XXI.—The Chlorobromoplatinates of Potassium.

By Lucius Pitkin.

At the November meeting of the Society I described a new platinum salt, having the composition, $K_2PtCl_4Br_2$, which was called the chlorobromoplatinate of potassium. Since that time, however, I have found that this salt forms one of a series between the double chloride and the double bromide of platinum and potassium, the series comprising five compounds, each formed by the replacement of one or more atoms of chlorine in the double chloride, by a corresponding atom of bromine.

It will be remembered that in my previous experiments, the compound salt was formed by the action of potassium bromide on platinum tetrachloride, in the proper proportions; here, however, a different method was adopted, as, owing to the very rapid absorption of water, it was found impossible to accurately weigh out the platinic chloride. The method adopted was that of allowing a mutual reaction to take place between the double chloride, and the double bromide of platinum and potassium, by means of solution, digestion at a gentle heat, and cautious crystallization.

Both of these salts are easily prepared, are easily kept dry, and by weighing out the proper proportions, and allowing the reaction to take place under the conditions mentioned above, all the possible substitutions of Br for Cl, in this series of salts, are readily accomplished.

The five salts found, form connecting links between the double chloride, on the one hand, and the double bromide, on the other, and will be described in their order according to the number of Br atoms replacing the Cl; they are:

K_2PtCl_5Br, potassium monobromopentachloroplatinate.
$K_2PtCl_4Br_2$, potassium dibromotetrachloroplatinate.
$K_2PtCl_3Br_3$, potassium tribromotrichloroplatinate.
$K_2PtCl_2Br_4$, potassium tetrabromodichloroplatinate.
$K_2PtClBr_5$, potassium pentabromomonochloroplatinate.

Potassium monobromopentachloroplatinate, $K_2PtBrCl_5$. This salt, forming the first of the series of substitution products, differs very little in appearance from the double chloride of platinum and potassium. It can be most advantageously formed by the combination of five equivalents of chloroplatinate of potassium, with one of bromoplatinate, or by weight, 2444.0 parts of the former to 755.8 parts of the latter. In my experiments, 4.888 grms of the double chloride

were used, and 1.5116 of the double bromide. After solution, they were gently heated for some hours, and then allowed to crystallize, the solution being concentrated between each crystallization; by this means, six crops of crystals were obtained.

Three crops of the crystals were analyzed, the first, second and third, the last three being perfectly similar in appearance to those analyzed, all of which gave results very close to the theoretical amount calculated from the formula assigned.

The method of analysis consisted in ascertaining the amount of platinum in each crystallization, the salts being decomposed by heat and oxalic acid.

The theoretical percentage of platinum in this salt is 37.05, and the result of the three analyses were :

1st crystallization, 36.97 per cent.
2nd crystallization. 37.04 per cent.
3rd crystallization, 36.99 per cent.

The crystals of this salt were very small, under the same conditions which were favorable to the development of much larger crystals in the salts containing more bromine, and, throughout the course of these experiments, the tendency to form crystalline masses, of a size proportionate to the amount of bromine present, was well marked. The crystalline form of the salt is an octahedron, sometimes modified to a cubo-octahedron, while, under the microscope, a few frond-like masses of crystals were discovered.

Potassium dibromotetrachloroplatinate, $K_2PtBr_2Cl_4$. This salt has been already described, in full, in the November number of this JOURNAL (Vol. I, No. 11); a description will, therefore, not be necessary, except to say that, under the microscope, it exhibits the same general characteristics as the monobromated salt, with perhaps a greater abundance of the frond-like forms, this probably being due to a more rapid crystallization on the slide.

Potassium tribromotrichloroplatinate, $K_2PtBr_3Cl_3$. The salts of the series containing three, four and five atoms of bromine now remain to be considered. Heretofore, it was necessary to resort to fractional crystallization, in order to prove that the supposed salt was not a mechanical mixture; now, however, the crystallizations afforded such large crystals, that it could be readily perceived by the eye that such was not the case, and an analysis of only one specimen of each salt was rendered necessary.

The theoretical amount of platinum in this compound is 31.73 per cent., and an analysis yielded a result of 31.77 per cent., fully establishing the formula given.

It can best be prepared, as in the case of the monobromated salt, by combining potassium chloroplatinate with the corresponding bromoplatinate, in the proper proportions, which are, in this case, one equivalent of each, or by weight, 488 of chloroplatinate, to 755 of the bromoplatinate.

As thus prepared, it is a salt of a clear, reddish-yellow color, crystallizing readily in octahedra and cubo-octahedra.

Examined under a power of two hundred diameters (a drop of a solution, 1 : 50, being spontaneously evaporated for this purpose), it still showed, among the crystals of more definite form, frond-like radiations.

Potassium tetrabromodichloroplatinate, $K_2PtBr_4Cl_2$. Another salt, having the formula $K_2PtBr_4Cl_2$, has been formed like the preceding, but altering the proportions used. In this case, 4.5336 grms of the double bromide of platinum and potassium were used, while 1.4658 grms of the double chloride were employed.

The salt has a fine, bright, reddish shade, crystallizes easily, and, upon analysis, yielded 29.79 per cent. of metallic platinum—the calculated percentage being 29.61.

Potassium pentabromomonochloroplatinate, K_2PtBr_5Cl. This salt, the last of the series, exhibits a beautiful, ruby-red color, crystallizes in brilliant, and quite large, octahedra, and resembles, in great part, the ordinary double bromide of platinum and potassium, which it approaches closely in composition. An analysis resulted in showing a platinum percentage of 27.93, while the theoretical percentage was calculated as 27.76.

All of these salts are sparingly soluble in cold water, greatly more so in hot, and are precipitated from aqueous solutions by the addition of alcohol, while none of them are affected in the slightest degree by polarized light.

It is evident that the corresponding salts of the other alkaline bases can be formed in precisely the same manner, but limited time prevents a further investigation into the subject.

The supposition is also reasonable, and indeed, very probable, that more complicated substitutions can take place, involving a greater number of atoms ; for instance, the formation of a salt, such as $K_8Pt_4BrCl_{23}$, in which one bromine atom is substituted in a multiple of the empirical formula assigned to platinum and potassium double chloride.

In concluding, my thanks are due to Mr. Aschman, of the School of Mines, for instruments and assistance, in the part relating to the microscopic character of these salts.

SCHOOL OF MINES, COLUMBIA COLLEGE, February 9th, 1880.