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Crystal Structure of Methanethiolatomercury(II) Chloride

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Abstract

The crystal structure of the title compound, MeSHgCl, has been determined by single-crystal X-ray diffraction at 295 K and refined by full-matrix least squares to a residual of 0·048 for 787 'observed' reflections. Crystals are monoclinic, $P2_1/c$, a 7·490(4), b 7·395(2), c 7·815(3) Å, β 92·93(4)°, Z 4, and are isostructural with the previously described MeSHgBr.

Introduction

In a previous report,[1] the structure determination of MeSHgBr has been described and shown to comprise a two-dimensional polymeric Hg/S/Br sheet; it was also noted that the cell dimensions correspond closely to those reported in an early crystallographic study of MeSHgCl, based on powder data.[2] In this note we report the structure determination of MeSHgCl by single-crystal methods; the structure of the bromide analogue has been described in detail previously and that of the chloride is so closely similar as not to justify more than the present brief report.

Crystallography

Crystal data.—CH_3ClHgS, M 283·1, monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 7·490(4), b 7·395(2), c 7·815(3) Å, β 92·93(4)°, $D_c(Z = 4)$ 4·350 g cm^{-3}. Monochromatic Mo Kα radiation, λ 0·7106$_9$ Å, μ_{Mo} 351·8 cm^{-1}. Specimen size: plate 0·25 by 0·20 (c, b as diagonals) by 0·03 (a) cm. $F(000)$ 488.

Structure determination.—Unique data set collected to $2\theta_{max}$ 60°, by means of a Syntex P$\bar{1}$ four-circle diffractometer in the $2\theta/\theta$ scan mode yielding 1259 independent reflections, 787 with $I > 3\sigma(I)$ being considered 'observed' and used in the refinement after absorption correction. (In the present case, satisfactory crystals were directly obtained by recrystallization of the complex from pyridine, in contrast to the bromide where the only specimens obtainable were poor in quality being obtained by cleavage of the micaceous leaves.) Full-matrix least-squares refinement, initiated by using the structural parameters of the bromide as an initial approximation, converged at R 0·048, R' 0·054, reflection weights being $[\sigma^2(F_o)+0\cdot0003(F_o)^2]^{-1}$. Hydrogen atoms were not located; all other atoms were refined with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+ \ldots +2U_{23}klb^*c^*)]$.

[1] Canty, A. J., Raston, C. L., and White, A. H., *Aust. J. Chem.*, 1979, **32**, 311.
[2] Johansson, A., *Ark. Kemi, Mineral. Geol.*, 1939, **13A**, 1.

Scattering factors: neutral atoms, corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[3,4] Material deposited: structure factor amplitudes.† Atom numbering follows that of the bromide.[1] Computation: X-RAY 76 program system, CYBER 73 computer.[5]

Results.—These are presented in Tables 1 and 2.

Table 1. Atom parameters for MeSHgCl

U_{ij} in Å^2

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Hg	0349(1)	1274(1)	2209(1)	36·9(5)	20·2(3)	36·4(4)	5·6(5)	4·3(3)	1·9(4)
Cl	2438(6)	1289(7)	−0529(5)	31(2)	30(2)	31(2)	1(3)	5(2)	3(2)
S	1559(6)	−1276(7)	3849(5)	26(2)	23(2)	28(2)	−1(2)	2(2)	1(2)
C	3725(29)	−1658(26)	2974(26)	25(12)	47(12)	46(11)	5(9)	−1(9)	9(9)

Table 2. Interatomic distances (Å) and angles (degrees)

Transformations of the asymmetric unit (x, y, z): i ($\bar{x}$, $\bar{y}$, $1-z$); ii ($\bar{x}$, $\bar{y}$, $\bar{z}$); iii (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$); iv ($\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$); v ($\bar{x}$, $y-\frac{1}{2}$, $\frac{1}{2}-z$); vi (x, $\frac{1}{2}-y$, $z-\frac{1}{2}$)

Atoms	Distance	Atoms	Angle	Atoms	Angle
		The mercury environment			
Hg–Cl	2·714(5)	Cl–Hg–S	101·8(1)	S–Hg–S^{iv}	163·1(1)
Hg–S	2·429(5)	Cl–Hg–S^{i}	169·2(1)	S^{i}–Hg–Cl^{ii}	94·5(1)
Hg···S^{i}	3·462(4)	Cl–Hg–Cl^{ii}	94·1(3)	S^{i}–Hg–Cl^{iii}	72·2(1)
Hg–Cl^{ii}	3·064(5)	Cl–Hg–Cl^{iii}	99·3(1)	S^{i}–Hg–S^{iv}	92·3(1)
Hg–Cl^{iii}	2·922(5)	Cl–Hg–S^{iv}	94·7(1)	Cl^{ii}–Hg–Cl^{iii}	166·5(1)
Hg–S^{iv}	2·427(5)	S–Hg–S^{i}	72·0(1)	Cl^{ii}–Hg–S^{iv}	86·5(1)
Hg···Hg^{iv,v}	3·764(2)	S–Hg–Cl^{ii}	88·5(1)	Cl^{iii}–Hg–S^{iv}	91·9(1)
		S–Hg–Cl^{iii}	89·2(1)	Hg^{iv}···Hg···Hg^{v}	158·26(3)
		The thiol			
S–C	1·81(2)	Hg–S–C	103·8(6)	Hg^{v}–S–C	106·1(7)
		Hg^{i}–S–C	138·8(7)		
		Sulfur and chlorine bridges			
		Hg–S–Hg^{i}	108·0(2)	Hg–Cl–Hg^{ii}	85·9(1)
		Hg–S–Hg^{v}	101·7(2)	Hg–Cl–Hg^{vi}	99·6(2)
		Hg^{i}–S–Hg^{v}	92·3(1)	Hg^{ii}–Cl–Hg^{vi}	77·9(1)

Discussion

As found for the isostructural bromide,[1] parallel chains (–Hg–SMe–)$_n$ linked into parallel sheets by triply bridging halogen atoms (coordinated to two mercury atoms in one chain and one mercury atom in an adjacent chain) give the mercury environment 'Hg(μ-SMe)$_2$(μ_3-Cl)$_3$' with an additional, weak, Hg···S^{i} contact.

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† Copies are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

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[4] Cromer, D. T., and Liberman, D., *J. Chem. Phys.*, 1970, **63**, 1691.
[5] 'The X-RAY System—Version of June, 1976' Technical Report TR-446, Computer Science Center, University of Maryland, U.S.A.