Studies on the Compounds of the Group V Elements with Mercury II.* On the Mercury arseno-iodide $Hg_3As_2I_4$ and Mercury antimono-iodide $Hg_3Sb_2I_4$

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The preparation, analysis and properties of the compounds $Hg_3As_2I_4$ and $Hg_3Sb_2I_4$ are described for the first time. The compounds were prepared in pure state by the action of metallic mercury on arsenic- and antimony triiodide respectively; they are well defined crystalline substances.

The chemical reactions described show that these compounds probably belong to the class of arsonium and stibonium compounds but the other possibilities are not excluded.

The crystals of the antimony derivative are tetragonal. The elementary cell containing 9 stoichiometric units of $Hg_3Sb_2I_4$ has the dimensions: $a = 21.22$ Å; $c = 8.09$ Å.

An improved procedure for the preparation of antimony triiodide is also described.

In a previous paper[1] the existence of a mercury phospho-iodide $Hg_3P_2J_2$ was reported and its preparation and properties were described. The next step in the investigation of this class of compounds consisted in the attempt to prepare the arsenic and antimony analoga by the same method, i. e. by the action of mercury on the corresponding triiodides. Though the conditions of the experiment were very similar, the compounds which would have the formula $Hg_3As_2J_2$ and $Hg_3Sb_2I_2$ could not be isolated, but there were obtained well defined crystalline substances of the composition $Hg_3As_2I_4$ and $Hg_3Sb_2I_4$.

The reaction between mercury and antimony triiodide was investigated for the first time by Granger[2]. He obtained a compound the composition of which he expressed with the formula $Hg_3Sb_4 . 2HgJ_2$ however we were not able to prove the existence of a defined compound of this composition.

The method of preparation of both arsenic and antimony compounds was essentially the same. The corresponding triiodide was heated in a sealed glass tube in carbon dioxide atmosphere for several hours with mercury in excess. In both cases the crude product was purified by being heated once more in the same manner. The mercuric iodide, as the main impurity, was thus removed by sublimation.

The arsenic compound is a reddish brown coarse powder composed of small sintered crystals which transmit light of a vivid red colour. The well formed single crystals could not be prepared and consequently neither morphological nor crystallographical data can be given.

The antimony derivative is also a coarse crystalline powder composed of small bright crystals which are far better developed. They are dark grey,

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* Paper I., see reference[1]

nearly black with a violet tinge. Observed in transmitted light they are dark red. Some cristals were suitable for crystallographic measurements and it was found they were tetragonal.

The X-ray difraction photographs enabled us to establish the unit cell dimensions as follows:

$$a = 21\cdot22 \text{ Å} \qquad\qquad c = 8\cdot09 \text{ Å}$$

The density determined picnometrically amounted to 5·46 g.cm^{-3} (calculated density: 5·52 g.cm^{-3}); thus the cell contains 9 formula units of $Hg_3Sb_2I_4$.

The both arsenic and antimony compounds are not soluble in any common inorganic or organic solvent. They are not changed noticeably by cold water and by cold acids. The boiling water acts slowly, the warm concentrated nitric and sulphuric acid destroy both the compounds quickly. In hydrochloric acid they blacken.

The arsenic compound is quite sensitive to light. It blackens after short exposure to daylight, but the action of light is limited only on the thin surface layer.

Both compounds are not sensitive to air at room temperature, but if heated they burn giving mercuric iodide, mercury and arsenic (antimony) oxides.

The chemical analysis of both compounds was carried out in the similar way and is described in the experimental part. The results of analysis agreed unambiguously with the formula $Hg_3As_2I_4$ and $Hg_3Sb_2I_4$ respectively.

Obviously, it was impossible to decide at the first moment to which class these compounds really belong. In order to establish the nature of these compounds, the remarkable effect of sulphuric acid and especially the action of alcalies on them was studied carefully.

Both compounds heated in concentrated sulphuric acid are destroyed with evolution of iodine. This behaviour is not a property of mercuric iodide. It was assumed therefore that iodine was not bound to with mercury.

The reaction with alkali was followed quantitatively. The arsenic and antimony derivatives were destroyed by the action of warm 6 N potassium hydroxide solution. During the reaction no gas evolution was observed. There remained a grey powdery residue in which small mercury drops were easily observable. The residue contained the total quantity of mercury, so that no trace of mercury could be detected in alkaline solution. This solution contained always the total amount of iodine, with a half of the total amount of arsenic (or antimony), the other half remaining in the residue in elementary state mixed with mercury.

The described reaction can be explained by assuming the formulae (AsI$_4$) (AsHg$_3$) and (SbI$_4$) (SbHg$_3$) with tetraiodo-arsonium and tetraiodo-stibonium cation respectively. The reaction of the arsonium compound with potassium hydroxide may be expressed therefore by the following equation:

$$(AsI_4)^+(AsHg_3)^- + 8\,OH^- + K^+ \rightarrow AsO_4^{3-} + 4\,I^- + KAs + 3Hg + 4\,H_2O$$
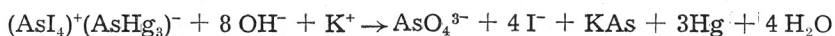
the same equation being valid for the stibonium compound.

The residue which is presumably the potassium arseno- or antimono-amalgam (or potassium arsenide resp. antimonide mixed with mercury) is

obviously stable in strong alkaline medium, since the evolution of hydrogen was not observed. When the residue was removed by filtration and the solution was acidified the half of the total iodine content was liberated:

$$AsO_4^{3-} + 2I^- + 2H^+ \rightarrow AsO_3^{3-} + I_2 + H_2O$$
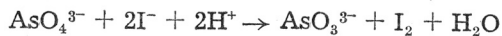
The other half of the iodine content remained in the solution in the state of iodide ion which was proved by precipitation with silver ion. The same is true for the antimony compound.

The residue of potassium arseno-amalgam lost its potassium content only after it had been thoroughly washed with water. The weight of washed residue was exactly as required by the above given formulae for the total mercury content increased by the half of the total content of arsenic or antimony.

In order to prove the above observation, another experiment was carried out in which the antimony derivative was destroyed in the same manner by 6N KOH solution, but then water was added and so the alkalinity reduced. After this the residue underwent further decomposition accompanied by gas evolution. The residue consisted of pure mercury. The filtrate contained all iodine in the state of iodide ions and consequently, also the total amount of antimony in the form of antimonite ions. This was obviosly due to the reduction of the antimonate ions by the action of hydrogen evolved in the process of dissolution of potassium antimonide in the hot alkaline solution.

In conclusion it is worthy to give a discussion about the probable structure of these compounds. Of course, we may hope that the final answer will be obtained from the X-ray structure analysis which is anticipated. But, now, in this stage of the investigation some assumptions and guessings about the structure are not to be despised. Before all, the chemical reactions described above together with the known crystallochemical data must be taken into account. The most probable explanation of the structure, at least for the antimony compound, is as follows:

The mercuro-arsenate $(AsHg)^-$ and mercuro-antimonate $(SbHg_3)^-$ are polymeric. Each arsenic (or antimony) atom is linked to six mercury atoms in a octahedral co-ordination. The $AsHg_6$ and $SbHg_6$ octahedra build up a three-dimensional network by sharing all corners. The question remains open whether there is enough space for the large iodo-arsonium and iodo-stibonium ions.

If, in the case of antimony compound, the sum of the corresponding metallic radii is assumed to be the Hg-Sb distance, i. e. 3.16 Å[3], then more than 27 mercury atoms and 18 antimony atoms would be required, what is in contradiction with the X-ray data obtained. Therefore, if the above assumption is valid, the Sb-Hg distance is longer. Assuming it to be 3,55 Å in the a axis direction and 4.05 Å in the c axis direction, then just the correct number of antimony and mercury atoms can be arranged in a $SbHg_3$ octahedral array. If the values 1.77 Å and about 2.70 Å are taken for the intermolecular iodine atom radius[4] and for Sb-I bond length[5] respectively, then the SbI_4-ions will have such a size that the cubooctahedral cavities of the $SbHg_3$-array will just be able to accommodate them.

The above assumption of a longer Hg-Sb distance as well as the use of the iodine intermolecular distance from the I_2 cristal structure may be also

justified. For, in the former case, we have an array of metal atoms carrying one negative charge per $SbHg_3$, in the latter case, there is one positive charge contracting the iodine atoms.

Of course, the assumed structure is idealized, while the actual structure is more or less deformed, which is proved also by its tetragonal symmetry instead of the cubic. It is difficult to suggest another structure which would explain the behaviour of the crystals in alkalies, i. e. the separation of mercury as well as two different states of antimony in the structure. An alternative may be suggested by the formula $Hg_3Sb.SbI_2.I_2$, with the iodine molecule enclosed in the structure, which would satisfy the above condition, but its crystal structure could be explained only by the first model.

EXPERIMENTAL PART

1. Preparation of $Hg_3As_2I_4$.

In a hard glass tube (1 cm. in diameter and 25 cm. in length) equal parts (e. g. 1·5 g.) of arsenic triiodide and mercury (2.3 gram-atoms of mercury to one mol of arsenic triiodide) were introduced after the air had been previously displaced by dry carbon dioxide. The tube was then sealed and heated continually for 10 hours in a vertical position in an aluminium block in such a manner that two thirds of the tube lenght were out of the aluminium block. The temperature was maintained constant and amounted to 250⁰C at the middle of the aluminium block. At the end of the preparation the outer part of the tube was filled with crystals of mercuric and mercurous iodide mixed with a small quantity of a brown powdery product and drops of mercury. The bottom of the tube was filled with reddish brown agglomerate of small crystals of $Hg_3As_2I_4$.
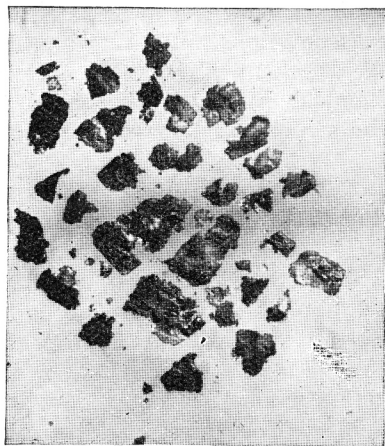

Fig. 1. Crystals of $Hg_3As_2I_4$. X20

Fig. 2. Crystals of $Hg_3Sb_2I_4$. X20

It was necessary to continue the heating for ten hours be in order to complete the separation of mercurous and mercuric iodide by sublimation. In preliminary experiments, when the heating lasted less then ten hours, the product contained always some mercury iodides as inpurities. A purification process consisting in heating the crude product in vacuo at 120⁰C was then undertaken, but the decomposition of the compound was slow. Only when the crude product was purified by heating in a sealed glass tube in the same manner as during the preparation, a pure compound was obtained.

2. *Preparation of* $Hg_3Sb_2I_4$.

The method for preparing the antimony derivative was similar. Equal parts (e. g. 6.4 g.) of antimony triiodide and mercury (2.5 gram-atoms of mercury to one mole of antimony triiodide) were heated in a sealed glass tube with dry carbon dioxide atmosphere in an aluminium block. At the begining the temperature was maintained during one hour at 108°C, then for one hour at 210°C and then finally for 4 hours at 300—310°C. The cooling of the block with the tube lasted two hours. In the cold outer part of the tube, mercury iodides, drops of mercury and a small amount of an undefined brown product were deposited. The crude product, which remained as a black crystalline cake at the bottom of the tube, was purified by being sealed again in a tube with CO_2 atmosphere and heated once more for 4 hours at 280°C and then slowly cooled. The sintered crystal agglomerate obtained in such a way was pure $Hg_3Sb_2I_4$. Heated in vacuo at 100—110°C it gave no sublimate of mercury or mercuric iodide.

3. *Chemical analysis.*

a) *Determination of mercury.* The mercury content was determined in both arsenic and antimony compound as previously described[1]. The analysis was carried out on samples from different preparations and the results were always in good agreement.

Arsenic derivative:
Found: Hg 47.60% required for $Hg_3As_2I_4$: Hg 47.76%
Antimony derivatives:
Found: Hg 44.43% required for $Hg_3Sb_2I_4$: Hg 44.48%

b) *Determination of arsenic, antimony and iodine.* The alkaline mass deprived of mercury was dissolved in warm water and then about 10 ml. of a sulphur dioxide solution were added in order to reduce arsenates (antimonates) and iodates. The solution was then acidified and filtered from glass chips and asbestos fibres and used for the determination of arsenic (antimony) and iodine.

At first the iodine content was determined by precipitation as AgI. The excess of silver ions in the filtrate was removed by adding a solution of potassium iodide; arsenic (antimony) was then precipitated as trisulphide[3].

The iodine content was also determined by titration method[4] after arsenic (antimony) was removed from the solution as sulphide. All results of the analyses which were carried out on samples from different preparations were in good agreement.

Arsenic derivative:
Found: As 11.70% required for $Hg_3As_2I_4$: As 11.90%
Found: I 39.81% required for $Hg_3As_2I_4$: I 40.30%
Antimony derivative:
Found: Sb 17.98% required for $Hg_3Sb_2I_4$: Sb 17.99%
Found: I 37.27% required for $Hg_3Sb_2I_4$: I 37.53%

4. *Reaction with alkalies*

The arsenic compound as well as the antimony compound is very sensitive to aqueous ammonia. In the experiments described here potassium hydroxide was used.

a) *Reaction of potassium hydroxide with the antimony compound.* The powdered substance (0.2966 g.) was covered in a beaker by pouring over a $6N$ potasisum hidroxide solution (30 ml.) and then slightly warmed on the water-bath. The grey residue was filtered, washed and weighed (0.1594 g.). The filtrate was acidified with dilute nitric acid. The acidification was accompanied by the liberation of iodine. The iodide ions were precipitated from the solution in the form of silver iodide by means of a silver nitrate solution. The weight of AgI amounted to 0.1023 g. The excess of silver ions was then removed from the solution by precipitation with potassium iodide, and filtered. Antimony was finally precipitated with hydrogen sulphide and determined as Sb_2S_3 (0.0365 g.).

The grey residue, which remained in Gooch crucible after the filtration of the alkaline solution, was washed with 20% hydrochloric acid. Antimony dissolved, while mercury remained undissolved. The weight of mercury amounted to 0.1329 g. The hydrochloric acid solution contained only antimony; no trace of mercury could be detected in this solution.

The above data gave the folloving percentages:

Grey residue, found: 53.75%
Required for (Hg_3Sb) $(Sb\,I_4)$: . . . . . . Hg_3Sb 53.41%
Found in grey residue: . . . . Hg 44.82%
Required for (Hg_3Sb) (SbI_4): . . . . Hg 44.48%
The antimony content in the grey residue found: Sb 8.93%
A half of the antimony content required for
(Hg_3Sb) (SbI_4):   . . . . Sb 8.995%
Antimony content in the KOH-solution, found: . .   Sb 8,82%
Iodide ion content in the acidified KOH-solution, found: I 18.64%
A half of the iodine content required for $(Hg_3Sb)(SbI_4)$: I 18.77%

The total iodine content was also conveniently determined in the alkaline solution. For this purpose a sulphur dioxide solution was added to the alkaline solution before it had been acidified and iodine content was then determined by titration[4]
    Found: I 37.49% Required for (SbI_4) (Hg_3Sb): . . I 37.53%
In order to show that potassium was bound to antimony in the antimony- and mercury-containing residue after the action of $6N$ KOH solution, the following experiment was carried out.

The powdered antimony compound (0.3445 g.) was covered with $6N$ KOH solution and slightly warmed as described above. Water (200 ml.) was then added and warmed again. The curdy part of the residue started to decompose with small explosions and gas evolution. After the reaction had ceased, the solution was filtered, the residue determined by weighing as pure mercury and iodide ion determined as previously described.

    Found: Hg 45˙30%   Required for SbI_4 Hg_3Sb: 44.45%
    Found: I   37 45%   Required for SbI_4 Hg_3Sb: 37.53%

b) *Reaction of potassium hydroxide with arsenic compound.* This reaction was also used in the study of arsenic compound. The results obtained did not agree as well as in the case of antimony compound. The reason might be searched in the fact that arsenic compound was never obtained in such a purity as the antimony compound. Besides, the reaction of alkali with the arsenic compound was carried out only in order to confirm the analogy of both arsenic and antimony compounds. The results were as follows:

Arsenic content in the grey residue, found: . . . As 5.66%
Arsenic content in the alkaline solution, found: . . As 6.20%
A half of the arsenic content required for
(AsI_4) (Hg_3As): . . . . As 5.95%
The content of mercury in elementary state in the grey
residue found: . . . . Hg 47.80%
Required for (AsI_4) (Hg_3As): . . . . . . Hg 47.76%
The iodine content in alkaline solution found: . . I 40.70%
Required for (AsI_4) (Hg_3As): . . . . . . I 40.30%

5. *Preparation of $Hg_3As_2I_4$ by the reaction of mercury with arsenic triiodide in chloroform solution.*

The equal parts of mercury and arsenic triiodide (e. g. 1.5 g.) in chloroform (50 ml.) were heated on water bath under reflux for 8 hours. The redish brown powder was deprived of the remaining drops of mercury by suspension and then thoroughly washed with warm chloroform.

The analysis was carried out as described above and gave as formula $Hg_3As_2I_4$.

    Found Hg 47.68% and As 11.02%

An attempt was made to prepare the antimony compound by the same procedure, but without success. The antimony triiodide dissolved in chloroform remained unchanged even after prolonged heating with mercury under reflux.

6. Crystallographic and X-ray data.

Well developped crystals of these substances could not be obtained. Occasionally a few small crystals of the antimony compound were obtained which enabled crystallographic and X-ray measurements. Some crystals were prism shaped and its tetragonal symmetry was easily determined, but some of them were tiny six-sided plates parallel to (100). No cleavage was observed at all.

The unit cell was determined from oscillation photographs. Filtered copper radiation was used.

7. The preparation of antimony triiodide .

Dry toluene (200 ml.) with antimony powder (7.5 g.) was allowed to boil in a conical flask under reflux. Iodine (23 g.) was gradually added in small portions and then the boiling maintained for three hours. The hot solution was filtered and allowed to stand for crystallization. The yield of pure product (m. p. 170°C) was 85% of the calculated. This procedure was found more convenient than that described previously[5]. The yield was also slighthly higher.

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IZVOD

Studije o spojevima žive s elementima V grupe.
II. O živinu arseno-jodidu Hg$_3$As$_2$J$_4$ i živinu antimono-jodidu Hg$_3$Sb$_2$J$_4$

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Opisana je po prvi put preparacija, analiza i svojstva spojeva s formulom Hg$_3$As$_2$J$_4$ i Hg$_3$Sb$_2$J$_4$. Ti su spojevi dobiveni grijanjem žive s arsenovim, odnosno antimonovim trijodidom. Neke kemijske reakcije, u prvom redu djelovanje alkalija, dale su dovoljno dokaza u prilog pretpostavci, da se radi zapravo o jodo-arsonijevu merkuri-arsenatu i jodo-stibonijevu merkuri-antimonatu, te da im treba pripisati formule (AsJ$_4$) (AsHg$_3$), odnosno (SbJ$_4$) (SbHg$_3$). Pretpostavlja se dalje, da atomi arsena, odnosno antimona, zajedno s atomima žive, čine u kristalnoj rešetki tih spojeva trodimenzijski polimer od AsHg$_6$, odnosno SbHg$_6$ oktaedara, koji imaju sve kutove zajedničke. U praznine koje preostaju mogli bi se smjestiti (AsJ$_4$)$^+$, odnosno (SbJ$_4$)$^+$ ioni. Kristali antimonova derivata su tetragonski. Veličina elementarne ćelije određena je rentgenografskim metodama.

Daje se i opis poboljšane metode za preparaciju antimonskoga trijodida.

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