The Decomposition of $Hg_3S_2Cl_2$ in Alkaline Solutions

S. ĎUROVIČ

*Crystallographic Laboratory McGill University, Montreal, P. Q., Canada**

With the aid of the qualitative X-ray phase analysis it has been shown that the product of the decomposition of $Hg_3S_2Cl_2$ in the solution of an alkaline hydroxide, consists of the mixture of both modifications of HgS and both modifications of HgO. The product is not an individual chemical compound Hg_3OS_2.

It is a well known fact that $Hg_3S_2Cl_2$ is decomposed by the alkaline solutions, leaving brownish-black residue of the total chemical composition of Hg_3OS_2 [1—8]. The individual authors, however, are not unified about the phase composition of this residue. Their opinions can be roughly divided into two groups:

1. The product of the decomposition consists of the mixture of HgS and HgO [1, 4, 8].

2. The product of the decomposition is an individual chemical compound Hg_3OS_2 [2, 5, 7].

Only two papers deal with an X-ray phase analysis of the residue. J. Lamure [6] found in its X-ray powder pattern the lines of γ-HgS (cubic) but claimed that the remaining significant lines cannot be assigned neither to $Hg_3S_2Cl_2$ nor to HgO (his paper does not contain the list of the diffraction lines). On the other hand S. S. Bacanov and L. I. Abaulina [7] claimed the existence of the mercuric oxide sulfide Hg_3OS_2 and documented it with the list of the diffraction lines.

During the determination of the crystal structure of γ-$Hg_3S_2Cl_2$ [9] and the redetermination of the crystal structure of α-$Hg_3S_2Cl_2$ [10] in this Laboratory, specimens of both modifications have been used in order to check the above opinions. The specimens in both single-crystal (average size 0.5 mm) and powdered form were boiled in 5 % solution of KOH and the brownish-black residue of the decomposition (controlled in the case of the powdered specimens by the determination of the liberated Cl^- in the solution) was analyzed by X-ray diffraction methods with following results:

1. Rotating-crystal photographs (Cu-radiation) were taken from the pseudomorphs of the residue after $Hg_3S_2Cl_2$ single crystals (the pseudomorphs preserved complete morphology of the original crystals). The photo-

* Present address: Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Dúbravská cesta, Czechoslovakia.

graphs had the character of powder diagrams, this being a proof of a destruction of the original structure. Few lines, however, exhibited textural maxima and these lines were identified as those of γ-HgS (cubic). This fact alone proves that the residue cannot be considered as an individual chemical compound.

2. Powder photographs (calibrated with silicon) were prepared in Guinier focusing camera (CoK_α-radiation, $1° \doteq 4$ mm), using the specimens obtained in two separate decomposition experiments from powdered crystals. The powder patterns obtained, were identical only as regards the positions of the diffraction lines. There were significant differences in the distribution of the intensities. Out of the total of 47 lines ($\Theta_{max} = 44°$), only 4 weakest ones were unidentifiable; the remaining lines were unequivocally assigned to the mixture consisting of 4 components: γ-HgS (cubic), α-HgS (hexagonal) [11], orthorhombic HgO [12] and hexagonal HgO [13]. The most important portion of the powder diagram of one specimen, together with the corresponding lines of the above components is schematically drawn in Fig. 1. The other specimen contained the same components in different proportions.

3. Common Debye-Scherrer patterns of the two above powdered specimens were taken (nickel-filtered Cu-radiation, camera diameter 57.2 mm, diameter of the cylindrical specimen 0.4 mm). The evaluation of these photographs (without an absorption correction) yielded a set of the „*d*-values" very close

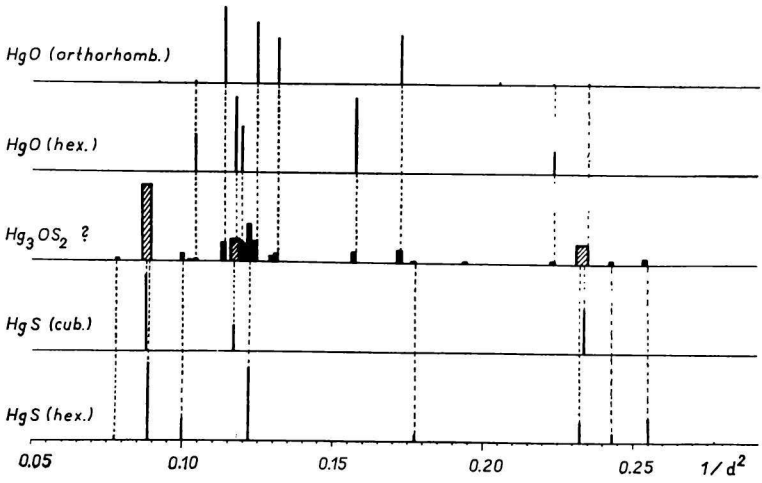

Fig. 1. The powder diffraction pattern of the decomposition product of $Hg_3S_2Cl_2$ in KOH solution (marked Hg_3OS_2?) together with the standard diffraction patterns of its components. The relative intensities are plotted versus $1/d^2$.
Diffuse lines shadowed.

to those, listed by S. S. Bacanov and L. I. Abaulina [7]. It can be, therefore, concluded that the above authors worked under similar experimental conditions. It is clear, however, that the „*d*-values" obtained in this way, cannot be considered as a proof of the existence of the chemical compound Hg_3OS_2, mainly because of the high absorption in the specimen and insufficient resolution.

The results of the X-ray phase analysis thus showed unequivocally that the product of the decomposition of $Hg_3S_2Cl_2$ in the solution of an alkaline hydroxide is a mixture of HgO and HgS (both modifications of each) and not an individual chemical compound Hg_3OS_2.

The author thanks to Dr. A. J. Frueh, Jr. (McGill University, Montreal) for his guidance and to National Research Council of Canada for the financial support.

ROZKLAD $Hg_3S_2Cl_2$ V ALKALICKÝCH ROZTOKOCH

S. Ďurovič

Ústav anorganickej chémie Slovenskej akadémie vied,
Bratislava

Pomocou kvalitatívnej röntgenografickej fázovej analýzy sa dokázalo, že rozkladný produkt $Hg_3S_2Cl_2$ v roztoku alkalického hydroxidu nie je osobitnou zlúčeninou Hg_3OS_2, ale zmesou oboch modifikácií HgS a oboch modifikácií HgO.

РАЗЛОЖЕНИЕ $Hg_3S_2Cl_2$ В ЩЕЛОЧНЫХ РАСТВОРАХ

С. Дюрович

Институт неорганической химии Словацкой академии наук,
Братислава

С помощью качественного рентгенографического фазового анализа было доказано, что в результате обработки $Hg_3S_2Cl_2$ щелочами получившийся продукт представляет с обой смесь двух модификаций HgS, а также двух модификаций HgO, а не является специальным химическим соединением Hg_3OS_2.

Перевел С. Дюрович

REFERENCES

1. Rose H., *Pogg. Ann.* ***13***, 59 (1828).
2. Poleck T., Goercki C., *Ber.* ***21***, 2415 (1888).
3. Bodroux M. F., *Compt. rend.* ***130***, 1398 (1900).
4. Naumann A., *Ber.* ***37***, 3600 (1904).
5. Denigès M. G., *Bull. Soc. chim. France* ***17***, 353 (1915).
6. Lamure J., *Compt. rend.* ***225***, 525 (1947).
7. Bacanov S. S., Abaulina L. I., *Izv. Sibir. otd. Akad. nauk SSSR* ***1961***, No. 10, 67.
8. Puff H., Private communication.
9. Ďurovič S., *Acta Cryst.* (in the press).

10. Frueh A. J., Gray N., *Acta Cryst.* ***B24***, 156 (1968).
11. Swanson H. E., Fuyat R. K., Ugrinic G. M., *NBS Circular 539, V. IV.*, 11—23 (1955).
12. Aurivillius K., *Acta Cryst.* ***9***, 685 (1956).
13. Aurivillius K., Carlsson I.—B., *Acta Chem. Scand.* ***12***, 1297 (1958).

Received July 31th, 1968

The address of the author:

Ing. Slavomil Ďurovič, CSc., Ústav anorganickej chémie SAV, Bratislava, Dúbravská cesta 5.