Crystal Structure of Tris(methylmercurio)sulphonium Perchlorate†

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Crystals of $[(CH_3Hg)_3S]ClO_4$ are tetragonal, space group $P4_1$ or $P4_3$, with a = 9.642(3), c = 12.808(6) Å, and Z = 4. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least squares to R = 0.045 (R' = 0.048) for 1 009 diffractometer data. The $[(CH_3Hg)_3S]^+$ cation adopts a trigonal-pyramidal structure with Hg–S and Hg–C bond lengths ranging from 2.383(10) to 2.405(9) Å, and from 2.04(4) to 2.10(4) Å, respectively. The S–Hg–C angles vary from 172.3(14) to 179.5(12)°, those at the apical sulphur atom from 95.5(3) to 106.5(4)°.

After it had been established that the structure of $2HgCl_2 \cdot HgO$ consists of pyramidal tris(chloromercurio)oxonium ions,[1] the analogous tris(methylmercurio)-oxonium and -sulphonium salts were prepared.[2,3] Due to the low quality of their crystals or their sensitivity to moisture, the structure of these compounds has not been definitely established until now. The present X-ray diffraction investigation of $[(CH_3Hg)_3S]ClO_4$ is the first example for this type of organomercury compound.

Results and Discussion

The structure of $[(CH_3Hg)_3S]ClO_4$ consists of $[(CH_3Hg)_3S]^+$ cations and perchlorate anions (Figure). The cations have a trigonal-pyramidal structure in which three Hg atoms form a triangle (see Table 1) while the sulphur atom is situated at the apex of the pyramid. The methyl-carbon atoms also form a triangle which is almost parallel to that of the mercury atoms. The height of the SHg_3 pyramid, *i.e.* the distance between the S atom and the least-squares best plane through the three Hg atoms, is 1.11(2) Å, while the distance between the best plane through the three C and the S atom is 1.97(2) Å. The angles at the S atoms are significantly different [95.5(3), 98.0(4), and 106.5(4)°], but similar to the values found *e.g.* in $Hg_3S_2Cl_2$.[4] The S–Hg–C bond angles vary from S–Hg(3)–C(3) of 179.5(12), with almost collinear bonds, to S–Hg(2)–C(2) and S–Hg(1)–C(1) of 172.3(14) and 174.6(10)°, respectively. The values of the three Hg–S bond lengths are similar [2.400(11), 2.405(9), and 2.383(10) Å] and a little, but not significantly, larger than the sum of the corresponding digonal covalent radii (2.36 Å).[5] Each of the Hg atoms is linked to one of the methyl-carbon atoms at distances of 2.04(4), 2.07(5), and 2.10(4) Å, in very good agreement with the values found for Hg–C bond lengths in numerous organomercurials.[6]

The Hg···O distances from mercury to the perchlorate oxygens range from 2.97(7) to 3.19(5) Å, while the shortest Hg···S contacts are 3.483(9) and 3.498(11) Å obviously indicating that there are not additional interactions between Hg and the neighbouring O and S atoms.[7] Consequently, the characteristic co-ordination of the Hg atoms is digonal.[5,8]

Table 1. Bond lengths, interatomic contacts (Å), and angles (°) with estimated standard deviations in parentheses for $[(CH_3Hg)_3S]ClO_4$

Hg(1)–S	2.400(11)	Cl–O(1)	1.50(4)
Hg(2)–S	2.405(9)	Cl–O(2)	1.27(5)
Hg(3)–S	2.383(10)	Cl–O(3)	1.46(6)
Hg(1)–C(1)	2.04(4)	Cl–O(4)	1.41(4)
Hg(2)–C(2)	2.07(5)		
Hg(3)–C(3)	2.10(4)		
Hg(1)···O(2$^{\rm I}$)	3.03(11)	Hg(3)···O(1$^{\rm II}$)	3.12(5)
Hg(1)···O(3$^{\rm II}$)	2.97(7)	Hg(3)···O(4$^{\rm I}$)	2.97(5)
Hg(2)···O(1$^{\rm III}$)	3.05(5)	Hg(1)···S$^{\rm I}$	3.498(11)
Hg(2)···O(1$^{\rm II}$)	3.19(5)	Hg(2)···S$^{\rm I}$	3.483(9)
Hg(2)···O(4$^{\rm III}$)	3.06(5)		
Hg(1)–S–Hg(2)	106.5(4)	O(1)–Cl–O(2)	116(6)
Hg(2)–S–Hg(3)	98.0(4)	O(1)–Cl–O(3)	102(4)
Hg(1)–S–Hg(3)	95.5(3)	O(1)–Cl–O(4)	112(3)
S–Hg(1)–C(1)	174.6(10)	O(2)–Cl–O(3)	110(8)
S–Hg(2)–C(2)	172.3(14)	O(2)–Cl–O(4)	107(4)
S–Hg(3)–C(3)	179.5(12)	O(3)–Cl–O(4)	109(3)

Symmetry code: I $-y, x, 0.25 + z$; II $y, 1 - x, -0.25 + z$; III $x, 1 + y, z$.

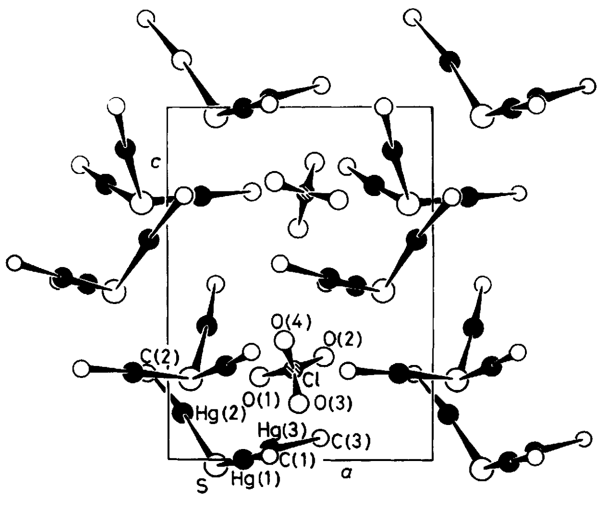

Figure. The crystal structure of $[(CH_3Hg)_3S]ClO_4$ viewed down b

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† *Supplementary data available* (No. SUP 56293, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg(1)	2 887(1)	1 321(2)	0
Hg(2)	617(1)	−1 457(1)	1 323(2)
Hg(3)	3 982(2)	−2 174(1)	203(2)
S	1 916(10)	−949(11)	−235(7)
C(1)	3 863(57)	3 196(43)	110(48)
C(2)	−734(33)	−1 873(57)	2 540(43)
C(3)	5 812(40)	−3 239(42)	580(41)
Cl	35(12)	5 208(10)	101(11)
O(1)	−830(49)	6 467(36)	−104(41)
O(2)	−623(127)	4 133(101)	393(83)
O(3)	685(57)	4 966(87)	−911(56)
O(4)	1 069(55)	5 464(53)	851(41)

Experimental

The crystals were prepared as described for the analogous nitrate.[5]

X-Ray Crystal Structure of $[(\mathrm{CH_3Hg})_3\mathrm{S}]\mathrm{ClO_4}$.—*Crystal data.* $\mathrm{C_3H_9ClHg_3O_4S}$, $M = 778.39$, tetragonal,* $a = 9.642(3)$, $c = 12.808(6)$ Å, $U = 1\,190.74$ Å^3, $Z = 4$, $D_c = 4.34$ g cm^{-3}, $F(000) = 1\,328$, $\mu(\text{Mo-}K_\alpha) = 375.75$ cm^{-1}. Systematic extinctions $00l$, $l \neq 4n$ indicated the space group to be $P4_1$ or $P4_3$.

The intensity data were collected from a crystal of size 0.10 × 0.08 × 0.21 mm on a Philips PW 1100 automatic diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å) in the range θ 3—30° using the ω—2θ scan technique (scan range 1.20°, scan rate 0.04° s^{-1}). The structure was solved by means of a three-dimensional Fourier synthesis based upon the positions of the Hg atoms obtained from the Patterson synthesis, using 1 009 [$I \geqslant 3\sigma(I)$] absorption-corrected reflections. It was refined by full-matrix least squares. Hydrogen atoms at their calculated positions (C–H 1.08 Å) were included in the refinement but were not refined. A weighting scheme with $w = 0.742/[\sigma(F_o)^2 + 0.000\,56\,F_o^2]$ was applied to the data and the refinement was terminated at $R = 0.045$ ($R' = 0.048$).

The atomic co-ordinates are given in Table 2. Computations were performed on the UNIVAC 1110 computer at Zagreb University Computing Centre using the SHELX system of programs.[10]

Acknowledgements

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* Initially the crystals were wrongly assigned to the monoclinic space group $P2_1/c$.[9]