

Ethyl ammonium selenite and Non-existence of Amidoselenites (selenosamates).

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Ethyl ammonium selenite.

In absence of water, selenion dioxide proves to be quite indifferent to ammonia in the cold or to its solution in ether. Although not very soluble in alcohol alone, it dissolves freely in alcoholic ammonia to become, in absence of water, a new salt, ethyl ammonium selenite, obtainable in the solid state, either by evaporating the alcohol or by precipitating the salt with dry ether. Hinsberg (*Ann.*, 1890, **260**, 40) has found that an alcoholic solution of selenion dioxide, free from all water, leaves on evaporation crystals of ethyl hydrogen selenite, which decompose slowly in dry air into alcohol and selenion dioxide again, or at once on contact with water into alcohol and selenious acid. He also obtained what appeared to be the aniline salt of this compound, in an impure state, by mixing and evaporating solutions of selenion dioxide in alcohol and aniline in ether, but only in absence of water. Water at once decomposed the salt into alcohol and the acid selenite of aniline.

The production of ethyl ammonium selenite acquires interest from the fact, that it can only be effected in the entire absence of water, to the action of which the salt is very

sensitive. The salt is also of interest because, in mode of formation and in properties, it closely resembles ethyl ammoniumsulphite (see preceding paper), although the work of Michaelis and Landmann (*Ann.*, 1887, **241**, 150) seems to have established that nothing analogous to a sulphonic constitution presents itself in alkyl selenites. One of us has also pointed out (*J. Chem Soc.*, 1886, **49**, 585) some special points of similarity of silver and mercury selenites to silver and mercury sulphites, although their alkyl derivatives are differently constituted (Michaelis and Landmann, *loc. cit.*).

The selenion dioxide for making the new salt was prepared from selenion of high purity, which had been obtained, years ago, from the 'red sulphur' of Japan, by M. Shimose and one of ourselves. The anhydride being very hygroscopic, special care had to be taken to ensure its freedom from hydration when used. The selenion was dissolved in nitric acid, the solution evaporated to dryness, and the residue repeatedly moistened with water and dried again by heat. The resulting selenious acid was kept for some time, in an open dish, close to the subliming point of the anhydride. Thus almost dehydrated, it was transferred hot to a glass tube in which it was several times sublimed in a current of dry oxygen. Finally it was again volatilised into and deposited in the well dried experimental vessel itself.

Great care was also taken to dry the alcohol in the usual way and then to keep it almost out of contact with the air. The ammonia too was well dried, not so effectively, perhaps, as the alcohol and anhydride, yet sufficiently so, as the result of its use proved.

The selenion dioxide with about five times its weight of

alcohol was treated with ammonia, in a freezing-mixture, until the gas passed unabsorbed. The ammonia causes the undissolved selenium dioxide to dissolve slowly, and the final product is a clear viscid liquid. This liquid, which is most sensitive to the decomposing action of the moisture of the air, can be dried up in a vacuum into a solid with silky lustre, but not to be got, in this way quite free from alcohol. Instead, therefore, of evaporating the liquid, it was poured into a small flask of well-dried ether, with as little exposure to air as practicable. The liquid does not dissolve in ether but, on shaking, the ether extracts the alcohol from it and leaves the solid salt adhering to the flask. After decanting off the ethereal solution and exposing the open flask for a night in a vacuum-desiccator, the salt was obtained dry and was then weighed in the flask.

The analysis was begun by dissolving the salt, in the flask itself, in water acidified with sulphuric acid. The solution, only slightly acid, was distilled for the alcohol, this being then estimated from the weight and specific gravity of the distillate. Distillation of the solution with alkali gave the ammonia, the residue being then heated at 150° for some hours with hydrochloric acid, again distilled with alkali, and no more ammonia got. The selenium was determined by precipitating it with sulphur dioxide in presence of much hydrochloric acid, heating to 100°, and collecting the selenium on a weighed filter. The mother-liquor, after concentration, gave no more selenium with sulphur dioxide.

The percentage numbers obtained were —

$C_2H_5(NH_4)SeO_3$:	sel. diox.,	63.79 ;	ammonia,	9.77 ;	alc.,	26.44.
Found :	„	64.09 ;	„	9.31 ;	„	—
„	„	65.94 ;	„	10.09 ;	„	24.16.

The deviations of the quantities found from those calculated are clearly attributable to slight decomposition of the salt by moisture into alcohol lost and acid ammonium selenite.

Ethyl ammonium selenite is crystalline, soluble in alcohol, insoluble in ether, exceedingly deliquescent, and at once decomposed by water into ammonium hydrogen selenite and alcohol. It cannot be heated or even kept long without decomposing, selenion being one of the products. Thus, after ten days or so in the desiccator, the decomposed salt may contain as much as 5 per cent. of its weight of free selenion, oxidised alcohol (acetic acid?) and ammonia having volatilised.

Non-existence of amidoselenites (selenosamates).

Since it is not easy to get normal ammonium selenite from its aqueous solution, on account of its great solubility and the readiness with which it loses much of its ammonia, Berzelius, Muspratt, and others have all had resort to an alcoholic solution of selenious acid, from which to precipitate the salt by gaseous ammonia. Now, when an alcoholic solution of ethyl ammonium selenite is exposed to moist air or mixed with a very little water, separation of ammonium selenite at once occurs, either normal or acid, according as much ammonia is present or not. The same behaviour has been noted by Hinsberg in an alcoholic solution of ethyl phenylammonium selenite. Moreover, the alcoholic solution of ethyl ammoniumsulphite behaves in a quite analogous way (see preceding paper). Accordingly, we have found that, unless precautions are taken to specially dry the materials and to exclude aerial moisture, the passage of ammonia into a solution of selenion dioxide in good ordinary absolute

alcohol very soon causes ammonium selenites of varying composition to precipitate. We are thus brought in contact with the experimental work of Cameron and Macallan (*Proc. Roy. Soc.*, 1888, **44**, 112), who obtained just such a precipitation by passing ammonia into a solution of selenion dioxide in absolute alcohol, the ammonia being described as having been carefully dried by passing it through a series of potash tubes. But the examination they made of their product and of a derivative of it led them to consider the two substances to be amidoselenites or selenosamates, and not merely selenites.

We have analysed and in other ways examined the products we have obtained in this way. The crystalline precipitate in presence of excess of ammonia is diammonium selenite and can be rendered dry and anhydrous, without decomposing it, in a potash desiccator, charged with a strongly ammoniacal atmosphere. It is a very alkaline and very deliquescent salt, which yields half its ammonia when its aqueous solution is distilled to a small volume. Exposed in a sulphuric-acid desiccator for 20 or 30 hours, it also loses half its ammonia, becoming the half-acid salt. Left for several months in such a desiccator, occasionally opened, it becomes the three-fourths-acid selenite. The results of the analyses of the three salts were very satisfactory, and were obtained when, so to speak, we did not know exactly what we were analysing. They are given as parts per hundred, in the following table:—

$(\text{NH}_4)_2\text{SeO}_3$:	selen. diox.,	68.09;	ammonia,	20.87
Found:	"	67.96;	"	21.02
$(\text{NH}_4)\text{HSeO}_3$:	"	76.03;	"	11.64
Found:	"	76.01;	"	10.88
$(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$:	"	80.73;	"	6.18
Found:	"	81.51;	"	6.22

It must be mentioned that the numbers for the selenion dioxide in the above two acid selenites differ very little, each to each, from those calculated for Cameron and Macallan's two selenosamates, while those for the ammonia are entirely out of agreement. But as these chemists adopted a method of questionable accuracy for determining the selenion, much weight cannot be laid upon these coincidences.

Now, we have tried repeatedly but fruitlessly to get these selenosamates, or any other salts which might be amido or imidoselenites. Some years ago, also, Mr. Toyotaro Kamiya tried, in this laboratory, to prepare Cameron and Macallan's selenosamates, at the instigation of one of us, who then wanted to see whether the acid salt, $(\text{NH}_4)\text{H}(\text{SeO}_2\text{NH}_2)_2$, might not be diammonium imidoselenite $\text{HN}(\text{SeO}_2\text{NH}_4)_2$, instead. But Mr. Kamiya reported failure to get products of uniform composition, or any having the composition of Cameron and Macallan's salts, or any which did not readily yield up all their nitrogen as ammonia when boiled with potassium hydroxide. To Mr. Kamiya we are indebted for the preparation and analysis, above given, of the salt which proved to be the three-fourths-acid ammonium selenite.

Having failed in our attempts to confirm the observation of Cameron and Macallan that dry ammonia causes precipitation in a solution of selenious anhydride in absolute alcohol; having obtained in these attempts only a very soluble salt, ethyl ammonium selenite; and having got precipitation, apparently such as theirs, only when moisture had in some way entered in, which precipitation was, however, of ammonium selenites only, we may proceed to point out what a lack of reliable evidence there is contained in their paper, for the existence of these salts.

In just such ways as the more acid ammonium selenite can be prepared from the normal or the less acid selenite, did Cameron and Macallan get the acid selenosamate from the normal selenosamate. No property of the selenosamates is recorded by which they are distinguishable from the acid selenites. It is indeed stated that a neutral solution gives hardly any precipitate with barium chloride until ammonia is added, but then that is equally true of a neutral solution of ammonium selenite, the normal salt being strongly alkaline.

The only difficulty, but it is a great one, in the way of regarding the selenosamates as being merely selenites lies in the fact that the quantities of ammonia found in the two salts are just those proper to the selenosamates and not in the least those proper to the selenites. This difficulty, we believe, may be legitimately surmounted, until further evidence is forthcoming, by calling in question the propriety of the methods of analysis by which such results were reached. In the first place, the normal selenosamate, described as continuously losing ammonia, was dried for analysis in a partial vacuum over sulphuric acid, and yet gave the right proportions of both selenion dioxide and ammonia very closely indeed. Secondly, the selenion dioxide was estimated by passing chlorine into the solution of the selenosamate and then precipitating barium selenate; it was therefore estimated by a method which H. Rose in 1861 (*Pogg. Ann.* **113**, 472; *Z. anal. Ch.*, **1**, 75) had condemned as being quite unsatisfactory and utterly unreliable for reasons given, and which has again been discredited by Boutzoureano (*Ann. Chim. Phys.*, 1889 [6] **18**, 296) as being far from giving good results. Lastly, they record no attempt to estimate the ammonia by direct distillation with alkali and give no reason for not

employing this method. Instead, they tried Kjeldahl's nitrogen process, which they found to give excellent results with one selenosamate but to be unsuitable for use in the analysis of the other. They offer no explanation of this remarkable difference, and we have to rely, without evidence, on the accuracy of the process in one case, though in the other indistinguishably similar case it is found to be unsuitable. After failing also in the use of the soda-lime process to determine the ammonia in the acid selenosamate, success was at last gained by using Dumas' nitrogen method. The chloroplatinate method was tried with both salts and gave indefinite results. It is certain that Cameron and Macallan, in some of their analyses of the acid selenosamate, got quantities of ammonia much below what they expected, thus favouring the supposition that this salt may have been the three-fourths-acid selenite. However that may be, we hold ourselves justified in asserting that there has not yet been given any reliable evidence that selenion dioxide and ammonia in presence of alcohol or water give any other compounds than selenites. It may, therefore, be said of selenion dioxide that, unlike sulphur dioxide, it forms only oxylic salts, whether with alkyl radicals, with amines, or with metals.

