

ART. XLIV.—*On the Iridium compounds analagous to the Ethylen and Protochloride of Platinum Salts*,\* by Prof. SAMUEL P. SADTLER, Ph.D., Pennsylvania College, Gettysburg, Pa.

AMONG the compounds which we are accustomed to call *organo-metallic*, those of  $\text{PtCl}_4$  and  $\text{PtCl}_2$  play perhaps the most important part. We can separate them, however, into the two great classes—those where the  $\text{PtCl}_4$  and  $\text{PtCl}_2$  enter by substitution into compound ammonia-atoms, and thus form bases more or less complex, but having still a certain connection; and those where the  $\text{PtCl}_4$  and  $\text{PtCl}_2$  take up organic radicals of different degrees of valence to form saturated compounds.

\* Extract from an Inaugural d'ssertation at the Univ. of Göttingen, April, 1871.

The range of this last class, as can be seen, is very wide; one of the most prominent of these compounds, however, and one which exercised for some time a very considerable influence upon the theoretical views held at that time, is the compound of  $\text{PtCl}_2$ , known as Zeise's salt, and discovered and investigated by him in 1830.

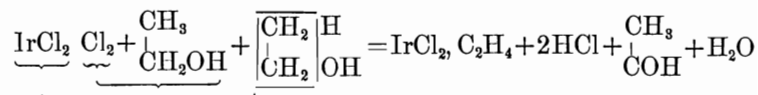
It is not necessary to recount here the controversy which took place between Zeise and Liebig on the subject. Suffice it to say that, by subsequent investigations of Griess and Martius and of Birnbaum, its formula is definitely settled as  $\text{PtCl}_4, \text{C}_2\text{H}_4, +\text{KCl}$ .

The investigation I now undertook was to see if a similar base of iridium could be prepared. Various considerations, stated at length in my original paper, led me to believe that iridium might not combine exactly as platinum did, in the formation of these salts.

After obtaining the double chloride of iridium and ammonium in the usual way, by decomposing the osmiridium, I made some tests as to the manner of formation of the salt. An attempt to form it by taking the double chloride of iridium and ammonium in solution, and, passing a stream of chlorine through to break up the chloride of ammonium, to then conduct ethylen gas into it, was unsuccessful. The method which succeeded most perfectly was to act upon iridium chloride. This was obtained by igniting the double chloride of iridium and ammonium, thus obtaining iridium oxide and metallic iridium, which was then heated with aqua regia in sealed tubes of bohemian glass to  $180^\circ$  or  $200^\circ\text{C}$ . This solution of  $\text{IrCl}_4$ , I then treated with absolute alcohol. On adding  $\text{KCl}$ , and allowing it to crystallize out, I got the greenish-brown crystals of the iridium-ethylen base. On subjecting them to an organic combustion, I obtained as products carbonic acid and water. They burned with a luminous flame, and answered, in short, all the tests applied to Zeise's platinum salt.

Another experiment, to see if ethylen gas would act directly upon the  $\text{IrCl}_4$ , reducing it and uniting at the same time, was unsuccessful.

It will thus be seen, that the only method of preparing the iridium-base is by the reducing action of alcohol on iridium chloride, according to the reaction:—



the products of which are iridium-ethylen-protochloride, hydrochloric acid, aldehyde and water.

The purifying of the necessary iridium was found to be a very long and tedious operation, the last traces of platinum

sticking very pertinaciously to the iridium salt. The processes in use also leave much to be desired in the way of completeness and expedition.

The method selected for separation was the method of Birnbaum, grounded upon the distinct and separate crystallization of the double cyanides of iridium and barium and platinum and barium. To convert the double chlorides of iridium and ammonium, and platinum and ammonium into the double cyanides of iridium and potassium, and platinum and potassium, after trying Wöhler's and Muckle's method and obtaining unsatisfactory results, I had recourse to Martius' method. This consists in mixing the dry impure chloride of iridium and ammonium with powdered cyanide of potassium, and fusing and then taking up with water the fused mass. After working some time with this method, with rather poor results, owing to the high heat required to bring the mass to fusion and the invariable decomposition of the newly formed double cyanides, resulting from the application of such a heat, I modified the method in several particulars. I found, on trying, that the black iridium oxide went very readily into solution in the fused cyanide of potassium. Taking, therefore, the double chloride of iridium and ammonium and igniting it to transform it into the iridium oxide, I proceeded after the following manner. Covering the bottom of the crucible with a bed of powdered KCy, I then added a mixture of KCy and iridium oxide, and exposed it to the flame of the blast-lamp. The fusing cyanide takes up quite readily the metallic oxide, and is soon in calm fusion. A reduction still takes place, but by no means to the extent experienced before. This is occasioned by the strong heat which has to be applied to get the mass into full fusion. Another modification which I then made has some advantages over this just described. It is to bring a few pieces of KCy to full fusion, and then keeping it so, to add a previously prepared mixture of the iridium oxide and finely pulverized cyanide of potassium to it, in small quantities at a time. The advantage here is, that, when the KCy has once been brought to fusion, it can be kept there with a comparatively small flame, and the reduction of the double cyanides does not occur so readily. It is true, that adding the iridium so slowly, the compound is kept in the fused state longer. My experience, however, leads me to prefer this latter plan, and I generally used it as giving the largest yield. Birnbaum's method proper is now used. The solution of the double cyanides, filtered off from any unattacked iridium oxide, contains a tolerably large excess of free KCy. This is destroyed by adding dilute HCl. When neutral, a concentrated solution of copper vitriol is added. The violet-colored precipitate of mixed double cyanides of iridium and platinum with copper is

washed by decantation with boiling water. While suspended therein, a strong solution of caustic baryta is added. The copper is thrown down as brown oxide of copper, and the double cyanides of iridium and platinum with barium are formed, which remain in solution. When the fluid reacts distinctly alkaline, after a minute or so boiling, it is filtered off, and then  $\text{CO}_2$  is passed through, until a neutral reaction is obtained. Filter off the precipitate of  $\text{BaCO}_3$ , and then concentrate for crystallization. The yellow platinum salt crystallizes out first in small crystals, with a play of colors from yellow to blue, being similar in their dichroic effects to most of the other double cyanides of platinum. The iridium salt crystallizes then in larger colorless prisms, which can be easily separated mechanically from the platinum crystals. The iridium crystals I ignited in a porcelain crucible, and having thus completely broken up the compound, drew out the baryta with boiling water. The iridium, after being well washed and ignited to completely oxidize it, was heated as before with aqua regia in a sealed tube to  $200^\circ\text{C}$ . The  $\text{IrCl}_4$  solution obtained was again treated with absolute alcohol, and, on addition of  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$ , the crystallized salts were obtained.

However the compounds which were now formed were, contrary to my expectations, not the ethylen salts pure and alone, but there was a simultaneous formation of what appear to be several distinct compounds. Although in one preparation of ammonium salt analyzed, the ethylen-protochloride-salt was isolated tolerably pure, yet, in the majority of the analyses, I had to do with a mixture difficult to separate even under the lens. The readiness with which these compounds decompose when subjected to recrystallization, even although one observes the precaution of keeping the solution distinctly acid, prevents any successful purifying that way. The preparation, therefore, had to be prepared for analysis by drying between bibulous paper, and then over  $\text{H}_2\text{SO}_4$  or at  $100^\circ$ , according as I wished to determine the percentage of water or not. A certain amount of  $\text{HCl}$  from the acid solutions therefore, adhering to the crystals, made the  $\text{Cl}$  determinations as a rule high. Still the results approximate sufficiently, these circumstances being taken into consideration, to the formulas given, to show that several distinct compounds are here formed. My first crystallization consisted of brownish-red octahedra, which when analyzed gave in three  $\text{Cl}$  determinations 42.13 pr. ct., 42.07 pr. ct. and 42.09 pr. ct.  $\text{Cl}$ , showing them to be simple  $\text{IrCl}_4(\text{KCl})_2$ , of which the percentage of  $\text{Cl}$  is 42.08 pr. ct.

I next got a crystallization of fine, sharply-formed monoclinic crystals of a reddish-brown color, which I think the analyses, although not perfectly conclusive, still go to show to be a new

compound. Several different crystallizations of it were analysed. It could not always be entirely separated from the slight crust of decomposed KCl which separated out along with and among the crystals.

Preparation No 1. Large well-formed crystals, with but very little foreign matter adhering to the sides.

·1567 grms. dried over  $\text{H}_2\text{SO}_4$  lost by heating to  $100^\circ$  ·0170 grms. = 10·85 pr. ct. :

gave ·0525 grms. metallic iridium = 33·50 pr. ct. :

gave also ·2275 grms.  $\text{AgCl}$  = ·0563 grms.  $\text{Cl}$  = 35·92 pr. ct.

·1610 grms. dried over  $\text{H}_2\text{SO}_4$  lost by heating to  $100^\circ$  ·0172 grms. = 10·68 pr. ct. :

gave — Ir. determination accidentally spoiled :

gave also ·2320 grms.  $\text{AgCl}$  = ·0574 grms.  $\text{Cl}$  = 35·65 pr. ct.

This we see at once cannot be any chloride of iridium and potassium. Its luminous flame, too, when burned, shows the same. Nor do the percentages agree with the simple potassic-ethylen iridium protochloride  $\text{IrCl}_2\text{C}_2\text{H}_4\text{KCl} + 2\text{H}_2\text{O}$  where the Ir. = 48·45 pr. ct. and  $\text{Cl}$  = 26·19 pr. ct.

If we reckon out the ratio of iridium to chlorine, we find it as 1 : 6, showing it to be an iridium-chloride compound. The large pr. ct. of loss on heating, the small Ir. and  $\text{Cl}$  pr. cts., when compared with double iridium and potassic chloride, and the luminous flame when burned, all go to show that an organic constituent must make the additional pr. ct. If we suppose now ethylen to enter here into the union with iridium chloride, hanging itself on, we can expect from the consideration of analogous compounds that 2 atoms of the bivalent radical  $\text{C}_2\text{H}_4$  would join the atom  $\text{PtCl}_4$ .

We would have on this supposition the formula  $\text{IrCl}_4(\text{C}_2\text{H}_4)_2(\text{KCl})_2 + \chi\text{H}_2\text{O}$ . Now this formula with 3 atoms  $\text{H}_2\text{O}$  gives Ir. = 32·93 pr. ct.,  $\text{Cl}$  = 35·61 pr. ct., and with 2 atoms  $\text{H}_2\text{O}$ , Ir. = 33·95 pr. ct.,  $\text{Cl}$  = 36·71 pr. ct. ; anhydrous it gives Ir. = 36·20 pr. ct. and  $\text{Cl}$  = 39·14 pr. ct.

The large pr. ct. of loss at  $100^\circ$  is not accounted for by  $3\text{H}_2\text{O}$ , which give only 9·03 pr. ct. ; but it is possible that in a compound where the organic constituent is so loosely connected with the rest, as must be the case here, a partial decomposition of the salt enters at  $100^\circ$  already.

In another preparation, also well crystallized, ·1822 grms. dried at  $100^\circ$  :

gave ·0678 grms. metallic iridium = 37·21 pr. ct. ;

gave also ·3063 grms.  $\text{AgCl}$  = ·0758 grms.  $\text{Cl}$  = 41·59 pr. ct.

In another preparation, indistinctly crystallized, ·0502 grms. dried at  $100^\circ$  :

gave ·0172 grms. metallic iridium = 34·26 pr. ct.

(Probably low from  $\text{HCl}$  mechanically admixed.)

In another preparation, also indistinctly crystallized, .3207 grms. dried at  $100^{\circ}$ :

gave .2125 grms.  $\text{AgCl}$  = .1268 grms.  $\text{Cl}$  = 39.53 pr. ct.

It will thus be seen the determinations, all things considered, agree close enough with the theoretical pr. cts. of the formula to make it very probable. The want of enough sufficiently-well crystallized material prevented me from making an organic combustion which might settle it definitely.

Several individual crystals of the first crystallization were very sharply and clearly formed, and I subjected them to examination under the microscope with a power of about 50 diameters. The faces were clearly to be made out. They belong to the monoclinic system, and their prevailing habitus in crystallization is a combination of the two lateral pinacoids with positive and negative pyramids accompanied by one macrodome on the ends. The faces observed in an examination of five distinct crystals were (according to Naumann)  $\infty P \infty$ .  $\infty P \infty + P$ .  $-P$ .  $+\frac{1}{2}P$ .  $-\frac{1}{2}P$ .  $+P \infty$ .  $-P \infty$ .

In considering the compounds of the iridium-base with  $\text{NH}_4\text{Cl}$ , we find again a mixture of crystallized salts.

Preparation No. 1 consisted of sharply crystallized needles that looked almost black, and only by transmitted light showed a brownish-green color. They were also monoclinic.

On analysis they prove, I think, to be the sought-for ethylen-iridium compound.

.0713 grms. dried over  $\text{H}_2\text{SO}_4$  lost on heating to  $100^{\circ}$  .0029 = 4.07 pr. ct.:

gave .0850 grms.  $\text{AgCl}$  = .0210 grms.  $\text{Cl}$  = 29.49 pr. ct. or 30.74 pr. ct. of salt dried at  $100^{\circ}$ .

The iridium determination was made with magnesium, and was inaccurate as before.

The formula  $\text{IrCl}_2\text{C}_2\text{H}_4\text{NH}_4\text{Cl} + \text{H}_2\text{O} = 367.5$  demands  $\text{Cl}$  = 28.98 pr. ct.,  $\text{H}_2\text{O} = 4.89$ , or anhydrous 30.47 pr. ct.  $\text{Cl}$ .

Preparation No 2 was of much smaller needles and of lighter color.

Analyses show it to be of very similar composition to the potassium salt described above.

.1207 grms. dried at  $100^{\circ}$  C.:

gave .0495 grms. metallic Ir. = 41.97 pr. ct.:

gave also .2068 grms.  $\text{AgCl}$  = .0512 grms.  $\text{Cl}$  = 43.37 pr. ct.

$\text{IrCl}_4(\text{C}_2\text{H}_4)_2(\text{NH}_4\text{Cl})_2 = .502$  gives Ir. = 39.25 pr. ct. and  $\text{Cl}$  = 42.43 pr. ct., and supposing it to lose some of the  $\text{C}_2\text{H}_4$  at  $100^{\circ}$ , as stated above,  $\text{IrCl}_4(\text{C}_2\text{H}_4)(\text{NH}_4\text{Cl})_2$  would give Ir. = 41.50 pr. ct. and  $\text{Cl}$  = 44.94 pr. ct.

The other two preparations of the ammonium salt analysed appeared under the lens to be mixtures of the iridium proto-

chloride-ethylen salt and the iridium chloride-ethylen salt given above.

The results were—

·1322 grms. dried at  $100^{\circ}$  :

gave ·0609 grms. metallic iridium = 46·07 pr. ct.

·1715 grms. dried at  $100^{\circ}$  :

gave ·0784 grms. metallic iridium = 46·95 pr. ct.

$\text{IrCl}_2 (\text{C}_2\text{H}_4) (\text{NH}_4\text{Cl}) + \text{H}_2\text{O}$  gives Ir. = 53·61 pr. ct.

$\text{IrCl}_4 (\text{Cl}_2\text{H}_4)_2 (\text{NH}_4\text{Cl})_2$  gives Ir. = 39·25 pr. ct.

The existence of the base  $\text{IrCl}_4 (\text{C}_2\text{H}_4)_2$ ,

I hope to settle definitely by renewed analyses of larger quantities.

While engaged with the preparation of the ethylen and iridium compound, the thought of the possibility of acetylen ( $\text{C}_2\text{H}_2$ ) uniting with  $\text{PtCl}_2$  or  $\text{IrCl}_2$  led me to make some experiments in that direction. After a number of endeavors to form a platinum salt and analyses of the products (a detailed account of which is given in the original paper), I obtained negative results only. The existence of such a salt is highly improbable.