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## On the Tris-methylmercury-oxonium Compounds

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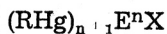
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The preparation and properties of tris-methylmercury-oxonium fluoborate  $(\text{CH}_3\text{Hg})_3\text{OBF}_4$  are described. A method for the preparation of methylmercury oxide  $(\text{CH}_3\text{Hg})_2\text{O}$  by dehydration of methylmercury hydroxide is given. The crystals of tris-methylmercury-oxonium fluoborate have a trigonal symmetry, the hexagonal cell being  $a = 23.85 \text{ \AA}$ ,  $c = 10.72 \text{ \AA}$ ,  $z = 18$ . The Patterson synthesis along the  $c$ -axis was computed.

Recent x-ray crystal structure analysis<sup>1,2</sup> has shown that mercuric oxychloride  $2\text{HgCl}_2 \cdot \text{HgO}$  is in reality a tris-chlormercury-oxonium chloride  $(\text{ClHg})_3\text{OCl}$ . This unexpected result led us to attempt the investigation of the possibility of the existence of other mercury-oxonium compounds with the mercury atom linked to the oxonium oxygen atom. In the group of mercury oxy-halides the additional representative with the oxonium structure has not yet been established<sup>3,4</sup>. There is little chance that some of them could be prepared because of the restricted conditions of the reaction for preparation and owing to the sensitivity of these compounds to water and their insolubility in organic solvents.

On the other hand, much more promising in this direction were the organic mercury compounds. The more so, since an organo-metallic oxonium compound was described previously, i. e. tris-trimethyltin-oxonium iodide<sup>5</sup>. From the very beginning we conceived our investigation on a broader basis with the aim to establish the possibility of preparation of organomercury sulphonium and selenonium compounds as well as the onium compounds of the elements of the 5th and the 7th group of the periodic table. Consequently we started the investigation of the onium compounds in the organomercurial series of the common formula:



where R = alkyl or aryl; E = O, S, Se, N, P, As, Sb, or I; X = halide or another common anion; n = number of unshared valence electrons of the element E.

Up to now we have been successful with the preparation of the alkylmercury-oxonium and sulphonium compounds, but concerning the nitrogen, phosphorus, arsenic and antimony derivatives we could prepare only the complex compounds of ammonia, phosphine and arsine<sup>6</sup>. The present com-

munication deals with the compounds of tris-methylmercury oxonium only, since the work has proceeded so far mostly in this direction.

The starting idea was that the reaction between the methylmercury oxide and methylmercury compounds  $\text{CH}_3\text{HgX}$  in an inert solvent might result in the formation of oxonium compounds  $(\text{CH}_3\text{Hg})_3\text{OX}$ . The more the Hg-X bond was ionic in its nature the better were the chances for such a reaction. That is why we endeavoured to accomplish this reaction with the use of methylmercury-fluoborate  $\text{CH}_3\text{HgBF}_4$ . Neither methylmercury oxide nor methylmercury fluoborate have been described up to now, so we decided to prepare the first by the dehydration of methylmercury hydroxide and the second by the neutralisation of the hydroxide with fluoboric acid.

Neutralisation of a solution of methylmercury hydroxide in methanol gave a crystalline product of a definite composition which corresponded — to our surprise — to the tris-methylmercury oxonium fluoborate which we had attempted to obtain in the second stage of the preparation only.

The explanation of this reaction issue could be given in two ways: (i) Fluoboric acid caused the formation of methylmercury oxide by dehydration of the hydroxide. The oxide then reacted subsequently with methylmercury fluoborate which originated from the other part of the hydroxide amount. (ii) The methylmercury hydroxide used was not pure but previously contained methylmercury oxide as an admixture.

Methylmercury hydroxide used in this reaction was prepared according to Slotta and Jacobi<sup>7</sup>. We checked carefully several times the preparation by this method and controlled the product on melting point and on mercury content after the recrystallisation and after keeping it in a dessicator. Slotta and Jacobi found in the product, which they had described as methylmercury hydroxide, the mercury content slightly higher. The melting point — according to them — was 137°C.

We found that the product, which corresponded by its mercury content to methylmercury hydroxide and which had a melting point of 131°C, increased its mercury content and heightened its melting point by merely standing in a vacuum dessicator over calcium chloride. We concluded therefore that (i) methylmercury hydroxide was transformed to oxide by dehydration and (ii) that »pure hydroxide« according to Slotta and Jacobi with the melting point 137°C was in reality methylmercury oxide.

The preparation of methylmercury oxide, which we produced subsequently, should be the proof for the above statement. The crude methylmercury hydroxide, prepared according to Slotta and Jacobi, was dissolved in dry toluene and one half of the solvent was removed by distillation. The remaining solution gave on cooling colourless, needlelike crystals, with the melting point 137°C and with a mercury content which corresponded exactly to methylmercury oxide. Hence, the water which the hydroxide lost at higher temperature distilled away together with toluene.

Moreover, the change in the composition of the »crude« hydroxide, caused by keeping it in a dessicator, was followed by means of powder x-ray photographs. Lines appeared which were subsequently established to belong to methylmercury oxyde.

Tris-methylmercury-oxonium fluoborate was therefore the product of the neutralisation reaction because the initial product had contained methylmercury hydroxide as well as the oxide. The question still remains open whether it contains tris-methylmercury-oxonium hydroxide or is a mixture of oxide and hydroxide. It is hoped that further investigation on the properties of methylmercury oxide, which is in our program, will throw some light in this direction.

Tris-methylmercury-oxonium fluoborate is a crystalline, colourless substance, stable in dry atmosphere, but sensitive to moisture. When pure it has not that detestable odour characteristic of methylmercury compounds.

It is easily soluble in methanol and from such a solution can be precipitated by addition of dry ethylether. It melts at 98°C under decomposition.

Tris-methylmercury-oxonium bromide was also prepared by condensation of methylmercury oxide with methylmercury bromide. Colourless leaflets turn yellow on exposure to light and decompose on standing. The powder photograph showed no lines of the initial components.

Tris-methylmercury-oxonium iodide was prepared by mixing a methanolic solution of methylmercury oxonium fluoborate and of potassium iodide. The square, plate-shaped, pale yellow crystals were not further examined due to their instability.

Reinecke's salt precipitates from methanolic solution of tris-methylmercury-oxonium fluoborate quantitatively an orange-red crystalline product of the composition  $[(\text{CH}_3\text{Hg})_3\text{O}][\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{H}_2\text{O}$ .

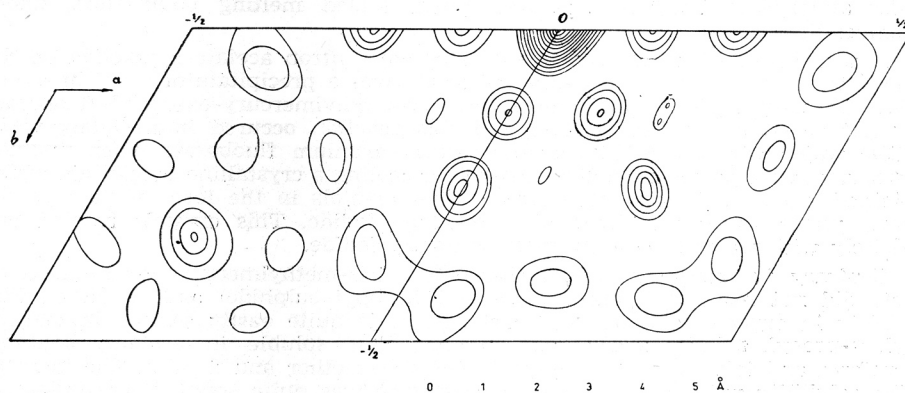


Fig. 1. Patterson projection along the hexagonal *c*-axis of the crystal of tris-methylmercury-oxonium fluoborate (contours at equal arbitrary levels). One half of the monoclinic cell is given, the transformation matrix to the true hexagonal cell being 120(110)000.

Precipitation of tris-methylmercury-oxonium by sodium tetraphenyl-borate has given no definite result up to now. Such a precipitation cannot be carried out in alcoholic solution, which is, by the way, known from the experience of the use of sodium tetraphenyl--borate in analytical practice<sup>8</sup>. On the other hand, solution in water should not be used for the reason stated above.

The results of the preliminary x-ray crystal analysis speak in favour of an oxonium structure. The rhombohedral unit cell of tris-methylmercury-oxonium fluoborate contains 18 formula units. Therefore the possibility for the determination of the molecule symmetry directly from the unit cell content and symmetry was ruled out. The Patterson synthesis ( $\chi_{y0}$ ) for a third of hexagonal cell was computed (Fig. 1). Most of the peaks belong to Hg—Hg vectors. There are Hg—Hg vectors which correspond to Hg—O distance of about 2.1 Å in agreement to previously found value<sup>2</sup>. The complete x-ray structure analysis is in progress.

The preparation of the analogous oxonium as well as other onium compounds derived from organomercurials is also in progress.

#### EXPERIMENTAL

##### 1. Preparation, analysis and properties of tris-methylmercury-oxonium fluoborate

A solution of methylmercury hydroxide (16 g.), which had been prepared by the method described by Slotta and Jacobi<sup>7</sup>, in methanol (50 ml.) was carefully neutralised with 40% fluoroboric acid. The solution was warmed with a small amount of charcoal, filtered and evaporated to dryness in vacuum at room temperature. The residue was dissolved in as little methanol as possible and filtered. A fifteen fold quantity of dry ether was then added to the filtrate. The small crystals which precipitated, were allowed to stay in the mother liquor overnight and grew to long colourless needles. The crystals were filtered, washed with a little dry ether and dried in vacuum (12 g.).

Tris-methylmercury-oxonium fluoborate crystallises in long colourless needlelike crystals which decompose by the action of atmospheric moisture. The odour characteristic of methylmercury compounds is then easily noticed. The crystals are stable in dry atmosphere. They melt at 98°C (in a sealed melting point tube) under decomposition.

A water solution of the compound gives with nitron acetate a reaction on the fluoborate anion and with potassium iodide it gives a precipitate of methylmercury iodide. In methanolic solution, however, tris-methylmercury-oxonium fluoborate does not react with nitron acetate, but this reaction occurred immediately when a little water was added. Tris-methylmercury-oxonium fluoborate when warmed in methanol with potassium iodide gave under cooling a crystalline precipitate which contained, except potassium fluoborate, larger crystals in the form of pale yellow square plates of tris-methylmercury-oxonium iodide. This crystals reacted immediately with water separating methylmercury iodide.

Contrary to trialkyl oxonium fluoborates tris-methylmercury oxonium fluoborate did not react with alkyl sulphides (dipropyl sulphide) and pyridine<sup>9</sup>. The solubility in organic solvents is remarkable. It is quite easily soluble in methyl, ethyl, *n*-propyl, *n*-butyl alcohol and pyridine, less soluble in acetone, benzene, chloroform and toluene and insoluble in petroleum ether and decalin. The increase of the solubility with the increasing temperature was quite small. Recrystallisation was therefore carried out as stated above by adding dry ether to the saturated methanolic solution.

Mercury was determined as follows: About 0.1 g. of methyl-mercury-oxonium fluoborate was dissolved in a few milliliters of water, 30 ml. of aqua regia were added and gently boiled under reflux for 20 minutes. Mercury was determined as mercuric sulphide in the usual way<sup>10</sup>.

The determination of the fluoborate ion was carried out by the nitron acetate method described by M. Lange<sup>11</sup>. It was found:

for  $(\text{CH}_3\text{Hg})_3 \text{OBF}_4$ : Hg calculated 80.21%, determined 80.73%  
 $\text{BF}_4$  calculated 11.63%, determined 11.14%.

A methanolic solution of Reinecke's salt added to the methanolic solution of tris-methylmercury-oxonium fluoborate gives quantitatively an orange-red crystalline precipitate which is insoluble in methanol, petroleum ether and chloroform, quite soluble in acetone but decomposes in water. The precipitate was washed several times with small portions of methanol in filter paper and dried at 65°C. The chromium content was determined in the precipitate as  $\text{Cr}_2\text{O}_3$  in the usual way.

For  $[(\text{CH}_3\text{Hg})_3\text{O}] [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\text{H}_2\text{O}$ :  $\text{Cr}_2\text{O}_3$  calculated 5.07%  
determined 5.31%.

### 2. Preparation and properties of methylmercury oxide.

Methylmercury hydroxide (5 g.), which had been prepared by the method according to Slotta and Jacobi<sup>7</sup>, was dissolved in dry toluene (100 ml.) at 75°C. The solution was filtered, distilled up to about 50 ml. and cooled to room temperature. The needleshaped crystals (4.5 g.) were filtered off, washed with a little dry petroleum ether and kept in vacuum. Melting point 137.5°C. The determination of mercury was carried out in the same way as described above.

For  $(\text{CH}_3\text{Hg})_2\text{O}$ : Hg calculated 89.41%, determined 89.71%.

Methylmercury oxide is stable in vacuum or in a dessicator over calcium chloride and sodium hydroxide. In free air it absorbs carbon dioxide readily. The existance of methyl-mercury carbonate was proved by analysis and by synthesis which will be described elsewhere.

Methylmercury oxide is quite easily soluble in water, alcohol, acetone and chloroform, less soluble in benzene, toluene, carbon tetrachloride and ethylether. The aqueous solution of methylmercury oxide is alkaline and gives all the reactions on methylmercury cation.

### 3. Tris-methylmercury-oxonium bromide.

A solution of methylmercury oxide in benzene was boiled with a 50% excess of methylmercury bromide. Colourless leaflets separate on cooling, turn yellow to brown on exposure to light and are soluble in methanol. Melting point 116°C. Mercury was determined by the method stated above.

For  $(\text{CH}_3\text{Hg})_3\text{OBr}$ : Hg calculated 80.90%, determined 81.30%.

### 4. Crystallographic and x-ray data.

The single crystals of tris-methylmercury-oxonium fluoborate were grown by slow evaporation of a solution in chloroform at room temperature. Needleshaped crystals have a hexagonal habit with prismatic and rhombohedral faces. The density as determined pycnometrically (in decalin) amounts to  $\rho = 4.11 \text{ g. cm.}^{-3}$ . The hexagonal unit cell has the dimensions

$$a = 23.85 \text{ \AA}, \quad c = 10.72 \text{ \AA}$$

and contains 18 formula units of  $(\text{CH}_3\text{Hg})_3\text{OBF}_4$  (calculated density  $\rho = 4.25 \text{ g. cm.}^{-3}$ ). The x-ray diffraction has a Laue-symmetry of 3 m, and condition  $-h + k + l = 3n$  is fulfilled for reflexion hkil. The probable space groups are (i) with all atoms in general positions  $R\bar{3}2$ ,  $R\bar{3}c$ ; (ii) with oxygen and boron on twofold axes:  $R\bar{3}c$ . The space groups  $R3m$  and  $R3m$  are omitted according to the criteria given by Kitaigorodskii<sup>12</sup>.

The reflections of the [0001] zone are recorded with the use of a Weissenberg goniometer on 4 films simultaneously. Relative intensities were determined visually. The absorption correction ( $\mu = 770 \text{ cm.}^{-1}$ ) was carried out for each reflexion by means of formulae previously described<sup>13</sup>. The Patterson synthesis (Fig. 1) in the (xyo) projection was computed with the use of Beevers-Lipson strips at the intervals of 1/60 of the cell edge for a third of the hexagonal unit cell.

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## IZVOD

## O tris-metilmerkuri-oksonium spojevima

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Opisana je preparacija i prikazana su svojstva tris-metilmerkuri-oksonium fluoborata  $(\text{CH}_3\text{Hg})_3\text{OBF}_4$ . Izrađena je metoda za preparaciju metilmerkuri oksida  $(\text{CH}_3\text{Hg})_2\text{O}$  dehidracijom metilmerkuri hidroksida. Kristali tris-metilmerkuri-oksonium fluoborata imaju trigonsku simetriju. Heksagonska elementarna ćelija ima dimenzije  $a = 23,85 \text{ \AA}$ ,  $c = 10,72 \text{ \AA}$ ,  $z = 18$ . Izračunata je Pattersonova sinteza u projekciji uzduž osi  $c$ .

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