

On a Mercuric Oxyfluoride

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Properties, preparation and analysis of a crystalline oxyfluoride defined by the formula $\text{HgF}(\text{OH})$ are described.

Crystallographic and X-ray investigations have shown that the crystals are orthorhombic with the space group D_{2h}^{13} or D_2^3 . The unit cell, which has the dimensions:

$$a = 4.93 \text{ \AA} \quad b = 5.95 \text{ \AA} \quad c = 6.86 \text{ \AA}$$

contains six stoichiometric units $\text{HgF}(\text{OH})$.

Defined mercuric oxyfluorides have not yet been described in the chemical literature. According to Finkener¹ the products^{2,3} previously described and obtained by the action of hydrofluoric acid on mercury or mercuric oxide, should be considered as mercuric oxyfluorides. Cox⁴ did not succeed in isolating even those oxyfluorides and he therefore concluded that these substances were only the mixtures of mercuric oxide and fluoride. By evaporation of the mercuric fluoride solution in hydrofluoric acid, Ruff⁵ obtained various products coloured from pale to deep yellow. He thought that they were oxyfluorides of various composition.

The present research was stimulated by the observation that a sample of mercurous fluoride, containing basic mercuric nitrate*, left, after heating on the water bath with hydrofluoric acid (40%) in a platinum crucible, pale yellow prismatic crystals which gave only the reactions on mercuric and fluoride ion but no reactions on mercurous ion. It was evident that the nitrate ion had acted as an oxidizing agent. Examinations described below showed that the crystals consisted of mercuric oxyfluoride having a constant composition corresponding to the formula $\text{HgF}(\text{OH})$.

The same compound was obtained under the same conditions when pure mercurous fluoride was used, but in this case the addition of nitric acid or sodium nitrate was necessary. In the absence of nitrate ion, mercurous fluoride remained unchanged. This fact proved the oxidizing action of nitrate ion in the above described preparation. At the same time it was established that this way of obtaining $\text{HgF}(\text{OH})$ from mercurous fluoride in hydrofluoric acid in the presence of nitrate ion was the best one, because it gave the least amount of by-products.

For the preparation of the oxyfluoride in the ordinary way from mercuric oxide and hydrofluoric acid the reverse could be said. The action of the acid begins already at the normal temperature and is increased by heating, giving plenty of crystals which change the colour from pale yellow to red-brown

* Obtained by mixing mercurous nitrate and sodium fluoride solutions.

of the tetralin was found to be 11.4 g. cm.^{-3} . Systematic extinctions were found to be of the type hOO , $h=2n$, OkO , $k=2n$ and hkO , $h+k=2n$. They lead to the space groups D_{2h}^{13} — $Pmmn$ or D_2^3 — $P2_12_12$, of which the first is the more probable one.

EXPERIMENTAL

1. The preparation of mercuric oxyfluoride

About 1–2 g. of mercurous fluoride, containing nitrate ion was dissolved in a platinum crucible with 40% hydrofluoric acid and it was evaporated slowly in darkness over the water bath just to dryness. A yellow residue, which contained the crystals as pale yellow needles was obtained. These needles were carefully separated from the residue and then collected. One of such preparations gave on average 10–20 mg. of crystals.

2. Chemical analysis

a) The determination of mercury.

The substance (from 0.010 to 0.050 g.) was dissolved in dilute nitric acid (about 0.2 cm.³) water added to 50 cm.³ and the excess of acid neutralized with dilute ammonia. 1 g. of potassium iodide, in the form of a 2% solution was added, heated nearly to boiling and precipitated with a boiling, concentrated aqueous solution of copper ethylene diamine nitrate. After being left for 12 hours the precipitate was filtered, dried in a vacuum desiccator and weighed as $[\text{Cu(en)}_2] [\text{HgJ}_4]^6$.

b) The determination of fluorine.

In one case the substance was carefully molten in a platinum crucible with sodium hydroxide and after cooling dissolved in water. In the filtrate the fluorine was estimated. An alternative which consisted in the fusion of the substance by means of the metallic sodium in a glass tube, proved to be more efficient. The excess of sodium was dissolved with alcohol after the reaction. Water was added and the solution filtered. The fluoride ion was precipitated with an alcoholic solution of triphenyltin chloride according to a previously described procedure⁷. The reagent was prepared according to Kotsheshkov¹⁰.

The accuracy of both methods was proved on test substances (mercuric chloride and sodium fluoride) with the corresponding amounts of mercury, respectively fluorine, which corresponded by weight to the investigated substances.

c) The determination of water.

In order to determine the water content, crystals were heated. At 105° they remained unchanged, at 120° they became brown, and at 150° they darkened totally and in the meantime they slowly lost in weight.

The average of a large numbers of analysis is following:

	Found	Theoretical
Hg	84.00%	84.78%
F	7.50%	8.03%
OH	—	7.19%

As the crystals could not be recrystallized, the substance for the analysis was selected in a mechanical way. All the impurities were probably not removed. This could explain some disagreement of the analysis, whose mean value is given; the accuracy being for mercury $\pm 0.10\%$ and for fluorine $\pm 0.50\%$.

3. Crystallographic and X-Ray measurements

All the necessary crystal-data, as well as the results of measurements are mentioned in the first part of this paper. For the powder photograph the »Unicam« vacuum powder camera of 19 cm. diameter was used. The sample was sealed

in a 0.3 mm. quartz capillary. The nickel filtered copper $K\alpha$ radiation was used. The spacings d_{hkl} and the relative intensities I_{hkl} are given in Table I.

TABLE I.
X-Ray Powder data for $HgF(OH)$
Cu/Ni radiation, the intensities photometrically measured

d_{hkl}	I	d_{hkl}	I
4.165	55	1.335	15
3.803	80	1.313	15
2.968	100	1.272	20
2.832	33	1.257	11
2.778	7	1.171	7
2.644	11	1.148	20
2.497	20	1.122	15
2.284	4	1.050	11
2.049	46	1.024	20
1.911	61	1.008	7
1.836	43	0.956	7
1.716	20	0.933	2
1.599	15	0.910	2
1.570	15	0.891	2
1.496	11	0.840	2
1.481	11	0.834	3
1.412	24	0.824	3

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IZVOD**O živinu oksifluoridu***C. Đorđević*

Opisana su po prvi put svojstva, preparacija i analiza živina oksifluorida, koji je priređen u kristalnom stanju, i kojemu je sastav definiran formulom $\text{HgF}(\text{OH})$.

Kristalografsko i rentgensko istraživanje pokazalo je, da su kristali rompski, a prostorne grupe D_{2h}^{13} ili D_2^3 . U elementarnoj ćeliji s dimenzijama:

$$a = 4.93 \text{ \AA} \qquad b = 5.95 \text{ \AA} \qquad c = 6.86 \text{ \AA}$$

nalazi se šest stehiometrijskih jedinica $\text{HgF}(\text{OH})$.

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