distort the bond angles in the silicon compound.

We are indebted for the furnishing of materials to Professor H. S. Booth of Western Reserve University, Professor Warren C. Johnson of the University of Chicago, Professor D. M. Yost of this Laboratory, Dr. Fred Stitt, and their associates. We also wish to thank Messrs. V. Schomaker and K. J. Palmer for assistance in preparing some of the photographs. To Professor Linus Pauling we express our appreciation of unfailing encouragement and help.

Summary

The molecular structures of seven phosphorus compounds have been investigated with the results shown in Table XI. The P–F bond distances in the PX_3 and POX_3 molecules are all close to 1.52 Å., and in PF_5 and PF_3Cl_2 are 1.57 and 1.59 Å. An increase in bond length with coördination number occurs at coördination number five but not four. The observed lengths are all smaller than the covalent radius sum, 1.74 Å. The P–Cl bond lengths show similar variations but the decreases below the radius sum, 2.09 Å., are only from 0.04 to 0.08 Å.

The XPX bond angles increase by 4° in going from PX_3 (102°) to POX_3 (106°). The P–O bond, 1.56 Å. in length, is a double bond and stands at angles of 112° to the three P–X bonds.

In Si_2H_6 the Si–Si bond length is 2.32 ± 0.03 Å., within 0.02 Å. of the length in elementary silicon. In $SiHCl_3$ and Si_2Cl_6 the Si–Cl bonds are 2.01 ± 0.03 Å., and 2.00 ± 0.05 Å.; the same value has been observed in $SiCl_4$. This value is 0.15 Å. below the Si–Cl radius sum. The ClSiCl angle in $SiHCl_3$ is distorted from the tetrahedral value by less than 1°.

PRINCETON, N. J. RECEIVED MAY 31, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 650]

The Crystal Structure of Cesium Aurous Auric Chloride, $Cs_2AuAuCl_6$, and Cesium Argentous Auric Chloride, $Cs_2AgAuCl_6$

BY NORMAN ELLIOTT AND LINUS PAULING

The substances cesium aurous auric chloride, $Cs_2AuAuCl_6$, and cesium argentous auric chloride, $Cs_2AgAuCl_6$, discovered by Wells,[1] are of interest because of their jet black color, which has been ascribed[2] to the presence of the same element or two closely similar elements in two valence states.[3] In a preliminary investigation carried out some time ago[4] the substances were found to be diamagnetic, showing that they contain gold and silver in the univalent and trivalent oxidation states rather than the bivalent state. Powder photographs were also prepared with molybdenum X-radiation. These photographs, each with about fifteen lines, were interpreted as showing the crystals to have a structure closely related to the cubic perovskite type, the unit cube, with $a_0 \cong 5.33$ Å. for each substance, containing 1 Cs at 000, 1 (Au,Ag) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and 3 Cl at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$. Although the agreement between the intensities of X-ray reflection calculated for this structure and the observed values was good in general, there were one or two points of pronounced discrepancy for each substance, and the conclusion was reached that the structures are actually distorted somewhat from the ideal perovskite arrangement.

In the course of the investigation described below X-ray powder photographs were prepared with copper and iron radiation, giving greater dispersion, and it was found that cesium aurous auric chloride is tetragonal, and contains the complex ions $[AuCl_2]^-$, which is linear, and $[AuCl_4]^-$, which is square. A similar structure occurs for heat-treated samples of cesium argentous auric chloride, which also exists in a cubic modification involving some randomness in atomic arrangement.

The Determination of the Structure of Cesium Aurous Auric Chloride.—Powder photographs of cesium aurous auric chloride were prepared with copper $K\alpha$ radiation filtered through nickel and with iron K radiation, the camera radius being 5.005 cm. The photographs show about fifty well-defined lines, occurring as multiplets near

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[1] H. L. Wells, *Am. J. Sci.*, **3**, 315 (1922).

[2] H. L. Wells, *ibid.*, **3**, 417 (1922).

[3] Norman Elliott, *J. Chem. Phys.*, **2**, 298 (1934); magnetic data for $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$.

[4] Norman Elliott, *ibid.*, **2**, 419 (1934).

the angles expected for reflections from a cubic crystal. This suggests that the unit of structure of the crystal is closely related to a cube. The observation that the cubic line {200} occurs as a doublet, with the outer component twice as strong as the inner one, suggests that the crystal is tetragonal. This is supported by the multiplet structure of the other lines, the octahedral reflections being single, reflections with two indices equal double, and those with all three indices different triple.

The tetragonal unit of structure with $a_0 = 7.49 \pm 0.02$ Å. and $c_0 = 10.87 \pm 0.02$ Å. accounts for the presence of all observed lines.[5] The lattice can be taken as body-centered, no reflections with $h + k + l$ odd being observed. No classes of planes other than those indicated by the lattice are absent on the photographs. The space group is accordingly $D_{4h}^{17} - I4/mmm$ or one of its subgroups with the same unit. It was found possible with the assumption of holohedry to determine an atomic arrangement which accounts completely for the X-ray data; it is accordingly probable that the space group of the crystal is D_{4h}^{17}.

The density of the substance was determined by displacement of benzene to have the value 4.57 g./cc. This corresponds to 1.94 $Cs_2AuAuCl_6$ per unit, the calculated value of the density for two molecules per unit being 4.72 g./cc. There are 4 Cs, 2 Au^{I}, 2 Au^{III}, and 12 Cl atoms to be located. The sets of equivalent positions for D_{4h}^{17} are[6]

2a: $000,\ \frac{1}{2}\frac{1}{2}\frac{1}{2}$
2b: $00\frac{1}{2},\ \frac{1}{2}\frac{1}{2}0$
4c: $0\frac{1}{2}0,\ \frac{1}{2}00,\ \frac{1}{2}0\frac{1}{2},\ 0\frac{1}{2}\frac{1}{2}$
4d: $0\frac{1}{2}\frac{1}{4},\ \frac{1}{2}0\frac{1}{4},\ \frac{1}{2}0\frac{3}{4},\ 0\frac{1}{2}\frac{3}{4}$
4e: $00z,\ 00\bar{z},\ \frac{1}{2}\frac{1}{2}\frac{1}{2} + z,\ \frac{1}{2}\frac{1}{2}\frac{1}{2} - z$
8h: $xx0,\ \bar{x}\bar{x}0,\ x\bar{x}0,\ \bar{x}x0,\ \frac{1}{2} + x\ \frac{1}{2} + x\frac{1}{2},\ \frac{1}{2} - x\frac{1}{2} - x\frac{1}{2},$
$\frac{1}{2} + x\frac{1}{2} - x\frac{1}{2},\ \frac{1}{2} - x\frac{1}{2} + x\frac{1}{2}$

together with 8f, 8g, 8i, 8j, and positions for sets of 16 and 32 equivalent atoms. The photographs show that the atoms are in positions close to those of the perovskite arrangement. This can be achieved only in the following way

2 Au^{III} in 2a
2 Au^{I} in 2b
4 Cs in 4d
4 Cl in 4e, with $z \cong 1/4$
8 Cl in 8h, with $x \cong 1/4$

(The assignment of Au^{III} to 2b and Au^{I} to 2a leads to the same structures.)

The parameters x and z were evaluated from the intensity data given in Table I. The ob-

TABLE I

POWDER PHOTOGRAPHIC DATA FOR CESIUM AUROUS AURIC CHLORIDE, COPPER RADIATION, λ = 1.539 Å.

hkl	*d* obsd., Å.	*d* calcd., Å.	*I* obsd.	*I* calcd.
002	5.46	5.43	100	128
110	5.28	5.22	200	250
112 200	3.76	3.75	2400	2230
103	3.28	3.26	13	16
121	3.21	3.20	9	7
202	3.11	3.08	16	14
004	2.71	2.72	300	340
220	2.645	2.647	600	660
114 301	2.414	2.420 2.425	50	52
310 222	2.369	2.370 2.390	100	106
204	2.200	2.200	300	315
312	2.169	2.177	600	660
105	2.097	2.112	4	2
224	1.892	1.910	450	420
400	1.868	1.872	200	209
006	1.804	1.809	10	10
411 314	1.790	1.793 1.787	26	27
402 330	1.774	1.772 1.767	26	30
116	1.712	1.735	200	191
332 420	1.678	1.698 1.674	300	333
404	1.537	1.546	200	214
226 235	1.498	1.508 1.510	18	18
334 501	1.483	1.485 1.483	13	13
510	1.466	1.467	13	13
136	1.439	1.450	200	213
244	1.423	1.430	175	172
152	1.415	1.417	175	185
008	1.360	1.358	30	32
118 440	1.320	1.335 1.323	110	131
208 530	1.276	1.292 1.283	50	50
336	1.262	1.272	75	76
600 352	1.248	1.230 1.250	200	214
228	1.207	1.220	100	87
444 620	1.190	1.192 1.184	200	188
156	1.140	1.147	100	114
604	1.133	1.136	40	45
408	1.100	1.100	75	67
264 0·0·10	1.085	1.086 1.086	100	112
338		1.085		
446	1.069	1.074	40	36
1·1·10 550	1.059	1.063 1.060	50	46
710		1.060		
248	1.050	1.053	55	57
356	1.043	1.045	140	147
370 554 266	0.986	0.983 0.988	150	140
3·1·10 714		.955 .998 .988		
372 644 528	.966	.968 .971 .976	150	136
448 4·0·10	.951	.948 .950	50	55
800 538	.937	.937 .939	35	32
3·3·10 802	.927	.924 .925	50	50
556 608	.917	.917 .917	75	87

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[5] This unit is obtained from the small pseudo-cubic unit by rotating about c through 45° and doubling c_0. It corresponds to the dimensions a_0 = 5.28 Å., c_0 = 5.44 Å. for the small pseudo-unit, with axial ratio 1.03.

[6] "International Crystal Structure Tables."

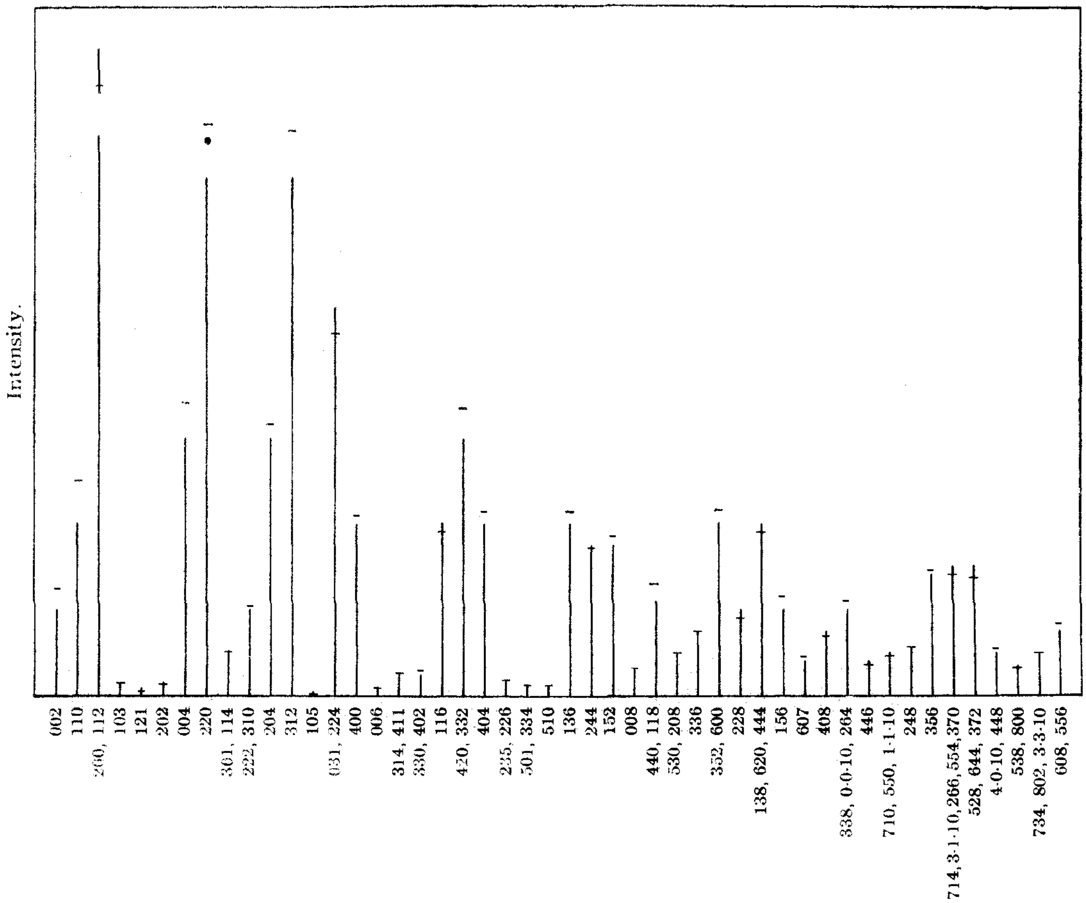

Fig. 1.—Calculated and observed intensities of reflections on powder photographs of cesium aurous auric chloride. The vertical lines show the observed values of the relative intensities, and the horizontal crossbars the calculated values.

served intensity values $I_{\text{obsd.}}$ were obtained from microphotometer records of the photographs and from visual estimates made on a series of photographs taken under identical conditions except for varied time of exposure. Intensity values were calculated with the equation

$$I_{\text{calcd.}} \sim \frac{1 + \cos^2\Theta}{\cos\Theta\,\sin^2\Theta}\,hF^2$$

in which h is the frequency factor and F the structure factor. F is given by the equation

$$F = f_{\text{Au}} + f_{\text{Au or Ag}}\cos 2\pi\frac{h+k}{2} + (-1)^{l/2}f_{\text{Cs}}\left\{\cos 2\pi\frac{h}{2} + \cos 2\pi\frac{k}{2}\right\} + 2f_{\text{Cl}}\left\{\cos 2\pi u(h+k) + \cos 2\pi u(h-k) + \cos 2\pi lv\right\}$$

Screening-constant f values were used,[7] without temperature correction. The parameter values obtained in this way, with especial emphasis on comparisons between adjacent lines on the photographs, are $x = 0.228 \pm 0.003$ and $z = 0.288 \pm 0.003$. The excellence of the agreement between observed and calculated intensities with these parameter values is shown in Table I and Fig. 1.

The Determination of the Structure of Cesium Argentous Auric Chloride.—Copper radiation photographs of samples of cesium argentous auric chloride which had been standing at room temperature since their preparation two to three years before were found to show only reflections (about thirty in number) which could be explained by a cubic unit of structure with $a_0 = 5.28 \pm 0.01$ Å., containing $\frac{1}{2}\,Cs_2AgAuCl_6$. The lines on the photographs are sharp, and the absence of fine structure comparable in magnitude with the clearly resolved CuKα_1-α_2 doublet for the wide-angle reflections shows that the approximation to a cubic structure is within 0.1%.

After the sample had been heated in a sealed evacuated tube at 350° for seventy-two hours and

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[7] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

cooled slowly to room temperature over a period of about five hours, it gave quite different X-ray photographs, the cubic lines being split into components similar to those for the aurous-auric compound, but with still greater separation. The photographs could be indexed completely on the basis of a tetragonal unit with $a_0 = 7.38 \pm 0.02$ Å. and $c_0 = 11.01 \pm 0.02$ Å. The unit is body-centered, and the observed reflections correspond to the space-group $D_{4h}^{17} - I4/mmm$ or one of its subgroups. The atomic arrangement described above for $Cs_2AuAuCl_6$, with Ag^I replacing Au^I and with the parameter values $x = 0.220 \pm 0.03$ and $z = 0.285 \pm 0.003$, accounts completely for the observed intensities, as shown in Table II and Fig. 2.

TABLE II

POWDER PHOTOGRAPHIC DATA FOR CESIUM ARGENTOUS AURIC CHLORIDE, COPPER RADIATION, $\lambda = 1.539$ Å.

hkl	*d* obsd., Å.	*d* calcd., Å.	*I* obsd.	*I* calcd.
101	6.12	6.10	40	50
002	5.50	5.50	25	26
110	5.24	5.22	50	46
112	3.77	3.77	600	637
200	3.685	3.690	250	270
103	3.275	3.280	50	49
202	3.055	3.054	50	44
004	2.750	2.750	170	163
220	2.601	2.598	260	290
114 301 123	2.436	2.430 2.393	30	29
		2.440		
222 310	2.329	2.350 2.325	18	15
204	2.206	2.203	150	136
105 132	2.145	2.107 2.140	265	270
321 303	2.050	2.05 2.06	30	36
224	1.896	1.890	250	220
006 400	1.842	1.830 1.835	125	105
215		1.825		
314 411	1.783	1.775 1.760	35	36
323		1.780		
330 402	1.735	1.732 1.740	135	145
116	1.678	1.690	25	21
332 420	1.655	1.652 1.644	160	170
206		1.640		
107 226	1.530	1.536 1.500	120	126
325 404		1.494 1.525		
316 510	1.444	1.440 1.442	120	117
217 424	1.415	1.418 1.412	100	105
512	1.400	1.395	100	107
415 433	1.382	1.384 1.380	25	20
503		1.381		
008	1.373	1.375	16	20
440	1.305	1.300	40	36
406 208	1.293	1.295 1.288	25	29
514 442	1.267	1.277 1.265	50	52
530 336		1.261 1.259		
532	1.232	1.229	60	55
600 426 435	1.220	1.225 1.223	60	62
505 228		1.222 1.222		
		1.215		
318 602	1.181	1.183 1.195	55	57
417 444		1.178 1.175		
620	1.170	1.167	55	56
622 516	1.138	1.140 1.135	75	74
534		1.145		
408	1.107	1.100	60	58
1·1·10	1.083	1.082	50	54
624	1.076	1.078	100	110
428	1.062	1.055	80	80
710 550	1.045	1.044 1.044	85	83
536		1.039		
640 712	1.026	1.024 1.025	120	130
3·1·10 518	1.003	0.994 0.997	90	100
556 716	0.910	.905 .905	100	110
628	.890	.888	90	85
5·1·10	.880	.875	90	85
804	.876	.873	50	45
5·3·10 558	.830	.836 .836	90	93
718		.836		

Discussion of the Structures.—The structure found for the tetragonal form of cesium argentous auric chloride (after heating at 350°) is shown in Fig. 3. The structure is closely related to the perovskite structure, the arrangement of the large cesium and chlorine atoms corresponding approximately to cubic closest packing, with the silver and gold atoms alternating in positions at the centers of chlorine octahedra. The distortion from the ideal perovskite structure is such as to show the presence of $[AgCl_2]^-$ and $[AuCl_4]^-$ complexes. Each silver atom has two closest chlorine atoms at the distance 2.36 Å., which is just the sum of the covalent radii for silver (with coördination number two) and chlorine;[8] the other four chlorine atoms of the distorted octahedron are 2.92 Å. from the silver atom. The $[Cl\text{-}Ag\text{-}Cl]^-$ complexes are linear, and are oriented parallel to the *c* axis of the crystal. Each gold atom has four nearest chlorine neighbors, arranged about it at the corners of a square, at the distance 2.30 Å., which is the sum of the covalent radii of trivalent gold and chlorine. The distance from the gold atom to the two other chlorine atoms in its neighborhood is 3.13 Å.

The linear configuration of the $[AgCl_2]^-$ complex ion is expected, in view of the analogy of the complex to the linear $[Ag(CN)_2]^-$ complex in the crystal $KAg(CN)_2$, studied by Hoard.[9] The square configuration of the chloroaurate ion $[AuCl_4]^-$ is similar to that observed[10] for the isoelectronic chloroplatinite ion $[PtCl_4]^=$, and is ex-

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[8] L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[9] J. L. Hoard, *ibid.*, **84**, 231 (1933).

[10] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

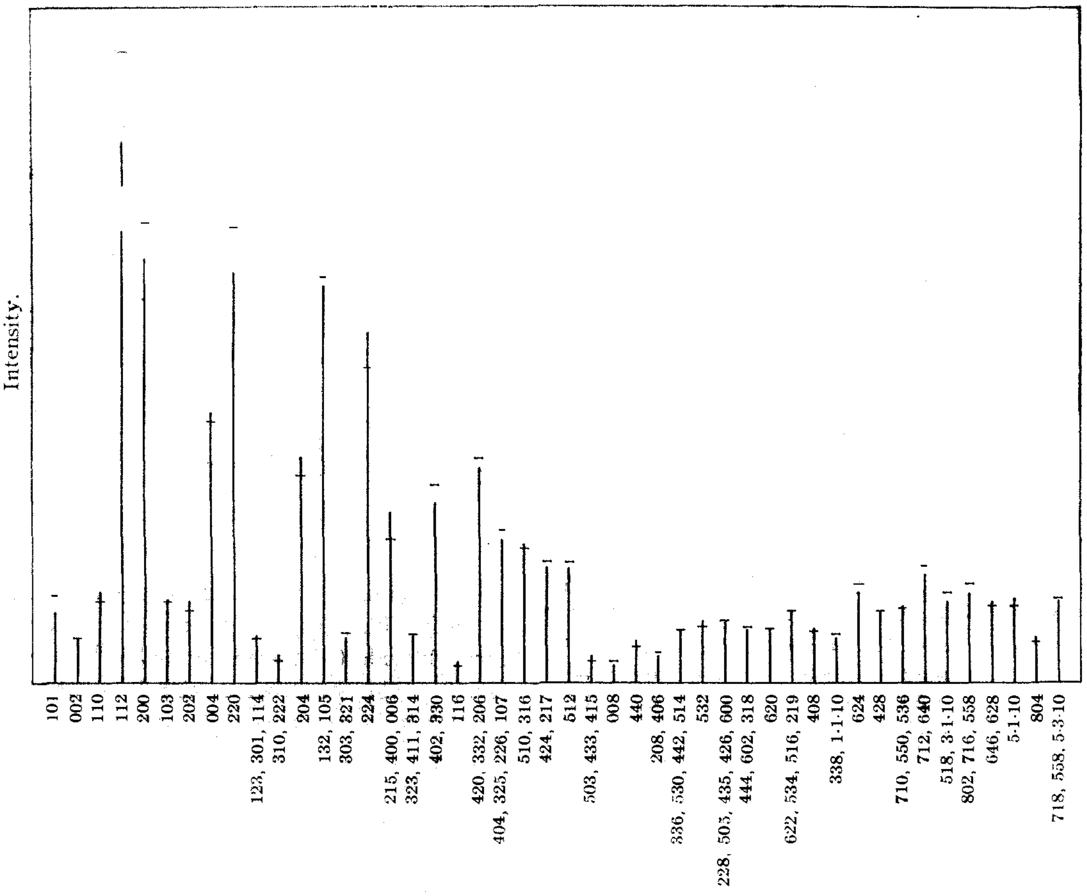

Fig. 2.—Calculated and observed intensities of reflections on powder photographs of the tetragonal modification of cesium argentous auric chloride. The vertical lines show the observed values of the relative intensities, and the horizontal crossbars the calculated values.

pected from quantum mechanical considerations.[11]

From these results it is seen that cesium argentous auric chloride is a compound of cesium dichloroargentite, $CsAgCl_2$, and cesium tetrachloroaurate, $CsAuCl_4$, with the stability of the compound to be attributed to the close packing of the pseudo-perovskite arrangement. The formula of the compound might well be written as $CsAgCl_2 \cdot CsAuCl_4$ or $Cs_2AgCl_2AuCl_4$.

The cubic modification of the substance must involve some randomness of atomic arrangement, since the X-ray data show that silver and gold atoms are randomly distributed in such a way as to give no reflections requiring a larger unit. It is probable that the crystal contains linear $[AgCl_2]^-$ complexes and square $[AuCl_4]^-$ complexes with random distribution and random orientation relative to its three orthogonal axes.

The structure found for cesium aurous auric chloride is similar to that of the tetragonal modification of the argentous auric compound. The structure involves linear $[AuCl_2]^-$ groups, with Au^{I}–Cl = 2.31 Å., and square $[AuCl_4]^-$ groups, with Au^{III}–Cl = 2.42 Å. The longer Au–Cl distances are Au^{I}–Cl = 2.98 Å. and Au^{III}–Cl = 3.13 Å.

There is some evidence that the structure found for this substance represents some deviation from the ideal structure. The axial ratio c/a for tetragonal $Cs_2AgAuCl_6$ is 1.491, whereas that found for $Cs_2AuAuCl_6$ is 1.452, which is considerably closer to the value for no distortion from the cubic perovskite structure, 1.414. It is to be expected, however, because of the very small difference in radii of silver and gold atoms, that the structures of the substances would be identical. The low value of the axial ratio of the aurous auric compound suggests that in the sample of this substance used for preparing the photographs the ideal structure with completely oriented complex ions had not been achieved,

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(11) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

and that some of the complexes were oriented in a random manner. Some further support for this idea is given by the value of the parameter x, which makes the Au^{III}–Cl distance 0.12 Å. larger than in the argentous auric compound; it seems likely that the change in intensities of the lines caused by the partial randomness of the structure has caused a small error in the parameter determination. An effort to test this hypothesis was made by heating the sample of $Cs_2AuAuCl_6$ to 350° for twenty-four hours; the photograph obtained of the sample after this treatment was identical with the earlier ones, however, showing that the partial randomness of structure, if it exists, represents the stable state at ordinary temperatures and not a metastable state.

An investigation of cesium aurous auric chloride and cesium argentous auric chloride has been reported recently by Ferrari,[12] leading to results different from ours. Ferrari reported the substances to give powder photographs (taken with iron radiation) corresponding to cubic units with $a_0 = 5.23$ Å. in each case, except that a few very faint lines were observed indicating the true units to have values of a_0 twice as large. He suggested a structure involving distortion from the ideal perovskite arrangement such as to give $[AuCl_6]^{=}$ complexes with the configuration of a regular octahedron. It seems to us improbable that this complex exists; and we believe that the samples studied by Ferrari represent random structures, as described above, with admixture of the tetragonal ordered modifications in sufficient amounts to give the faint extra lines which he observed.

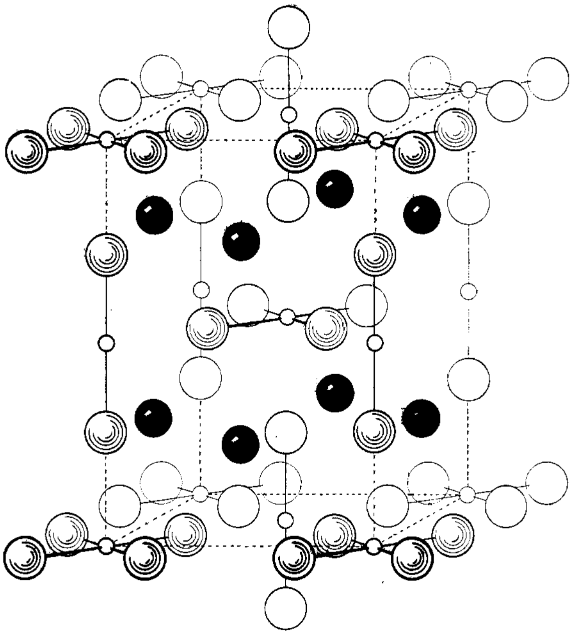

Fig. 3.—The atomic arrangement in tetragonal crystals of $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$. Large full circles represent cesium atoms, large open circles chlorine atoms, and small circles gold and silver atoms.

Summary

Crystals of tetragonal cesium aurous auric chloride have a body-centered unit of structure, with $a_0 = 7.49 \pm 0.02$ Å., and $c_0 = 10.87 \pm 0.02$ Å. containing 2 $Cs_2AuAuCl_6$. The space group is $D_{2h}^{17} - I4/mmm$, and the atoms are in the following positions of this space group: 2 Au^{III} in 2a; 2 Au^{I} in 2b; 4 Cs in 4d; 4 Cl in 4e, with $z = 0.288 \pm 0.003$; 8 Cl in 8h, with $x = 0.228 \pm 0.003$. Tetragonal cesium argentous auric chloride, $Cs_2AgAuCl_6$, has a similar unit, with $a_0 = 7.38 \pm 0.02$ Å., and $c_0 = 11.01 \pm 0.02$ Å., and a similar atomic arrangement (with Ag^{I} replacing Au^{I}), the parameter values being $z = 0.285 \pm 0.003$ and $x = 0.220 \pm 0.003$. These crystals contain linear $[AgCl_2]^-$ and $[AuCl_2]^-$ ions, similar to $[Ag(CN)_2]^-$, and square coplanar $[AuCl_4]^-$ ions, similar to the $[PdCl_4]^{=}$ and $[PtCl_4]^{=}$ ions.

In addition a metastable cubic modification of $Cs_2AgAuCl_6$, capable of conversion into the stable tetragonal modification by heating, was studied. The apparent unit of structure of this is cubic, with $a_0 = 5.28 \pm 0.01$ Å. It contains $\frac{1}{2}$ $Cs_2AgAuCl_6$, and appears to have the perovskite structure, with $\frac{1}{2}$(Ag + Au) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, Cs at 000, 3 Cl at approximately $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$. It is probable that the crystal contains $[AgCl_2]^-$ and $[AuCl_4]^-$ complexes with random distribution among the positions and orientations provided by the perovskite structure. Evidence for the existence of a similar modification of $Cs_2AuAuCl_6$ is given by the work of Ferrari.

PASADENA, CALIF. RECEIVED MAY 31, 1938

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(12) A. Ferrari, *Gazz. chim. ital.*, **67**, 94 (1937).