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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(2,3,4,5-TETRAFLUOROPHENYL)MERCURY *

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Summary

During studies on the preparation of perfluoro-*o*-phenylenemercury, bis(2,3,4,5-tetrafluorophenyl)mercury was isolated as a by-product and characterised by spectroscopic and X-ray techniques.

Introduction

The decarboxylation of mercury(II) tetrafluorophthallate is known [1] to produce perfluoro-*o*-phenylenemercury, $(C_6F_4Hg)_3$. Investigation of a sample of crystals, grown by sublimation in the open air, from such a preparation showed that a small quantity of bis(2,3,4,5-tetrafluorophenyl)mercury is also produced.

Experimental

Mercury(II) tetrafluorophthallate was prepared by precipitation on mixing a warm aqueous solution of tetrafluorophthallic acid (Bristol Organics Ltd.) with a warm filtered solution of mercury(II) acetate. The precipitate was filtered, dried at 110°C and then small batches of this compound decarboxylated and sublimed onto a water-cooled probe by heating to about 300°C under vacuum. Purification was accomplished by vapour diffusion of water into a filtered *N*,*N*-dimethylformamide solution of the crude product, followed by drying at 150°C. A recrystallization of this bulk product from cyclohexanone, followed by drying in an oven, produced a small quantity of feathery crystals on the neck of the flask.

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* Part III of a Series; for Part II see ref. 9.

TABLE 1

THERMAL PARAMETERS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	417 (4)	475 (5)	651 (6)	7 (8)	309 (4)	91 (8)

	U		U
C(1)	587 (48)	C(6)	448 (35)
C(2)	474 (37)	F(2)	765 (32)
C(3)	555 (43)	F(3)	794 (33)
C(4)	496 (33)	F(4)	833 (30)
C(5)	534 (41)	F(5)	729 (31)

The parameters refer to the equations $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2\,U_{23}b^*c^*kl + \ldots)]$ and $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$.

Crystal data

$C_{12}H_2F_8Hg$, $M = 498.7$, Monoclinic, $a = 11.786(4)$, $b = 4.871(6)$, $c = 13.114(5)$ Å, $\beta = 127.4(1)°$, $U = 598.0$ Å^3, $Dx = 2.78$ Mg m^{-3}, $Z = 2$, $F(000) = 456$, Mo—K_α radiation, $\lambda = 0.71069$ Å, $\mu = 12.47$ mm^{-1}. Crystal size 0.1 × 0.025 × 0.9 mm. Absent reflections, $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$ conform uniquely with space group $P2_1/c$ (No. 14).

The intensities and refined cell dimensions were collected on a Stoë automatic 2-circle Weissenberg diffractometer allowing the measurement of 911 reflections for which $I > 3\sigma(I)$. Corrections were made for Lorentz, polarisation and absorption effects. The structure was solved by heavy atom methods and refined by full-matrix least squares refinement with unit weights to a final conventional R of 5.1%. Anisotropic parameters were allowed for mercury and isotropic parameters for the light atoms (except hydrogen which was not included) (Table 1). In the final cycle the maximum shift/error was 0.25 and no interpretable features were observed on the final difference map. Calculations were carried out using the XRAY 72 [2] and SHELX [3] packages as implemented by the University of Manchester Regional Computer Centre. Scattering factors were taken from International Tables for Crystallography Vol. IV [2].

Results and discussion

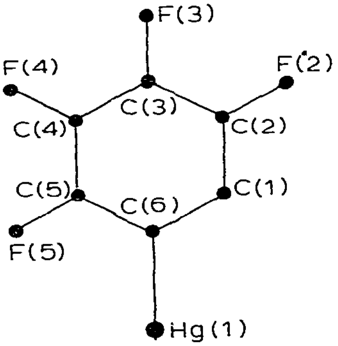
Bis(2,3,4,5-tetrafluorophenyl)mercury, like diphenylmercury [4] and bis-(4-methylphenyl)mercury [5], crystallizes in the space group $P2_1/c$ with the heavy atom in a centrosymmetric special position (Table 2, Fig. 1). The rings are coplanar thus maximising the separation of the two *ortho* fluorine atoms and minimising their electrostatic repulsion. When the 6-fluorine atoms are present, as in bis(pentafluorophenyl)mercury [6], the electrostatic repulsion has to be reduced by tilting the rings relative to each other. Bis(2,3,4,5-tetrafluorophenyl)mercury is ordered, unlike 2,3,3′,4,4′,5,5′,6,6′-nonafluorobiphenyl [7], presumably due to a combination of the above electrostatic effect

TABLE 2

POSITIONAL PARAMETERS $(\times 10^3)$ WITH STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
Hg(1)	0	500 [a]	500 [a]
C(1)	223 (2)	−58 (4)	621 (2)
C(2)	323 (2)	119 (4)	630 (2)
C(3)	329 (2)	145 (4)	530 (2)
C(4)	251 (1)	−14 (5)	427 (1)
C(5)	158 (2)	−194 (4)	422 (2)
C(6)	145 (2)	−219 (4)	516 (2)
F(2)	408 (1)	3 (3)	233 (1)
F(3)	424 (1)	332 (3)	537 (1)
F(4)	253 (1)	9 (4)	327 (1)
F(5)	83 (1)	−364 (3)	317 (1)

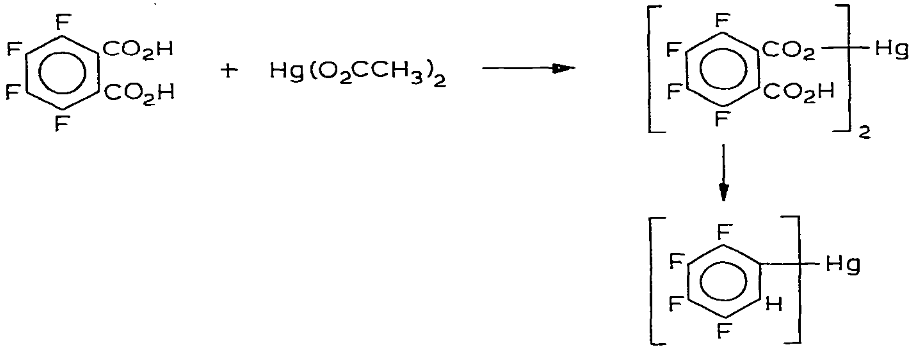
[a] Fixed by symmetry considerations.



and a weak H—F interaction (which is sterically possible). The difference in crystal packing between bis(pentafluorophenyl)mercury and the other phenylmercurials may explain the early report of a variable melting point for the former compound [8]. If, on fresh sublimation, the crystal packing were determined solely by Van der Waals' considerations about the heavy atom, then a meta-stable, co-planar configuration of low melting point could well result.

The bond lengths and angles (Tables 3 and 4) in the rings are normal for a phenyl system. The carbon—mercury bond length at 2.096(16) Å is also within normal values for this distance: the six unique carbon—mercury separations in orthorhombic tribenzo[*b*,*e*,*h*][1,4,7]trimercuronin [9] fall in the range 2.07—2.13 Å and in bis(pentafluorophenyl)mercury [6] the values are both 2.10 Å.

The decarboxylation of mercury(II) tetrafluorophthallate shows the relative ease of elimination of carbon dioxide from a highly fluorinated aromatic system, compared with the unsubstituted case: mercury(II) phthallate monodecarboxylates only [10]. The isolation of bis(2,3,4,5-tetrafluorophenyl)mercury was unexpected since it could not be detected in the infra-red spectrum of the bulk product; subsequent thermogravimetric analysis showed it to comprise only about 1% of the mercurials produced. It possibly arises from the following reaction sequence.



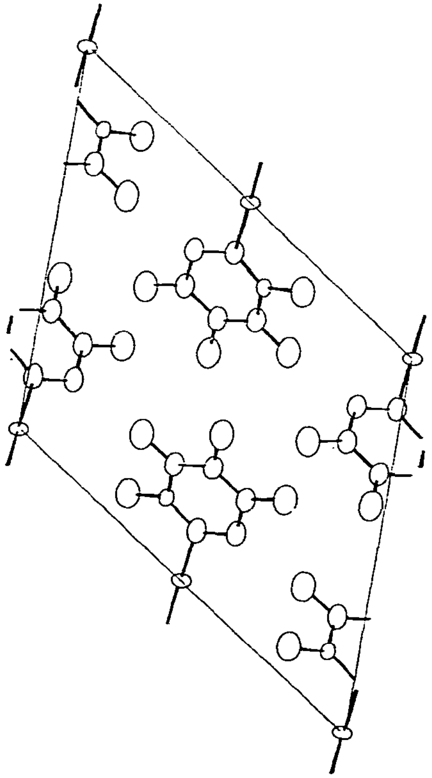


Fig. 1. Contents of the unit cell projected down the *b* axis.

TABLE 3

BOND-LENGTHS (Å) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Hg(1)—C(6)	2.096 (16)
C(6)—C(5)	1.336 (22)
C(5)—C(4)	1.380 (26)
C(4)—C(3)	1.325 (25)
C(3)—C(2)	1.369 (22)
C(2)—C(1)	1.405 (23)
C(1)—C(6)	1.346 (23)
C(2)—F(2)	1.388 (21)
C(3)—F(3)	1.394 (21)
C(4)—F(4)	1.337 (17)
C(5)—F(5)	1.378 (21)

TABLE 4

BOND-ANGLES (°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

C(6)—Hg(1)—C(6)	180.0 [a]
C(1)—C(6)—Hg(1)	119.8 (1.2)
C(5)—C(6)—Hg(1)	120.4 (1.3)
C(5)—C(6)—C(1)	119.8 (1.7)
C(6)—C(1)—C(2)	117.7 (1.6)
C(1)—C(2)—C(3)	120.4 (1.7)
C(1)—C(2)—F(2)	121.8 (1.7)
C(3)—C(2)—F(2)	118.0 (1.8)
C(2)—C(3)—C(4)	121.0 (0.8)
C(2)—C(3)—F(3)	119.8 (1.7)
C(4)—C(3)—F(3)	119.1 (1.6)
C(3)—C(4)—C(5)	117.3 (1.5)
C(3)—C(4)—F(4)	122.4 (1.9)
C(5)—C(4)—F(4)	120.1 (1.7)
C(4)—C(5)—C(6)	123.4 (1.7)
C(4)—C(5)—F(5)	115.5 (1.5)
C(6)—C(5)—F(5)	120.9 (1.7)

[a] Fixed by symmetry considerations.

Insufficient sample was found to produce a completely confirmatory IR spectrum, but the major peaks were in agreement with literature values [11]. The mass spectrum confirmed the empirical formula as $C_{12}H_2F_8Hg$ and showed the only major degradative pathway to be cleavage of the C—Hg bond (i.e. loss of C_6F_4H or HC_6F_4Hg).

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References

1 P. Sartori and A. Golloch, Chem. Ber., 101 (1968) 2004.
2 XRAY System (1972), Tech. Rep. TR-192; Computer Science Centre, University of Maryland, College Park, Maryland.
3 G.M. Sheldrick (1975); SHELX, a Program for Crystal Structure Determination.
4 D. Grdenic, B. Kamenar and N. Nagl, Acta Cryst. B, 33 (1977) 587.
5 N. Mathew and N.R. Kunchur, Canad. J. Chem., 48 (1970) 429.
6 N.R. Kunchur and N. Mathew, Chem. Commun., (1966) 71.
7 M.J. Hamor and T.A. Hamor, Acta Cryst. B, 34 (1978) 863.
8 P.L. Coe, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1962) 3227.
9 D.S. Brown, A.G. Massey and D.A. Wickens, Acta Cryst. B, 34 (1978) 1695.
10 L. Pesci, Atti. Accad. Naz. Lincei Rc., 101 (1901) 362.
11 H.B. Albrecht and G.B. Deacon, J. Organometal. Chem., 57 (1973) 77.
12 International Tables for Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974, p. 99.