

## TRIMERCURATED ACETALDEHYDE. THE CRYSTAL STRUCTURE OF $[\text{OHg}_3\text{CCHO}]\text{NO}_3 \cdot \text{H}_2\text{O}$

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### Summary

The product of mercuration of acetaldehyde in aqueous mercuric-nitrate is a hydrated oxonium nitrate of tris(mercuri) acetaldehyde,  $[\text{OHg}_3\text{CCHO}]\text{NO}_3 \cdot \text{H}_2\text{O}$ , the crystal structure of which has been determined. The crystals are tetragonal, space group  $P4_2/m$  with four formula units in the unit cell of dimensions  $a$  10.755(3) and  $c$  6.763(2) Å. The structure was determined by means of X-ray diffractometry and refined by full-matrix least-squares method to an  $R$  value of 0.038. Mercuration of acetylene gives the same product but in polycrystalline form as shown by X-ray powder diagrams. The  $\text{Hg}_3\text{CCHO}$  units are interconnected by oxonium oxygen atoms to a polymeric columnar  $[\text{OHg}_3\text{CCHO}]_n^{n+}$  cation. The nitrate ions show positional disorder. The geometry of the column is defined by a flat  $\text{Hg}_3\text{O}$  oxonium pyramid and a slightly distorted  $\text{Hg}_3\text{CC}$  tetrahedron, with  $\text{Hg}-\text{O}$  and  $\text{Hg}-\text{C}$  bond distances of 2.04(1) to 2.08(1) Å.

### Introduction

The products of mercuration of acetaldehyde by aqueous solutions of mercuric oxo-acid salts were formulated as salts of dimercurated acetaldehyde,  $\text{XHg}(\text{=Hg})\text{CHO}$ , where  $X$  is  $\text{NO}_3$  [1],  $\text{ClO}_3$  or  $\text{ClO}_4$  [2]. The nitrate was found to be identical with the product obtained by passing acetylene into aqueous mercuric nitrate [1,3], while the products of a prolonged action of acetylene on mercuric salts in aqueous solution were considered to be basic salts of trimercurated acetaldehyde,  $\text{XHgC}(\text{Hg}_2\text{O})\text{CHO}$ , where  $X$  is  $\text{NO}_3$  [4],  $\text{ClO}_3$  or  $\text{ClO}_4$  [2]. With aqueous solutions of mercuric halides acetylene gives halides of trimercurated acetaldehyde,  $(\text{XHg})_3\text{CCHO}$ , where  $X$  is  $\text{Cl}$  [5] and  $\text{Br}$  [6]. This was confirmed recently by determination the crystal structure of the corresponding DMF and DMSO solvates [7,8]. Our assumption that the nitrate [1] was also a derivative of trimercurated acetaldehyde has now been confirmed by the structure analysis reported below. We decided against studying the chlorate and perchlorate since they are extremely explosive, as shown

by a previous report [2] and by our own experience. But, since preparative conditions are the same the analogous trimercurated acetaldehyde structure can reasonably be assumed for both the chlorate and perchlorate.

## Results and discussion

The needle-shaped transparent crystals of mercurated acetaldehyde were obtained as described by Hofmann [1] from a mixture of an ethanolic acetaldehyde solution and aqueous mercuric-nitrate, but not as the only product. Suitable crystals of A were separated mechanically from a microcrystalline by-product as well as from the crystals of a different form, examination of which is under way. The crystals of A are insoluble in water and organic solvents, and cannot be recrystallized. The results of the chemical analysis differed slightly from those reported previously [1,3] and agreed better with the formula for the nitrate of mercurated acetaldehyde (B) obtained from acetylene [2] and the X-ray powder diagrams of A and B were, in fact, identical. The formula involving one molecule of crystal water, i.e.,  $[\text{OHg}_3\text{-CCHO}]\text{NO}_3 \cdot \text{H}_2\text{O}$ , which gave the best agreement with the chemical analysis, was subsequently confirmed by determination of the loss in weight of the specimen in vacuo. Thus, mercuration of either acetaldehyde or acetylene in aqueous mercuric-nitrate solution gives the trimercurated acetaldehyde. It followed that the compound formulated by Hofmann as the basic nitrate,  $\text{OHg}_2\text{Hg}(\text{NO}_3)\text{CCHO}$  [4], was actually the nitrate of the mercurated oxonium,  $[\text{OHg}_3\text{CCHO}]^+$ . Mercurated oxonium cations are frequently found in the structure of oxo- and hydroxo-mercury halides and oxo-acid salts [9]. The presence of the O-Hg-C linkage was previously proposed in the light of the crystal structure of Hofmann's base [10], but could not be confirmed since only microcrystalline specimens were obtainable. The  $[\text{OHg}_3\text{CCHO}]$  framework in the present structure is thus the only known representative of infinite O-Hg-C linkages for organomercurials.

## Description of the structure

The structure of oxonium tris(mercuri)acetaldehyde nitrate hydrate,  $[\text{OHg}_3\text{C-CHO}]\text{NO}_3 \cdot \text{H}_2\text{O}$ , projected on (001) is shown in Fig. 1.

The  $\text{OHg}(2)\text{CCHO}$  moieties lie in the mirror planes and are arranged along the *c* axis direction by  $4_2$  symmetry operation. They are connected by the  $\text{Hg}(1)$  mercury atoms, which are located in eightfold general positions, almost half-way between the mirror planes, so that the O-Hg-C and C-Hg-O bridges are formed. Thus, each O(2) oxygen atom belongs to one  $\text{Hg}(2)$  atom in the same mirror plane and to two  $\text{Hg}(1)$  atoms above and below this plane. The  $\text{Hg}(1)_2\text{Hg}(2)\text{O}(2)$  oxonium pyramids thus formed are interconnected to the  $\text{Hg}(2)\text{Hg}(1)_2\text{C}(1)\text{C}(2)$  tetrahedra by sharing the  $\text{Hg}(1)$  and  $\text{Hg}(2)$  corners. The resulting polymeric  $[\text{OHg}_3\text{CCHO}]_n^{n+}$  cations form endless columns extending along and parallel to the *c* axis direction (Fig. 2). The  $\text{Hg}_3\text{O}^+$  oxonium pyramid is defined (Table 1) by the O(2)- $\text{Hg}(2)$  and O(2')- $\text{Hg}(1)$  bond distances of 2.04(2) and 2.06(1) Å (twice), by corresponding angles of 112.6(10) and 118.8(6)° (twice) and the pyramid height of 0.37 Å. The distances in the  $\text{Hg}_3\text{CC}$  tetrahedron are 2.08(1) (twice) and 2.06(2) Å for the C(1)- $\text{Hg}(1)$  and C(1)- $\text{Hg}(2)$  bonds, 1.55(4) Å for the C(1)-C(2) bond and 106.9(10) to 113.4(17)° for the tetrahedral angles at the C(1) atom. In an alternative description the columns may

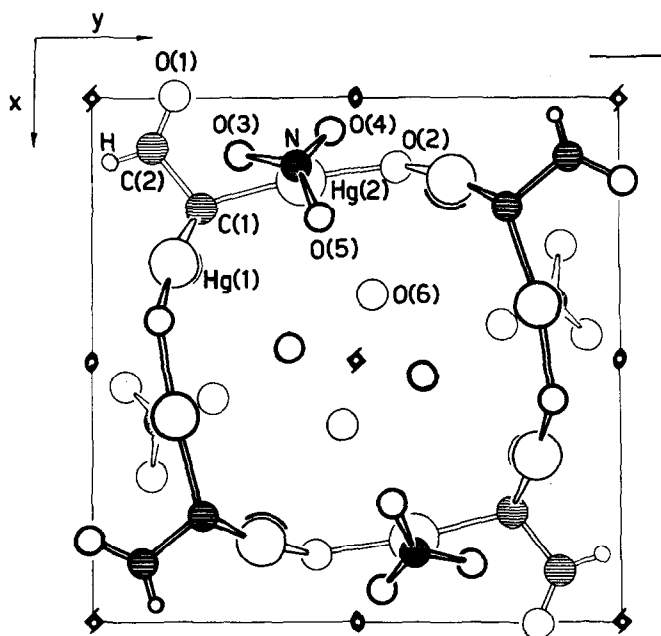


Fig. 1. The unit cell of  $[\text{OHg}_3\text{CCHO}]\text{NO}_3 \cdot \text{H}_2\text{O}$  projected along the  $c$  axis direction.

be visualized as composed of four parallel  $-\text{C}-\text{Hg}-\text{O}-\text{Hg}-$  zig-zag chains, displaced in pairs for  $c/2$ , and interconnected by the  $\text{Hg}(2)$  mercury atoms. The aldehyde groups,  $\text{C}(2)\text{HO}(1)$ , point outward the column. The middle of the twelve membered  $(-\text{C}-\text{Hg}-\text{O}-\text{Hg}-)_3$  rings formed in this way is occupied by one nitrate ion. In an idealized structure, required by the space group symmetry, the nitrate ions should lie in the mirror plane. Since the rings are too large to provide close interatomic contacts between the nitrate oxygen atoms and the mercury atoms, the nitrate ions

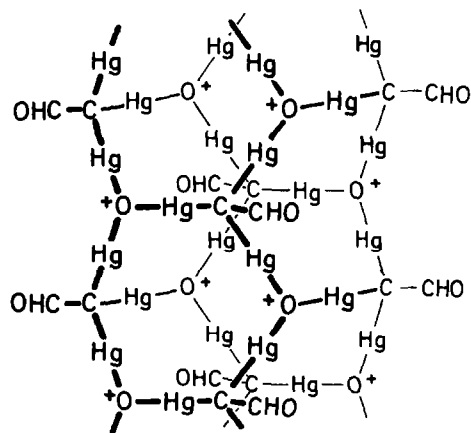


Fig. 2. The structural formula of the polymeric  $[\text{OHg}_3\text{CCHO}]_n^{n+}$  cation.

TABLE 1

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°), WITH STANDARD DEVIATIONS IN PARENTHESES<sup>a</sup>

Hg(1)–C(1)	2.08(1)	C(1)–Hg(1)–O(2 <sup>i</sup> )	176.4(8)
Hg(1)–O(2 <sup>i</sup> )	2.06(1)	C(1)–Hg(2)–O(2)	176.3(9)
Hg(2)–C(1)	2.06(2)	Hg(1)–C(1)–Hg(1 <sup>iii</sup> )	107.0(10)
Hg(2)–O(2)	2.04(2)	Hg(1)–C(1)–Hg(2)	111.2(7)
C(1)–C(2)	1.55(4)	Hg(1)–C(1)–C(2)	106.9(10)
C(2)–O(1)	1.22(4)	Hg(2)–C(1)–C(2)	113.4(17)
N–O(3)	1.23(5)	Hg(1 <sup>iii</sup> )–O(2)–Hg(1 <sup>iv</sup> )	112.6(10)
N–O(4)	1.27(7)	Hg(1 <sup>iii</sup> )–O(2)–Hg(2)	118.8(6)
N–O(5)	1.30(7)	C(1)–C(2)–O(1)	121.7(27)
O(4)···O(4 <sup>v</sup> )	2.67(6)	O(4)···Hg(2)	2.66(5)
O(2)···O(2 <sup>vi</sup> )	3.31(3)	O(5)···Hg(2 <sup>ix</sup> )	3.14(5)
O(1)···O(2 <sup>vii</sup> )	3.20(4)	O(5)···Hg(1 <sup>x</sup> )	2.99(5)
O(3)···Hg(1)	2.84(4)	O(6)···Hg(2)	2.66
O(4)···Hg(1 <sup>iii</sup> )	2.70(4)	O(6)···O(6 <sup>xi</sup> )	2.88
O(4)···Hg(1 <sup>viii</sup> )	2.98(4)	O(6)···O(5 <sup>iii</sup> )	2.71

<sup>a</sup> Transformation of the asymmetric unit ( $x, y, z$ ): (i)  $1 - y, x, 1/2 + z$ ; (ii)  $x, y, -z$ ; (iii)  $y, 1 - x, 1/2 - z$ ; (iv)  $y, 1 - x, z - 1/2$ ; (v)  $-x, 1 - y, 1 - z$ ; (vi)  $-x, 1 - y, -z$ ; (vii)  $-x, -y, -z$ ; (viii)  $-y, x, 1/2 - z$ ; (ix)  $x, y, 1 + z$ ; (x)  $y, 1 - x, 1/2 + z$ ; (xi)  $1 - x, 1 - y, z$ .

are displaced from the mirror plane statistically equally above and below this plane (see Experimental). Such a positional disorder leads to closer Hg···O contacts as O(4)···Hg(1<sup>iii</sup>) and O(4)···Hg(2) of 2.70(4) and 2.66(5) Å, as well as O(3)···Hg(1) and O(4)···Hg(1<sup>viii</sup>) of 2.84(4) and 2.98(4) Å, each are less than or equal to the sum of the Van der Waals' radii [9,11]. The location of the water molecule with its oxygen atom in the mirror plane is justified by the hydrogen bridge contacts with the nitrate-ion oxygen at the minimum distance of 2.71 Å.

## Experimental

### Preparation of $[OHg_3CCHO]NO_3 \cdot H_2O$

(A) *From acetaldehyde.* A solution of freshly distilled acetaldehyde (0.26 g) in ethanol (10 ml) was added to a solution of  $Hg(NO_3)_2 \cdot H_2O$  (9.4 g) in water (100 ml) acidified with 20%  $HNO_3$  (1.5 ml) and the mixture was kept in the dark for several days. The crop of crystals was transferred to a block of filter papers and the needle-shaped crystals were separated mechanically from the admixed solid material with a thin glass rod. Analyses. Found: Hg, 81.34; N, 1.98.  $C_2H_3Hg_3NO_6$  calcd.: Hg, 81.45; N, 1.90%. The density of  $6.26 \text{ g cm}^{-3}$  was determined pycnometrically using decalin.

(B) *From acetylene.* As described by Korshak and Zamyatina [3], acetylene was absorbed into a solution of  $Hg(NO_3)_2 \cdot H_2O$  (26.4 g) in 2% aqueous  $HNO_3$  (75 ml). Since the white precipitate turned gray in contact with acetylene, only a fixed volume (650 ml) of acetylene (from a gas burette) was allowed to be taken up by the

TABLE 2

ATOMIC COORDINATES, THERMAL PARAMETERS<sup>a</sup> AND THE SITE OCCUPATION FACTOR (OCC) FOR OXONIUM TRIS(MERCURI)ACETALDEHYDE NITRATE HYDRATE

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	occ	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Hg(1)	0.3177(1)	0.1648(1)	0.2469(1)		0.0257(4)	0.0356(4)	0.0174(3)	0.0029(3)	0.0000(3)	0.0009(3)
Hg(2)	0.1649(1)	0.3952(1)	0.0		0.0387(6)	0.0204(5)	0.0205(5)	0.0001(5)	0.0	0.0
C(1)	0.212(2)	0.210(2)	0.0		0.020(11)	0.019(11)	0.010(10)	-0.002(9)	0.0	0.0
C(2)	0.098(3)	0.122(3)	0.0		0.043(16)	0.038(15)	0.019(13)	-0.009(13)	0.0	0.0
O(1)	-0.008(2)	0.162(2)	0.0		0.014(9)	0.043(13)	0.111(25)	0.002(9)	0.0	0.0
O(2)	0.130(2)	0.582(2)	0.0		0.061(14)	0.022(9)	0.012(9)	0.004(9)	0.0	0.0
N	0.129(4)	0.394(4)	0.467(8)	0.5	0.072(15)					
O(3)	0.114(4)	0.282(3)	0.439(7)	0.5	0.091(16)					
O(4)	0.066(4)	0.459(4)	0.346(7)	0.5	0.088(14)					
O(5)	0.227(4)	0.441(4)	0.552(8)	0.5	0.098(15)					
O(6)	0.370	0.533	0.0		0.1					

<sup>a</sup> Anisotropic thermal parameters in the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$ .

solution in a stoppered conical flask. The heavy crystalline precipitate was filtered off, washed with 2% HNO<sub>3</sub>, then with water, ethanol and ether (yield 14.4 g). The mercury content of 79.14% found for the air-dried specimen, in agreement with that previously reported [3], increased to 80.53% when a specimen was dried in desiccator. Further loss of water was slow, and the calculated value of 81.45% for mercury was never attained, confirming that water is strongly adsorbed by the microcrystalline precipitate.

#### *X-ray diffraction experiments*

*X-ray powder analysis.* X-ray powder photographs of the A and B specimens in the Lindemann glass capillaries (2R 0.3 mm) were taken with a Unicam S25 oscillation-rotation camera (Cu-K<sub>α</sub> radiation). Distinct and sharp lines matched exactly by superimposing the photographs of A and B.

*X-ray single crystal diffractometry.* Preliminary crystal data were determined using oscillation and Weissenberg techniques, and more extensive data with a Philips PW 1100 computer controlled diffractometer (graphite-monochromatized Mo-K<sub>α</sub> radiation, λ 0.7107 Å).

*Single crystal data.* Single crystals were prepared from acetaldehyde as described above under A: C<sub>2</sub>H<sub>3</sub>Hg<sub>3</sub>NO<sub>6</sub>, mol. wt. 738.82, tetragonal-dipyramidal, *a* 10.755(3), *c* 6.763(2) Å, *V* 782.3 Å<sup>3</sup>, *D*<sub>obs</sub> 6.26, *D*<sub>calc</sub> 6.273 g cm<sup>-3</sup>, *Z* = 4, space group *P*4<sub>2</sub>/*m*, *F*(000) 1240, Mo-K<sub>α</sub> radiation (λ 0.7107 Å), μ(Mo-K<sub>α</sub>) 599 cm<sup>-1</sup>, crystal dimensions (mm from centroid): (100)0.028, (100)0.028, (010)0.021, (010)0.021, (101)0.143, (101)0.146, (001)0.154; maximum, minimum transmission coefficients 0.126, 0.039.

*Intensity measurements.* Integrated intensities of 1666 reflections from a needle-shaped specimen were collected over the range of 2° < θ < 28° on a computer controlled automatic diffractometer Philips PW 1100 (graphite monochromatized Mo-K<sub>α</sub> radiation, ω-2θ scan, scan width 1.2°, scan speed 0.04° s<sup>-1</sup>). Unit cell parameters were obtained by the least-squares method from the data for 20 automatically centered reflections. The intensity data for three standard reflections measured periodically showed a variation of about ± 4% and the intensities were corrected accordingly. Correction for the absorption [12], Lorentz and polarization effects were applied. From the total of 835 independent reflections, obtained after the equivalent reflections had been averaged, 782 reflections with *I* > 3σ(*I*) were used in the structure determination and refinement. The atomic scattering factors were given by Cromer and Mann [13], with corrections for the real and imaginary parts of the anomalous dispersion [14].

*Determination and refinement of the structure.* The mercury atoms were located by the Patterson method. Three cycles of the isotropic least squares refinement with the mercury coordinates led to the *R* index of 0.10. When the carbon, carbonyl oxygen and oxonium oxygen atoms, revealed from the Fourier synthesis, were included in the refinement with anisotropic thermal parameters for mercury, the *R* index of 0.049 was obtained. The location of the nitrate ion in the mirror plane followed from the difference Fourier synthesis but with an orientational disorder. The density peaks belonging to the nitrate ion appeared out of the mirror plane, symmetrically above and below it, with half of the expected density height. In the subsequent refinement this disorder of the nitrate ion position was taken into account. Atoms of the nitrate ion were included in the refinement as a rigid group. They were placed in the general positions with the site occupation factor of 0.5.

Poorly resolved peaks in the fourfold position with the coordinates of 0.370; 0.533; 0.000 were ascribed to the water oxygen atoms. Their positions could not be refined and were kept fixed in the refinement. The final refinement, with the anisotropic thermal parameters for all non-hydrogen atoms, except the atoms of the nitrate ion and the water molecule, resulted in an *R* value of 0.038. In the last difference Fourier map a peak with the coordinates of 0.146, 0.033, 0.000, at a distance of 1.09 Å from the C(2) carbonyl carbon atom, was ascribed to the hydrogen atom. The atomic coordinates are listed in Table 2 (with their e.s.d.'s, site occupation factor and thermal parameters).

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. 15.

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