On the Mercury Phosphoiodide $Hg_3P_2I_2$

D. GRDENIĆ, S. ŠĆAVNIČAR and M. KESLER

M. Granger[1]) decribed the preparation and the properties of mercury phosphide Hg_3P_4. The present authors repeated Granger's experiments and obtained a crystallized compound showing the same properties but with a composition given by the formula: $Hg_3P_2I_2$. No compound which contained only phosphorus and mercury could be obtained by the method described.

The crystals are monoclinic, belonging to the space group $C_2{}^5h - P2_1/c$. The elementary cell containing 12 stoichiometric units $Hg_3P_2I_2$ has the dimensions.

$a = 13.07$ Å $\quad b = 12.44$ Å $\quad c = 17.16$ Å $\quad \beta = 120.2^0$

The method of preparation and analysis, the chystallographic and chemical data of the substance are given. The investigations of its structure by X-ray methods is in progress.

The crystal chemistry of mercury compounds with the elements of the 5b subgroup is better known only in the case of nitrogen. From the mercury compounds with arsenic only the crystal structure of $(Bu_3As)_2(HgBr_2)_2$ has hitherto been investigated[2]) and its As—Hg bond length determined. The bond length P—Hg is still unknown. In order to determine this bond length we chose the compound described by Granger[1]) as Hg_3P_4, because the other mercury phosphides quoted in chemical literature[3]) do not occur in crystals. Granger's compound is described in Abegg's handbook[4]) and it is mentioned also in Groth's work[5]). The compound seemed to be very interesting and we believed that a knowledge with its structure would also be of some importance for the crystal chemistry of the metal phosphides.

The compound was prepared according to the Granger's method by heating mercury and diphosphorus tetraiodide in a sealed glass tube. Single crystals suitable for crystallographic measurements are very rare. We succeded in obtaining only a few examples about 1 mm long and 0,5 mm thick. The crystals have a high metalic lustre and a dark violet colour. They may be easily powdered to a reddish brown powder, but no cleavage has been observed. Thin crystals viewed by transmitted light are ruby red. After Granger's description the crystal habit is hexagonal. Our crystals have also such a habit, but the goniometric and roentgenographic measurements showed that the crystals were really monoclinic prisms elongated

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[1]) M. Granger, Ann. chim. phys., [VII] **14** (1898) 5.

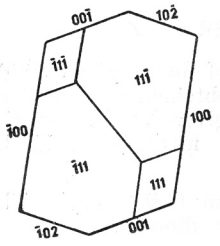
[2]) R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, J. Chem. Soc., **1940**, 1209.

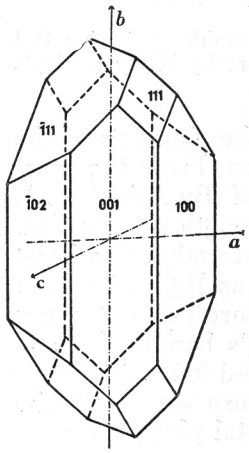
[3]) L. Moser and A. Brukl, Z. anorg. allg. Chem., **121** (1922) 252, described amorphous precipitates of Hg_3P and Hg_3P_2.

[4]) R. Abegg, Handbuch der anorganischen Chemie, II, 2, Leipzig 1905, p. 633.

[5]) P. Groth, Chemische Krystallographie, I, Leipzig 1906, p. 60.

in the direction of the b-axis (Fig. 1). The following faces were always observed: {100}, {001}, {$\bar{1}$02}, {$\bar{1}$11}, {111}, and ocasionally {010}, {110}, {011}, {$\bar{1}$01}, {021}, {$\bar{1}$12}, $\bar{1}$22}, {$\bar{2}$11}, and {$\bar{2}$12}.
The axis ratio is $a:b:c = 1{\cdot}058 : 1 : 1{\cdot}358$ (from unit cell edges determined by X-ray method: $a:b:c = 1{\cdot}051 : 1 : 1{\cdot}379$).





We attempted to grow the crystals by sublimation in an atmosphere of carbon dioxide in a sealed glass tube by a method which was in principle similar to that already described by Ruston and Rüdorff[6] but with no success. The sublimation was accompanied by decomposition and only small crystals were obtained. The products of the decomposition attracted our attention and in order to study them the following experiments were performed. The substance was heated several hours in a sealed glass tube filled with dry carbon dioxide. The temperature was kept constant 250°C at the bottom and 150°C at the top of the tube. The products of the decomposition were mercury, phosphorus (which usually burst into flames when the tube was opened) and big, tetragonal, yellow crystals of mercurous iodide. Under those conditions no other products of the decompositions could be observed.

The chemical analysis was carried out on several examples from different preparations and gave the brutto formula $Hg_3P_2I_2$. The equation for the decomposition is therefore

$$2\ Hg_3P_2I_2 = 2\ Hg + P_4 + 2\ Hg_2I_2$$

A little higher values for mercury were obtained. This may be explained by the fact that the usual methods of cleaning (recrystallisation and sublimation) could not be applied. The impurities may be mechanical or enclosed in the crystal lattice during the growing of crystals.

All the chemical properties of our crystals are the same as described by Granger for his phosphide. In addition, the particular resistance against nitric acid may be pointed out. The fuming nitric acid acts very slowly even on heating under reflux.

When we began the investigation we assumed that $Hg_3P_2I_2$ probably contained a P-P bond and that it was necessary for its preparation to take diphosphorus tetraiodide. It was shown, however, that this is not the case since the reaction of the phosphorus triiodide with mercury, carried out in the same manner, gave the same product.

As for the structure of $Hg_3P_2I_2$, no definite conclusions can be made at present, but it is very probable that mercury phosphoiodide is analogous to a mercury nitrogen compound belonging to the group of Millon's base

[6] W. R. Ruston and W. Rüdorff, Bull. soc. chim. Belges, **56** (1947) 97.

salts. If this asumption is valid the correct formula would be $[Hg_3P_2I]^+ I^-$ and the compound is a mercury-iodophosphonium iodide. But we do not exclude other possibilities and detailed X-ray analysis will decide.

The unit cell and the space group was determined by the usual X-ray method using oscillation photographs. The filtered CuK radiation was used. The unit cell has the dimensions

$$a = 13{\cdot}07 \text{ Å} \quad b = 12{\cdot}44 \text{ Å} \quad c = 17{\cdot}16 \text{ Å} \quad \beta = 120{\cdot}2^0$$

The density determined picnometrically is 7·69 g. cm^{-3}. The unit cell contains therefore 12 stoichiometric units of $Hg_3P_2I_2$ (the calculated density is 7·62 g. cm^{-3}). The reflexions with indices *hkl* were all observed. Absent reflexions were *0k0* for *k* odd and *h0l* for *l* odd. Thus the spase group is C_{2h}^5 —$P2_1/c$.

EXPERIMENTAL

1) Preparation of $Hg_3P_2I_2$. In a hard glass tube (2 cm in diameter and 30 cm in length) the diphosphorus tetraiodide (20 g) and mercury (40 g) were introduced and the air expelled with dry carbon dioxide. The tube was then sealed and heated for 10 hours continually in an aluminum block. The temperature was maintained constant and amounted to 330—340°C at the bottom and 250°C in the middle of the tube. Such a temperature gradient is necessary for the separation of reaction products. The tube must be cooled slowly (2—3 hours). The lower part of the tube was filled with the crust of small crystals of $Hg_3P_2I_2$ mixed with mercurous iodide, drops of mercury and a little scarlet amorphous phosphorus. The upper part was filled with orange and yellow crystals with the mercurous iodide as the main component. But they contained also mercuric iodide and probably the nondefined compounds of unchanged phosphorus iodide with mercury iodides[7]). The crystal crust was ground, mixed with potassium iodide (20 g), water was added, the precipitate warmed on a water bath and washed by decantation. The residual mercury was dissolved by warming with dilute nitric acid (20%) on a water bath. The nitric acid was renewed 5 times each hour. The product was washed with water and alcohol and dried on a water bath. The yield was 28 g or 88% of the calculated amount.

2) Preparation of the crystals. Since an attempt to grow the crystals from the pure product by sublimation gave no results, we tried to obtain single crystals directly from the reaction of the preparation in the tube. For this purpose many preparations were carried out by the method described above but only a tenth of that quantity was taken. The dimensions of the glass tube were thus suitably reduced (1 cm in diameter and 20 cm in length). Only a few well developed crystals were obtained as a result of many preparations.

[7]) A yellow mercury phosphorus iodide Hg_2PI_3 was allready prepared by Venturoli and was described by O. Dammer, Handbuch der anorganischen Chemie, II, 2, Stuttgart 1894, p. 919.

3) Chemical analysis. The method according to Volhard[8]) gave always a mercury sulphide containing phosphorus. Therefore a modified Souberain and Liebig's[9]) method was applied. The substance was mixed with a finely powdered mixture of sodium hydroxide and magnesium oxide (2 : 1). The reaction was carried out in a long glass test tube. The test tube was filled as follows. At first the pure mixture of sodium hydroxide and magnesium oxide was introduced, then this mixture plus substance, again pure mixture, then mixture of magnesium oxide with sodium peroxide and finally a few asbestos fibres. The test tube was then drawn and bent three times at right angles. The middle part was blown to a bulb in order to serve as recipient for mercury and water. The heating began from the asbestos towards the end of the test tube. After the main part of the mercury was distilled, the whole mass was heated strongly to expell the last traces of mercury. The bulb with the mercury was cut off, the mercury dissolved in a little dilute nitric acid and determined as sulphide. The test tube still warm was lowered in cold water and the mass dissolved by addition of dilute sulphuric acid to neutrality. The traces of separated iodine were reduced with some drops of a sulphur dioxide solution. The iodine was then determined iodometrically by the method described by Viebeck and Becher[10]).

Found	Hg 66.05% I 27.60%
Required for $Hg_3P_2I_2$	Hg 65.58% I 27.66%

Phosphorus can also be determined in the content of the test tube but in this case the separation of the silicic acid from the glass would be necessary. Therefore for the phosphorus determination the reaction was carried out in a nickel crucible and the phosphoric acid determined as $Mg_2P_2O_7$ by the usual method.

Found	P 6.16%
Required for $Hg_3P_2I_2$	P 6.76%

4) Preparation of $Hg_3P_2I_2$ from the phosphorus triiodide. 2 g of phosphorus triiodide and 8 g of mercury was sealed in a glass tube and heated for 15 hours in the manner described above. The results of the chemical analysis for the mercury and iodine were practically the same as for the product prepared from diphosphorus tetraiodide.

The X-ray photographs were taken in the Physical Institute (Faculty of Science) by kind permission of its Director Professor M. Paić.

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[8]) See F. P. and W. D. Treadwell, Kurzes Lehrbuch der analytischen Chemie, II, Wien 1943, p. 138.

[9]) H. Meyer, Die Analyse und Konstitutionsermittlung der organischen Verbindungen, Leipzig 1931, p. 125.

[10]) See F. Pregl and H. Roth, Quantitative organische Mikroanalyse, Wien 1947, p. 139.

IZVOD

O živinom fosfojodidu $Hg_3P_2J_2$

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Granger[1]) je opisao priređivanje i svojstva živinog fosfida Hg_3P_4. Mi smo ponovili Granger-ove pokuse i dobili kristaliziran produkt istih svojstava, no sastav mu je odgovarao formuli $Hg_3P_2J_2$. Spoj, koji bi sadržavao samo fosfor i živu, nismo mogli dobiti pomoću opisane metode.

Kristali su monoklinski i pripadaju prostornoj grupi C_5^{2h} — $P2_1/c$. Elementarna stanica sadrži 12 stehiometrijskih jedinica $Hg_3P_2J_2$ i njene su dimenzije:

$$a = 13{,}07\ \text{Å} \qquad b = 12{,}44\ \text{Å} \qquad c = 17{,}16\ \text{Å} \qquad \beta = 102{,}2^0$$

Dajemo opis metode priređivanja, te kristalografske i kemijske podatke. U pripremi je istraživanje kristalne strukture rentgenografskim metodama.

Rentgenski snimci učinjeni su u Fizičkom institutu prirodoslovno-matematskog fakulteta susretljivošću upravitelja profesora M. Paića.

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