

The Crystal Structure and Magnetic Susceptibility of Caesium Argentous Auric Chloride, $\text{Cs}_2\text{AgAuCl}_6$, and Caesium Aurous Auric Chloride, $\text{Cs}_2\text{AuAuCl}_6$

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Citation: *The Journal of Chemical Physics* **2**, 419 (1934); doi: 10.1063/1.1749500

View online: <http://dx.doi.org/10.1063/1.1749500>

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The Crystal Structure and Magnetic Susceptibility of Caesium Argentous Auric Chloride, $\text{Cs}_2\text{AgAuCl}_6$, and Caesium Aurous Auric Chloride, $\text{Cs}_2\text{AuAuCl}_6$

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(Received April 30, 1934)

The triple salts $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$ have been investigated by means of magnetic susceptibility measurements and x-ray powder photographs in order to obtain information regarding the general nature of these compounds. Both compounds were found to be diamagnetic. X-ray powder-photographic data lead to a cubic structural unit with $a_0 = 5.33\text{\AA}$ for both crystals. The observed intensity values are in general agreement with the perovskite structure. Small discrepancies, however, suggest that the atomic arrangement varies slightly from the ideal perovskite structure. The detailed nature of the distortion was not determined. The bearing of these results on the valence type of the substances is discussed.

IN 1922 Wells¹ discovered an interesting series of triple salts when he attempted to prepare a caesium silver auric chloride, $\text{Cs}_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$, analogous to Pollard's² ammonium silver auric chloride, $(\text{NH}_4)_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$. The substance he obtained was a jet black, finely-divided powder with the stoichiometric formula $\text{Cs}_2\text{AgAuCl}_6$ and properties quite unlike those of Pollard's salt. Further investigation led to the discovery of several other triple salts having the formulae $\text{Cs}_2\text{AuAuCl}_6$, $\text{Cs}_4\text{CuAu}_2\text{Cl}_{12}$ and $\text{Cs}_4\text{HgAu}_2\text{Cl}_{12}$. All of these compounds crystallize isomorphously, as shown by solid solution formation, and have colors varying from black to light yellow.

In order to obtain information regarding the valence of the metals and the general nature of these compounds, I have investigated two of them, $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$, at the suggestion of Professor Linus Pauling, by means of x-ray powder photographs and magnetic susceptibility measurements. The results of the study are contained in this paper.

We can formulate four reasonable structure types for these salts; (1) Each heavy metal atom may be bivalent and not attached by covalent bonds to other heavy metal atoms. (2) Both heavy metal atoms may be bivalent, the two being joined by a covalent bond forming the group $\text{Ag} : \text{Au}$ in the case of $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Au} : \text{Au}$ in the case of $\text{Cs}_2\text{AuAuCl}_6$. (3) One heavy metal atom may be univalent and the other trivalent. (4) Each heavy metal atom may

resonate between a univalent and a trivalent state.

If the first suggested structure were correct, the compounds would contain groups with an odd number of electrons and hence be paramagnetic. A measurement of their specific magnetic susceptibilities was therefore made by the Gouy method. Both compounds proved to be diamagnetic. The value $\chi = -0.33 \times 10^{-6}$ c.g.s.m. was found for $\text{Cs}_2\text{AgAuCl}_6$ and $\chi = -0.25 \times 10^{-6}$ c.g.s.m. for $\text{Cs}_2\text{AuAuCl}_6$. The results eliminate a structure with each heavy metal atom bivalent and separate, and we must consider the three remaining structure types.

X-ray powder photographs of $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$ were prepared by using molybdenum radiation filtered through zirconia. These were not entirely satisfactory, the lines being rather faint and difficult to measure. However, it was possible to measure about fifteen lines on each photograph. The regular spacing of the lines suggested at once that the crystals are cubic, and, on assigning indices, all the lines could be accounted for on the basis of cubic units with $a_0 = 5.33 \pm 0.02\text{\AA}$ for both $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$. The lines which occur, together with their estimated intensities, are shown in Figs. 1 and 2. No lines occurred requiring a larger unit.

These cubic units contain only one-half of a stoichiometric molecule, $\text{Cs}_2\text{AgAuCl}_6$ or $\text{Cs}_2\text{AuAuCl}_6$, as estimated from the atomic volumes of the constituent atoms. The calculated values of the density are 4.266 g/cm^3 and 4.753 g/cm^3 , respectively, for $\text{Cs}_2\text{AgAuCl}_6$ and $\text{Cs}_2\text{AuAuCl}_6$.

¹ Wells, *Am. J. Sci.* **3**, 315 (1922).

² Pollard, *Am. J. Sci.* **3**, 257 (1922).

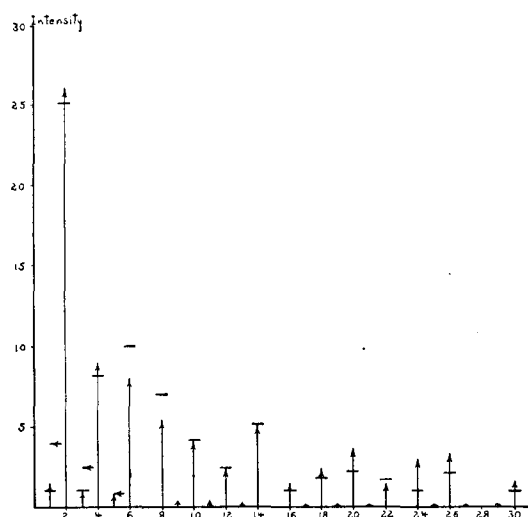


FIG. 1. Powder-photographic x-ray data for $\text{Cs}_2\text{AgAuCl}_6$. Relative intensities calculated for arrangement *A* are shown by vertical arrows. Horizontal arrows indicate the relative intensities calculated for arrangement *B*. Arrangements *A* and *B* give the same intensities for those lines for which $h^2+k^2+l^2$ is even. Horizontal bars show the observed intensity values.

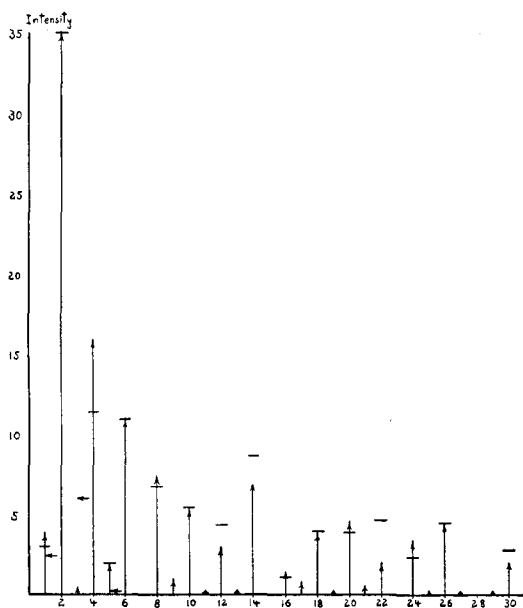


FIG. 2. Powder-photographic x-ray data for $\text{Cs}_2\text{AuAuCl}_6$. The symbols are the same as for Fig. 1.

No directly measured density values are available for comparison. If these are the true units of structure, the silver compound must contain Ag and Au atoms distributed at random in equivalent positions. We shall first proceed on

the assumption that units with $a_0 = 5.33\text{\AA}$ are the true units of structure.

The theory of space groups provides only two ways of arranging 1 M ($M = \text{Ag}, \text{Au}$), 1 Cs, and 3 Cl in a cubic unit of structure. These are the following arrangements *A* and *B*.

Arrangement <i>A</i> :	Arrangement <i>B</i> :
Cs at 000	M at 000
M at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Cs at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
Cl at $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$	Cl at $0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$

The only difference in these forms is the exchange in position of Cs and M.

With the f -values of Pauling and Sherman,³ values of the intensity of reflection from various planes for these two arrangements were calculated according to the usual intensity formula, including the Lorentz, polarization, and frequency factors. Visual estimates of the intensities were made and compared with the theoretical intensities. The results are shown in Figs. 1 and 2. The positions of the vertical arrowheads give the relative calculated intensities for arrangement *A*, and those of the horizontal arrowheads show the values for arrangement *B*. For $h^2+k^2+l^2$ even, both arrangements have the same values. Horizontal bars indicate observed intensities. It is seen that arrangement *B* is in pronounced disagreement with experiment even for simple planes. Thus (111), $h^2+k^2+l^2 = 3$, for $\text{Cs}_2\text{AuAuCl}_6$ is not observed, though calculated for arrangement *B* to be over ten times as strong as (210), $h^2+k^2+l^2 = 5$. Hence the atomic arrangement is *A*. This is known as the perovskite structure. It may be described as a cubic close-packed arrangement of the large atoms Cs and 3 Cl with the smaller metal atoms, *M*, introduced at the centers of octahedra with six chlorine atoms for corners, each chlorine atom forming a corner of two such octahedra.

The agreement in the observed and calculated intensities is sufficiently good to show that this arrangement must be the actual structure of these crystals or very close to it. Therefore, structure type 2 containing Ag : Au and Au : Au complexes is not correct.

If the perovskite structure were the actual structure of these compounds, equivalence of all the gold atoms would be required in $\text{Cs}_2\text{AuAuCl}_6$;

³ Pauling and Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

that is, structure type 4, involving resonance of each metal atom between the univalent and trivalent state, would be correct. However, there are some small discrepancies. The calculated and observed intensities of the lines $h^2+k^2+l^2=24$ in Fig. 1 and $h^2+k^2+l^2=22$ in Fig. 2 show definite disagreement when compared with the values of neighboring lines. These discrepancies are sufficient to eliminate the perovskite structure and the valence type 4. It is

probable that the structures are based on a larger unit and that the atomic arrangement is a distortion of the perovskite structure so that the six chlorine atoms are brought closer to the trivalent gold atom (valence type 3) than to the univalent gold or silver atom. The data are not sufficiently extensive to permit the detailed discussion of this point. We hope to continue the investigation and to determine completely the structure of these crystals.

The Line Absorption Spectrum of Crystalline $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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(Received March 24, 1934)

The line absorption spectrum of chrome alum has been photographed at five temperatures from 85° to 14°K. The variation with temperature of the intensities of certain of these lines suggests the existence of one or more excited lower levels. At 14°K a new group of faint, sharp lines appears near 4500Å. A general discussion of the nature of energy levels in solids is presented and the possible energy states which could give rise to the observed lines are examined theoretically.

IT is commonly known that the outermost electrons in the atoms of a substance determine most of its chemical and many of its physical properties. Therefore, given a reasonably complete knowledge of those energy states of the substance which involve the outer electrons, one should be able to predict most of its properties. Conversely every property of the substance should give some information concerning its energy levels. Though the work of correlation is as yet far from being fully developed, considerable progress has been made. Thus, for example, the energy states of many monatomic and diatomic gases have been related to such properties as heats of activation and dissociation, entropy, magnetic susceptibility and the like. In the case of polyatomic gases and solids progress has been slower due to the greater complexities of the problem but now that the nature of the difficulties is better understood, more rapid headway is being made.

With gases a study of the spectra both in emission and absorption has provided by far the

most direct and fruitful method of determining energy states. Unfortunately, in the case of most solids the emission spectra are not characteristic and the absorption spectra at room temperature consist usually of wide structureless bands showing none of the detail which is so necessary if an analysis is to be made. Nevertheless, if particular compounds are chosen, and especially if they are cooled to very low temperatures, sharp absorption lines can be obtained and the energy levels may be deduced as in the case of gases.

Up to the present most of the work on the spectra of solids has been done with compounds of the rare earth metals, chiefly because they are rich in lines which become sharp at higher temperatures than do the lines of commoner compounds. The reasons for this have been discussed in a previous paper.² The chief disadvantage of working with the rare earth compounds is that their properties are not as well known as might be desired, mainly due to the fact that they are not available in any quantity for experimental purposes. Moreover, the spectra

¹ DuPont Fellow in Chemistry 1932-33; Shell Research Fellow in Chemistry 1933-34.

² Spedding and Nutting, *J. Am. Chem. Soc.* **55**, 496 (1933).