

## The Crystal Structure of Cesium Enneachlordithalliate, $\text{Cs}_3\text{Ti}_2\text{Cl}_9$

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## The Crystal Structure of Cesium Enneachlordithalliate, $\text{Cs}_3\text{Ti}_2\text{Cl}_9$

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$\text{Cs}_3\text{Ti}_2\text{Cl}_9$  is shown to possess a rhombohedral unit of structure with  $a_0 = 9.58\text{\AA}$ ,  $\alpha = 83^\circ 48'$ , containing two molecules. The crystals exhibit extensive and quite perfect  $60^\circ$  twinning on the basal plane, so that most specimens simulate complete sixfold symmetry, but when this is taken into consideration, a structure based upon  $D_{3d} - R\bar{3}c$  accounts well for observed intensity data. The

structure may be described conveniently as an aggregate of  $\text{Cs}^+$  and  $\text{Ti}_2\text{Cl}_6^{-3}$  groups packed together in such manner that all large atoms fit into an approximately closest-packed arrangement. The  $\text{Ti}_2\text{Cl}_6^{-3}$  group is considered to be a covalent complex. The derived structure is compared with the known structures of  $\text{Cs}_3\text{As}_2\text{Cl}_9$  and  $\text{KMgF}_3$ .

### INTRODUCTION

IN the course of a search for compounds of trivalent thallium which would lend themselves to structural investigations, we have examined cesium enneachlordithalliate,  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ , first prepared by Pratt.<sup>1</sup> While this compound can scarcely be considered remarkable for the simplicity of its structure, it has proved more amenable to treatment than other thallic salts, which seem in general to crystallize with highly complex structures. We have determined from x-ray data the atomic arrangement existing within crystals of  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ , leading to some interesting results with regard to the coordination and bonding properties of  $\text{Ti}^{\text{III}}$  in addition to accounting for the stability of crystals of this formula.

### DETERMINATION OF THE STRUCTURE

In accordance with the results of Pratt, we were able to prepare clear stable crystals of  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  with two different habits: Very thin

uniaxial hexagonal plates and hexagonal prisms, depending upon the relative concentrations of  $\text{CsCl}$  and  $\text{TiCl}_3$  in the solutions from which the compound crystallized. The compound is highly absorbing, but as the plates were less than 0.1 mm in thickness, it was possible to get x-ray data from various types of transmission photographs. We have for the most part worked with the plates, although such data as were obtained for the prisms are in agreement with the derived structure.

Most of our Laue photographs, prepared with the incident beam exactly perpendicular to the basal plane, show no deviation from the symmetry of  $D_{6h}$ . In two cases, however, we found exceedingly thin crystals which gave excellent Laue photographs showing only the symmetry of  $D_{3d}$ . With either type of crystal the smallest hexagonal unit which accounts for the numerous data of our Laue and oscillation photographs is one with  $a_0 = 12.8\text{\AA}$ ,  $c_0 = 18.30\text{\AA}$ . Our value of the axial ratio,  $c_0/a_0 = 1.43$ , agrees within the limit of error with the crystallographic value,  $\sqrt{3} \cdot 0.8257 = 1.430$ .

That we have to deal with extensive and quite

<sup>1</sup>Pratt, *Am. J. Sci.* **149**, 397 (1895). See also Groth, *Chem. Kryst.* Engelmann, Leipzig 1, 437 (1908).

perfect twinning on the basal plane is rendered highly probable by the following considerations: We find that the sixfold symmetry of the one type of photograph can be completely reproduced both as to the positions and relative intensities of all spots by the simple process of superposition of two of the threefold patterns after one of them has been rotated through  $60^\circ$  about  $c$ . We simply average the intensities of  $\{HI \cdot L\}$  and  $\{HI \cdot \bar{L}\}$  of the threefold pattern to get the corresponding intensities of either form in the sixfold pattern.

All of the data of the threefold photographs, moreover, are accounted for by the rhombohedral unit with one-third the volume of the hexagonal unit. This unit, which has  $a_0 = 9.58 \pm 0.04\text{\AA}$ ,  $\alpha = 83^\circ 48' \pm 15'$ , contains  $2\text{Cs}_3\text{Ti}_2\text{Cl}_9$  and leads to a calculated density of  $4.32\text{ g/cc}$ , is to be accepted as the true one.

The regular vanishings<sup>2</sup> observed are  $\{hhl\}$  with  $l$  odd. The space-groups accounting for these are  $C_{3v}^6 - R\bar{3}c$  and  $D_{3d}^6 - R\bar{3}c$ .

The crystal radius<sup>3</sup> for coordination number six of  $\text{Cl}^-$  is  $1.81\text{\AA}$ . A hexagonal unit of 6 layers made up of 72 spheres of this size in closest-packing would have  $a_0 = 12.54\text{\AA}$ ,  $c_0 = 17.72\text{\AA}$ . Our hexagonal cell contains 54  $\text{Cl}^-$  and 18  $\text{Cs}^+$ , the latter with radius  $1.69\text{\AA}$  only slightly smaller than that of  $\text{Cl}^-$ . As we find  $a_0 = 12.8\text{\AA}$ ,  $c_0 = 18.3\text{\AA}$ , it appears highly probable that cesium and chlorine ions are to be found in a nearly closest-packed arrangement in  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ . Remembering that within this hexagonal cell we must have the rhombohedral lattice points at  $\frac{2}{3}\frac{1}{3}\frac{1}{3}$  and  $\frac{1}{3}\frac{2}{3}\frac{2}{3}$ , and adding the quite reasonable assumption that two cesium ions are not to be in contact with each other, we are led to a unique distribution (excepting small distortions) of the 18  $\text{Cs}^+$  and 54  $\text{Cl}^-$  within the hexagonal cell. We may conveniently symbolize this ideal arrangement, which is made up of identical layers, as follows: Let  $A$  represent a closest-packed layer containing 3 Cs and 9 Cl with Cs at  $0\frac{1}{3}, \frac{1}{3}\frac{1}{3}, \frac{2}{3}\frac{2}{3}$ ,  $B$  a similar layer with Cs at  $0\frac{2}{3}, \frac{2}{3}\frac{2}{3}, \frac{1}{3}\frac{1}{3}$ . The sequence of layers along  $c$  is then  $ABABAB \dots$ , corresponding to hexagonal closest-packing (see Fig. 1).

If thallium and cesium atoms are not to be in

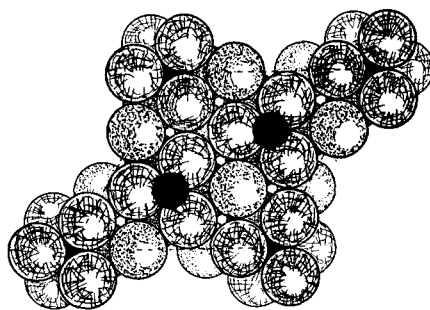


FIG. 1. Packing drawing of two layers parallel to  $(00 \cdot 1)$  showing the undistorted closest-packed structure. Cesium may be distinguished from chlorine atoms by the type of shading.

contact, and the resulting structure is to possess rhombohedral symmetry, the 12 Ti are to be placed in approximate positions given by  $Z \cong \pm 1/12$  and  $\pm 5/12$  relative to each rhombohedral lattice point. Each Ti is then surrounded by 6 Cl. This undistorted or ideal structure can be developed from either  $C_{3v}^6$  or  $D_{3d}^6$ , in both cases with highly specialized parameter values. A careful study of the structure reveals no reason for eliminating the centers of symmetry and twofold axes, and we accordingly assume  $D_{3d}^6$  to be the correct space-group.

Using the rhombohedral notation of Wyckoff<sup>4</sup> proper to  $D_{3d}^6$ , we have the following assignment of positions: 4 Ti in  $4c$ ,  $uuu$ , etc. 6 Cs in  $6e$ ,  $v\bar{v}o$ , etc. 6 Cl in  $6e$ ,  $w\bar{w}o$ , etc. 12 Cl in  $12f$ ,  $xyz$ , etc. We expect  $u \cong 1/12$ ,  $v \cong \frac{2}{3}$ ,  $w \cong \frac{1}{6}$ ,  $x \cong \frac{1}{3}$ ,  $y \cong \frac{1}{6}$ ,  $z \cong 0$ .

The basal plane reflections deserve special consideration since they involve but two parameters. Only the even orders appear of course, for which

$$S_{(nnn)} = 4f_{\text{Ti}} \cos 6\pi nu + 6(f_{\text{Cs}} + f_{\text{Cl}}) + 12f_{\text{Cl}} \cos 2\pi n(x+y+z).$$

Intensities were calculated from the formula

$$I = C \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} n |S|^2.$$

The  $f$ -values of Pauling and Sherman<sup>5</sup> are used

<sup>2</sup> Astbury and Yardley, *Tabulated Data for the Examination of the 230 Space-Groups by Homogeneous X-Rays*, Phil. Trans. **224**, 221 (1924).

<sup>3</sup> Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927).

<sup>4</sup> R. W. G. Wyckoff, *The Analytical Expression of the Results of the Theory of Space-Groups*, 2nd Ed., p. 157. Carnegie Institution of Washington, 1930.

<sup>5</sup> Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

throughout this paper. No temperature factor is included. The extremely thin plate-like but very strongly absorbing crystals used for these photographs were so small as always to be completely bathed in radiation; the effective cross section taken from the beam was proportional therefore to  $\sin \theta$ , or to  $n$ .

A comparison of calculated with observed intensities for the first four orders from (111) with  $u=0.098$ ,  $x+y+z=\frac{1}{2}$  (the value for undistorted closest-packing) is given in Table I.

TABLE I. Comparison of calculated with observed intensities for (nnn) reflections.  $u=0.098$ ,  $x+y+z=\frac{1}{2}$ .

$n$	Observed intensity	Calculated intensity*
2	16	16
4	24	29
6	8	18
8	1	4

\* Temperature factor not included.

The agreement is quite satisfactory, but is seriously impaired if the value of  $u$  be changed by more than about 0.002. A small deviation of the chlorine parameter ( $x+y+z=3Z$ , where  $Z$  is the parameter along the hexagonal axis) from the ideal value  $\frac{1}{2}$  is to be expected, although exerting a nearly inappreciable effect upon the calculated intensities.

Table II contains a comparison of calculated with observed intensities for a group of reflections which do not depend upon the thallium parameter using the closest-packed values for cesium and chlorine. The technique here employed was that of transmission through a thin plate which was completely bathed in radiation, and the formula used in calculation was similar in form to that for

TABLE II. Comparison of calculated with observed intensities for reflections independent of  $u$ .  $v=\frac{2}{3}$ ,  $x=\frac{1}{3}$ ,  $y=\frac{1}{6}$ ,  $z=0$ ,  $w=\frac{1}{6}$ .

(hkl)	Intensity		(hkl)	Intensity	
	Obs.	Calc.*		Obs.	Calc.*
101	24	24	633	5	9.7
202	0	0.04	844	3	13.
303	16	32	10.5.5	0	2.5
404	0	0.09	415	4	10
505	<1	1.5	527	1.5	4.8
606	6	18	213	5	5.6
211	48	67	325	1	1.2
422	36	54	314	2	2.5

\* Temperature factor not included.

(nnn) reflections except for the omission of the factor  $n$ . The intensity comparisons of Table II provide strong evidence that we have arrived at essentially the correct structural type, although small deviations from the ideal parameter values are probably indicated. A change of  $\pm 0.01$ – $0.02$  from the value  $\frac{2}{3}$  of the cesium parameter, which affects the calculated intensities quite appreciably, is certainly dimensionally admissible. A change in either direction decreases somewhat the calculated intensities of all the reflections with appreciable structure factors of Table II excepting the last three, which are increased. We have not been able to decide in which direction the parameter value should be moved, so that we are giving interatomic distances in Table III for  $v=\frac{2}{3}$ .

TABLE III. Interatomic distances in  $\text{Cs}_2\text{Tl}_2\text{Cl}_6$ .

Atom	Neigh- bors	Separation	Atom	Neigh- bors	Separation
Tl	3 Cl <sub>I</sub>	2.66Å	Cl <sub>I</sub>	2 Cl <sub>I</sub>	3.39Å
Tl	3 Cl <sub>II</sub>	2.54	Cl <sub>I</sub>	2 Cl <sub>II</sub>	3.77
Cs	2 Cl <sub>I</sub>	3.70	Cl <sub>I</sub>	2 Cl <sub>II</sub>	3.75
Cs	2 Cl <sub>I</sub>	3.83	Cl <sub>I</sub>	2 Cl <sub>II</sub>	3.80
Cs	2 Cl <sub>II</sub>	3.76	Cl <sub>II</sub>	2 Cl <sub>II</sub>	3.78
Cs	2 Cl <sub>II</sub>	3.62	Cl <sub>II</sub>	2 Cl <sub>II</sub>	3.68
Cs	4 Cl <sub>II</sub>	3.74	Cl <sub>II</sub>	1 Cl <sub>II</sub>	3.68

The intensity data of Tables I and II were obtained from twinned crystals, but include only planes which possess structure factors independent of the type of twinning postulated.

## DISCUSSION OF THE STRUCTURE

A diagram illustrating the closest-packing of the cesium and chlorine atoms of two layers is shown in Fig. 1. Disregarding the thallium atoms, which are introduced in positions of rhombohedral symmetry, the fundamental translation along  $c$  of the closest-packed arrangement is just the thickness of two layers. As placed in the derived structure each Tl is surrounded by 6 Cl, but pairs of  $\text{TlCl}_6$  octahedra share faces to give  $\text{Tl}_2\text{Cl}_9$  groups. In the two molecule rhombohedral unit, we find a  $\text{Tl}_2\text{Cl}_9$  group of symmetry  $D_3$  at the origin and an equivalent group at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . These groups fit together along the threefold axes to form closest-packed columns, which are bound together by cesium ions in such manner as

to complete the closest-packing in three dimensions.

The radius ratio of the univalent radii,<sup>6</sup>  $r_{\text{Tl}^{+3}}/r_{\text{Cl}^{-}}=0.635$ , indicates that thallic thallium should show a coordination number of six (or perhaps more) toward chloride ion if the ionic model be a good approximation. The mere existence in this structure of the complex  $\text{Tl}_2\text{Cl}_9$  groups, in which  $\text{TlCl}_6$  octahedra share faces, is enough to show that the ionic model is unsatisfactory. It seems very improbable that a solution containing a mixture of truly ionic  $\text{Tl}^{3+}$ ,  $\text{Cl}^{-}$  and  $\text{Cs}^{+}$  (or ionic complexes) would give rise to crystals in which the thallium atoms are placed so near together in pairs, although crystals of this composition have actually a rather wide range of stability. We conclude therefore that the  $\text{Tl}_2\text{Cl}_9$  ion is essentially a covalent complex, and we find that an assignment of parameter values for chlorine differing but little from the ideal set together with the experimentally determined value for the thallium parameter give rise to interatomic distances in agreement with this view. With  $x=0.336$ ,  $y=0.176$ ,  $z=-0.005$  and  $w=0.153$ , we find  $\text{Tl}-\text{Cl}_\text{I}=2.66\text{\AA}$ ,  $\text{Tl}-\text{Cl}_\text{II}=2.54\text{\AA}$  and the  $\text{Cl}-\text{Cl}$  separations given in Table III. These  $\text{Tl}-\text{Cl}$  separations may be compared with the sum of the ionic radii,<sup>7</sup>  $2.76\text{\AA}$ ,

and the covalent bond distance,  $2.55\text{\AA}$ , obtained by adding the "octahedral" radius<sup>8</sup> of  $\text{Tl}^{\text{III}}$  to the covalent radius of chlorine (for which the "tetrahedral" and "normal" radii are equal). Because of the mutual repulsions of the (somewhat ionic) thallium atoms within the complex and to the less favorable bond angle,  $79^\circ 20'$  as against  $96^\circ 20'$ , the  $\text{Tl}-\text{Cl}$  bonds involving the shared chlorine atoms are somewhat weaker than the others. The value of  $w$  is assumed so as to make the shared face of the complex have somewhat shortened edges, in analogy to what is observed in truly ionic crystals. A change in this value of  $w$  together with a possible small change from the value of the thallium parameter as determined would modify slightly the bond angle and interatomic distance for  $\text{Tl}-\text{Cl}_\text{I}$ .

The structure of  $\text{Cs}_3\text{Tl}_2\text{Cl}_9$  is related to the structures of  $\text{Cs}_3\text{As}_2\text{Cl}_9$ <sup>9</sup> and  $\text{KMgF}_3$  by virtue of the fact that all of them are based upon closest-packing of the large cations and anions, which occur in the ratio one to three. Characteristic molecular aggregates are, however, very different within the three structures, for we find, respectively,  $\text{Tl}_2\text{Cl}_9^{-3}$ ,  $\text{AsCl}_3$  and  $\text{MgF}_6^{-4}$  occurring as rather well-defined groups.

We are indebted to Professor Linus Pauling for invaluable suggestions during the course of this work.

<sup>6</sup> Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927). Ibid. **51**, 1010 (1929).

<sup>7</sup> Linus Pauling, J. Am. Chem. Soc. **49**, 765 (1927).

<sup>8</sup> Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).

<sup>9</sup> Hoard and Goldstein, J. Chem. Phys. **3**, 117 (1935).