PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XVIII.—*A new Double Salt of Thallium.*

By R. J. FRISWELL.

THE platino-cyanides are well known for their tendency to form double salts, and I have now to lay before the Chemical Society some experimental results which show that this tendency is capable of development in a direction not hitherto contemplated.

Sometime since I wished to prepare some specimens of the platino-cyanides; amongst others, that of thallium. I could find no description of the method of preparation, and so had to discover a suitable process.

It occurred to me that the necessary reaction might take place between thallious carbonate COTlO_3 , and potassic platino-cyanide, and I accordingly mixed a small quantity of the solutions of the two salts. The solutions were both very hot, as thallious carbonate is but slightly soluble in cold water, and a hot solution begins to deposit it if only slightly chilled.

The mixed solutions were left to cool slowly in a covered beaker, and after a short time, while the solution was yet very warm, masses and tufts of splendid bronze green dichroic crystals began to grow from the sides and bottom of the beaker, and from the surface of the solution. These I collected with as little injury as possible, by detaching them by gentle shaking, and then pouring the whole on to a filter. The mother-liquor was removed by a slight washing with perfectly cold distilled water, in which the crystals proved almost insoluble. (In subsequent preparations I found it desirable to omit this as it spoiled the lustre of the crystals.) The crystals were dried at 100° in a water-oven, and were found to be of a magnificent crimson red by transmitted light, while the reflected colour was an intense bronzy green of strong metallic lustre. So vivid is this latter colour by daylight, that a friend to whom I exhibited them took them for brass filings.

I at first thought that this salt was the platino-cyanide I wanted, but soon found that this was not the case, as it effervesced strongly when treated with acids, evolving a quantity of carbonic anhydride, the effervescence continuing for a considerable time and a pale pink residue being left. I found that the platino-cyanide of thallium was yellowish white and completely destitute of dichroic tints, and that it could be prepared by decomposing baric platino-cyanide with an

equivalent quantity of thallious sulphate, filtering off the baric sulphate formed, and crystallising. It being evident that the salt I had obtained was not the platino-cyanide of thallium, I proceeded to make analyses.

0.2991 grm. was burnt with granular oxide of copper in vacuo, and the gases passed over ignited metallic copper, the vacuum being produced by means of a Sprengel pump, as described by Frankland and Armstrong in their paper on water analysis.* The gases were pumped off and analysed; they gave 5.089 per cent. of carbon, and 4.697 N. Repeated determinations of the nitrogen gave 4.607, 4.679, and 4.586. The carbon came out rather higher, the mean of five experiments giving 5.204.

The thallium was estimated as thallious iodide (TII), by precipitating with potassic iodide in a solution made alkaline with ammonia, which renders the iodide very insoluble.

0.3452 grm. gave 0.3890 thallious iodide, equivalent to 0.2395 thallium or 69.37 per cent. 0.4965 grm. gave 0.5596 TII, equal to 0.3448 Tl, or 69.24 per cent. Mean 69.305 per cent.

The platinum was estimated by fusing the salt with potassic disulphate, which converted the thallium into thallious sulphate, decomposed and liberated the cyanogen and carbonic anhydride, and left the platinum in the metallic state.

0.2635 grm. gave 0.0446 grm. Pt, or 16.88 per cent.

These results suggest that the salt is a compound of 1 molecule of thallious carbonate with 1 molecule of thallious platino-cyanide, or $\text{PtTl}_2\text{Cy}_4, \text{COTlO}_2$; the molecular weight of this compound is 1177.4, and theory requires the following percentage composition:—

Found (average).		
C ₅	5.10	5.20
N ₄	4.76	4.66
O ₃	4.08	3.96 by loss.
Pt.....	16.76	16.88
Tl ₄	69.30	69.30

100.00   100.00   Tl = 204.0   Pt = 197.4

The salt, when treated with warm nitric acid, effervesced evolved carbonic anhydride, and left a pink residue. This was well washed with warm water and boiled, when it dissolved, and on cooling, crystallised out in long colourless needles. These were burnt as before. 0.3242 gave 6.785 per cent. carbon and 7.916 nitrogen, results corresponding to thallious platino-cyanide, which contains 6.76 per cent. carbon and 7.86 nitrogen.

The salt may be prepared by mixing 4.334 grms. of $\text{Pt K}_2\text{Cy}_4, 3\text{OH}_2$

* Journal of the Chemical Society [2], vi, page 90.

with 9.360 grms. of thallious carbonate, when the following reaction takes place :—

When the salt is treated with potassic iodide, it is decomposed as follows :—

It may also be prepared by mixing 7.094 grms. of thallious platino-cyanide with 4.680 grms. of thallious carbonate when simple combination takes place.

Also by mixing 4.384 of baric platino-cyanide with 9.360 of thallious carbonate, when the reaction occurs as follows :—

The formation from potassic platino-cyanide is very curious, and is also a delicate reaction, as a crystal of thallious carbonate is at once stained red if moistened with solution of potassic platino-cyanide.

The salt is nearly insoluble in cold water, and is dissolved with difficulty by hot. The aqueous solution is absolutely colourless, and, unless very concentrated, does not deposit the salt on cooling. It, however, deposits white crystals, which are either a hydrate, or merely a mixture of the two constituents deposited simultaneously, but I have not yet determined which, though I am strongly inclined to the latter view.

To recrystallise the salt, it is best to use a hot aqueous solution of thallious carbonate, made so dilute that it does not deposit on cooling. I have examined the aqueous solution with the spectroscope, but have found no absorption bands, though, from the deep colour of the crystals, I expected to do so.

The crystals under the microscope appear to be hexagonal prisms, terminated by planes at right angles to the longer axis. Some crystals I have observed with splinters broken off from them longitudinally, somewhat in the way that a glass rod will break if struck on the end. The fracture in this direction is conchoidal, and shows no signs of cleavage planes.

What the crystalline form really is, I am unable to say. But if, as I presume, is generally admitted, the formation of a true double salt depends upon the isomorphism of its constituent salts, and the resultant is isomorphous itself with those constituents, then this platino-cyano carbonate of thallium must belong to the trimetric system, to which thallious carbonate belongs,* as does also thallious platino-cyanide.

I use the term true double salt above, in reference to this compound, advisedly, and mean thereby an actual molecular combination, and not a body of a more complicated nature, such as an alum.

* Watts's Dictionary of Chemistry, vol. v., page 753.

My best thanks are due to Mr. J. J. Day, for the kind assistance he has rendered me in performing the combustions of the salt.

DISCUSSION.

THE President thought the communication just read was an important contribution to the knowledge of the double cyanides. It appears that the compound is formed only at the moment of solidification; it is an interesting phenomenon to see the beautifully coloured crystals shooting out from the colourless mother-liquor. With regard to Mr. Friswell's view that the new salt is a *molecular* combination of thallious carbonate and thallious platinio cyanide, the President was inclined to dispute this. If it is to be considered as a molecular compound at all, then it must be a triple, not a double, salt, for certainly there are three molecules in it, viz., thallious cyanide, platinous cyanide, and thallious carbonate. Now, such a definitely crystalline body may with greater probability be regarded as an *atomic* compound, the platinum affording the link between the thallious cyanide and the thallious carbonate, thus:—

Such a representation would also make the formation of the salt appear very simple. The idea of viewing the double cyanides as atomic compounds ought to receive more attention than chemists hitherto have given to it. These cyanides are much too stable to be regarded as mere loose molecular combinations.

Professor Williamson thought that most chemists are in the habit of considering the double cyanides as atomic compounds; there is hardly any alternative but to look upon so great a number of atoms as bound together by atomic forces. As to the particular mode of representation, however he had some hesitation in exactly following it.

Mr. Spiller inquired whether the thallium was disguised in the salt, or whether it gave the usual reactions, and if the latter was the case, whether *all* the thallium could be precipitated?

Mr. Friswell replied that the metal gave all the known reactions, and that potassic iodide and hydrochloric acid precipitate the whole of it.

Mr. Perkin inquired whether the pink colour of the residue that was left on treating the new salt with an acid may not be due to an admixture of some undecomposed salt?

Mr. Friswell replied that it was not.

The President asked Dr. Gladstone whether physical observation could not throw some light on the formation of these crystals from a colourless liquid.

Dr. Gladstone thought that this new double cyanide would be an interesting material to investigate. From the change of colour of the crystals from the colourless liquid he would assume that a molecular change had taken place.

The President suggested that an examination of the isomeric cyanides where the nitrogen is trivalent in one case, and quinquivalent in the other, should reveal differences in the refractive powers.

Dr. Gladstone said that he had determined the refractive indices of several isomeric bodies and found them to be different. The nitrous element in such bodies has a greater power of retarding the motion of light than it has in ordinary nitrates, for instance potassic nitrate.

Dr. Müller and Dr. Mills observed that there are many cases known where colourless solutions deposit coloured crystals, such as mercuric iodide, the double cyanide of lead and platinum, &c.

NOTE.—Since writing the above, a further examination of the salt has induced me to modify my views with regard to its constitution, and to incline to those expressed by the President in the discussion which followed the paper. Having obtained some very large and clean crystals, I examined them very carefully with the microscope, and found them to be *square* prisms; fortunately, also, I obtained some crystals which appeared to taper to a point when seen by the naked eye. These when magnified could be easily seen to be composed of a number of cubes, arranged in steps and terminating in a single minute cube. Another and conclusive proof of their not belonging to the

rhombic system was the fact that they exerted no action on polarized light.

The fact of there being so complete a change in crystalline form tends, I think, to show that the salt is not a molecular compound.

I hope to be able to obtain similar compounds with the other carbonates which will, no doubt, throw more light on this point.

R. J. F.