THE DOUBLE CADMIUM AND MERCURIC IODIDES OF SUBSTITUTED AMMONIUM BASES.

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The Double Cadmic Iodides.

In a paper[1] to the Chemical Society, it has been shown that when chloroplatinic acid or cupric chloride is added to a strong solution of an alkylammonium iodide, a precipitate is obtained of double platinic or cupric iodide, notwithstanding the fact that cupric iodide does not exist by itself. The formation of such salts suggested further investigation as to the general applicability of this method by which such interesting results had been achieved. Accordingly, it was thought advisable to try the same experiment with cadmium and mercury, the more so as cupric copper ought naturally to belong to the second group of Mendeléef's classification. However, the nature of the double iodides with these metals differs essentially from those formed with cupric copper. In the former case, the metallic iodide is stable and the iodide of the substituted ammonium base is not essential for its formation: while in the latter case, the metallic iodide is highly unstable and it is by the simultaneous combination with the alkylammonium iodide that the existence of its double iodide becomes at all possible. Consequently, no special care has to be taken to prepare these double iodides with cadmium, it being only necessary to add cadmium chloride to the substituted ammonium iodide. Since cadmium iodide itself can be obtained in solution, a solution of it is therefore also directly employed instead of cadmium chloride, which, however, gives the same result. The only point of difference is that in the use of cadmium chloride, the substituted ammonium iodide has to be kept in considerable excess, while in the case of cadmium iodide, this condition is not at all necessary. The precipitation of these double salts takes place immediately with the heavily substituted ammonium iodides, the reaction not being successful in leading to a precipitate with the lower members, however strong the interacting solutions may be.

Ragland[2] obtained several double cadmium halides, including iodides, with the lower members only, which are very soluble, by the crystallization of cadmium iodide with amine hydriodides. Now, cadmium iodide forms two types of salts, *viz.*, $2NR_4I.CdI_2$ and $NR_4I.CdI_2$. It is the former type that is generally produced and the latter type is produced only in exceptional cases.

Tetramethylammonium Cadmium Iodide, $2N(CH_3)_4I.CdI_2$.—This compound is obtained as a white precipitate by adding a solution of cadmium chloride to an excess of tetramethylammonium iodide. The same result

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[1] *J. Chem. Soc.*, **103**, 426 (1913).

[2] *Am. Chem. J.*, **22**, 417 (1899).

is also obtained by adding cadmium iodide solution to the substituted ammonium iodide. The salt is washed with water and dried in the steam chamber. It is a white powder, slightly soluble in water.

0.3408 gave 0.0559 CdO; Cd = 14.35; $2C_4H_{12}NI.CdI_2$ required Cd = 14.58%.

The cadmium is estimated according to the method of Barth and Hlasiwetz,[1] which consists in repeated treatment of the salt with fuming nitric acid and evaporation on the water bath and finally igniting and weighing as oxide.

Tetraethylammonium Cadmium Iodide, $2N(C_2H_5)_4I.CdI_2$.—This salt is obtained similarly to the previous salt by adding cadmium chloride and also the iodide to a solution of tetraethyl ammonium iodide. The salt is washed with water and dried in the steam chamber. It is a white powder.

0.3121 gave 0.0441 CdO; Cd = 12.37; $2C_8H_{20}NI.CdI_2$ requires Cd = 12.72%.

Trimethyl-p-tolylammonium Cadmium Iodide, $2N(CH_3)_3C_7H_7I.CdI_2$.—This compound is obtained as usual by adding cadmium iodide to a solution of the alkylammonium iodide. During the precipitation, it has a slight tendency to first separate as an oil. The precipitate, after being washed and dried as usual, consists of a white powder.

0.4025 gave 0.0549 CdO; Cd = 11.95; $2C_{10}H_{16}NI.CdI_2$ requires Cd = 12.17%.

Tetrapropylammonium Cadmium Iodide, $N(C_3H_7)_4.ICdI_2$.—Instead of forming a double salt of the type $2NR_4I.CdI_2$, as with the other members, it forms a salt of the type $NR_4I.CdI_2$. Copper also forms the same type of salt with tetrapropylammonium iodide, as was pointed out in my paper on the double platinic and cupric iodides. Hence it appears that the weight of the base is alone responsible for the formation of the other type of salt. This is obtained as usual by adding a solution of cadmium chloride or cadmium iodide to a solution of tetrapropylammonium iodide. The precipitate is filtered, washed and dried.

0.2844 gave 0.0531 CdO; Cd = 16.33; $C_{12}H_{28}NI.CdI_2$ requires Cd = 16.70%.

Pyridinium Cadmium Iodide, $2C_5H_5NHI.CdI_2$.—To a strong solution of pyridine hydriodide, cadmium iodide is added, when immediately a white cloudiness is produced, which disappears on shaking. The production of the white cloudiness and its immediate disappearance, continues for some time on addition of CdI_2, when all of a sudden, a thick mass of crystals deposits at the bottom. The same result is also obtained by using a solution of cadmium chloride with an excess of pyridine hydriodide. It is also observed that if, instead of adding cadmium iodide to pyridine hydriodide, the latter be added to the former, a similar haziness and its immediate disappearance take place. The crystallin precipitate obtained above is filtered, washed and dried at 100°. The salt consists of a

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[1] *Ann.*, 122, 104 (1862).

white powder, moderately soluble in water and hence during the preparation its precipitation is delayed.

0.7006 gave 0.1190 CdO; Cd = 14.27; $2C_5H_6NI.CdI_2$ requires Cd = 14.36%.

α-Picolinium Cadmium Iodide, $2C_5H_4(CH_3)NHI.CdI_2$.—The method of preparation of this compound is precisely the same as that of the preceding compound, the same phenomena being noticed in this case too. But unlike the previous compound, its precipitation is almost immediate. The salt is dried as usual.

0.2854 gave 0.0443 CdO; Cd = 13.59; $2C_6H_8NI.CdI_2$ requires Cd = 13.86%.

Quinolinium Cadmium Iodide, $2C_9H_7NHI.CdI_2$.—When a solution of cadmium iodide is added to a solution of quinoline hydriodide, a white cloudiness is first formed, which soon collects to a reddish brown oil. After a time, the oil solidifies to a mass of crystals, which is broken up and washed. The solidification of the oil can be much hastened by stirring with a glass rod. As the separation of the double iodide as an oil and its consequent solidification to a hard mass presents considerable difficulties in the matter of washing, the following method has been employed in which a white crystallin precipitate can be obtained without passing through the intermediate stage of an oil. For this purpose, first only a small quantity of cadmium iodide is added when the precipitate formed solidifies on shaking. Now on gradually adding cadmium iodide with shaking, the precipitate increases without any sign of a liquid appearing. The crystals are finally collected, washed to free them from adhering mother liquor and dried at 100°. This method applies to all the double salts of quinoline, which have a tendency to become oily, and it was successfully employed in the case of double quinoline mercuric nitrite.[1] The salt as obtained above is a white powder, sparingly soluble in water.

0.5929 gave 0.0829 CdO, Cd = 12.24; $2C_9H_8NI.CdI_2$ requires Cd = 12.72%.

The Double Mercuric Iodides.

The tendency to double salt formation is particularly marked in the case of mercury and oftentimes two types of salt could be obtained by varying the conditions of preparation.

Mercuric iodides dissolve freely in solutions of the alkali and ammonium iodides and out of those solutions, numerous double salts have been prepared by different investigators. Hofmann,[2] boiled a solution of tetraethylammonium iodide with mercuric iodide but though the mercuric iodide did not dissolve, it was changed into a yellow powder, having the formula $2N(C_2H_5)_4I.5HgI_2$. In the same paper, he mentions the formation of a compound by adding a large excess of mercuric chloride to

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[1] Ray, Rakshit and Datta, *J. Chem. Soc.*, **101**, 616 (1912).

[2] *Ann.*, **78**, 273 (1851).

tetraethylammonium iodide. The compound according to him contains 6 mols NEt_4I, 30 mols $HgCl_2$, one mol $NEt_4I.2^1/_2HgI_2$ and 5 mols HgI_2. But as will be shown later, he obtained an impure mixture of varying composition, the irregular proportions of the compound further confirming this.

While the present investigation was in progress, Dehn[1] prepared a series of double iodides having the general formula $NR_4I.HgI_2$ by dissolving mercuric iodide in solutions of the amine iodides and crystallizing out of the solution the respective double iodides.

Risse[2] prepared two types of salts with tetramethyl- and tetraethylammonium iodides, by the interaction of polyiodides of the tetraalkylammonium bases with mercury. By the interaction with an alcoholic solution of tetraalkylammonium triiodide, a salt of the type $NR_4I.HgI_2$ and by a similar interaction with tetraalkylammonium tetraiodide, a salt of the type $2NR_4I.3HgI_2$, were obtained.

Muller[3] prepared the compound $2N(C_2H_5)_4I.3HgI_2$ by the interaction of trimercuramine, N_2Hg_3, with ethyliodide.

Smiles[4] prepared double mercuric iodides of the sulfonium bases by the interaction of sulfonium iodide with mercuric iodide in acetone solution, as also from dialkylsulfide-mercuric iodide and alkyl iodide. He obtained by these interactions salts of the type $SR_3I.HgI_2$.

By following up the method of double decomposition described before, two types of salt have been obtained by slightly varying the conditions of precipitation. When an aqueous solution of mercuric chloride is added to an excess of alkylammonium iodide, a white to yellowish white precipitate is formed which has been found of the type $2NR_4I.HgI_2$. If the addition of mercuric chloride be continued, the precipitate changes to yellow, and the salt is of the type $2NR_4I.3HgI_2$. If the addition be further continued, the precipitate changes into red iodide of mercury. The decomposition of the yellow precipitate by excess of mercuric chloride speaks of the superior affinity of iodine for mercury. The successive steps in the reaction may be represented thus:

$$2NR_4I + HgCl_2 = 2NR_4Cl + HgI_2$$
$$2NR_4I + HgI_2 = 2NR_4I.HgI_2$$
$$2NR_4I.HgI_2 + 4NR_4I + 2HgCl_2 = 4NR_4Cl + 2NR_4I.3HgI_2$$
$$2NR_4I.3HgI_2 + HgCl_2 = 2NR_4Cl + 4HgI_2.$$

The crude precipitate which Hofmann obtained is evidently an impure mixture and not any definit compound.

[1] THIS JOURNAL, 34, 290 (1912).

[2] *Ann.*, **107**, 223 (1858).

[3] *Ann.*, **108**, 6 (1858).

[4] *J. Chem. Soc.*, **77**, 160 (1900).

Instead of using mercuric chloride, a solution of mercuric iodide in potassium iodide is used. With this solution the addition of an excess does not decompose the precipitate into pure mercuric iodide. When the interacting solutions are strong, the type $2NR_4I.HgI_2$ is produced: but this is decomposed by water and is changed into the other type $2NR_4I.3HgI_2$, which is the most stable of all and is prepared by the interaction of dilute solutions, using an excess of potassium mercuric iodide solution. It is necessary to point out that this method fails to give precipitates with lightly substituted ammonium iodides on account of their ready solubility and also on account of their unstable nature if the compounds break up into mercuric iodide in the presence of water.

Tetramethylammonium Mercuric Iodide (*a*), $2N(CH_3)_4I.HgI_2$.—The salt is obtained by adding a strong solution of potassium mercuric iodide to a large excess of strong solution of tetramethylammonium iodide. It is obtained as a yellowish white precipitate, which is filtered and washed with only a small quantity of water. The salt has a great tendency to pass into the more stable type, *viz.*, $2N(CH_3)_4I.3HgI_2$ when treated with water, some tetramethylammonium iodide being washed away. The salt after being dried at 100° was analyzed.

0.3477 gave 0.0972 HgS; Hg = 24.09; $2C_4H_{12}NI.HgI_2$ requires Hg = 23.36%.

The salt when boiled with dilute nitric acid decomposes quantitatively into mercuric iodide, which remains behind as a brick-red precipitate. A quantitative experiment indicates that the decomposition is quantitative. All the subsequently described double iodides decompose similarly.

Tetramethylammonium Mercuric Iodide (*b*), $2N(CH_3)_4I.3HgI_2$.—This is obtained as a bright yellow precipitate by adding a dilute solution of potassium mercuric iodide to a dilute one of tetramethylammonium iodide to completion of precipitation. The salt, after being dried, consists of a bright lemon-yellow powder.

1.0087 gave 0.4085 HgS; Hg = 34.90; $2C_4H_{12}NI.3HgI_2$ requires Hg = 34.01%.

In addition to these types, Risse prepared a salt of the type $N(CH_3)_4I.HgI_2$. Hence tetramethylammonium iodide altogether forms three types of salts, *viz.*, (1) $2N(CH_3)_4I.HgI_2$, (2) $N(CH_3)_4I.HgI_2$ and (3) $2N(CH_3)_4I.3HgI_2$. Of these the type No. 3 is found to be produced more frequently and easily and is perhaps the most stable of the double salts.

Tetraethylammonium Mercuric Iodide (*a*), $2N(C_2H_5)_4I.HgI_2$.—When a strong solution of potassium mercuric iodide is added to a strong solution of tetraethylammonium iodide, a pale yellowish flocculent precipitate comes down. This salt during washing has the tendency to turn deep yellow as is observed with tetramethylammonium iodide. When the tendency of deepening is found, the process of washing is discontinued and the precipitate allowed to dry in the steam oven. After drying it consists of a fine lemon-yellow powder.

0.4036 gave 0.1167 HgS; Hg = 20.25; $2C_8H_{20}NI.HgI_2$ requires Hg = 20.66%.

Tetraethylammonium Mercuric Iodide (*b*), $2N(C_2H_5)_4I.3HgI_2$.—On conducting the precipitation in a dilute solution, using an excess of potassium mercuric iodide, this compound is obtained as a bright yellow precipitate, which is washed carefully with water and allowed to dry in the steam oven. The salt consists of a fine, bright lemon-yellow powder.

0.3469 gave 0.1270 HgS; Hg = 31.55; $2C_8H_{20}NI.3HgI_2$ requires Hg = 31.98%.

Tetrapropylammonium Mercuric Iodide, $2N(C_3H_7)_4I.HgI_2$.—It is interesting to note that tetrapropylammonium iodide forms this type of salt only, even if the interaction be carried out in a highly dilute solution, using a large excess of potassium mercuric iodide. This behavior with tetrapropylammonium iodide is determined by the heaviness of the base, the first type being so stable that water is unable to transform it into the other variety. The salt is obtained as a white precipitate by adding a solution of potassium mercuric iodide to a solution of tetrapropylammonium iodide, either strong or dilute. The salt on drying at 100° consists of a white crystallin powder.

0.3561 gave 0.0756 HgS; Hg = 18.30; $2C_{12}H_{20}NI.HgI_2$ requires Hg = 18.52%.

Trimethyl-p-tolylammonium Mercuric Iodide (*a*), $2N(CH_3)_3TolI.HgI_2$.—To a strong solution of trimethyl-*p*-tolylammonium iodide a strong solution of potassium mercuric iodide is added when a yellow oil separates, which solidifies specially readily by stirring, to a yellowish white mass of crystals. The separation of the oil can be prevented by starting with a ready formed crystal of the substance. The salt is sucked to free it from adhering mother liquor, washed with a small quantity of water and allowed to dry in the steam chamber.

0.2310 gave 0.0455 HgS; Hg = 19.51; $2C_{10}H_{16}NI.HgI_2$ requires Hg = 19.84%.

Trimethyl-p-tolylammonium Mercuric Iodide (*b*), $N(CH_3)_3p\text{-}TolI.HgI_2$.—To a dilute solution of the alkylammonium iodide, a solution of potassium mercuric iodide is added, when a yellowish haziness is produced without immediate precipitation, evidently due to the separation of an oil, which gradually solidifies, forming solid crusts at the sides. The crystals are transferred, washed carefully and dried in the steam chamber. It consists of a pale yellow crystallin powder.

0.4172 gave 0.1327 HgS; Hg = 27.42; $C_{10}H_{16}NI.HgI_2$ requires Hg = 27.36%.

Pyridinium Mercuric Iodide, $2C_5H_5NHI.HgI_2$.—Pyridine hydriodide forms this type of salt only and is obtained by adding a solution of potassium mercuric iodide to a solution of pyridine hydriodide. It was washed and dried in the steam chamber. The other type of salt could not be obtained with it. It consists of a yellow powder.

0.2930 gave 0.0777 HgS; Hg = 22.85; $2C_5H_6NI.HgI_2$ requires Hg = 23.14%.

Quinolinium Mercuric Iodide, $2C_9H_7NHI.HgI_2$.—Quinoline like pyridine forms this type of salt and is obtained as a yellow precipitate, which was washed and dried in the desiccator.

0.3050 gave 0.0706; Hg = 19.95; $2C_9H_8NI.HgI_2$ requires Hg = 20.66%.

Trimethylsulfonium Mercuric Iodide (*a*), $2S(CH_3)_3I.HgI_2$.—This is obtained as a white precipitate by adding potassium mercuric iodide to an excess of a strong solution of trimethylsulfonium iodide. The salt is sucked to free it from the adhering mother liquor.

0.2907 gave 0.0773 HgS; Hg = 22.92; $2SC_3HgI.HgI_2$ requires Hg = 22.83%.

Trimethylsulfonium Mercuric Iodide (*b*), $2S(CH_3)_3I.HgI_2$.—To a dilute solution of trimethylsulfonium iodide, a solution of potassium mercuric iodide is added, when a white flocculent precipitate is first formed, which turns faintly yellow by adding more of the potassium mercuric iodide solution. Finally, an excess of the reagent was added. The salt is dried at 100° and had a faint yellow tinge.

0.1949 gave 0.0747 HgS; Hg = 33.01; $2SC_3HgI.3HgI_2$ requires Hg = 32.79%.

Smiles obtained a salt of the type $S(CH_3)_3I.HgI_2$, as pointed out before. So trimethylsulfonium iodide altogether forms three types of salts: (1) $2S(CH_3)_3I.HgI_2$, (2) $S(CH_3)_3I.HgI_2$ and (3) $2S(CH_3)_3I.3HgI_2$. Of these the salt No. 3 is the most stable, since the first salt is transformed into the third with excess of water and the salt No. 2 has to be prepared from acetone solutions.

Now ammonium iodide forms a salt of the type $2NH_4I.HgI_2$[1], but this and also the salts with the alkali metals are decomposed by water into pure mercuric iodide. The same type of salt is also formed with the substituted ammonium bases but on treatment with water, they pass into the more stable type, *viz.*, $2NR_4I.3HgI_2$. In the case of very heavily substituted bases, the stability of the type $2NR_4I.HgI_2$ is so great that they do not pass into the other variety when treated with water. So there is noticeable a remarkable transition of the stability of the double salts.

Investigations on similar lines are being continued.

My thanks are due to Prof. P. C. Ray for the interest he has taken in the above investigation.

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A COMBINATION SPECIFIC GRAVITY BOTTLE AND DILATOMETER.

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For determining the changes in specific gravity and volume which sugar solutions exhibit under varying conditions, the writer has made use of a combination specific gravity bottle and dilatometer. As the instrument

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[1] Doubin, *Compt. rend.*, 141, 385 (1905).