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TRIMERCURATED ACETALDEHYDE AS THE MERCURATION PRODUCT OF ETHANOL. THE CRYSTAL STRUCTURE OF $(ClHg)_3CCHO \cdot DMF$ AND $(BrHg)_3CCHO \cdot DMSO$

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Summary

The product obtained by boiling an ethanolic solution of mercuric chloride with sodium acetate (Hofmann, 1899) has been identified as tris(chloromercuri)acetaldehyde. The analogous bromomercuri derivative is obtained by using mercuric bromide. Both compounds crystallize from DMSO of DMF solution as the one-to-one solvates. The crystal structure of $(ClHg)_3CCHO \cdot DMF$ (A) and $(BrHg)_3CCHO \cdot DMSO$ (B) has been determined by X-ray diffraction methods and refined by full-matrix least-squares to the conventional R indices of 0.087 and 0.079, respectively. The mean value of the Hg—C bond length is 2.09(9) Å in A and 2.04(7) Å in B.

Introduction

When ethanol is mercurated with mercuric oxide and alkali [1] an oxide-hydroxide of permercurated methane, $(CHg_4O)_n(OH)_{2n}$, is obtained as established by the X-ray crystal structure analysis of its $C(HgX)_4$ derivatives with X = CF_3COO [2], CN [3], CH_3COO [4] and Cl [5].

A different mercuration product of ethanol is the subject of the present paper. It is obtained by boiling an ethanolic solution of mercuric chloride with sodium acetate and was formulated as $C_2Hg_4Cl_4$ [6]. We found that the product was badly contaminated with mercurous chloride. The chemical analysis of the purified product, as well as its IR and NMR spectra, indicated tris(chloromercuri)acetaldehyde, $(ClHg)_3CCHO$, as the only mercuration product. This has been confirmed by X-ray structure analysis of the 1/1 solvate with dimethylformamide (DMF), and that of a similar solvate of $(BrHg)_3CCHO$ with dimethylsulfoxide (DMSO).

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Results and discussion

The IR absorption band at 1620 cm^{-1} of the mercuration product, indicating the presence of the carbonyl group, was too strong to be attributed to impurity. On the other hand, X-ray powder diffractogram of the original mercuration product consisted almost only of the peaks which had been unambigously assigned to mercurous chloride. Exhaustive digestion of the product with nitric acid gave a white crystalline powder, free from mercurous chloride. The amount of mercurous chloride found in the crude product corresponded to the amount of mercuric chloride required for the oxidation of ethanol to acetaldehyde according to the equation:

$$C_2H_5OH + 5\ HgCl_2 + 5\ NaOCOCH_3 \rightarrow$$
$$(ClHg)_3CCHO + Hg_2Cl_2 + 5\ NaCl + 5\ CH_3COOH\ , \qquad (1)$$

i.e., two of five $HgCl_2$ moles totally consummed. The reaction with mercuric bromide was analogous. Subsequently, bromine (chlorine) water was conveniently used to separate mercurous bromide (chloride) from the mercurated acetaldehyde since the latter is only slowly transformed to bromal (chloral) [7,8]. Since mercurous halides are insoluble in DMF and DMSO, trimercurated acetaldehyde is conveniently extracted from the crude product with one of these solvents. The pure 1/1 solvates are precipitated by the addition of acetone to the filtrate.

Tris(chloromercuri)acetaldehyde, as a well defined substance, was described for the first time by Biltz and Mumm [7] who obtained it by passing acetylene into a dilute aqueous solution of mercuric chloride. The bromine analogue was obtained in the same way [8]. The mercuration product of ethanol we obtained was identical with the tris(chloromercuri)acetaldehyde obtained by mercuration of acetylene.

Description of the structures

The asymmetric units of the crystal structure of $(ClHg)_3CCHO \cdot DMF$ (A), and $(BrHg)_3CCHO \cdot DMSO$ (B) are depicted in Fig. 1 and 2, respectively. The crystal structure of each solvate consists of discrete molecules. The interatomic distances and bond angles are given in Table 1. The variations in the Hg—C bond distances can be ascribed to the variability of the intensity data due to the decomposition of the specimen under X-rays during the measurement (see Experimental). The accuracy of the light atom coordinates were most affected and is lower than is usual for the methods used.

Nevertheless, the values of the Hg—C bond lengths, having mean values of 2.09 (A) and 2.04 Å (B), agree with those observed previously in the permercurated methane derivatives [2—4] as well as in chloromercuriacetaldehyde [9] and bis(chloromercuri)methane [10]. The difference might be attributed to the different nature of the halogen in A and B. The distortion of the $CCHg_3$ tetrahedron is evident from the unequality of the Hg···Hg edges as well as from the Hg—C—Hg bond angles (Table 1). It is mainly due to the dissimilar effective coordination about the mercury atoms. Thus the mercury—oxygen interactions

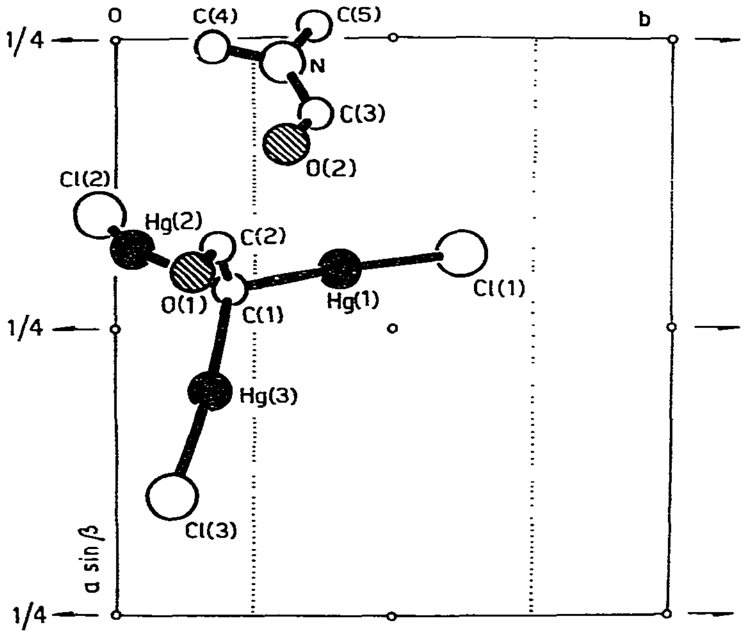

Fig. 1. The asymmetric unit in the structure of $(ClHg)_3CCHO \cdot DMF$ (A) viewed along the c-axis direction.

are strong for Hg(1) in both A and B, but with Hg(2) only in B, the corresponding Hg···O distances being less than the sum of the Van der Waals radii [11,12]. The interactions with Hg(3) are not strong, either in A or in B, the effective coordination of the Hg(3) being a distorted octahedron. The mean values of the Hg···Hg tetrahedron edges and the Hg—C—Hg angles of 3.40 Å and 109° in A,

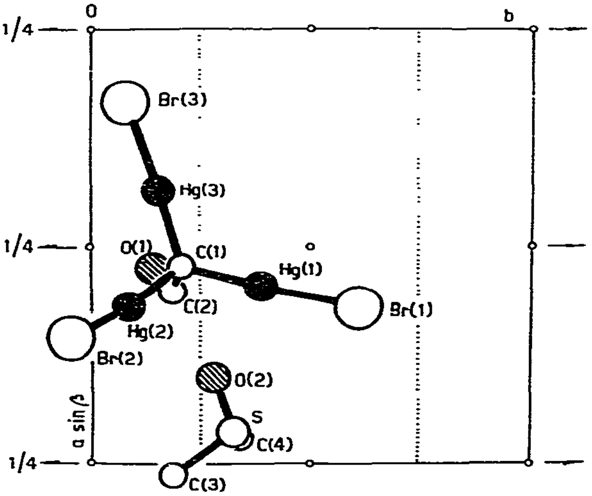

Fig. 2. The asymmetric unit in the structure of $(BrHg)_3CCHO \cdot DMSO$ (B) viewed along the c-axis direction.

TABLE 1

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°), WITH STANDARD DEVIATIONS IN PARENTHESES [a]

Distances		Distances		Angles	
Compound (A)					
C(1)—Hg(1)	2.15(6)	Hg(1) ... Hg(2)	3.261(4)	Hg(1)—C(1)—Hg(2)	101(3)
C(1)—Hg(2)	2.07(8)	Hg(1) ... Hg(3)	3.520(4)	Hg(1)—C(1)—Hg(3)	113(3)
C(1)—Hg(3)	2.06(7)	Hg(2) ... Hg(3)	3.412(5)	Hg(2)—C(1)—Hg(3)	112(4)
Hg(1)—Cl(1)	2.30(1)	Hg(1) ... O(2)	2.75(5)	C(1)—Hg(1)—Cl(1)	176(2)
Hg(2)—Cl(2)	2.34(2)	Hg(1) ... O(1)^{iii}	2.80(6)	C(1)—Hg(2)—Cl(2)	175(2)
Hg(3)—Cl(3)	2.30(2)	Hg(1)^{iii} ... Cl(2)	3.35(3)	C(1)—Hg(3)—Cl(3)	172(2)
C(1)—C(2)	1.50(13)	Hg(2) ... O(2)	3.03(6)	Hg(1)—C(1)—C(2)	105(4)
C(2)—O(1)	1.26(9)	Hg(2) ... O(1)^{iii}	3.25(5)	Hg(2)—C(1)—C(2)	109(4)
N—C(3)	1.48(11)	Hg(2)^{ii} ... Cl(1)	3.40(2)	C(1)—C(2)—O(1)	121(5)
N—C(4)	1.40(12)	Hg(3) ... O(1)	3.15(6)	O(2)—C(3)—N	129(8)
N—C(5)	1.49(11)	Hg(3) ... Cl(1)^{i}	3.21(2)	C(3)—N—C(4)	109(7)
C(3)—O(2)	1.06(10)	Hg(3)^{ii} ... Cl(1)	3.34(2)	C(3)—N—C(5)	133(6)
		Hg(3) ... Cl(2)^{ii}	3.46(2)	C(4)—N—C(5)	118(6)
Compound (B)					
C(1)—Hg(1)	2.05(5)	Hg(1) ... Hg(2)	3.276(3)	Hg(1)—C(1)—Hg(2)	107(2)
C(1)—Hg(2)	2.03(5)	Hg(1) ... Hg(3)	3.537(2)	Hg(1)—C(1)—Hg(3)	119(3)
C(1)—Hg(3)	2.05(6)	Hg(2) ... Hg(3)	3.423(2)	Hg(2)—C(1)—Hg(3)	114(3)
Hg(1)—Br(1)	2.442(5)	Hg(1) ... O(2)	2.80(4)	C(1)—Hg(1)—Br(1)	178(2)
Hg(2)—Br(2)	2.434(5)	Hg(1) ... O(1)^{iii}	2.84(4)	C(1)—Hg(2)—Br(2)	168(2)
Hg(3)—Br(3)	2.428(6)	Hg(1) ... Br(2)^{ii}	3.570(5)	C(1)—Hg(3)—Br(3)	175(2)
C(1)—C(2)	1.64(7)	Hg(2) ... O(2)	2.77(4)	Hg(1)—C(1)—C(2)	103(3)
C(2)—O(1)	1.22(4)	Hg(2) ... O(1)^{iv}	3.17(3)	Hg(2)—C(1)—C(2)	108(3)
S—O(2)	1.49(5)	Hg(3) ... O(1)	2.95(4)	C(1)—C(2)—O(1)	122(4)
S—C(3)	1.82(7)	Hg(3)^{ii} ... Br(1)	3.311(6)	O(2)—S—C(3)	109(3)
S—C(4)	1.82(8)	Hg(3) ... Br(1)^{v}	3.431(5)	O(2)—S—C(4)	102(3)
		Hg(3) ... O(1)^{iv}	3.36(2)	C(3)—S—C(4)	97(3)
		Hg(3) ... Br(2)^{ii}	3.477(5)		

[a] Transformation of the asymmetric unit (x, y, z): (i) $1-x, 1-y, 1-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $1-x, -y, -z$; (v) $1-x, 1-y, -z$.

as well as 3.41 Å and 113° in B, satisfy the tetrahedral geometry within the limits of error.

Experimental

Characterization of the mercuration products

Spectral data. The IR spectra in the region of 4000—400 cm^{-1} were recorded on a Perkin—Elmer infrared grating spectrophotometer Model 337 using KBr discs. The ^{1}H NMR spectra were measured with a JEOL SQ 90 high resolution spectrometer at 90 MHz in DMSO-d_6 solution with TMS as internal standard.

Tris(chloromercuri)acetaldehyde. A mixture of absolute ethanol (200 ml), mercuric chloride (40 g), and anhydrous sodium acetate (10 g) was refluxed gently for 20 h. The white crystalline solid was filtered off, washed with water and (instead of being treated with nitric acid (30%) as described by Hofmann [6]) was dried in vacuo and weighed (16.5 g). The X-ray powder diffractogram of the solid was practically identical with that of mercurous chloride. The weak peaks of the mercuration product, merged with the back-ground, were hardly noticeable.

Suspension of the solid (10 g) in chlorine water (100 ml) was shaken for one hour, the remaining solid filtered off, washed with water and dried in vacuo. Yield: 6.0 g, dec. at 210°C. Found: C, 3.11; H, 0.24; Cl, 14.39; Hg, 80,17; $C_2HCl_3Hg_3O$ calcd.: C, 3.21; H, 0.14; Cl, 14.20; Hg, 80.33%. A few weak peaks in the X-ray diffractogram proved a low degree of crystallinity. None of the peaks could be attributed to mercurous chloride. The mercury content of the filtrate after chlorine water treatment, as determined by complexometric titration, corresponded to 3.96 g Hg_2Cl_2 (required by eq. 1: 3.865 g Hg_2Cl_2). Infrared absorptions: 1620s, 1600sh, 1380m, 1370m, 1350m, 1075s, 1013w, 612w and 522m cm^{-1}.

Tris(chloromercuri)acetaldehyde, obtained according to Biltz and Mumm [7], showed identical IR spectra, X-ray diffractogram, chemical analysis data, and gave the same solvates with DMF and DMSO.

Tris(chloromercuri)acetaldehyde DMSO-solvate. The original solid (4.20 g), obtained as described above, was dissolved in DMSO (6 ml) at room temperature, the insoluble residue (Hg_2Cl_2) was filtered off, washed with DMSO (2 ml), then (using a separate receiver) with acetone (5 ml) and finally dried in vacuo and weighed: 1.63 g, (calculated according to the eq. 1: 1.62 g). The combined filtrate and DMSO washing liquor was treated with acetone (10 ml) and ethanol (20 ml), the mixture was stirred and left for 2 h, then the precipitate was filtered off, washed with acetone and dried in a desiccator. The product (2.6 g) was dissolved in DMSO (2.6 ml), the solution left for 8 to 10 days at room temperature, and the crystals filtered off, washed with acetone and dried in a desiccator (2.3 g); dec. at. 190°C. Found: C, 5.74; H, 1.11; Cl, 12.74; Hg, 72.73. $C_4H_7Cl_3Hg_3O_2S$ calcd.: C, 5.81; H, 0.85; Cl, 12.86; Hg 72.74%. Infrared absorptions: 2980sh, 2890sh, 2810sh, 2670sh, 1605sh, 1578s, 1425m, 1400m, 1360m, 1083s, 1008s, 950m, 930vw, 892vw, 805sh, 704w, 667vw, 594m and 516m cm^{-1}. ^1H NMR: peak at 9.2 ppm (in respect to TMS) indicated proton of the CHO group.

Tris(chloromercuri)acetaldehyde DMF-solvate. From the solution of tris-(chloromercuri)acetaldehyde (2.5 g), obtained as described above, in DMF (28 ml), the solvate was precipitated with acetone (28 ml) and ethanol (56 ml), then after 2 h was filtered off and dried in vacuo (1.95 g; 70%), dec. at 195°C. Found: C, 7.48; H, 1.35; Cl, 12.52; Hg, 73.38. $C_5H_8Cl_3Hg_3NO_2$ calcd.: C, 7.30; H, 0.98; Cl, 12.93; Hg, 73.19%. Infrared absorptions: 2940sh, 2910sh, 2840sh, 2680sh, 1638s, 1580s, 1485w, 1430m, 1410w, 1380m, 1365vw, 1250w, 1090s, 1005w, 658m, 592m and 523m cm^{-1}.

Tris(bromomercuri)acetaldehyde. The mercuration was carried out with absolute ethanol (200 ml), mercuric bromide (53 g) and anhydrous sodium acetate (10 g) as described above for tris(chloromercuri)acetaldehyde. Bromine water was used to remove mercurous bromide from the solid obtained. The pale-yellow solid was filtered off, washed with water, warm ethanol and dried in vacuo (9.5 g), dec. at 215°C. Found: C, 2.91; H, 0.28; Br, 26.89; Hg, 67.96. $C_2HBr_3Hg_3O$ calcd.: C, 2.72; H, 0.11; Br, 27.16; Hg, 68.19%. Infrared absorptions: 1620s, 1600sh, 1380w, 1370w, 1365w, 1075s, 1008vw, 573w and 515m cm^{-1}.

Tris(bromomercuri)acetaldehyde DMSO-solvate. The solvate was obtained from a solution of tris(bromomercuri)acetaldehyde (2.45 g) in DMSO (8 ml) by precipitation with acetone (8 ml) and ethanol (20 ml). The white crystalline solid was filtered off and dried in vacuo. Yield: 2.1 g (78%), dec. 185°C, Found: C, 5.26; H, 0.83; Br, 25.12; Hg, 62.76. $C_4H_7Br_3Hg_3O_2S$ calcd.: C, 5.00; H, 0.73; Br, 24.95; Hg, 62.64%. Infrared absorptions: 2980sh, 2890sh, 2810sh, 2680sh, 1680vw, 1565s, 1425w, 1405vw, 1390vw, 1355vw, 1305w, 1075s, 1008s, 945m, 930vw, 895sh, 700w, 668vw, 578m and 510s cm^{-1}.

Tris(bromomercuri)acetaldehyde DMF-solvate. The solvate was obtained from a solution of tris(bromomercuri)acetaldehyde (2.75 g) in DMF (22 ml) by precipitation with acetone (22 ml) and ethanol (30 ml). The white crystalline solid was filtered off and dried in vacuo. Yield: 2.1 g (70%), dec. 170°C. Found: C, 6.36; H, 1.32; Br, 25.06; Hg, 62.96. $C_5H_8Br_3Hg_3NO_2$ calcd.: C, 6.28; H, 0.84; Br, 25.09; Hg, 62.97%. Infrared absorptions: 2945sh, 2910sh, 2840sh, 2790sh, 1635s, 1575s, 1480vw, 1420w, 1400w, 1370w, 1245w, 1080s, 1000w, 658m, 575m and 512m cm^{-1}.

X-ray diffraction experiments

X-ray powder diffractometry. X-ray powder diffractograms were recorded on a General Electric XRD-6 diffractometer with a proportional counter using nickel filtered Cu-K_α radiation. For the reference diffractogram mercurous chloride reagent grade, E. Merck, Darmstadt, was used.

X-ray single crystal diffractometry. Crystal data were determined preliminary using oscillation and Weissenberg techniques and finally with a Philips PW 1100 computer controlled diffractometer (graphite monochromatized Mo-K_α radiation, λ 0.7107 Å).

Single crystal data. Single crystals of tris(chloromercuri)acetaldehyde DMF-solvate, $(ClHg)_3CCHO \cdot DMF$ (A), and tris(bromomercuri)acetaldehyde DMSO-solvate, $(BrHg)_3CCHO \cdot DMSO$ (B), were obtained from the solution of the corresponding mercurated acetaldehyde in DMF and DMSO, respectively. Acetone was added to each solution to the 1/1 volume ratio and the mixture allowed to stand several days at room temperature.

A: $C_5H_8Cl_3Hg_3NO_2$, mol. wt. 822.25, monoclinic, a 12.76(2), b 10.12(1), c 11.39(1) Å, β 115.3(1)°, V 1330 Å^3, D_{obs} 4.155, D_{calc} 4.106 g cm^{-3}, $Z = 4$, space group $P2_1/c$ (No. 14), $F(000) = 1408$, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 358.4 cm^{-1}, crystal dimensions (mm from centroid) (100) 0.015, ($\bar{1}$00) 0.015, (010) 0.075, (001) 0.087, (00$\bar{1}$) 0.063, (0$\bar{1}$1) 0.055, maximum, minimum transmission coefficients 0.365, 0.085.

B: $C_4H_7Br_3Hg_3O_2S$, mol. wt. 960.66, monoclinic, a 11.30(1), b 10.38(1), c 11.41(1) Å, β 95.7(1)°, V 1331 Å^3, D_{obs} 4.97, D_{calc} 4.79 g cm^{-3}, $Z = 4$, space group $P2_1/c$ (No. 14), $F(000) = 1632$ Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 448.7 cm^{-1}, crystal dimensions (mm from centroid) (100) 0.007, ($\bar{1}$00) 0.007, (010) 0.06, (11$\bar{5}$) 0.135, ($\bar{1}\bar{1}$5) 0.135; maximum, minimum transmission coefficients 0.511, 0.038.

Intensity measurements. The integrated intensities of 1014 (A) and 1840 (B) reflections with $I > 3\sigma(I)$ were collected within the interval of $2° < \theta < 30°$ using $\omega - 2\theta$ scan technique, with scan range 1.6°, scan rate 0.08 s^{-1} for A and 1.2°, 0.04 s^{-1} for B. The crystal specimens darkened under the influence of

TABLE 2

ATOMIC COORDINATES AND THERMAL PARAMETERS[a] OF TRIS(CHLOROMERCURI)ACETALDEHYDE DMF-SOLVATE (A) AND TRIS(BROMOMERCURI)ACETALDEHYDE DMSO-SOLVATE (B)

Compound (A)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	0.3958(2)	0.4045(2)	0.3324(3)	557(19)	287(12)	341(23)	−39(13)	222(19)	−30(15)
Hg(2)	0.3642(3)	0.0974(2)	0.2371(3)	677(21)	340(13)	307(23)	−29(15)	267(20)	−54(17)
Hg(3)	0.6061(3)	0.1692(2)	0.5132(3)	555(19)	378(13)	352(23)	16(14)	179(19)	−29(16)
Cl(1)	0.3708(16)	0.6217(13)	0.2654(18)	924(148)	249(76)	474(155)	86(81)	455(140)	55(83)
Cl(2)	0.3038(19)	−0.0258(16)	0.0452(19)	1163(184)	518(99)	392(159)	−227(112)	437(157)	−241(106)
Cl(3)	0.7931(17)	0.1016(16)	0.6389(21)	660(135)	645(107)	504(168)	20(109)	−203(135)	−103(126)

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
N	0.039(6)	0.301(6)	−0.029(8)	7.6(21)	C(1)	0.432(6)	0.206(6)	0.407(8)	6.0(22)
C(3)	0.127(8)	0.356(8)	0.094(10)	8.7(31)	C(2)	0.357(5)	0.187(5)	0.477(7)	2.6(15)
C(4)	0.011(8)	0.173(9)	−0.007(11)	10.5(33)	O(2)	0.179(5)	0.306(5)	0.181(6)	8.9(20)
C(5)	−0.024(6)	0.358(7)	−0.162(8)	7.6(26)	O(1)	0.398(4)	0.141(4)	0.591(5)	6.8(16)

Compound (B)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	0.5924(1)	0.3881(1)	0.1236(1)	373(8)	332(6)	414(9)	24(6)	36(7)	−27(6)
Hg(2)	0.6385(1)	0.0848(1)	0.1934(1)	389(9)	390(7)	369(9)	−6(6)	−4(7)	31(6)
Hg(3)	0.3724(1)	0.1555(1)	0.0366(2)	346(8)	454(7)	525(10)	2(6)	36(8)	−27(7)
Br(1)	0.6392(5)	0.6114(4)	0.1774(4)	725(33)	410(18)	540(28)	25(19)	80(25)	−45(18)
Br(2)	0.7158(4)	−0.0484(4)	0.3591(4)	548(29)	630(24)	621(32)	48(21)	−81(26)	−175(22)
Br(3)	0.1705(5)	0.0790(5)	−0.0124(5)	410(26)	826(31)	896(43)	46(23)	−37(28)	71(27)
S	0.9255(11)	0.3254(11)	0.2382(16)	424(69)	581(63)	1378(145)	−8(54)	72(86)	−53(74)

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
C(3)	1.023(7)	0.186(6)	0.262(7)	12.0(23)	C(2)	0.605(3)	0.187(3)	−0.051(3)	3.5(8)
C(4)	0.939(7)	0.342(6)	0.081(7)	11.3(22)	C(1)	0.548(5)	0.203(5)	0.075(5)	7.2(15)
O(2)	0.800(4)	0.283(3)	0.239(3)	8.5(11)	O(1)	0.549(3)	0.140(2)	−0.137(3)	5.3(7)

[a] Anisotropic thermal parameters ($\times 10^4$) in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$.

X-ray during the intensity data collection. Three standard reflections, monitored every hour (A) and 1.5 hour (B), had weakened by a factor 3.93 and 1.52 for A and B, respectively, by the end of the measurement. Each set of data collected within the given time interval was corrected by a decay factor obtained for the standard reflections over this preriod.

Determination and refinement of the structure. The structure were solved by means of three-dimensional Fourier synthesis, based upon the mercury atom coordinates obtained from the Patterson synthesis, and then refined by full-matrix least-squares method. Weights of $1/(\sigma I)$ were alloted to all reflections. The anisotropic temperature factors were assigned to the mercury and halogen (A,B) and to the sulphur atom (B). Correction for the absorption [13], Lorentz and polarization effects were applied. The final values of the reliability indices were R 0.087, R_w 0.094 for A and R 0.077, R_w 0.089 for B. The atomic scattering factors were those of Cromer and Mann [14] with corrections for the real and imaginary parts of the anomalous dispersion [15]. The final values of atomic coordinates and thermal parameters with e.s.d.'s are listed in Table 2. A list of observed and calculated structure factors can be obtained from the authors on request. Calculations were carried out on the UNIVAC 1110 of the SRCE, University Computing Centre, Zagreb, using the programmes described in ref. 16.

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