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MERCURETIN AS THE CONDENSATION POLYMER OF TRIS(ACETOXYMERCURI)ACETIC ACID. THE CRYSTAL STRUCTURE OF $(ClHg)_3CCOOH \cdot DMSO$

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Summary

It has been confirmed that the compound obtained by melting mercuric acetate (Stromeyer, 1809; Dimroth, 1902), named mercuretin (Marsh and Fleming Struthers, 1927), is identical with the compound prepared by heating mercuric acetate in acetic anhydride (Sand and Singer, 1903). Mercuretin, prepared by both routes, has been identified as the condensation polymer of tris(acetoxymercuri)acetic acid, $AcO[HgC(HgOAc)_2COO]_nH$, with $n \sim 10$. Its hydrolysis in dilute hydrochloric acid gives tris(chloromercuri)acetic acid as the only mercury-containing product. The crystal structure of tris(chloromercuri)acetic acid dimethylsulfoxide solvate, $(ClHg)_3CCOOH \cdot DMSO$, has been determined by X-ray diffraction methods and refined by full-matrix least-squares to the conventional R_w index of 0.074. The Hg-C bond length was fixed at 2.06 Å in the final refinement, which gave a mean value of 2.33(3) Å for the Hg-Cl bond length.

Introduction

The name mercuretin was given by Marsh and Fleming Struthers [1] to the compound which Stromeyer obtained in 1809 by melting mercuric acetate [2]. These authors were the first to determine the formula $C_2H_2O_2Hg$ for mercuretin, and they pointed out that it "was probably the first organometallic compound to be discovered".

Unaware of Stromeyer's observation, Dimroth reported that mercuric acetate when heated above melting point "is converted into mercurated acetic acid" [3]. At much the same time Sand and Singer [4] reported that the "internal salt" of trimercurated acetic acid (I), was formed by heating mercuric acetate in acetic anhydride; the chemical properties of the product were satisfactorily explained by this formulation, and its composition expressed as $C_6H_6O_6Hg_3$.

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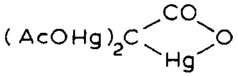
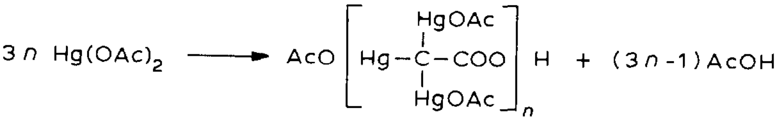


(I)

Marsh and Fleming Struthers [1] were the first to suggest that the same compound was probably obtained either by heating mercuric acetate in acetic anhydride [4] or by melting it [2]. Mercuretin was the reaction product in both cases, and acetic anhydride acted only as a solvent, as previously assumed [4]. We have confirmed that the products are indeed, identical, but the structural formula suggested by Marsh and Fleming Struthers is not compatible with our results: mercuretin is a derivative of trimercurated not dimercurated acetic acid.

Results and discussion

In view of our previous studies on mercurated acetaldehyde [5,6], the formula proposed by Sand and Singer [4] seemed to us to be close to the correct solution if polymerisation of the mercurated acetic acid were assumed instead of internal cyclisation. Mercuretin is therefore formed by "self-mercuration" of mercuric acetate in a process analogous to that whereby benzoic and salicylic acid [3] or acetamide [7] are mercurated by melting corresponding mercuric salts. Consequently, the formation of mercuretin from mercuric acetate may be represented by the overal equation:



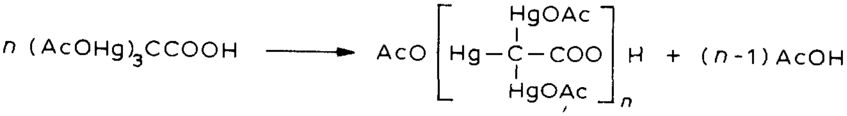
$$3n\ \mathrm{Hg(OAc)_2} \longrightarrow \mathrm{AcO}\left[\begin{array}{c}\mathrm{HgOAc}\\ |\\ \mathrm{Hg{-}C{-}COO}\\ |\\ \mathrm{HgOAc}\end{array}\right]_n \mathrm{H} + (3n-1)\,\mathrm{AcOH} \qquad (1)$$

The value of *n* can be estimated from the mercury content (% Hg) found in the mercuration product, i.e., 76.89 [4], 77.4 [1] and 76.84 (this work), according to the table:

n	1	2	10	20	100	∞
% Hg	71.99	74.67	76.96	77.26	77.50	77.56

The highest calculated % Hg value of 77.56 for $n = \infty$, which would correspond to the "internal salt", was not found. The lowest % Hg value of 71.99, for $n = 1$, corresponds to tris(acetoxymercuri)acetic acid, $\mathrm{(AcOHg)_3CCOOH}$.

Tris(acetoxymercuri)acetic acid should be formed by acetic acid cleavage of mercuretin, and we did , in fact, obtain it from a solution of mercuretin in boiling glacial acetic acid as tiny lustrous crystalline leaflets. It is therefore the parent monomer of mercuretin, into which it polymerises by condensation with release of acetic acid:



$$n\ \mathrm{(AcOHg)_3CCOOH} \longrightarrow \mathrm{AcO}\left[\begin{array}{c}\mathrm{HgOAc}\\ |\\ \mathrm{Hg{-}C{-}COO}\\ |\\ \mathrm{HgOAc}\end{array}\right]_n \mathrm{H} + (n-1)\,\mathrm{AcOH} \qquad (2)$$

We found that tris(acetoxymercuri)acetic acid released acetic acid spontaneously, slowly at room temperature and faster on heating, until mercuretin with % Hg of 76.91. ($n \sim 10$) was regenerated. The crystals of tris(acetoxymercuri)acetic acid were not suitable for X-ray structure analysis.

Tris(chloromercuri)acetic acid, first reported by Hofmann [8,9], was obtained as a microcrystalline solid by digestion of mercuretin with dilute hydrochloric acid. Well developed crystals of its one-to-one solvate with dimethylsulphoxide, $(ClHg)_3CCOOH \cdot DMSO$, made possible a successful X-ray structure analysis reported here.

Mercuretin for the present investigation was prepared by heating mercuric acetate in acetic anhydride [4]. The method gives pure mercuretin as a coarse white powder. It is not soluble in aqueous alkali but is converted by it into a fine powder, the "free base" of mercuretin, whose composition corresponds to the polymeric tris(hydroxymercuri)acetic acid with one molecule of water per one monomer unit, $HO[(H_2O)Hg(HOHg)_2CCOO]_nH$, with $n \sim 10$.

Stromeyer's method [1,2] is not convenient for preparative purposes since decomposition of the product by the heat of reaction cannot be completely avoided. As mercuric acetate is consumed by self-mercuration the mixture solidifies and stirring is no longer possible. The crude product is always contaminated with mercurous acetate and other, unidentified, decomposition products. Traces of methylmercuric chloride can be clearly recognized by its characteristic repulsive smell when the crude product is treated with hydrochloric acid.

The alkali-soluble precipitate, obtained by Marsh and Fleming Struthers [1] from mercuric acetate in boiling glacial acetic acid, was a polymer of acetoxymercuriacetic acid, $AcO[HgCH_2COO]_nH$, with $n \sim 6$, as shown by Wells and Kitching [10], whose results we confirmed in repetition of their experiments.

The structure of $(ClHg)_3CCOOH \cdot DMSO$

The asymmetric unit of the crystal structure is depicted in Fig. 1. The arrangement of molecules is similar to that for the analogous DMSO solvate of tris(chloro-

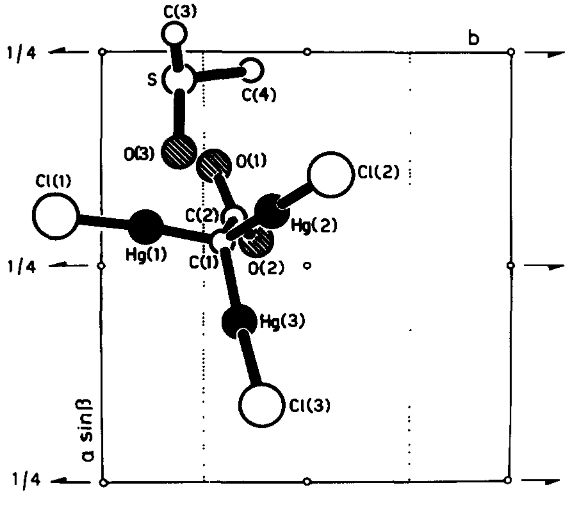


Fig. 1. The asymmetric unit in the structure of $(ClHg)_3CCOOH \cdot DMSO$ viewed along the c-axis.

mercuri)acetaldehyde [11], in accordance with the fact that they have the same space group symmetry and approximately the same unit cell geometry. The interatomic distances and bond angles are listed in Table 1. The main feature of the structure is the slightly deformed Hg_3CC tetrahedron in which the mean values of the Hg–C–Hg and Hg–C–C angles are 111(3)° and 108(4)°, respectively. The deformation is due to the intermolecular interaction manifested by the Hg...O distances of 2.73(8) (the DMSO oxygen) and 2.85(5) Å (carboxyl oxygen), which are less than the sum of the Van der Waals' radii [12,13].

Experimental

Characterization of the mercuration products

Spectral data. The IR spectra in the region of 4000–180 cm^{-1} were recorded on a Perkin–Elmer spectrophotometer Model 580 D using KBr discs.

Preparation of mercuretin

(A) From molten mercuric acetate. Mercuric acetate (15.0 g) was slowly heated with stirring, for which a thermometer was used. When a clear melt was obtained (180 °C) the heating was discontinued. A sudden temperature increase, to above about 200 °C, indicated the beginning of the exothermic reaction, the melt becoming turbid and sticky and then solidifying (about 40 minutes after the mercuric acetate melted). Acetic acid was finally removed by re-heating the contents to 135 °C. The product (12.6 g) was washed with hot 2% acetic acid until the sample of the solid did not blacken on treatment with aqueous sodium hydroxide. The solid was then

TABLE 1

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

C(1)–Hg(1)	2.06(7)	Hg(1)...Hg(2)	3.343(4)
C(1)–Hg(2)	2.07(8)	Hg(1)...Hg(3)	3.482(5)
C(1)–Hg(3)	2.06(7)	Hg(2)...Hg(3)	3.352(6)
Hg(1)–Cl(1)	2.33(2)	Hg(1)...O(3)	2.73(8)
Hg(2)–Cl(2)	2.35(3)	Hg(1)...O(2) [e]	2.85(5)
Hg(3)–Cl(3)	2.32(2)	Hg(1)...Cl(2) [d]	3.56(2)
C(1)–C(2)	1.54(8)	Hg(2)...O(3)	3.07(7)
C(2)–O(1)	1.37(6)	Hg(2)...O(2) [a]	3.15(5)
C(2)–O(2)	1.27(8)	Hg(2)...Cl(1) [c]	3.32(2)
S–O(3)	1.63(6)	Hg(3)...Cl(1) [b]	3.33(2)
S–C(3)	1.83(12)	Hg(3)...Cl(1) [c]	3.33(2)
S–C(4)	1.83(9)	Hg(3)...Cl(2) [d]	3.37(2)
Hg(1)–C(1)–Hg(2)	108(4)	Hg(3)–C(1)–C(2)	108(5)
Hg(1)–C(1)–Hg(3)	115(3)	C(1)–C(2)–O(1)	115(5)
Hg(2)–C(1)–Hg(3)	109(3)	C(1)–C(2)–O(2)	123(4)
C(1)–Hg(1)–Cl(1)	173(2)	O(1)–C(2)–O(2)	122(5)
C(1)–Hg(2)–Cl(2)	177(2)	O(3)–S–C(3)	108(4)
C(1)–Hg(3)–Cl(3)	177(2)	O(3)–S–C(4)	103(3)
Hg(1)–C(1)–C(2)	110(3)	C(3)–S–C(4)	97(5)
Hg(2)–C(1)–C(2)	106(4)		

[a] Transformation of the asymmetric unit (x,y,z): $1-x$, $1-y$, $1-z$. [b] $1-x$, $-y$, $1-z$. [c] $1-x$, $1/2+y$, $3/2-z$. [d] $1-x$, $y-1/2$, $3/2-z$. [e] x, $1/2-y$, $1/2+z$.

washed with ethanol and dried in a vacuum desiccator over NaOH pellets. Yield 7.8 g (63%), dec. 235 °C. Found: C, 10.02; H, 0.91; Hg, 76.10. $C_2H_4O_2(C_6H_6O_6Hg_3)_{10}$ calcd.: C, 9.52; H, 0.83; Hg, 76.96%. The IR spectrum was identical with that of mercuretin (B).

(B) From mercuric acetate in acetic anhydride. Mercuric acetate (20.0 g, finely ground and dried) in acetic anhydride (150 ml, freshly redistilled) was heated on the water bath with stirring until a sample did not turn yellow on treatment with aqueous sodium hydroxide (about 4 h). The voluminous precipitate was filtered off, washed with acetic anhydride and diethyl ether, and kept in a vacuum desiccator over NaOH pellets to the constant weight. Yield: 14.5 g (88.5%). Found: C, 9.79; H, 0.90; Hg, 76.84. $C_2H_4O_2(C_6H_6O_6Hg_3)_{10}$ calcd.: C, 9.52; H, 0.83; Hg, 76.96%. IR max (cm^{-1}) 3390mbr, 2930vw, 1578s, 1520sh, 1408m, 1307m, 1260sh, 1047vw, 1015w, 950vw, 920vw, 823sh, 735vw, 705sh, 685w, 646w, 620vw, 570sh, 470vw, 387vw, 243vw and 325vw.

Tris(chloromercuri)acetic acid

From mercuretin (A). Finely ground mercuretin (A) (5.0 g), was covered with 5% HCl (150 ml) and the mixture was left at room temperature with occasional shaking. Afther 1 h the liquid was decanted off and the treatment repeated. The solid was filtered off, washed with dilute HCl (2%), water, and ethanol, and dried over $CaCl_2$. Yield: 4.52 g (92%). Found: C, 3.39; H, 0.63; Cl, 13.60; Hg, 78.36. $C_2HCl_3Hg_3O_2$ calcd.: C, 3.14; H, 0.13; Cl, 13.90; Hg, 78.65%. The IR spectrum was identical with that of the tris(chloromercuri)acetic acid prepared from mercuretin (B).

From mercuretin (B). Mercuretin (B) (5.0 g) was treated with dilute hydrochloric acid in the way as described above. Yield: 4.67 g (95%). Found: C, 3.23; H, 0.22; Cl, 13.55; Hg, 78.72. $C_2HCl_3Hg_3O_2$ calcd.: C, 3.14; H, 0.13; Cl, 13.90; Hg, 78.65%. IR max (cm^{-1}) 3420vwbr, 3000vw, 2915vw, 2760vw, 2600vw, 1623s, 1605s, 1585sh, 1403vw, 1350vw, 1275s, 1245s, 975vw, 930vw, 805vw, 773vw, 695vw, 545m, 417m, 330sh and 315m.

Tris(chloromercuri)acetic acid · DMSO solvate

Tris(chloromercuri)acetic acid (2.0 g) was dissolved in DMSO (6 ml) and ethanol (30 ml) was added. The crystalline precipitate was filtered off, washed with ethanol, and dried. Yield: 2.09 g (95%), dec. 225 °C. Found: C, 5.71; H, 0.99; Cl, 12.41; Hg, 71.35. $C_4H_7Cl_3Hg_3O_3S$ calcd.: C, 5.70; H, 0.84; Cl, 12.61; Hg, 71.36%.

The DMSO solvate was also prepared from the product obtained by the hydrochloric-acid digestion of molten mercuric acetate (see above). Mercurous chloride, the main impurity which is insoluble in DMSO, was filtered off and the filtrate diluted with a fivefold volume of ethanol. The crystalline precipitate was the pure 1/1 DMSO solvate of tris(chloromercuri)acetic acid as indicated by chemical analysis. Found: C, 5.77; H, 1.16; Cl, 12.26; Hg, 71.50. $C_4H_7Cl_3Hg_3O_3S$ calcd.: C, 5.70; H, 0.84; Cl, 12.61; Hg, 71.36%. IR max (cm^{-1}) 3420wbr, 3000vw, 2900vw, 2720vw, 2540w, 1620sh, 1605s, 1432vw, 1414vw, 1401vw, 1315w, 1235s, 1215sh, 1002s, 953s, 903vvw, 711vw, 667w, 578w, 415sh, 400w, 380w, 341w and 315m.

The hydrated tris(hydroxymercuri)acetic acid polymer ("base of mercuretin")

Finely-ground mercuretin (5.0 g) was covered with 10% aqueous KOH (50 ml) and the mixture was kept for 2 h at room temperature with occasional shaking. The solid was filtered off, washed thoroughly with water, and dried over $CaCl_2$ to constant weight (3.7 g; 81.3%), dec. 175 °C. Found: C, 3.29; H, 0.80; Hg, 84.81. $HO[(H_2O)Hg(HOHg)_2CCOO]_nH$, for a mean value of $n = 10$, calcd.: C, 3.38; H, 0.57; Hg, 84.56%.

Alternatively, the base was prepared by aqueous hydrolysis: mercuretin (2 g) was repeatedly boiled (three times were necessary) with water (50 ml) until the absence of acid reaction. The solid was filtered off, washed with water, and dried, and was shown to be identical with the base described above, as confirmed by elemental analysis. IR max (cm^{-1}) 3380mbr, 1627w, 1485m, 1307s, 965w, 827vw, 710sh, 642vw, 609w, 548vw, 518m, 387vw and 325w.

Tris(acetoxymercuri)acetic acid

Finely ground mercuretin (2.0 g) was added in portions to warm glacial acetic acid (120 ml) with shaking. The mixture was subsequently heated to boiling and the clear solution was left overnight at room temperature. The voluminous jelly-like precipitate of microscopic crystals was filtered off and washed with diethyl ether. Yield: 1.15 g (54%). A second crop of the product (0.74 g) was obtained from the filtrate. Found: C, 11.44; H, 1.37; Hg, 71.91. $C_8H_{10}Hg_3O_8$ calcd.: C, 11.50; H, 1.21; Hg, 71.99%.

The decrease in weight of the sample at room temperature after three days was 5.5%, the mercury content increasing to 75.50%. In drying pistol at 100 °C, after a decrease of 6.2% the weight remained constant. Found: Hg, 76.91. Mercuretin, $CH_3COO[Hg(CH_3COOHg)_2COO]_nH$, for $n = 10$, calcd.: Hg, 76.96%. IR max (cm^{-1}) 3415mbr, 2935vw, 1577s, 1405m, 1375w, 1307m, 1255sh, 1145sh, 1045vw, 1015w, 923vw, 818vw, 735vw, 687m, 647w, 615vw, 480vwbr, 390vw and 323vw.

X-Ray diffraction experiment

X-Ray single crystal diffractometry. Preliminary crystal data were determined by oscillation and Weissenberg techniques and detailed data on 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)acetic acid DMSO solvate, $(ClHg)_3CCOOH \cdot DMSO$, were obtained by slow crystalisation from a solution of tris(chloromercuri)acetic acid (prepared as described above) in dimethylsulphoxide to which acetone had been added.

$C_4H_7Cl_3Hg_3O_3S$, mol. wt. 843.29, monoclinic, a 12.427(6), b 10.351(5), c 11.40(4) Å, β 115.4(1)°, V 1324.7 Å^3, D_{obs} 4.42, D_{calc} 4.229 g cm^{-3}, $Z = 4$ formula units, space group $P2_1/c$, $F(000) = 1148$, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) 361.3 cm^{-1} crystal dimensions (mm from centroid): (100) 0.006, $(\bar{1}00)$ 0.006, $(\bar{2}34)$ 0.097, $(05\bar{1})$ 0.067, $(0\bar{5}1)$ 0.067, $(1\bar{5}\bar{2})$ 0.065, $(\bar{2}\bar{3}6)$ 0.097, $(2\bar{2}\bar{5})$ 0.097; maximum, minimum transmission coefficients 0.645, 0.142.

Intensity measurement. Integrated intensities of 979 reflections with $I > 2\sigma(I)$ were collected within the interval $2° < \theta < 30°$ using the ω–2θ scan technique, with scan range 1.8°, scan rate 0.06 s^{-1}. Three standard reflections, monitored every 1.5 h, had weakened by a factor of 1.14 by the end of the measurements . Each set of data collected within a given time interval was corrected by a decay factor obtained from the variation of the standard reflections.

Determination and refinement of the structure. The structure was solved by means of three-dimensional Fourier synthesis, based upon the mercury atom coordinates

TABLE 2

ATOMIC COORDINATES FOR TRIS(CHLOROMERCURI)ACETIC ACID·DMSO

Atom	*x*	*y*	*z*
Hg(1)	0.4034(3)	0.1056(2)	0.5716(2)
Hg(2)	0.3682(3)	0.4164(3)	0.6271(3)
Hg(3)	0.6207(3)	0.3343(3)	0.6071(3)
Cl(1)	0.3802(18)	−0.1122(15)	0.6052(16)
Cl(2)	0.2876(22)	0.5512(19)	0.7350(20)
Cl(3)	0.8185(15)	0.3926(20)	0.6770(19)
S	0.0668(20)	0.1890(21)	0.4699(19)
O(1)	0.268(4)	0.274(4)	0.329(4)
O(2)	0.436(4)	0.374(4)	0.334(4)
O(3)	0.201(6)	0.186(6)	0.587(6)
C(1)	0.442(6)	0.292(6)	0.540(6)
C(2)	0.381(4)	0.323(4)	0.394(5)
C(3)	−0.039(8)	0.176(8)	0.542(8)
C(4)	0.044(8)	0.361(8)	0.428(8)

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, chlorine and sulphur atom. Correction for absorption [14], Lorentz and polarization effects were applied. In the course of refinement it turned out that positions of C(1) and C(2) atoms were influenced by the number of reflections included. We assumed that this arose because of certain types of reflections, the absorption cerrection was not satisfactory due to the unsuitable shape of the crystal. Thus, in the final refinement the Hg–C and C–C distances were fixed at 2.06 and 1.54 Å, respectively. The final value of the reliability index was $R = 0.08$ and $R_w = 0.074$. The atomic scattering factors were those of Cromer and Mann [15] with corrections for the real and imaginary parts of the anomalous dispersion [16]. The final values of atomic coordinates with e.s.d.'s are listed in Table 2. Lists of thermal parameters and 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. 17.

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