

ART. XXI.—*On the Cæsium and Rubidium Chloraurates and Bromaurates*; by H. L. WELLS and H. L. WHEELER.
With their Crystallography; by S. L. PENFIELD.

A STUDY of the compounds to be described was undertaken in the hope that some crystallographic analogy would exist between them and the alkaline pentahalides described in a previous article.* No such analogy has been found in spite of

* This Journal. xliv, 42.

the similarity of such formulæ as $\text{CsCl} \cdot \text{Cl}_2\text{I}$ and $\text{CsCl} \cdot \text{Cl}_2\text{Au}$, but since some of these gold salts have never been described and as they show some interesting relations among themselves, our results are deemed worthy of publication.*

Th. Rosenblatt,† in an article on the solubility of the chloraurates, states that the cæsium and rubidium salts lose their water of crystallization almost completely when dried over sulphuric acid. He gives no statement of the amount of water, but refers to his dissertation of 1872 which is inaccessible to us. He mentions, however, that the crystals of both salts belong to the monoclinic system, so that it is probable that the compounds he obtained were the ones that we have found to be anhydrous.

The compounds that have been prepared are CsAuCl_4 , $2\text{CsAuCl}_4 \cdot \text{H}_2\text{O}$, CsAuBr_4 , RbAuCl_4 and RbAuBr_4 . We have attempted in each case to obtain bodies containing more cæsium and rubidium, but no evidence of their existence has been found.

An investigation of the corresponding iodine compounds was also undertaken, but, on account of the instability of auric iodide, we did not obtain any pure or well crystallized products.

Preparation:—The salts are so insoluble that they form precipitates when moderately concentrated solutions of the component salts are mixed, and the products are readily recrystallized from water or from the mother liquors. It is usually immaterial whether the solutions are neutral or acid or whether the gold or alkaline halide is in excess, but the salt $2\text{CsAuCl}_4 \cdot \text{H}_2\text{O}$ requires special conditions for its preparation, for it is apparently formed only when a large excess of gold chloride is present and when the solution does not contain much free acid. We have used four atoms of gold to one of cæsium in making this salt, but it usually requires repeated trials under these conditions before it is obtained free from the anhydrous compound. The two salts are however so distinct in form that there is no difficulty in distinguishing them.

Properties:—The color of CsAuCl_4 and of $2\text{CsAuCl}_4 \cdot \text{H}_2\text{O}$ is golden-yellow; RbAuCl_4 is yellowish-red; the two bromides are black; but give a dark red powder.

All the salts are sparingly soluble in water, especially when cold, and the cæsium compounds are less soluble than the rubidium. All of them are only slightly soluble in alcohol and insoluble in ether.

* The announcement by Professor Remsen (Am. Chem. Jour., xiv, 89), that he and Mr. H. C. Jones proposed to examine the gold-rubidium halides, was not made until after the work described in this article had been completed.

† Berichte, xix, 2535.

Methods of analysis.—The crystals were prepared for analysis by quickly pressing them between smooth filter-papers and finally allowing them to become air-dry. The hydrous caesium chloraurate, however, loses its water and becomes opaque on exposure. It was therefore dried as rapidly and thoroughly as possible on paper and was put into a weighing-tube as soon as some of the fragments began to lose their transparency.

Gold was determined by precipitation with ammonium oxalate or with sulphurous acid. The filtrate from the metallic gold was used either to determine the alkali-metal as normal sulphate or the halogen by the usual gravimetric method. Water was determined by the method used in the combustion of organic compounds, the halogens being held back by a mixture of lead chromate and lead oxide. The absence of water in the anhydrous compounds was established by the use of the same process.

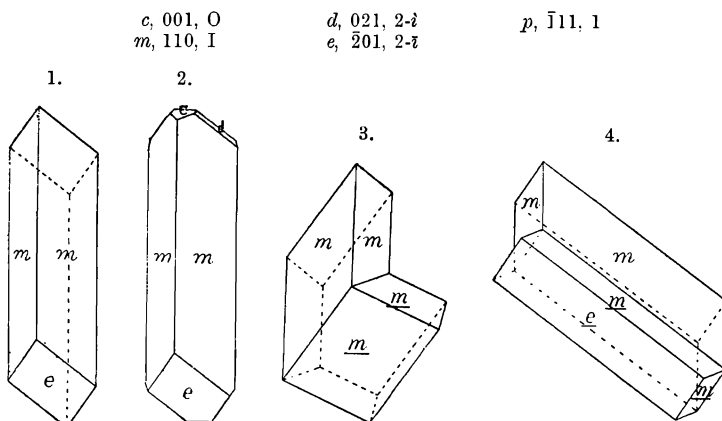
ANALYSES.

	Found.			Calculated for CsAuCl_4
Cæsium	28.11			28.16
Gold	41.61			41.77
Chlorine	29.91			30.06
	<hr/>			
	99.63			
	Found.			Calculated for $2\text{CsAuCl}_4 \cdot \text{H}_2\text{O}$
Cæsium	27.23	----	----	27.63
Gold	40.23	----	----	40.99
Chlorine	29.07	----	----	29.50
Water	2.32	2.37*	2.20*	1.87
	<hr/>			
	98.86			
	Found.			Calculated for CsAuBr_4
Caesium	20.73	----		20.45
Gold	30.32	30.26		30.34
Bromine	49.31	----		49.21
	<hr/>			
	100.36			
	Found.			Calculated for RbAuCl_4
Rubidium	----			20.14
Gold	45.53			46.46
Chlorine	32.98			33.40

* From a separate product.

	Found.	Calculated for RbAuBr ₄
Rubidium	-----	14.18
Gold	32.54	32.73
Bromine	-----	53.08

Crystallography.—The crystallization of CsAuCl₄, CsAuBr₄, RbAuCl₄ and RbAuBr₄ is monoclinic. The four salts form an isomorphous group and are identical in crystalline habit. The forms which have been observed on them are:



The crystals are prismatic and are usually terminated by e , fig. 1. When other faces are present they are always small, as represented in fig. 2. The pyramid p , which is not shown in the figure, frequently occurs as a small face, replacing the edge between d and e . Among the crystals of CsAuBr₄, several twins were observed, having $p, 11\bar{1}$ as the twinning plane, fig. 3, while fig. 4 represents a crystal of RbAuBr₄, twinned about $e, 20\bar{1}$. The letters belonging to the parts in twin position are underlined. Both kinds of twins are abnormally developed as represented in the figures. In all four compounds the cleavage is perfect parallel to the base.

The rubidium salts, being the most soluble, form readily in large crystals, several centimeters in length. The chloride, especially, yielded magnificent crystals, which frequently were only limited in length by the size of the vessel and volume of the solution containing them. The cæsium salts are less soluble and were made in small prisms, seldom over 5^{mm} in length. The crystals were frequently hollow or cavernous at the extremities, this was especially true of the two bromides. The faces, for the most part, gave excellent reflections of the signal on the goniometer.

The axial ratios are as follows:

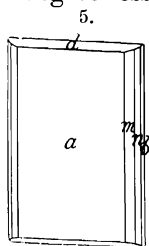
CsAuCl ₄		CsAuBr ₄	
$\hat{a}:\hat{b}:\hat{c}$	$= 1:1255:1:0\cdot7228$	$\hat{a}:\hat{b}:\hat{c}$	$= 1:1359:1:0\cdot7411$
β	$= 71^{\circ} 36'$	β	$= 70^{\circ} 24\frac{1}{2}'$
RbAuCl ₄		RbAuBr ₄	
$\hat{a}:\hat{b}:\hat{c}$	$= 1:1954:1:0\cdot7385$	$\hat{a}:\hat{b}:\hat{c}$	$= 1:1951:1:0\cdot7256$
β	$= 75^{\circ} 32'$	β	$= 76^{\circ} 53\frac{1}{2}'$

In the following tables the angles which were chosen as fundamental are marked by an asterisk.

CsAuCl ₄				CsAuBr ₄			
Measured.		Calculated.		Measured.		Calculated.	
$m \wedge m$, $110 \wedge \bar{1}\bar{1}0$	$= *93^{\circ} 46'$			$m \wedge m$, $110 \wedge \bar{1}\bar{1}0$	$= *93^{\circ} 53'$		
$m \wedge c$, $110 \wedge 001$	$= 77^{\circ} 36'$			$m \wedge c$, $110 \wedge 001$	$= *76^{\circ} 46'$		
$m \wedge d$, $110 \wedge 021$	$= 44^{\circ} 6'$			$m \wedge d$, $110 \wedge 021$	$= 43^{\circ} 23'$		
$d \wedge p$, $021 \wedge \bar{1}\bar{1}1$	$= 44^{\circ} 7'$			$d \wedge p$, $021 \wedge \bar{1}\bar{1}1$	$= 32^{\circ} 23'$		
$d \wedge e$, $021 \wedge \bar{2}01$	$= *75^{\circ} 17'$			$d \wedge e$, $021 \wedge \bar{2}01$	$= 75^{\circ} 31'$		
$m \wedge e$, $\bar{1}\bar{1}0 \wedge \bar{2}01$	$= *60^{\circ} 36'$			$m \wedge e$, $\bar{1}\bar{1}0 \wedge \bar{2}01$	$= *60^{\circ} 41'$		
$c \wedge e$, $001 \wedge \bar{2}01$	$= 64^{\circ} 20'$			$c \wedge e$, $001 \wedge \bar{2}01$	$= 62^{\circ} 9'$		
$m \wedge m$, Reëntrant angle of twin,				$m \wedge m$, Reëntrant angle of twin,			
RbAuCl ₄				RbAuBr ₄			
Measured.		Calculated.		Measured.		Calculated.	
$m \wedge m$, $110 \wedge \bar{1}\bar{1}0$	$= *98^{\circ} 21'$			$m \wedge m$, $110 \wedge \bar{1}\bar{1}0$	$= *98^{\circ} 40'$		
$m \wedge c$, $110 \wedge 001$	$= *80^{\circ} 36'$			$m \wedge c$, $110 \wedge 001$	$= *81^{\circ} 30'$		
$m \wedge d$, $110 \wedge 021$	$= 44^{\circ} 57'$			$m \wedge d$, $110 \wedge 021$	$= 45^{\circ} 12\frac{1}{2}'$		
$d \wedge p$, $021 \wedge \bar{1}\bar{1}1$	$= 31^{\circ} 26'$			$d \wedge p$, $021 \wedge \bar{1}\bar{1}1$	$= 31^{\circ} 35\frac{1}{2}'$		
$d \wedge e$, $021 \wedge \bar{2}01$	$= 72^{\circ} 28'$			$d \wedge e$, $021 \wedge \bar{2}01$	$= 72^{\circ} 26'$		
$m \wedge e$, $\bar{1}\bar{1}0 \wedge \bar{2}01$	$= *62^{\circ} 12'$			$m \wedge e$, $\bar{1}\bar{1}0 \wedge \bar{2}01$	$= 62^{\circ} 21\frac{1}{2}'$		
$c \wedge e$, $001 \wedge \bar{2}01$	$= 60^{\circ} 4'$			$c \wedge e$, $001 \wedge \bar{2}01$	$= 59^{\circ} 59'$		
$d \wedge d$, $021 \wedge 021$	$= 110^{\circ} 20'$			$d \wedge d$, $021 \wedge 021$	$= 110^{\circ} 4\frac{1}{2}'$		
$m \wedge m$, Reëntrant angle of twin,				$m \wedge m$, Reëntrant angle of twin,			

In their axial ratios the two caesium salts are very similar, as are also the two rubidium salts, while the rubidium compounds differ considerably from those of caesium, especially in the relation of \hat{a} to the other axes and in the angles β . It is therefore evident that the replacement of one metal by another in these salts has a considerable influence upon their form, whereas, as we have shown, such a replacement in the caesium and rubidium trihalides has little or no effect. There seems to be no regularity in the influence of the replacement of chlorine by bromine in these gold salts, for in the caesium compounds the chloride has a slightly shorter axis \hat{c} and a greater angle β than the bromide, while in the rubidium salts exactly the reverse is true in both cases. This unexpected relation between the chlorides and bromides has been confirmed by repeating the measurements, especially of the angle $m \wedge c$, using both crystal and cleavage faces. It is certain that this angle is about a degree greater with the chloride than with the bromide in

the cæsium salts, while in the rubidium compounds it is about a degree less.



The crystallization of $2\text{CsAuCl}_4 \cdot \text{H}_2\text{O}$ is orthorhombic. This salt was repeatedly made but only one crop of crystals was obtained which was suitable for measurement. These were thin plates, having the habit shown in fig. 5. They were not over 5^{mm} in length and were only a fraction of a millimeter thick. On removal from the mother liquor, or from a moist atmosphere, the transparent plates rapidly became opaque and the faces lost their luster so that only approximate measurements could be obtained.

The forms which were observed are:

$$\begin{array}{l} a, 100, i\bar{i} \\ b, 010, i\bar{i} \end{array}$$

$$\begin{array}{l} m, 110, \bar{1} \\ n, 120, i\bar{2} \end{array}$$

$$d, 101, 1\bar{1}$$

The axial ratio is as follows:

$$\bar{a} : \bar{b} : \bar{c} = 0.625 : 1 : 0.24$$

The following measurements were made.

$$\begin{array}{ll} a \wedge m, 100 \wedge 110 = \text{about } 32^\circ & a \wedge b, 100 \wedge 010 = \text{about } 96^\circ \\ a \wedge n, 100 \wedge 120 = \text{ " } 51^\circ & d \wedge d, 101 \wedge 101 = \text{ " } 42^\circ \end{array}$$

Under the polarizing microscope the crystals show parallel extinction and, in convergent light, an acute bisectrix normal to $a, 100$. The plane of the optical axes is the base. The divergence of the axes is large, the hyperbolæ opening out beyond the field of the microscope. The axes of elasticity are:

$$\bar{a} = c, \quad \bar{b} = a, \quad \bar{c} = b.$$

The double refraction is therefore positive.

The change which the crystals undergo when exposed to dry air is a molecular rearrangement, accompanied by loss of water and, probably a change to the anhydrous salt which was described above. This rearrangement is a beautiful sight when studied with the microscope in polarized light. The change commences a few minutes after the crystals are removed from the mother liquor, and in less than ten minutes has usually advanced to such an extent that the crystals are no longer transparent. The crystals at first show a uniform action on polarized light, then from different parts of the surface the rearrangement, which is marked by aggregate polarization, commences. It advances, shooting out in various directions in a manner resembling the growth of ammonium chloride crystals under the microscope, until the whole field is covered and light is finally no longer transmitted.

Sheffield Scientific School, April, 1892.