CXCIX.—*Silver-mercuroso-mercuric Oxynitrates and the Isomorphous Replacement of Univalent Mercury by Silver.*

By Prafulla Chandra Rây.

I have already shown that the action of silver nitrite on a solution of mercuroso-mercuric nitrite is similar to that of the alkali nitrites with the addition that, not only is mercury separated, but metallic silver is also deposited in shining, minute crystals. There is, however, no evolution of nitrogen nor any change in the radicle NO_2 (Proc., 1899, **15**, 103).

Owing to the sparing solubility of silver nitrite, my former experiments were made with boiling solutions. Now, however, the conditions have been somewhat modified. Mercurous and silver nitrites are rubbed to a fine paste with the minimum quantity of water, dilution with more water being then effected gradually, and the pale yellow filtrate evaporated under diminished pressure over sulphuric acid. By this procedure, it was expected that a double salt of the type described in the preceding paper would be formed in which the place of the alkali nitrite would be taken by silver nitrite; but lemon-yellow, crystalline products resulted containing both mercurous and mercuric mercury, as well as silver, and the acid radicle was *nitrate* instead of nitrite.

Although mercuroso-mercuric nitrite is quite stable in solution, it cannot be isolated in the solid state, for when the solution is concentrated by spontaneous evaporation mercuroso-mercuric oxynitrates crystallise out in succession (Trans., 1905, **87**, 174). In the present instance, as the reaction takes place in the cold, only a small proportion of mercurous nitrite is replaced by silver nitrite, owing to its slight solubility, and the solution thus contains a mixture of silver mercuric nitrite and mercuroso-mercuric nitrite. During the process of concentration two reactions evidently proceed side by side:

$$3Hg_2(NO_2)_2 = 4NO + 3Hg_2O \cdot N_2O_5.$$
$$3Hg(NO_2)_2 = 4NO + 3HgO \cdot N_2O_5.^*$$

Thus, although silver nitrite is a stable salt and can be crystallised without undergoing decomposition, it is here slowly converted into nitrate owing to the formation of nitric acid. Had there been no silver salt present, the first crop of crystals would have consisted of α-oxymercurosic nitrate, $HgO \cdot 2Hg_2O \cdot N_2O_5$. A salt of this type was, indeed, formed amongst others, but, as will be shown below, a portion of mercurous mercury was in each case replaced by its equivalent of silver. It is to be regretted that as the salts were of a microcrystalline form, they could not be examined crystallographically.

Method of Analysis.—The finely-powdered substance was dissolved in the minimum quantity of cold dilute nitric acid. Silver and mercurous mercury were precipitated by the addition of pure sodium chloride, the mercuric mercury remaining in solution. The precipitate, after careful washing with water, was treated with hydrochloric acid and one or two crystals of potassium chlorate and gently warmed, the solution being then largely diluted with water and set aside to allow the silver chloride to subside. The filtrate now represented mercurous mercury, although, of course, oxidised to the mercuric state. Analysis of two different preparations of this typical salt are given below.

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* And possibly also according to the equation $Hg(NO_2)_2 = HgNO_3 + NO$ (Trans. 1904, **85**, 527).

Owing to the fact that mercurous chloride is appreciably soluble in sodium chloride, the mercuric mercury often appears slightly higher:

	Found.	
	Preparation I.	Preparation II.
Mercurous mercury (Hg′)	57·80	54·83
Silver	6·13	6·77
Mercuric mercury (Hg″)	19·50	17·85
Nitrogen	2·85	—

The ratio (Hg′·Ag) : Hg″ : N in I is approximately 4 : 1 : 2.
,, (Hg′·Ag) : Hg″ in II is 4 : 1.

It should be understood that the ratio of the metals is not invariably as 4 : 1, as is shown by the analyses of two successive crops of another preparation:

	Found.		
	Preparation III.		
	1st crop.	2nd crop.	Preparation IV.
Hg′	58·98	45·81	48·04
Ag	7·92	4·15	3·79
Hg″	10·47	26·23	30·67
N	5·80	4·04	3·60

The ratios (Hg′·Ag) : Hg″ : N are respectively 7 : 1 : 8, 2 : 1 : 2, 1·8 : 1 : 1·7.

Judging from the distribution of the base and acid, it will be seen that preparations I and II are the most basic, and preparation III the least, whilst that represented by the second crop of preparation III stands intermediate between the two.

Discussion of Results.

The silver and mercurous nitrites were not weighed out in fixed proportions, but simply dissolved together by trituration in a mortar with cold water; hence at the start the components in solution often varied within wide limits. As a result of an extensive investigation on the "conjugated sulphates of the copper-magnesium group" (*Proc. Roy. Soc. Edin.*, 1888, **15**, 267), it was proved by the author that if the components are dissolved in equivalent proportions and successive crops collected at intervals, the crystals contain the component sulphates in definite proportions. Thus in the case of copper cobalt potassium sulphate two successive crops had Cu : Co = 5 : 4, whilst in the third crop the ratio was at 1 : 1 (*loc. cit.*, p. 275). In the case of iron zinc ammonium sulphate, the first three fractions had the same composition with the ratio of Fe : Zn = 1 : 3; the next three fractions had also identical composition, only the ratio of the two metals was as 2 : 5. In short, it was established that the change in composition between two "crops" was not in any sense *continuous*, but distinctly *abrupt* (*loc. cit.*, p. 281).

In the present instance, it is also evident that within fairly wide limits in the distribution of the components in solution the ratio of $Hg'':(Hg'\cdot Ag) = 1:4$, and that in successive crops the change in the ratio of the metals is abrupt and not in slow gradations. Thus, in preparation III, whilst the first crop had $Hg'':(Hg'\cdot Ag) = 1:7$, the ratio in the second was as 1 : 2. In preparation IV, the first crop which was analysed had the ratio of $Hg'':(Hg'\cdot Ag) = 1:1{\cdot}8$ instead of 1 : 2; it will be seen that it approached in composition the second crop of preparation III. This apparent anomaly appears to be due to the fact that a salt was actually formed in which $Hg'':(Hg'\cdot Ag):N = 1:2:2$; but owing to delay in collecting it another salt richer in mercuric mercury had already begun to be deposited. In other words, this is a case of overlapping of two consecutive crops.

It is, of course, well known that in the case of a solution containing isomorphous mixtures the ordinary laws of solubility hold good—the first crop being rich in the least soluble constituent; but as the latter is to a large extent fractionally removed from the field by the first and second crystallisations, the conditions begin to alter in the reverse direction, the mother-liquor gradually becoming richer in the more soluble constituent, and this is no doubt the reason why in the second crop of preparation III the proportion of mercurous mercury and silver $(Hg'\cdot Ag)$ diminished. Although in the present series of oxynitrates the ratio between Hg'' and $(Hg'\cdot Ag)$ appears in simple integers, the criterion of isomorphism is equally satisfied. Thus in both the preparations I and II, while the ratio of $Hg'':(Hg'\cdot Ag)$ remains constant, the percentage of the different metals varies.*

A few words on the position of univalent mercury in the periodic system may not be out of place here. Throughout the investigation on mercurous nitrite and hyponitrite, which has been going on during the last twelve years, very marked and striking similarity in properties has been found to obtain between these compounds and their silver analogues (compare Trans., 1897, **71**, 350; *Annalen*, 1901, **316**, 253; Proc., 1907, **23**, 89). The isomorphous replacement of univalent mercury by silver still further emphasises this family likeness. The univalent metals, copper, silver, and gold, have been placed in the first group surrounded by brackets as members of the odd series. Copper and silver isomorphously replace each other in a number of native sulphur compounds as also in the complicated triple thiocyanates.† But the relationship of these two metals with gold is

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* Compare "Haben die isomorphen Körper die Fähigkeit, miteinander krystallisirbare Mischungen zu bilden, in welchen die Mengen der Bestandtheile in einem irrationalen Verhältniss zu einander stehen. Diese Eigenschaft bietet zugleich auch das beste, ja einzige Kriterium für die Isomorphie."—Dr. Arzruni in *Neu Handwörterbuch d. Chem.*, Article: "Isomorphie."

† Groth's "Chemical Crystallography," trans. by Marshall, p. 73.

at best very remote. In view of the evidence now adduced, it would appear more rational to substitute mercury for gold and relegate the latter to its more congenial place in the eighth group immediately after platinum. Univalent mercury should be regarded as quite a distinct metal from bivalent mercury ; the former is related by ties of closest affinity to silver, whilst the latter is related to members of the second group, namely, magnesium and zinc.*

From the foregoing investigation, it follows that when a solution containing mercuroso-mercuric nitrite and silver mercuric nitrite is allowed to evaporate spontaneously, a series of hydrated silver-mercuroso-mercuric oxynitrates crystallises out, in each of which mercurous mercury is isomorphously replaced by silver. It is worthy of note that the present series of compounds are all basic and hydrated.† They retain their lustre untarnished, and do not lose water over sulphuric acid in a vacuum ; they give up water, however, readily when heated. It would appear that the predominant partner, univalent mercury, impresses its own characteristics upon silver, for silver as a rule does not form basic or hydrated salts (compare Rây, *Zeitsch. anorg. Chem.*, 1896, **12**, 374).

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