

ART. XXXII.—*On the Double Halides of Tellurium with Potassium, Rubidium and Cæsium*; by H. L. WHEELER.

THE existence of double halides of tellurium with potassium, sodium and ammonium was first indicated by Berzelius.* He described the methods by which he obtained them, but gave no analyses of the compounds. Later, Rammelsberg† investigated the double chlorides of tellurium with potassium and ammonium, with the object of determining their composition. He arrived at the formulæ $8\text{KCl} \cdot 3\text{TeCl}_4$ and $8\text{NH}_4\text{Cl}$.

* Pogg. Ann., xxxii, 577.

† Berlin Monats. Ber., 1875, 379.

3TeCl_4 . It will be shown beyond that the formula of the potassium compound at least must have been obtained from analyses of impure products. Von Hauer* analyzed the double bromide of tellurium and potassium, and concluded that the salt had the composition represented by the formula $2\text{KBr} \cdot \text{TeBr}_4 \cdot 3\text{H}_2\text{O}$. I have reinvestigated this salt and found it to contain two molecules of water and not three. Probably Von Hauer analyzed the salt without previously having dried it sufficiently or without having taken precautions to remove included water which the crystals always contain. He dehydrated this salt and used it in his work on the atomic weight of tellurium.

More recently Wills† determined the atomic weight of tellurium by means of the same salt. He does not give any analyses of the hydrous compound, but states that the salt contains water and gives directions for dehydrating it. Rammelsberg in his "Handbuch der krystallographisch-physikalischen Chemie" (p. 289) quotes the formula of the dehydrated compound from Wills' work and assigns to this Baker's‡ measurements, which do not belong to it, but to the hydrated compound with the three supposed molecules of water of crystallization. The present investigation has shown that the anhydrous salt is isometric, the hydrous one being orthorhombic.

Ramsay§ says that "By mixing aqueous solutions of the constituent halides, tellurium halides combine thus: TeCl_4 , 2KCl , TeBr_4 , 2KBr , TeI_4 , 2KI . These compounds form reddish crystals. Few attempts have been made to prepare double halides." Although a thorough search of the literature on this subject has been made, in connection with the present work, no analyses of the double chloride or iodide could be found. Berzelius's work as regards their preparation and Rammelsberg's attempt to determine the formula of the chloride comprise all the work that has been done on these two salts. It must be concluded that the formulæ given by Ramsay were deduced by analogy with the double bromide, especially since his statements in regard to color, method of preparation and composition only apply, in all respects, to the double bromide.

It will be seen from the above summary that very little satisfactory work has been done on this class of compounds, and, therefore, the present investigation has been undertaken with the view of making a thorough study of the double

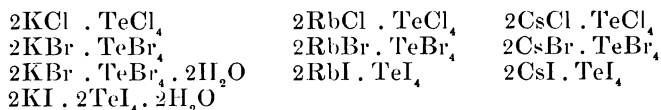
* Journ. prakt. Chem., lxxiii, 98.

† Jour. Chem. Soc., xxxv, 711.

‡ Jour. Chem. Soc., xxxv, 711.

§ System of Inorganic Chemistry, edition of 1891, p. 168.

halides of tellurium with potassium, rubidium and cæsium. As a result the following compounds have been prepared :



It is to be noticed that all of these compounds conform to the usual type of double halides of tetravalent metals in containing the alkali metal and tellurium in the ratio of two atoms of the former to one of the latter, and no indications of the formation of salts of a different type were observed. The anhydrous double halides of tellurium crystallize in the isometric system, with an octahedral habit, and it is an interesting fact that this form seems to be characteristic for anhydrous double halides of this type. The cæsium and rubidium salts are new compounds, as well as the crystallized, anhydrous, double potassium bromide. New formulæ have been assigned to the hydrous potassium double bromide and to the double iodide of potassium. A considerable difference is shown in the affinity of the double halides of tellurium and potassium for water of crystallization. The double chloride is anhydrous and no hydrous form of it was observed, the double bromide was prepared in both the hydrous and the anhydrous forms, while the iodide was obtained only with water of crystallization. This water was more firmly held than in the case of the hydrous bromide, as was shown by the fact that it formed from hot solutions and did not as readily effloresce.

The methods used in the preparation of pure material for this work, and which deserve to be mentioned on account of giving satisfactory results, are given below. The tellurium was obtained by purifying the commercial product by precipitation with sulphurous acid, according to the method of Divers and Shimosé.* The halides of tellurium were prepared from this material in the usual way.

Cæsium chloride was obtained in a pure state by the method of Godeffroy.† The bromides and iodides were obtained in the usual manner from the carbonate, the latter having been prepared from the pure chloride by converting into nitrate, then into oxalate and igniting the latter, as suggested by J. L. Smith,‡ for the conversion of potassium chloride into carbonate. The rubidium was purified by Allen's§ acid tartrate method. In the case of the potassium salts, Kahlbaum's pure material was used.

* Jour. Chem. Soc., xlvii. 439.

† This Journal, II, xvi, 373.

‡ Ber. d. chem. Ges., vii, 375.

§ Ibid., II, xxxiv, 367.

The methods by which the double halides were obtained will be given with the description of the salts.

Method of Analysis.

The anhydrous salts were removed from the mother liquor, and, after pressing on filter paper, were dried in the air. The hydrous compounds were rapidly crushed on smooth filter paper, and, as soon as it was certain that no included water was retained by the fragments, they were placed in weighing tubes. Portions of about one-half a gram were taken for analysis. In order to determine the halogens, silver sulphate was added to the solution of the weighed sample in water containing a little sulphuric acid. The silver halide was washed, ignited and weighed in the usual manner. After the removal of the excess of silver by means of hydrochloric acid, tellurium was removed with hydrogen sulphide. This separation of tellurium, best in warm solution, has been found to be complete in a few minutes and in a condition that admits of filtration without inconvenience. The sulphide of tellurium, filtered on asbestos in a Gooch crucible, was washed with water containing a little hydrogen sulphide, then treated with a solution of bromine in dilute hydrochloric acid, which readily dissolves the moist sulphide. An excess of nitric acid was then added to this solution and the whole evaporated on the water bath, the resulting tellurous acid, being transferred to platinum, was ignited and weighed as TeO_2 . The alkali metals were determined by evaporating the filtrate from the tellurium sulphide to dryness, with an excess of sulphuric acid. The residues were then converted into normal sulphate by ignition in a stream of ammonia, as suggested by Krüss for potassium sulphate. In the case of the hydrous salts, water was determined by heating them in an air bath to constant weight; the residues were analyzed and found to correspond in composition to the anhydrous salts. The atomic weights used in the calculation of the results were the following:

Te, 125; K, 39.1; Rb, 85.5; Cs, 133; Cl, 35.5; Br, 80; I, 127.

Solubility.

The salts are all decomposed by water. The double bromides, however, show an interesting difference in their deportment with this reagent. Potassium tellurium bromide dissolves in a small amount of water, but, if an excess of water is added, tellurous acid separates, as has been observed by Wills.* Rubidium tellurium bromide also dissolves in a

* loc. cit.

little hot water completely, the difference being shown on cooling, when a considerable portion of the tellurium separates as tellurous acid. While in the case of the cæsium salt both hot and cold water, in large and small amounts, fail to dissolve the salt, the result being immediate decomposition. Only a small part of the tellurium in this case goes into solution. Most of these double salts can be conveniently recrystallized from dilute solutions of the corresponding acid. The exceptions are potassium-tellurium chloride, which is decomposed by this treatment, and cæsium-tellurium iodide, which is practically insoluble in hydriodic acid. The fact, first noticed by Godeffroy,* that double halides, containing the metals potassium, rubidium and cæsium, generally decrease in solubility from potassium to cæsium, which has frequently been noticed in this laboratory, is again well illustrated by these compounds. For the determination of the solubility of these salts in acids, they were finely powdered, and saturated solutions were then prepared by digesting a mixture of the acid and an excess of the salt for about a week, at ordinary temperature. This was done in a closed flask. Weighed portions of these solutions were evaporated to dryness and the residues dried at 100° and weighed. These solubilities were all taken at 22°, and the results are the average of two or more closely agreeing determinations.

	100 parts HCl	100 parts HCl
	Sp. gr. 1·2 dissolve	Sp. gr. 1·05 dissolve
2RbCl . TeCl ₄	0·34 parts.	13·09 parts.
2CsCl . TeCl ₄	0·05 “	0·78 “
	100 parts HBr	100 parts HBr
	Sp. gr. 1·49 dissolve	Sp. gr. 1·08 dissolve
2KBr . TeBr ₄	6·57 parts.	62·90 parts.
2RbBr . TeBr ₄	0·25 “	3·88 “
2CsBr . TeBr ₄	0·02 “	0·13 “

The double tellurium chlorides, described in this article, are more soluble than the bromides, and the bromides more soluble than the iodides. The solubility of these compounds in strong alcohol shows the same gradation as their solubility in acids, the cæsium salts being practically insoluble in this menstruum, while the rubidium salts dissolve to a trifling but clearly perceptible extent, and the potassium salts dissolve considerably or are decomposed with separation of the potassium halide, or both solution and decomposition take place, according to the salt experimented with.

* Ber. d. Chem. Ges., viii, 9.

The Chlorides.

The crystals of the three chlorides have a pale yellow color, resembling that of the well known ammonium phosphomolybdate precipitate, the shade becoming somewhat lighter from the caesium to the potassium salts.

Cæsium tellurichloride, 2CsCl. TeCl₄.—In the preparation of this compound, and also in the preparation of the rubidium and potassium double chlorides, the tellurium tetrachloride is most conveniently made by converting tellurium into tellurous oxide by means of aqua regia, evaporating to dryness to expel nitric acid and then dissolving the residue in hot hydrochloric acid. An aqueous solution of caesium chloride, added to this, produces a precipitate, even in quite dilute solutions. There must be an excess of hydrochloric acid present to prevent the separation of tellurous acid. On boiling and adding more water, if necessary, this precipitate dissolves. The solution, left to cool, deposits small brilliantly lustrous octahedrons. It is a general fact with these double halides, that an excess of one or the other of the constituents does not affect their composition. This is shown in this particular case by the fact that it can be recrystallized from strong solutions of tellurium or of caesium chlorides.

		Analysis gave:		Calculated.
Cs	43·44	43·90	44·63	44·04
Te	20·65	----	21·41	20·69
Cl	35·93	35·14	----	35·27

This compound is perfectly stable in the air. It does not melt below the boiling point of sulphuric acid. It can be precipitated from its solution in dilute hydrochloric acid by the addition of concentrated hydrochloric acid. A portion of the salt, finely pulverized, was treated with water at ordinary temperature. This produced a voluminous white precipitate, which was washed with cold water and dried in the air.

	Analysis gave:	Calculated for H ₂ TeO ₃ .
Te	71·43	71·43
H ₂ O	7·52	10·29
O	17·76	18·28
Cl	2·49	
Cs	0·80	

The oxygen which was not given off in the form of water on heating the substance was calculated by difference. From the above analysis the conclusion may be drawn, that the precipitate produced by the action of water on this salt is essentially tellurous acid, a small amount of oxychloride of tellurium

being present. Hot water dissolves some of this tellurous acid, and, on cooling slowly, the anhydride separates in the characteristic form of colorless octahedrons.

Rubidium tellurichloride, $2RbCl \cdot TeCl_4$.—The preparation of this salt was in every way analogous to that of the cæsium tellurium chloride. However, since this salt is far more soluble than the corresponding cæsium compound, no precipitate was obtained in dilute solutions. The mixture of the hydrochloric acid solution of the constituents was concentrated by evaporation, and, when cooled, crystals separated. These were in the form of octahedrons, somewhat larger than the cæsium salt.

Analysis gave :		Calculated for $2RbCl \cdot TeCl_4$.	
Rb	33·50	33·83	33·59
Te	24·34	----	24·56
Cl	----	----	41·85

This salt remains permanent in the air. From the dilute hydrochloric acid solution, concentrated hydrochloric precipitates it unaltered. Water decomposes it, evidently in the same way as the cæsium salt.

Potassium tellurichloride, $2KCl \cdot TeCl_4$.—To prepare this salt in a pure state an excess of tellurium chloride is necessary. The analyzed material was obtained by spontaneous evaporation of the constituents in a solution of dilute hydrochloric acid, twice as much tellurium chloride being present as required by the formula. Under these conditions it was found to separate in the form of light yellow octahedrons, which, under the microscope, were shown to be free from potassium chloride.

Analysis gave :		Calculated for $2KCl \cdot TeCl_4$.	
		Ratio.	
K	17·37	·44	18·79
Te	30·29	·24	30·03
Cl	49·47	1·39	51·18
	97·13		

The salt, therefore, has the formula $2KCl \cdot TeCl_4$. The crystals deliquesce somewhat in moist air and the analyzed material retained a small amount of water, as is shown by the deficiency in the above analysis. It is not probable that the salt contains water of crystallization, for the crystalline form and optical properties show that it is isomorphous with the anhydrous salts. This salt is the most unstable as well as the most soluble of the anhydrous double halides described in this article. It is readily dissolved by dilute hydrochloric acid.

Strong hydrochloric acid separates potassium chloride. It therefore cannot be precipitated from its solutions by the addition of strong hydrochloric acid, as in the case of the other chlorides. Alcohol also separates potassium chloride. Water apparently effects the same decomposition as in the case of the caesium and rubidium chlorides. The tendency of potassium chloride to separate along with the salt explains why Rammelsberg's analysis came high in regard to the potassium chloride. His results corresponded to a mixture of two molecules of KCl and three molecules of $2\text{KCl} \cdot \text{TeCl}_4$. Experiments with the calculated quantity of the constituents invariably resulted in the separation of potassium chloride or potassium chloride mixed with the yellow $2\text{KCl} \cdot \text{TeCl}_4$. Experiments with the method given by Ramsay* for the preparation of this salt, by mixing aqueous solutions of the constituents, resulted in the decomposition of the tellurium chloride, and the resulting white precipitate failed to dissolve until considerable hydrochloric acid was added. Attempts to prepare the compound by concentrating the mixture of the constituents by the aid of heat invariably resulted in failure. In certain cases, on cooling such solutions, a mass of colorless slender prisms was obtained, which will be described in a future article.

The Double Bromides.

The crystals of the anhydrous bromides have a brilliant red color resembling that of the mineral crocoite. The powders of the salts have a color that is similar to that of a mixture of equal parts potassium bichromate and red lead. The powder of the hydrous bromide has the color of mercuric oxide, but, by loss of water, this soon changes to that of the anhydrous salt.

Cæsium telluribromide, $2\text{CsBr} \cdot \text{TeBr}_4$.—This double halide can easily be prepared by mixing finely divided tellurium with caesium bromide in dilute hydrobromic acid, then adding bromine in excess. The presence of free acid is necessary to prevent the separation of tellurous acid. When the tellurium has disappeared, the solution is concentrated by the aid of heat, and, on cooling, bright red crystals of the pure salt are deposited. These are generally somewhat larger than the crystals of the double chloride.

	Analysis gave:			Calculated.
Cs	30·90	30·87	30·91	30·54
Te	14·29	13·60	14·03	14·35
Br	55·01	---	55·32	55·11

* loc. cit.

This salt remains unaltered in the air. It can be separated from its solution in dilute hydrobromic acid by the addition of concentrated acid. It does not melt below the boiling point of sulphuric acid. Attempts to prepare a hydrous salt according to the methods used for the preparation of $\text{TeBr}_4 \cdot 2\text{KBr} \cdot 2\text{H}_2\text{O}$ were without success.

Rubidium telluribromide, $2\text{RbBr} \cdot \text{TeBr}_4$.—The directions given for the preparation of the corresponding cæsium compound apply also in the preparation of this salt. If the solutions are strong, the compound separates as a bright red precipitate, but if dilute, on concentrating by means of heat or spontaneous evaporation, it crystallizes in brilliant red octahedra.

	Analysis gave :	Calculated.
Rb	22·02	22·04
Te	-----	16·11
Br	62·07	61·85

This salt is stable in the air. Like the corresponding cæsium salt, this separates from its solutions by the addition of concentrated hydrobromic acid. When it is dissolved in a little water and the solution is cooled slowly, colorless octahedrons of TeO_2 separate. The latter product was found to be impure, containing a small amount of bromine. On heating, the salt decrepitates slightly and melts at a high temperature. Efforts to prepare a hydrous salt according to the methods used for the preparation of $2\text{KBr} \cdot \text{TeBr}_4 \cdot 2\text{H}_2\text{O}$ were without success.

*Potassium telluribromides, $2\text{KBr} \cdot \text{TeBr}_4$ and $2\text{KBr} \cdot \text{TeBr}_4 \cdot 2\text{H}_2\text{O}$.**—For the preparation of these salts, a mixture of the constituents was made as described in the case of the cæsium double bromide. The solution invariably deposited crystals of the anhydrous salt when it had been concentrated by heat, but, by spontaneous evaporation of the filtrate, the hydrous salt was obtained. On recrystallizing either of these salts from water or from dilute hydrobromic acid, the anhydrous salt is obtained when the solution has been saturated by boiling and then allowed to cool, but if the solution is left to deposit crystals at ordinary temperature the hydrous modification is obtained. The crystals of these different compounds closely resemble each other in color and appearance. The anhydrous variety crystallizes in octahedrons modified by the cube. The orthorhombic crystals of the hydrous salt look like distorted crystals of the other. This being the case, and since

* Described by Von Hauer as containing three molecules of water of crystallization.

the crystals of the hydrous compound can be obtained much larger than those of the anhydrous salt, both Von Hauer and Wills selected these for their work, while the more easily obtained anhydrous salt was overlooked. The hydrous salt is readily distinguished from the anhydrous one by its deportment on exposure to a dry atmosphere. The latter is stable, but under these conditions the hydrous compound rapidly effloresces, losing its luster, the faces of the crystals becoming superficially covered with a light reddish yellow and opaque layer of the anhydrous salt. Crystals which had been exposed to dry air for several days and were completely covered with this layer were found, on crushing, to remain unaltered in the interior and to have still retained included water in addition to their water of crystallization. This was shown by the fact that the crushed crystals gave a stain of the mother liquor to filter paper. This property of the hydrous crystals explains why Von Hauer assigned three molecules of water to this salt instead of two. The material for analysis of the hydrous salt was selected from crystals varying in size from 7 to 13^{mm} in diameter. These were very rapidly crushed on smooth filter paper, to remove included water, and immediately corked up in the weighing tube and analyzed. A close examination of the fragments, before and after weighing, gave no evidence of loss of water from the substance by efflorescence. The analyses were from three different crops.

	Analysis gave:		Calculated for 2KBrTeBr ₄ · 2H ₂ O.		Calculated for 2KBrTeBr ₄ · 3H ₂ O.
K	10·90	11·07	10·73	10·87	10·61
Te	17·59	17·29	17·46	17·38	16·96
Br	66·35	66·36	66·34	66·74	65·11
HO	5·33	5·53	5·73	5·01	7·32

These results make it evident that the salt contains two molecules of water, and not three as has generally been supposed. The water in this salt was determined by heating it in an air bath to constant weight. The temperature was maintained between 150°–160°, and finally, to be sure that all the water had been driven off, the residues were analyzed in two cases.

	Analysis gave:		Calculated for 2KBr · TeBr ₄ .
K	11·71	11·52	11·44
Te	18·29	18·58	18·30
Br	70·25	70·09	70·26

Analyses of products obtained by cooling hot saturated solutions gave the following results:

				Calculated for 2KBrTeBr ₄ .
K	11·67	11·70	----	11·44
Te	18·06	----	----	18·30
Br	70·24	70·20	69·40	70·26

The Double Iodides.

These salts are all black. The powder of the cæsium salt is pure black, that of the rubidium and potassium salts is grayish black.

Cæsium telluriiodide, 2CsI. TeI₄.—In order to prepare this salt, and also in the case of the rubidium and potassium compounds, tellurium tetraiodide was made by treating tellurous oxide with hydriodic acid. The iodide of tellurium is sparingly soluble in hydriodic acid, but, on mixing this solution with a solution of cæsium iodide, an amorphous black precipitate was obtained, even in very dilute solutions.

	Analysis gave:	Calculated for 2CsI. TeI ₄ .
Cs	23·37	23·07
Te	10·51	10·84
I	65·17	66·09

This compound resisted all attempts to prepare it in a crystalline form. It is insoluble in cæsium iodide and in hydriodic acid, hence warming in the mother liquor failed to dissolve the salt. It is decomposed slowly by cold water, rapidly by hot, and apparently tellurous acid or anhydride separates. This generally is impure, being mixed with a dark colored residue containing iodine. On exposure the salt slowly loses iodine. In the open capillary it does not melt below the boiling point of sulphuric acid.

Rubidium telluriiodide 2RbI. TeI₄.—This compound was prepared by mixing the constituents in the same manner as in the preparation of the corresponding cæsium salt. If the solutions are only moderately concentrated, a black amorphous precipitate is produced. Unlike the corresponding cæsium salt, it dissolves, to a slight extent, on warming in the mother liquor, and on cooling, black microscopic octahedrons are produced.

	Analysis gave:	Calculated for 2RbI. TeI ₄ .
Rb	16·83	16·17
Te	----	11·81
I	72·07	72·02

This iodide is stable on exposure. Water effects the same decomposition as in the case of the cæsium salt. A small portion of this salt dissolves in strong alcohol, giving the color of a weak iodine solution.

Potassium telluriiodide, $2KI \cdot TeI_4 \cdot 2H_2O$. — This compound can most conveniently be prepared by boiling tellurium iodide in a strong solution of potassium iodide in dilute hydriodic acid. The solution, filtered while hot from any undissolved tellurium iodide, deposits long black prisms on cooling. These crystals attain considerable size, about 30^{mm} in length, when a large excess of potassium iodide is used. The mother liquor, on evaporation in a desiccator, deposits more of the salt, but the crystals have a different habit.

	Analysis gave :			Calculated for $2KI \cdot TeI_4 \cdot 2H_2O$.
K	8.41	8.70	8.39	7.81
Te	12.25	12.95	12.30	12.48
I	75.97	----	76.68	76.11
H ₂ O	3.57	----	----	3.60

For the determination of water in this compound the crystals were rapidly pressed on paper and immediately analyzed. It was found that the salt could be dehydrated at a temperature between 110°–115°, the resulting anhydrous salt being stable at that temperature. This was shown by an iodine determination in the residue. Analysis gave 78.78 per cent. of iodine, calculated for $2KI \cdot TeI_4$, 78.94.

This salt is far more stable in the air than the corresponding bromide, but the crystals lose their luster in dry air, becoming dull black on account of a superficial efflorescence.

Crystallography.

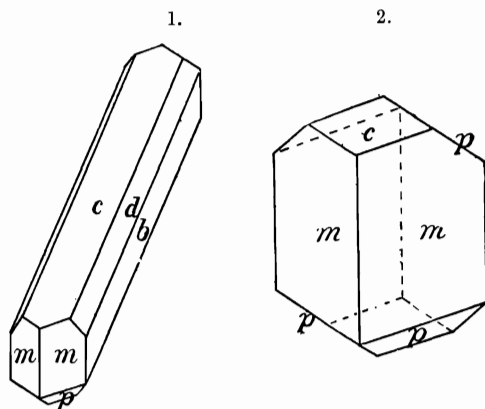
The crystallization of the anhydrous alkali-tellurium halides is isometric. The chlorides were obtained in octahedrons with little or no modification, the bromides in combination of octahedron and cube. The chlorides and bromides were measured and also proved to be isotropic by examination in polarized light. Of the anhydrous iodides, the rubidium salt was the only one obtained in crystals, and these were too small to measure, but appeared under the microscope as combination of octahedron and cube. They were so opaque that they could not be tested in polarized light.

The two hydrous salts, $2KBr \cdot TeBr_4 \cdot 2H_2O$ and $2KI \cdot TeI_4 \cdot 2H_2O$ although analogous to each other in their composition, differ in crystallization. The bromide is orthorhombic as has been shown by Baker* also by Grailich and Lang in Rammelsberg's Handbuch.† That the hydrous potassium tellurium bromide obtained in the present work is identical with that described by the above authors is shown by measurements of the crystals. The crystallization of the salt $2KI \cdot TeI_4 \cdot 2H_2O$ is

* Loc. cit.

† Loc. cit.

monoclinic. Two different habits were observed; long prisms, developed in the direction of the clino axis were obtained from hot solutions (fig. 1). The mother liquor from these, on standing, gave shorter prisms in which the domes and clinopinacoids were wanting (fig. 2).



The forms observed were:

$$\begin{array}{lll} m & 110 & c & 001 & d & 031 \\ p & 111 & b & 010 & & \end{array}$$

The axial ratio is as follows:

$$a : \bar{b} : c' \cdot 7047; 1; \cdot 5688 \text{ B} = 100 \wedge 001 = 59^\circ 7' 16''$$

The crystals gave fair reflections of the signal on the goniometer. Measurements chosen as fundamental are indicated by an asterisk.

		Calculated.	Measured.
$m \wedge m''$	$110 \wedge 1\bar{1}0$	$62^\circ 20'$	$62^\circ 26'$
$m \wedge b$	$110 \wedge 010$	$58^\circ 50'$	$58^\circ 50' *$
$b \wedge c$	$010 \wedge 001$	90°	90°
$m \wedge c$	$110 \wedge 001$	$63^\circ 57'$	$63^\circ 57' *$
$m \wedge p$	$110 \wedge 1\bar{1}1$	$60^\circ 42'$	$60^\circ 42' *$
$c \wedge p$	$001 \wedge 1\bar{1}1$	$55^\circ 21'$	$55^\circ 22'$
$b \wedge d$	$010 \wedge 031$	$34^\circ 20'$	$34^\circ 25'$
$b \wedge p$	$010 \wedge 1\bar{1}1$	$61^\circ 42' 49''$	$61^\circ 42' 30''$
$m \wedge m'$	$110 \wedge 1\bar{1}0$	$117^\circ 40'$	$117^\circ 33'$
$c \wedge m'$	$001 \wedge 1\bar{1}0$	$116^\circ 3'$	$116^\circ 11'$

The crystals were too opaque for any optical examination.

In conclusion the author wishes to express his indebtedness, to Prof. H. L. Wells for valuable advice and for the interest that he has taken in this work, and to Prof. S. L. Penfield under whose direction the crystallography of these salts was investigated.

Sheffield Scientific School, January, 1893.