	151(3)
C(8)—O(1)	128(3)	130(3)
C(8)—O(2)	125(3)	121(3)
C(7)—F(1)	129(3)	
C(7)—F(2)	132(3)	
C(7)—F(3)	129(3)	
Hg...O(2)	303.4(15)	290.7(15)
Hg...O(1) ⁱⁱ	295.2(15)	299.4(14)
Hg...O(2) ⁱ		316.0(14)
Hg...O(2) ⁱⁱⁱ		281.9(14)
Hg...O(2) ^{iv}	282.8(15)	
Hg...F(1) ^v	318.8(14)	

<i>Angles (°)</i>	<i>Compound (A)</i>	<i>Compound (B)</i>
C(1)—Hg—O(1)	176.6(7)	176.6(6)
C(1)Hg...O(1) ⁱⁱ	110.2(7)	
C(1)—Hg...O(2) ^{iv}	90.8(6)	
O(1)—Hg...O(1) ⁱⁱ	72.0(5)	
O(1)—Hg...O(2) ^{iv}	87.0(5)	
O(1) ⁱⁱ ...Hg...O(2) ^{iv}	79.2(5)	
C(1)—Hg...O(2)		131.0(7)
C(1)—Hg...O(2) ⁱⁱⁱ		92.8(6)
O(1)—Hg...O(2)		49.6(5)
O(1)—Hg...O(2) ⁱⁱⁱ		88.4(5)
O(2)...Hg...O(2) ⁱⁱⁱ		129.8(4)
C(6)—C(1)—C(2)	123(2)	118(2)
C(1)—C(2)—C(3)	119(2)	120(2)
C(2)—C(3)—C(4)	119(2)	123(2)
C(3)—C(4)—C(5)	120(2)	117(3)
C(4)—C(5)—C(6)	126(2)	125(3)
C(5)—C(6)—C(1)	113(2)	118(2)
C(7)—C(8)—O(1)	114(2)	114(2)
C(7)—C(8)—O(2)	120(2)	122(2)
O(1)—C(8)—O(2)	126(2)	124(2)
C(8)—C(7)—F(1)	111(2)	
C(8)—C(7)—F(2)	112(2)	
C(8)—C(7)—F(3)	111(2)	
F(1)—C(7)—F(2)	108(2)	
F(1)—C(7)—F(3)	109(2)	
F(2)—C(7)—F(3)	107(2)	

Symmetry code:

- (i) $-x, -y, 1-z$; (ii) $-x, -y, -z$; (iii) $x+1, y, z$; (iv) $x, y+1, z$;
(v) $-x, -y-1, -z$.

as one would expect so that it is still difficult to say that the trifluoroacetate ion, in comparison with the acetate ion has any particular effect on the elongation of the mercury-carbon bond length.

The surrounding of the mercury atom, *i.e.* its effective coordination, in both compounds (A) and (B) is similar. In the structure of (A) the mercury atom, apart from being bonded to the phenyl-carbon atom and to the trifluoroacetato-oxygen atom, is additionally surrounded by two oxygen atoms [Hg...O(2)^{iv} of 282.8 and Hg...O(1)ⁱⁱ of 295.2 pm] from two symmetrically related neighbouring trifluoroacetato ligands (Figure 2). The next closest contacts are Hg...O(2) and Hg...F(1)^v of 303.4 and 318.8 pm, respectively. The closer approach of F(1)^v to the mercury atom is hindered by the C(6)—H...F(1)^v contact in which the H...F(1)^v distance amounts to 274 pm (the hydrogen atom position is calculated at a distance of 100 pm from the C(6) carbon atom). In (B) the effective coordination of the mercury atom is also four: apart from its covalent bonding to the phenyl-carbon and to the acetato-oxygen atom there are two additional acetato-oxygen atoms surrounding mercury at distances of 281.9 and 290.7 pm (Figure 3). Further mercury-to-oxygen contacts are Hg...O(1)ⁱⁱ and Hg...O(2)ⁱ of 299.4 and 316.0 pm, respectively. The closer approach of O(1)ⁱⁱ to mercury is hindered by the O(1)...O(1)ⁱⁱ contact of 299 pm. In such a way the coordination sphere of mercury includes only those oxygen atoms which are at Hg...O distances approximately equal or smaller than the sum of the van der Waals radii of mercury and oxygen (154.0+140.0 pm).^{6,7}

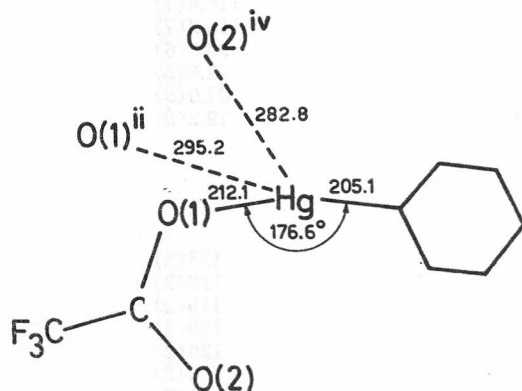


Figure 2. The effective coordination of mercury in phenylmercury(II) trifluoroacetate.

The bond lengths and angles within phenyl rings, trifluoroacetate or acetate ions are in agreement with the values found in similar compounds.^{8,9}

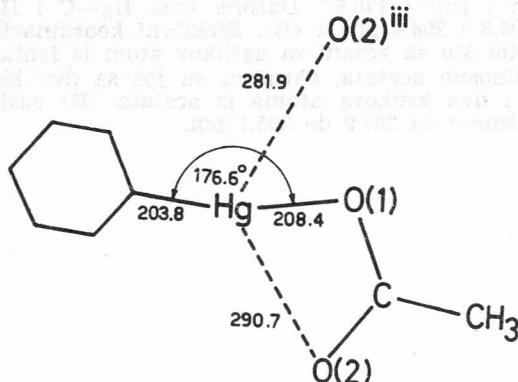


Figure 3. The effective coordination of mercury in phenylmercury(II) acetate.

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REFERENCES

1. D. Grdenić, *Izvj. Jugoslav. centr. krist. (Zagreb)*, **12** (1977) 5 (in English).
2. B. Kamenar and M. Penavić, *Inorg. Chim. Acta* **6** (1971) 191.
3. F. Swarts, *Bull. Soc. Chim. Belg.* **48** (1939) 176.
4. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974, p. 99.
5. A. Domenicano, R. Spagna, and A. Vaciano, *Atti Accad. Naz. Lincei Mem. Cl. Sci. Fis. Mat. Nat.*, Ser. 2a, **47** (1969) 331.
6. D. Grdenić, *Quart. Rev.* **19** (1965) 303.
7. D. Grdenić, *Connections in the Crystal Structures of Mercury Compounds*, in the book: *Structural Studies on Molecules of Biological Interest* (A Volume in Honour of Prof. Dorothy Hodgkin), Edit. by G. Dodson, J. P. Glusker and D. Sayre, Clarendon Press, Oxford, 1981, p. 207.
8. D. Grdenić, B. Kamenar and A. Nagl, *Acta Cryst.* **B33** (1977) 587.
9. J. Halfpenny and R. W. H. Small, *Acta Cryst.* **B34** (1978) 3758.

SAŽETAK

Kristalna struktura fenilživa(II)-trifluoroacetata i utočnjavanje kristalne strukture fenilživa(II)-acetata

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Kristalna struktura fenilživa(II)-trifluoroacetata (A) određena je postupkom teškog atoma na osnovi rendgenskih difraktometrijskih podataka i utočnjena metodom najmanjih kvadrata do faktora pouzdanosti $R = 0,051$. Struktura fenilživa(II)-acetata (B) ponovno je određena i utočnjena, također na osnovi difraktometrijskih podataka, da bi se dobile što točnije vrijednosti za duljine veza i kuteva i tada mogli usporediti s onima nađenim u strukturi (A). Utočnjavanje za (B) završeno je kod faktora $R = 0,069$. Oba spoja, (A) i (B), imaju u suštini jednaku molekulsku strukturu: karakteristična koordinacija žive je digonska sa skoro kolinearnim C—Hg—O vezama. U obje strukture kut kod ato-

ma žive je identičan i iznosi $176,6^\circ$. Duljine veza Hg—C i Hg—O su 205,1 i 212,1 pm u (A), a 203,8 i 208,4 pm u (B). Efektivni koordinacijski broj žive je četiri: atomi žive, osim što su vezani za ugljikov atom iz fenila i kisikov atom iz trifluoroacetata odnosno acetata, okruženi su još sa dva kisikova atoma iz trifluoroacetata (A) i dva kisikova atoma iz acetata (B) susjednih molekula. Ovi razmaci Hg...O iznose od 281,9 do 295,1 pm.