# CIX.—Imidosulphonates. Part II. By Edward Divers, M.D., F.R.S., and TAMEMASA HAGA, D.Sc. (Japan), F.C.S.

THIS communication to the Society is supplementary to that which appeared in 1892 (Trans., 61, 943). It contains an account of some imidosulphonates not there described, and a collation of our results with those obtained by Berglund, called for by the existence of some It was this chemist, now deceased, radical differences between them. who first made known the existence of imidosulphonates, although several of them had been already obtained and described by others. under various names and formulæ. His important memoir on these salts was published in Swedish, but summaries of it by Clève and by himself, respectively, appeared in the journals of the French and German Chemical Societies. References to all are given in our first paper. In English, also, a good summary was first published by Watts in the 2nd Supplement of his Dictionary; this had escaped our notice, and, up to the time of publishing our first paper, we had only seen the account in the Berichte, and an appreciative notice of the Swedish paper in Raschig's paper on "Fremy's Sulphazotised Salts." But, soon after that, Dr. Raschig spontaneously sent us, with the greatest kindness, his own copies of Berglund's Swedish papers on "Imidosulphonic acid" and "Amidosulphonic acid." A perusal of these led, us to resume work on the subject, with the intention only of examining into the differences between his results and ours, but we went further afield, and prepared a few new salts, because they promised to be of interest.

For convenience of reference, we follow in this paper the order of description observed in the former paper, and reproduce, as briefly as possible, matters of interest in Berglund's paper in Swedish, not to be found in chemical literature outside it. A full list of the salts prepared by him is given by Watts (op. cit.).

Berglund's first source of imidosulphonates was ammonia and chlorosulphonic acid, but afterwards he prepared them from potassium nitrite and sulphite, following Fremy, with modifications, which do not call for notice here.

# Alkali Imidosulphonates.

Ammonium Imidosulphonates.—Berglund failed to get normal ammonium imidosulphonate, the statement in Watts' Dictionary that he did being erroneous. He believed Rose's "vitreous sulphatammon" to be this salt, but we find that, both before and after its crystallisation from water, it is the two-thirds normal imidosulphonate, and that Rose's "flocculent sulphatammon," not noticed by Berglund, is anhydrous normal ammonium imidosulphonate. To Woronin is due the accurate distinction between the two salts.

The mother liquor of the crystals of the two-thirds normal ammonium imidosulphonate ("parasulphatammon") gave Rose, on evaporation, his so-called "deliquescent salt;" this, Berglund, judging from his later paper on "Amidosulphonic acid," considered to have been a mixture of amidosulphonate and the two-thirds normal imidosulphonate with ammonium acid sulphate.

Sodium Imidosulphonates .- That, contrary to Fremy's experience, sodium nitrite can be sulphonated as easily as potassium nitrite, was ascertained independently by Raschig and by us about the same time; later, we prepared the normal and two-thirds normal sodium salts, as well as some compound salts. Berglund, however, had prepared the normal sodium salt (and also the mercury sodium salt) from ammonium imidosulphonate by boiling it with sodium hydroxide till all ammonia had been expelled; he found it more satisfactory, however, to precipitate the two-thirds normal potassium salt by adding potassium chloride to the ammonium salt, and to boil the product with a solution of sodium hydroxide and chloride; on cooling, the normal sodium salt was deposited. His description of this salt, so far as it goes, agrees with ours. The crystalline salt, which he sometimes got in place of the ordinary normal sodium salt, and which he believed to be that salt in the anhydrous state, we take to have been a double salt of normal sodium imidosulphonate and potassium chloride.

He did not obtain the two thirds normal sodium imidosulphonate, or its compounds with ammonium nitrate and with potassium nitrate, or sodium ammonium imidosulphonate.

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## Barium Imidosulphonates.

Berglund's account of normal barium imidosulphonate agrees with ours; he was really the first to prepare this salt, and did himself an injustice in crediting Woronin and Jacquelain with its previous preparation. Woronin never analysed his preparation, which was almost certainly a double salt, and, although Jacquelain did carefully analyse his, the result shows it to have been a barium ammonium salt. Berglund found that the normal barium salt gave up its  $5H_2O$  almost entirely at  $100^\circ$ ; we maintain the accuracy of our statement that it loses water only very slowly, even at  $115^\circ$  (see further on this point our account of the strontium salt). Barium imidosulphonate is soluble in a solution of ammonium chloride.

Two-thirds normal barium imidosulphonate was fully described by Berglund, his account agreeing with ours.

Double salts of barium with the alkalis received peculiar treatment by Berglund. He did not formally recognise their existence, and relegated to footpotes observations which, he admitted, made their existence probable. He could not satisfactorily formulate the composition he found them to have, and for him they remained as impure barium salt only. Our own work confirms his results, and makes it possible to give formulæ to his preparations. First, there is  $Ba_{12}K_8H(NS_2O_6)_{11}$ ,11H<sub>2</sub>O, which he constantly obtained when he added normal potassium imidosulphonate to barium chloride. Had he thought of introducing the atom of hydrogen there is in the above formula, he would probably not have considered his analytical results as incapable of interpretation. A sodium salt, described by us, comes very near to this salt, being Ba<sub>11</sub>Na<sub>8</sub>(NS<sub>2</sub>O<sub>6</sub>)<sub>10</sub>,13H<sub>2</sub>O; for, if we subtract a molecule of the two-thirds normal barium salt, BaHNS<sub>2</sub>O<sub>6</sub>, from his formula and write Na for K, we get ours. Evidently, either salt is mainly BaK(or Na)NS<sub>2</sub>O<sub>6</sub> with a little Ba<sub>3</sub>(NS<sub>2</sub>O<sub>6</sub>)<sub>2</sub>. Bvadding two-thirds normal potassium salt to ammonia and barium chloride, he got  $Ba_{12}K_7(NH_4)_2(NS_2O_6)_{11},79H_2O.$ Lastly, the salts  $Ba_6(NH_4)_2H(NS_2O_6)_5,21H_2O$  and  $Ba_7(NH_4)(NS_2O_6)_5,22H_2O$ ; all three having an obvious relation to the first. We have described a still more ammoniated salt, Ba<sub>5</sub>(NH<sub>4</sub>)<sub>2</sub>(NS<sub>2</sub>O<sub>6</sub>)<sub>4</sub>,8H<sub>2</sub>O. All these double salts of barium are granular and powdery, and quite unlike the peculiarly soft, clinging, pure barium salt.

#### Strontium Imidosulphonates.

According to Berglund, normal strontium and normal calcium imidosulphonates are, in properties, water of crystallisation, and conditions of formation, as like each other as two salts can be, but unlike the normal barium salt. This account of the normal salts puzzled us, but when we found his description of the properties and method of preparation of the calcium salt applied perfectly, so far as it goes, to a salt described by us in our first paper, which we had found to be calcium sodium imidosulphonate, we lost all confidence as to the accuracy of his account. We therefore studied the strontium salts for ourselves, having omitted to do so when preparing our first paper.

Normal strontium imidosulphonate, according to Berglund, gradually separates in acicular prisms when a solution of strontium chloride, moderately concentrated, is mixed with one of either normal sodium imidosulphonate or of diammonium imidosulphonate to which ammonia has been added. Its composition is expressed by the formula  $Sr_3(NS_2O_6)_{2,6}H_2O$ , and it loses only two-thirds of its water, even at  $130-140^\circ$ .

In preparing it, it is unnecessary, he said, to take any care to have the strontium chloride in excess, although it is very important to keep the barium chloride in excess when preparing the normal barium imidosulphonate.

Normal strontium imidosulphonate, according to our experience, cannot be obtained by mixing together strontium chloride and normal sodium imidosulphonate, strontium sodium imidosulphonate being formed in this way; the normal salt, however, can be obtained from this in the same way as the normal barium salt is prepared from a barium potassium or barium sodium salt, namely, by dissolving it in dilute hydrochloric acid and pouring the solution at once into a slight excess of a warm, concentrated solution of strontium hydroxide, repeating the operation twice, or until all the sodium has been removed. So long as the reprecipitated salt contains sodium, it is a hard, granular precipitate, but, when it is free from sodium, it separates in glistening, thin, scaly crystals, which felt together into soft, voluminous flocks, and these, dried on the tile, form coherent flakes, retaining water in their interstices with great obstinacy, like the barium salt, to which it has, indeed, much resemblance. It is more soluble in water than the barium salt, and is actually soluble in hot water to a considerable extent. For analysis, we comminuted its flaky masses, and pressed the particles between filter paper till it seemed quite dry; but, on exposure to air for days, such a preparation continuously loses water, and much of it before the crystalline lustre sensibly diminishes.

The freshly dried salt contains  $12H_2O$ , as the following numbers show:

	Strontium.	Sulphur.	Water.
Calculated	31.75	15.51	26.13
Found	31.86	15.49	

Tested after 14 days' exposure, the water amounted to only 7 mols., 5  $\times$  2

although efflorescence had only then just become apparent. The strontium was then 35.61 per cent., calculation for  $7H_2O$  giving 35.66 per cent.

By decomposing the normal hydroxy-lead imidosulphonate with ammonium hydrogen carbonate, so as to obtain a weak solution of normal ammonium imidosulphonate, and then evaporating to a small volume, we obtained a concentrated solution of the two-thirds normal ammonium salt, the strength of which we determined by analysis. To it we added enough ammonia to make it a little more alkaline than the normal salt, and then mixed it with a slight excess of a concentrated solution of strontium chloride and left it to stand. Only a very small quantity of precipitate formed, but, on adding excess of somewhat concentrated ammonia water, allowing the whole to evaporate nearly to dryness in a desiccator over anhydrous potassium carbonate, and then adding water, a white, opaque powder was left, which, on analysis, proved to be normal strontium imidosulphonate, with a slight quantity of ammonia in addition. Our calculation is for a pure strontium salt with  $5\frac{1}{2}$  mols. water. The salt may. however, be regarded as having only 5 mols. water. We determined the alkalinity of the salt, and this expressed as strontium, shows it to be more than a third of the total strontium. The excess of base may be regarded as consisting of ammonium, the presence of a little of which was established.

	Calc.	Found.
Strontium	37.00	37.01
Alkalinity, as strontium	12.33	12.66
Sulphur	18.04	17.98

When a solution of the normal strontium salt, with  $12H_2O$ , is boiled, a nearly insoluble sandy precipitate is formed; this is a slightly basic<sup>\*</sup> strontium salt with about  $5H_2O$ . The calculation given is for normal strontium imidosulphonate with  $5H_2O$ .

	Calc.	Found.
Strontium	37.47	39.02
Sulphur	18.27	18.36

An opaque, powdery salt is also precipitated when the mixed solutions of strontium chloride and normal ammonium imidosulphonate are boiled; it contains a very little ammonia, and is, no doubt, a slightly basic ammoniacal strontium salt. We have not quantitatively analysed it.

We have not attempted to prepare the two-thirds normal strontium

<sup>\*</sup> We have got results indicating the existence of a hemihydroxy-salt,  $(HOSr)_3NS_2O_6$ , corresponding with the lead salt, but have not had time to establish the fact.

salt, although it could, no doubt, be easily got like the calcium salt (p. 1626). Berglund prepared a solution of it, but found the salt so soluble and so difficult to crystallise that he did not examine it.

Strontium sodium imidosulphonate is obtained when solutions of normal sodium imidosulphonate and strontium chloride are mixed. Probably, the proportions matter little, but we have used 2 mols of the imidosulphonate to 3 mols. of the strontium salt in moderately concentrated solutions. When the salts are mixed, precipitation occurs, but the precipitate redissolves on shaking, and soon small prisms of the strontium sodium salt separate. The salt is sparingly soluble, and resembles the calcium sodium salt described in our first paper. Like that salt, too, it contains  $3H_2O$ , its formula being  $SrNaNS_2O_{6,}3H_2O$ .

		For	and.
	Calc.		~
Strontium	25.84	25.96	25.97
Sodium	6.81		6.69
Sulphur	18.93	18.89	
Water	15.95		

Berglund got granular precipitates of a strontium potassium salt soon after mixing normal potassium imidosulphonate solutions with strontium chloride solutions. Calculating from his results, we find the salt was represented by the formula  $Sr_{12}K_8H(NS_2O_6)_{11},13H_2O$ , in close agreement with the composition of his barium potassium precipitates, as calculated by us.

# $Calcium \ Imidosul phonates.$

Berglund states that, on mixing solutions of normal sodium imidosulphonate and of calcium chloride, he got the normal calcium salt, whereas we always got the calcium sodium salt described in our first paper. Berglund's description and ours agree, and, as Berglund estimated the calcium from the weight of the residue left on ignition, the difference between this and the weight of the residue left by the sodium calcium salt would be within the limits of error of an ordinary analysis. Berglund's salt is quite unlike the normal calcium salt which we now describe for the first time.

Normal Calcium Imidosulphonate.—The true normal salt can be prepared by acting on the insoluble normal silver salt with its equivalent of calcium chloride in solution, decanting from silver chloride, and evaporating the solution in a desiccator till the new salt crystallises out. It is only sparingly soluble in water when once separated from solution, and crystallises in rectangular prisms and tables, stable in the air. It is strongly alkaline to litmus. Its composition is expressed by  $Ca_3(NS_2O_6)_{2,8}H_2O$ .

	Calc.	Found.
Calcium	19.60	19.60
Sulphur	20.92	21.06

Berglund states that the normal calcium salt is also got from a mixed solution of ammonium imidosulphonate, and calcium chloride. This mixture gave us no insoluble salt.

Two-thirds Normal Calcium Imidosulphonate.—This salt is obtained by decomposing normal silver imidosulphonate by two-thirds of its equivalent of calcium chloride and one-third of its equivalent, or, for safety, just a very little less, of hydrochloric acid. The solution, when evaporated in a desiecator, becomes a mass of radiating prisms. Crushed and drained dry, the salt is permanent in the air, at least for some days. Its reaction is slightly acid to litmus. Its formula is CaHNS<sub>2</sub>O<sub>6</sub>,3H<sub>2</sub>O.

			Calc.	Found.
Calcium		••••••	14.87	14.70
Sulphur	• • • • • • ·	<b></b>	23 79	23.59

Calcium Sodium Imidcsulphonate, CaNaNS<sub>2</sub>O<sub>6</sub>,3H<sub>2</sub>O, is described in our first paper, and has been referred to above as being what we get by following Berglund's directions for preparing his normal calcium salt. The mercury calcium salt will be found described on page 1630.

### Lead Imidosulphonates.

We have indicated the existence of an unstable salt,  $PbHNS_2O_6$ , in solution, and Berglund has done the same. The crystalline, normal hydroxy-lead imidosulphonate,  $(HO)_5Pb_4NS_2O_6$ , has also been described by both of us, and our accounts agree; his way of preparing it, however, was to add ammonia gradually to mixed solutions of diammonium imidosulphonate and lead acetate so long as the amorphous precipitate at first produced gives place to a crystalline one; when the last formed amorphous precipitate no longer changes, acetic acid is added until this has just been converted into the crystalline precipitate.

The amorphous precipitate he found to be a basic lead imidosulphonate of varying composition. We have shown in our first paper, however, that a basic salt can be uniformly obtained of the composition,  $(HOPb)_{\circ}NS_{2}O_{6}$ .

#### Silve: Imidosulphonates.

Berglund has described only the normal silver salt. We have described this and two other crystalline, well characterised salts,  $Ag_2NaNS_2O_6$  and  $AgNa_2NS_2O_6$ , the latter being obtained when silver nitrate is added to excess of normal sodium imidosulphonate. According to Berglund, however, the precipitate in that case is richer in silver than the normal salt. This is explicable when we consider that he worked with very dilute solutions, for, as we have pointed out, the salt,  $AgNa_2NS_2O_6$ , is partly decomposed by much water into silver oxide and two-thirds normal sodium imidosulphonate.

# Mercury Imidosulphonates.

Oxymercuric Hydrogen Imidosulphonate, HN(SO<sub>3</sub>HgO)<sub>2</sub>Hg (Divers and Haga); Normal Oxymercuric Imidosulphonate, Hg[N(SO3Hg)20]2 (Berglund).-These basic mercuric imidosulphonates differ in that the proportion of sulphur to mercury in ours is  $S_4$ : Hg<sub>6</sub>, whilst in Berglund's it is  $S_4$ :  $Hg_5$ . His salt was prepared from mercury potassium imidosulphonate and mercuric nitrate, and ours from normal sodium imidosulphonate and mercuric nitrate; they ought, therefore, to have been the same. Berglund tried the use of normal potassium imidosulphonate, and thus got a more basic product, but this he attributed to the presence of mercuric oxide or basic nitrate in the precipitate. As Berglund was strongly impressed by the tendency of mercury to displace the imidic hydrogen, whilst we were similarly struck with the fact that whenever sulphuryl occurs in combination with oxylic mercury in a precipitated salt, that mercury functions as the bivalent radicle, -HgOHgOHg-, it will be seen that Berglund's ratio of sulphur to mercury accords with his preconception, and not with ours, and that our ratio accords with our preconception, and not with his.

To make sure that we had not been mistaken, we made further experiments; but, before describing these, we have two adverse comments to make on Berglund's experiments.

One is as to the precipitation of mercuric oxide or basic nitrate inferred by him. However prepared, our product has always been one of the whitest of precipitates, only assuming a faint buff tint when kept for some time at  $100^{\circ}$  or higher, in the dry state. The presence of very little oxide of basic nitrate should have shown itself by a yellowish tinge. No precipitate that we have tested either of the present salt, of the oxymercuric sodium salt (first paper, p. 983), of the mercurous salt (this paper, p. 1630), or of the mercurosic salts (this paper, p. 1632), has ever shown the presence of nitric acid in it. Moreover, Berglund's supposition that mercuric oxide or basic nitrate might be precipitated is not probable, when it is considered that the mother liquor of the precipitating salt is much more strongly acid than the solution of mercuric nitrate used.

The other matter is the unlikelihood of mercury taking or retaining the imidic relation in a salt precipitating from such very acid mother liquors; for, as we have shown in our first paper, dilute nitric acid replaces such mercury by hydrogen. Directly the attempt is made to lessen the quantity of nitric acid sufficiently to permit of mercury

taking the imidic relation, sodium or potassium also enters the salt. For we then find that we pass displacing half the oxylic mercury. abruptly from  $HN(SO_3HgO)_2Hg$  to  $Hg < N(SO_3HgO)_2Hg$ .

Experiment I.-To excess of very dilute mercuric nitrate (necessarily acid) was added a very dilute solution (1 in 50) of mercury sodium imidosulphonate. The crystalloidal precipitate, washed by decantation with much water, was dried on a tile; both the salt and the mother liquor were free from sulphate. Composition: Mercury, 73.70 per cent.; sulphur, 7.98 per cent.; sodium, 0.08 per cent.

Experiment II.-Mercuric nitrate solution, 250 c.c., prepared from 6 grams of mercuric oxide dissolved in  $l_{\frac{1}{6}}$ th equivalent of nitric acid, 250 c.c. of a solution containing 4 grams of mercury sodium imidosulphonate; the voluminous, crystalline precipitate formed on mixing these solutions, after being washed once with dilute nitric acid, and then repeatedly with water, was drained dry on a tile; it weighed  $6\frac{1}{2}$  grams, or four-fifths of the calculated quantity. It was free from sulphate, as was also the mother liquor. Composition: Mercury, 73.44 per cent.; sulphur, 7.94 per cent.; sodium, 0.08 per cent.

Experiment III.-Dissolved 2.8 grams of mercury potassium imidosulphonate in 250 c.c. water, and added it to 3 grams of concentrated mercuric nitrate solution containing almost 1.5 grams of mercury A crystalline precipitate formed at once; after a few as nitrate. moments' active stirring, the precipitate was allowed to settle, and the bright mother liquor was decanted into another vessel containing 4.5 grams more of the mercuric nitrate solution; a second precipitate was thus obtained. Both were washed by decantation, and drained on tiles. The first weighed 2 grams; the second, 1.5 grams; by calculation, each would have weighed 2.9 grams, had none remained dissolved, according to the equations,

1.  $HgN_2(SO_3)_4K_4 + 2Hg(NO_3)_2 + 2H_2O = HN(SO_3)_2Hg_3O_2$  $+ 2KNO_3 + 2HNO_3 + HN(SO_3)_2K_2;$ 2.  $HN(SO_3)_2K_2 + 3Hg(NO_3)_2 + 2H_2O = HN(SO_3)_2Hg_3O_2$  $+ 2KNO_3 + 4HNO_3$ .

The first precipitate contained mercury, 72.85 per cent.; sulphur, 8.03 per cent.; potassium, 0.3 per cent. The second contained mercury, 72.61 per cent.; sulphur, 8.11 per cent.; potassium, 0.38 per cent. It will be seen that in no case is alkali metal absent, the quantity present being markedly greater in the case of potassium than in that of sodium, and that the potassium is slightly higher if more nitric This apparently strange result is due to the fact acid is present. that nitric acid dissolves mercuric imidosulphonate, but has no action on the two-thirds normal potassium or sodium salts.

The results of the above experiments, together with those described in our first paper, can, we think, leave no doubt that the basic mercuric salt has the composition  $HN(SO_3HgO)_2Hg$ , the percentage numbers for which are—mercury, 74.35; sulphur, 7.93; the potassium in the precipitates of Experiment III fully accounts for the slight deficiency of mercury in them. As already stated, it is probable that Berglund got his analytical results as a consequence of the presence of unobserved potassium.

Mercury Ammonium Imidosulphonate.—When the mercury calcium salt, described later (p. 1630), was decomposed with just enough ammonium hydrogen carbonate, a secondary decomposition set in after a very few minutes; that is to say, at first calcium carbonate was precipitated with effervescence due to escape of carbon dioxide; but after stirring well, till the effervescence had subsided, the solution began again to effervesce and deposit a basic mercuric calcium salt, possibly analogous to the sodium salt, and, therefore,

 $\mathrm{Hg} <_{\mathrm{N(SO_3HgO)_2Hg}}^{\mathrm{N(SO_3HgO)_2Hg}}$ 

The precipitate proved to be a mixture of calcium carbonate and basic mercuric calcium imidosulphonate, roughly separable by dilute nitric acid; whilst the mother liquor was a solution of normal and twothirds normal ammonium imidosulphonate, with a very little mercury calcium imidosulphonate, or the equivalent of these salts. No amidated mercury salt was produced.

Bergland also tried to make the mercury ammonium salt from the mercury barium salt and ammonium sulphate, but failed. The salt, therefore, appears to be incapable of continued existence.

Mercury Potassium Imidosulphonate.—According to Berglund, dilute nitric acid has no action on this salt, but, as we have pointed out, it is converted into the insoluble two-thirds normal potassium salt and mercuric nitrate.

Mercury Sodium Imidosulphonate.—This salt was described by us fully, under the belief that Berglund had not prepared it, in which we were mistaken. We have again prepared and examined the salt, and now find it contains 5 atoms of water, and not 6, which agrees with Berglund's results. The formula is therefore  $HgN_2(SO_3)_4Na_{4,5}H_2O$ . We have also found now that the salt left in a vacuum over sulphuric acid for weeks loses all its water, and not merely two-thirds of it, as stated in our first paper. Berglund dried his salt at  $100^\circ$ .

Oxymercuric Sodium Imidosulphonate.—Berglund had no knowledge of such a salt as the basic mercury sodium salt, described in our first paper, or of a corresponding potassium salt. It is interesting, however, to find that on mixing normal mercury potassium imidosulphonate with silver nitrate even in excess, he was unable to

get the mercury silver salt, but only a mercury silver potassium salt. His formula for this salt,  $Hg < _{N(SO_3Ag)_2}^{N(SO_3Ag)_2}, 3H_2O$ , is strictly analogous to ours for the basic mercury sodium salt,

$${
m Hg} < _{N({
m SO_{3}HgO})_{2}Hg}^{N({
m SO_{3}HgO})_{2}Hg}, {
m 3H_{2}O}$$

(instead of 4H<sub>2</sub>O, formerly adopted by us).

Mercury Calcium Imidosulphonate.—Although Berglund obtained and described mercury barium, mercury strontium, and mercury magnesium imidosulphonates, he failed to get the corresponding calcium salt, on account of its being so soluble in water. We have prepared it by dissolving mercuric oxide in a warm solution of twothirds normal calcium imidosulphonate, filtering, evaporating, crystallising, and, finally, recrystallising from water. It forms small, brilliant prisms.

	Mercury.	Calcium.	Sulphur
Calculated	25.90	10.36	16.58
Found	25.92	10.20	16.61

A compound of this salt with mercuric chloride, which can be formulated as  $ClHg_2(NS_2O_6Ca)_3, 12H_2O$ , and, therefore, be compared with apatite, was got in good, although small, crystals by treating oxymercuric hydrogen imidosulphonate with calcium chloride solution in the proportion  $HNS_2O_6Hg_3O_2$ : CaCl<sub>2</sub>. The solution, filtered from the mercuric oxychloride, and evaporated in a desiccator, gave the salt in question. By dissolving this in water and precipitating by absolute alcohol, the mercuric chloride can, for the most part, be removed, but only with great loss of the imidosulphonate, as the latter also is soluble in alcohol.

	Mercury.	Calcium.	Sulphur.	Chlorine.
Calculated	30.92	9.28	14.84	2.74
Found	31.00	9.32	14.55	2.63

Mercurous Imidosulphonate.—No mercurous imidosulphonate has yet been described. There seems to be only one, a basic salt, having  $Hg'_4: S_2$ , formed when two-thirds normal sodium imidosulphonate is added to mercurous nitrate in powder which has been stirred up with hot water until it has all passed into solution except a little of the soft, voluminous, basic nitrate, the latter being quite free from any yellow, granular particles. As the nitric acid liberated dissolves some of the salt, a third, at least, of the imidosulphonate remains in solution; the normal sodium imidosulphonate would, therefore, be preferable to use, were its use not subject to a disturbing effect, to be noticed presently. The mercuric nitrate should be in some excess, about one-fifth more than the calculated quantity. The equation expressing the reaction is

$$4(H_{g}NO_{3})_{2} + H_{2}O + 2HN(SO_{3}Na)_{2} = O[Hg_{4}N(SO_{3})_{2}]_{2} + 4NaNO_{3} + 4HNO_{3}.$$

Of the sodium salt, 1.05 gram, dissolved in about 150 c.c. water, added, with stirring, gradually to 4.5 grams of mercurous nitrate in about 20 c.c. of water, gave a precipitate weighing 2.75 grams, and nitric acid in solution weighing 0.33 gram, the ratio of these weights being in accordance with the above equation. The precipitate was free from nitrate and sulphate, and the mother liquor contained no sulphuric acid.

The new salt is flocculent and quite white, and, most probably, has the constitution expressed by the formula  $O[Hg'_2N(SO_3)_2Hg'_2]_2, 6H_2O$ .

	Mercury.	Sulphur
Calculated	77.22	6.18
Found	77.27	6.18

It loses very little in weight at  $100^{\circ}$  or  $120^{\circ}$ , and part of that loss will be due to volatilisation of mercury, for the salt becomes very grey; when more strongly heated, it becomes nearly black temporarily, and then white again. Then, or while still black, the altered salt gives some mercuric chloride as well as mercurous chloride when triturated with a solution of sodium chloride. At an incipient red heat, the whitened, altered salt fuses and effervesces, evolving nitrogen, but no sulphur dioxide. The black-red liquid consists mainly of the mercury sulphates.

Mercurous imidosulphonate dissolves in dilute nitric acid much more readily than mercuric imidosulphonate does, and the addition of sodium chloride to the solution precipitates all the mercury. Triturated with sodium chloride solution, the salt becomes of a permanent, dull, and somewhat greenish-orange colour, though quite free from the mercuric radicle; and the sodium chloride solution becomes very alkaline to litmus, no doubt because of the formation of normal sodium imidosulphonate. Concentrated hydrochloric acid soon causes, even in the cold, the formation of some mercury and mercuric chloride and, on heating, this change becomes complete.\* Concentrated solution of potassium iodide at once, in the cold, dissolves it, all but half its mercury left as metal.

Normal sodium imidosulphonate converts it into mercury and the sparingly soluble mercuric sodium imidosulphonate, and this makes it undesirable to use the normal sodium salt for preparing the mercurous salt. When it is used, a blue-grey cloud of mercury is

<sup>\*</sup> Owing to the production of amidosulphonic acid (see our paper on this acid).

formed, but by incessant and violent stirring for 10 minutes from the time of adding the normal sodium salt, not in excess, to the mercurous nitrate (which may here be used in a very dilute nitric acid solution), the grey precipitate becomes almost completely white, and is then the mercurous imidosulphonate. Thus prepared, we have found it to contain 78.20 and 78.55, instead of 77.22 per cent. of mercury, but the right quantity of sulphur, namely, 6.20 (twice), theory requiring 6.18 per cent.

Mercurosic Imidosulphonates .- Berglund found that mercuric potassium imidosulphonate when added to a solution of mercurous nitrate deposited some oxymercuric imidosulphonate only after standing some time. He must therefore have used a solution of mercurous nitrate containing an unnecessary excess of nitric acid, for precipitation is immediate if but little nitric acid is present.

The precipitate varies in composition with the proportions of the salts used, but still within well-marked limits. The variation is very great in the quantities of bivalent and univalent mercury, but very small indeed in the total quantities of mercury and of sulphur. The composition of the precipitates is such that they may be regarded as the oxymercurous imidosulphonate just described, modified in having one-half to three-eighths of its mercurous radicles replaced by mercuric radicles, for it varies within the limits expressed by

the formulæ  $O < \overset{Hg''N(SO_3)_2Hg'_2}{Hg''N(SO_3)_2Hg'_2}$ ,  $3H_2O$  and  $0 < \stackrel{Hg''N(SO_3)_2Hg'_2}{Hg''N(SO_3)_2Hg'_2}, 0 < \stackrel{Hg''N(SO_3)_2Hg'_2}{Hg'_2N(SO_3)_2Hg'_2}, 6H_2O.$ 

They differ from the purely mercurous salt in having only half as much water of hydration, and they cannot be represented as mixtures of the known oxymercurous salt with the known oxymercuric salt.

The compound

O[Hg"N(SO<sub>3</sub>)<sub>2</sub>Hg'<sub>2</sub>]<sub>2</sub>,3H<sub>2</sub>O (atomic ratios Hg"<sub>4</sub> : Hg'<sub>8</sub> : S<sub>8</sub>)

is obtained by adding mercuric sodium imidosulphonate, a salt neutral to litmus, to half its weight of normal mercurous nitrate. which makes 3Hg" be present for every 2Hg'2, and leaves a neutral, or even alkaline, mother liquor. The mercurous nitrate is used in the form described in the preparation of oxymercurous imidosulpho-After adding the mercuric sodium imidosulphonate to it, the nate. mixture is well stirred to insure the completion of the action, and until the mother liquor has just lost its acidity. The precipitate s white, settles quickly, and can be freely washed; when dry, its colour is dull. It contains nearly all  $\left(\frac{15}{16}\right)$  of the mercury of the nitrate, but only  $\frac{4}{7}$  of the mercuric radicle, and even only  $\frac{2}{7}$  of the imidosulphonic radicle, its mother liquor being very rich in imidosulphonate, and this gives assurance that there is no mercurous

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nitrate in the precipitate. Neither precipitate nor mother liquor contains any sulphate.

	Calc.	Found.
Univalent mercury	$49.45$ $1_{74.17}$	50·76 \ <sub>73·99</sub>
Bivalent mercury	24.72∫ ****	23.23∫
Sulphur	7.91	7.87
Sodium		0.04

In the analysis, the two mercury radicles were estimated by dissolving the salt in dilute nitric acid, diluting the solution, precipitating mercurous chloride by dilute hydrochloric acid, and precipitating the mercury in the filtrate as sulphide. After the salt has been hydrolysed in a sealed tube by hydrochloric acid for sulphur estimation, the mercuric radicle is found increased in quantity at the expense of the mercurous radicle; the oxygen in the air sealed up in the tube having given rise to the increase of mercuric radicle, as shown by the lessened pressure (Hada, this vol., p. 1676).

The compound  $O < Hg''N(SO_3)_2Hg'_2, O < Hg''N(SO_3)_2Hg'_2, 6H_2O$ (atomic ratios  $Hg''_3: Hg'_{10}: S_8$ ) is obtained if the mercurous nitrate is in excess, about five parts being taken for every two parts of mercuric sodium imidosulphonate, which provides  $7Hg'_2$  for every  $2Hg''_2$ . The precipitate has much the same appearance as that obtained when the imidosulphonate is taken in excess, and contains nearly  $\frac{3}{4}$  of the mercury of the nitrate used. The mother liquor is accordingly comparatively rich in mercurous salt; it is also acid. Both the mother liquor and precipitate are free from sulphate, and the precipitate from nitrate. The dry precipitate is dull white.

	Calc.	Found.
Univalent mercury	62·89 \ <sub>73.37</sub>	62·11 ] 72·57
Bivalent mercury	$10.48 \int 73.57$	11·46 <b>/</b> ****/
Sulphur	7.22	7.20
Sodium		0.01

It will now be seen how remarkably the percentages of sulphur and of total mercury approach each other in the two precipitates, widely as the ratio of the two mercury radicles varies. We append the results of analyses of two other preparations; they support the conclusions drawn from the above extremes.

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	А.	в.
Univalent mercury	59·90 \ <sub>72·78*</sub>	73.46+
Bivalent mercury	12.88∫ 1210	10 101
Sulphur	7.04	7.56

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