

Crystal Structure and Phase Transition of Cesium Trichlorostannate(II)

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Cesium trichlorostannate(II), CsSnCl_3 , crystallizes at room temperature as monoclinic crystals of space group No. 14, $P2_1/n$ with $a=16.10 \text{ \AA}$, $b=7.425 \text{ \AA}$, $c=5.748 \text{ \AA}$, $\beta=93^\circ.2$. There are four CsSnCl_3 units per unit cell. Pyramidal trichlorostannate(II) groups are packed with cesium atoms into a layer structure with atoms near planes of $z=\pm\frac{1}{4}$. The crystals are frequently twinned with (100) as twin plane. An irreversible phase transition occurs near 117°C . Two cubic phases seem to be present in the high temperature form. The structure of the low temperature form was determined from a twinned crystal using automatically collected counter data. Refinement was carried out by a full-matrix least-squares method to an R -value of 11%. The structures of the high temperature forms were not determined for lack of single crystal material.

According to the one electron approximation a number of elements may exist in a valence state where their outer electrons have $4s^2$ or $5s^2$ configurations. Divalent germanium and divalent tin compounds fall within this classification. The structures of cesium-trichlorogermanate(II)¹ and of pilocarpinium-trichlorogermanate(II)² have been studied in this laboratory and the crystal structure of CsSnCl_3 was investigated for comparing Ge(II)- and Sn(II)-compounds. CsGeCl_3 and CsSnCl_3 are not isostructural and neither of them is isostructural with CsPbCl_3 .³ Differential thermal analysis in conjunction with microscopic investigations and with X-ray investigations at various temperatures showed that CsSnCl_3 exhibits a phase transformation near 117°C . The transformation is irreversible in contradistinction to the phase transformations observed with the analogous germanium(II) and lead(II) compounds. It is even questionable if the high temperature form of CsSnCl_3 can be described as a single compound.

EXPERIMENTAL

Chemistry. A hot solution of 300 mg CsCl dissolved in 1 ml glycerol was mixed with another hot solution containing 400 mg $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ in 1 ml glycerol. Needle-shaped colourless crystals were obtained at slow cooling of the mixture.

Analysis. Found: Cl 28.4; Sn 34.2. Calc. for CsSnCl_3 ; Cl 29.7; Sn 33.2.

X-Ray technique. Unit cell and space group were established from Weissenberg, precession, and retigraph films using Co- and Cu-radiations. A Guinier powder diagram did not show lines from Cs_2SnCl_6 . The powder diagram was indexed on the basis of the cell constants obtained from single crystal measurements. A crystal of dimensions $0.5 \times 1.0 \times 5 \text{ mm}^3$ was mounted along the needle direction which was the c -axis and intensities were measured with a linear diffractometer of the Arndt and Phillips⁴ design. Mo-radiation was employed. Balanced filters SrO , ZrO_2 in conjunction with a pulse-height analyser and a scintillation counter insured simulation of a monochromatic $\text{MoK}\alpha$ -beam. The intensities measured were symmetry related in pairs.

The diffractometer data were reduced to relative structure factors using an ALGOL program⁵ which evaluated intensities, calculated averages over symmetry related reflexions, L_p -corrections, and standard deviations. 2000 independent reflexions were measured. 1700 of these had an intensity greater than twice their standard deviations estimated as the square root of the total number of counts in an intensity measurement.

Powder photographs were obtained using a Guinier-de Wolff camera. A sample holder, which could be heated electrically to 200°C was employed for making exposures at various temperatures. A precession camera was used for taking photographs at 120°C by blowing a stream of warm air over the crystal. Precession photographs at that temperature have the appearance of powder photographs although orientation effects are discernible.

CRYSTAL DATA

Crystal system: monoclinic, $a=16.10 \text{ \AA}$, $b=7.425 \text{ \AA}$, $c=5.748 \text{ \AA}$, $\beta=93^\circ.2$, space group $P2_1/n$ (No. 14). Density measured (pycnometer): 3.45 g/cm^3 , calc. 3.46 g/cm^3 . Four CsSnCl_3 units per unit cell.

The coordinates and their estimated standard deviations are given in Table 1. Thermal parameters are given in Table 2 and interatomic distances in Table 3. Table 4 gives observed and calculated structure factors. The atomic scattering factors used were taken from *International Tables*, Vol. III.

Table 1. Atomic coordinates as fractions of cell edges with their standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cs	0.1534	(1)	0.5002	(3)	0.7504	(3)
Sn	0.3917	(1)	0.4713	(3)	0.2610	(3)
Cl(1)	0.2532	(4)	0.3134	(9)	0.2705	(11)
Cl(2)	0.4565	(5)	0.1660	(11)	0.2673	(13)
Cl(3)	0.3784	(6)	0.4763	(12)	0.8165	(12)

Table 2. Anisotropic temperature factor parameters U_{ij} in $\text{\AA}^2 \times 10^3$ with standard deviations.

Atom	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{33}	$\sigma(U_{33})$	U_{12}	$\sigma(U_{12})$	U_{13}	$\sigma(U_{13})$	U_{23}	$\sigma(U_{23})$
Cs	38	(1)	35	(1)	46	(1)	2	(1)	0	(0)	-11	(2)
Sn	35	(1)	23	(1)	26	(1)	-4	(1)	0	(0)	2	(1)
Cl(1)	35	(3)	24	(3)	38	(3)	-4	(3)	2	(1)	4	(6)
Cl(2)	34	(4)	42	(4)	56	(4)	15	(3)	2	(2)	3	(8)
Cl(3)	60	(6)	44	(4)	35	(3)	-4	(4)	0	(2)	26	(7)

Table 3. Interatomic distances, l , in Å and angles, v , in degrees with standard deviations.

Atoms	l	$\sigma(l)$	
Sn—Cl(2)	2.50	(1)	
Sn—Cl(1)	2.52	(1)	
Sn—Cl(3) ₁	2.55	(1)	
Sn—Cl(3)	3.21	(1)	
Sn—Cl(1) ₂	3.45	(1)	
Sn—Cl(3) ₃	3.77	(1)	
Cs—Cl(2) ₄	3.41	(1)	
Cs—Cl(1)	3.55	(1)	
Cs—Cl(2) ₅	3.59	(1)	
Cs—Cl(3) ₅	3.59	(1)	
Cs—Cl(1) ₆	3.59	(1)	
Cs—Cl(2) ₂	3.59	(1)	
Cs—Cl(3)	3.63	(1)	
Cs—Cl(1) ₅	3.85	(1)	
Cs—Cl(3) ₇	3.94	(1)	
Cs—Cl(1) ₂	4.14	(1)	
Cs—Sn ₅	4.569	(1)	
	v	$\sigma(v)$	
Cl(1)—Sn—Cl(2)	86.9	(2)	
Cl(2)—Sn—Cl(3) ₁	92.3	(3)	
Cl(1)—Sn—Cl(3) ₁	90.2	(3)	
Symmetry relations			
Atom	x	y	z
Atom ₁	x	y	$z - 1.0$
Atom ₂	$0.5 - x$	$0.5 + y$	$0.5 - z$
Atom ₃	$1.0 - x$	$1.0 - y$	$1.0 - z$
Atom ₄	$x - 0.5$	$0.5 - y$	$0.5 + z$
Atom ₅	$0.5 - x$	$0.5 + y$	$1.5 - z$
Atom ₆	x	y	$1.0 + z$
Atom ₇	$0.5 - x$	$y - 0.5$	$1.5 - z$

STRUCTURE DETERMINATION

Many of the crystals prepared exhibited twinning and the one used for data collection was no exception. The twin plane is (100). Thus the reciprocal a^* -axes coincide for the two crystals and the b^* -axes are antiparallel. The reflexions on reciprocal lattice planes $h0l$, $h1l$... etc. show in general separate reflexions from both twins except that reflexions $h, k, 3n$ from one twin coincide with reflexions $h + n, k, 3n$ from the second twin. For these reflexions the observed intensities are the sum of the intensities from both crystals. Well separated reflexions were measured for both twins using film data as well as diffractometer data and it was estimated that the ratio of the volumes of the two crystals was $Q = V_{II}/V_I = 0.403$. The observed intensity of a reflexion of type $h, k, 3n$ can be expressed as

$$I(h, k, 3n)_{\text{obs}} = I_I(h, k, 3n) + I_{II}(\bar{h} + n, k, 3n)$$

Table 4. Observed and calculated structure factors.

h	k	l	Observed	Calculated
1	0	0	100	100
2	0	0	400	400
3	0	0	900	900
4	0	0	1600	1600
5	0	0	2500	2500
6	0	0	3600	3600
7	0	0	4900	4900
8	0	0	6400	6400
9	0	0	8100	8100
10	0	0	10000	10000
11	0	0	12100	12100
12	0	0	14400	14400
13	0	0	16900	16900
14	0	0	19600	19600
15	0	0	22500	22500
16	0	0	25600	25600
17	0	0	28900	28900
18	0	0	32400	32400
19	0	0	36100	36100
20	0	0	40000	40000
21	0	0	44100	44100
22	0	0	48400	48400
23	0	0	52900	52900
24	0	0	57600	57600
25	0	0	62500	62500
26	0	0	67600	67600
27	0	0	72900	72900
28	0	0	78400	78400
29	0	0	84100	84100
30	0	0	90000	90000
31	0	0	96100	96100
32	0	0	102400	102400
33	0	0	108900	108900
34	0	0	115600	115600
35	0	0	122500	122500
36	0	0	129600	129600
37	0	0	136900	136900
38	0	0	144400	144400
39	0	0	152100	152100
40	0	0	160000	160000
41	0	0	168100	168100
42	0	0	176400	176400
43	0	0	184900	184900
44	0	0	193600	193600
45	0	0	202500	202500
46	0	0	211600	211600
47	0	0	220900	220900
48	0	0	230400	230400
49	0	0	240100	240100
50	0	0	250000	250000
51	0	0	260100	260100
52	0	0	270400	270400
53	0	0	280900	280900
54	0	0	291600	291600
55	0	0	302500	302500
56	0	0	313600	313600
57	0	0	324900	324900
58	0	0	336400	336400
59	0	0	348100	348100
60	0	0	360000	360000
61	0	0	372100	372100
62	0	0	384400	384400
63	0	0	396900	396900
64	0	0	409600	409600
65	0	0	422500	422500
66	0	0	435600	435600
67	0	0	448900	448900
68	0	0	462400	462400
69	0	0	476100	476100
70	0	0	490000	490000
71	0	0	504100	504100
72	0	0	518400	518400
73	0	0	532900	532900
74	0	0	547600	547600
75	0	0	562500	562500
76	0	0	577600	577600
77	0	0	592900	592900
78	0	0	608400	608400
79	0	0	624100	624100
80	0	0	640000	640000
81	0	0	656100	656100
82	0	0	672400	672400
83	0	0	688900	688900
84	0	0	705600	705600
85	0	0	722500	722500
86	0	0	739600	739600
87	0	0	756900	756900
88	0	0	774400	774400
89	0	0	792100	792100
90	0	0	810000	810000
91	0	0	828100	828100
92	0	0	846400	846400
93	0	0	864900	864900
94	0	0	883600	883600
95	0	0	902500	902500
96	0	0	921600	921600
97	0	0	940900	940900
98	0	0	960400	960400
99	0	0	980100	980100
100	0	0	1000000	1000000

$$I(\overline{h+n}, k, 3n)_{\text{obs}} = I_{\text{I}}(\overline{h+n}, k, 3n) + I_{\text{II}}(h, k, 3n)$$

$$I_{\text{II}}(h, k, l) = Q \cdot I_{\text{I}}(h, k, l)$$

$$I_{\text{I}}(h, k, 3n) = [I(h, k, 3n)_{\text{obs}} - Q \cdot I_{\text{obs}}(\overline{h+n}, k, 3n)] / (1 - Q^2)$$

Thus for reflexions with $l=0$ the intensities are multiplied with $1/(Q+1)$.

Later an untwinned crystal was found and selected reflexions were measured for obtaining a check on the corrections applied. The corrections were carried out using a computer program written by F. R. Poulsen. Because of the twinning no absorption correction was employed.

An approximate absolute scale and an average temperature factor was found from a Wilson plot. The program applied was D50 written by Danielsen.⁶

The systematic extinctions found were $h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$. Consequently the monoclinic space group $P2_1/n$ (No. 14) was assumed.

The three dimensional Patterson function was used for the structure determination. The peaks Cs—Cs, Cs—Sn, and Sn—Sn were assumed to be undistinguishable. We were therefore expecting peaks from 8 heavy atoms per unit cell which would cause 28 vectors. The symmetry of the Patterson function reduces the number of independent vectors in an asymmetric unit to ten. The atomic positions of the heavier atoms were found using the "Minimum-function" principle. The positions found were refined using the atomic scattering factor of tin for both positions with the program D45 of Danielsen.⁷

An R -value of 30% was obtained. A Fourier synthesis was calculated using the signs determined by the two heavy atoms. Three new atoms, presumably chlorine atoms, appeared in the Fourier map. They all had a distance of 2.5 Å from one of the heavy atoms, the four atoms forming a pyramid. This heavy atom was considered a tin atom and the other heavy atom was consequently assumed to be cesium. The structure was refined by successive use of Fourier and difference Fourier-methods and least-squares methods. A final difference-Fourier map showed no significant details.

The following programs were used: Fourier calculations were performed on a GIER computer using a program written by Lauesen,⁸ block-diagonal least-squares and weight analysis were computed with Grønbaek-Hazell's program G3⁹ also on GIER and full-matrix and other auxiliary computations were carried out on a 7090 computer at NEUCC using the program-system X-Ray-63 by Stewart.¹⁰

The weights (w) used in the least-squares refinements were $1/(\mu F)^2$ where $\mu F = \sqrt{st + (1+a)F_o^2 - |F_c|}$ where $st = \sigma(F_o^2) + 0.002|F_o|^2/\xi$. $\sigma(F_o^2)$ is from the counting statistics and ξ is the distance from the reciprocal lattice point to the rotation axis. If $\xi < 0.05$ st is increased with $|F_o|^2(0.05 - \xi)/0.05$ in order to downweight reflexions for which the Lorentz correction is subject to a large uncertainty. The parameter a was adjusted to make the average value of $w(|F_o| - |F_c|)^2$ largely independent of the size of F_o . Convergence in the least-squares computations were obtained at an R -value of 10.9% using 1139 reflexions.

DISCUSSION

The chemistry of bivalent tin has recently been reviewed by Donaldson.¹¹

If we accept the description that a gaseous Sn^{2+} ion has a $5s^2$ electron configuration we may expect a number of possible types of compounds:

1) "Ionic" compounds with structures dominated by geometrical and electrostatic packing considerations.

2) "Covalent" compounds using sp^3 hybrid orbitals on the tin atom. Pyramidal structures should be expected.

3) "Crystal-field" stabilizations of varying degrees leading to various distortions of an octahedral structure.

The choice of description varies from compound to compound. If there is only a small energy difference between a structure based upon description 1) and another based upon 2), one could assume that both a low temperature form with a high degree of ordering ("directional valencies") and a high temperature form with a more "random" structure are possible. This description applies to CsGeCl_3 ,¹ to CsSnCl_3 , and to $\text{Cs}_3\text{Sb}_2\text{Cl}_9$.¹² Phase transitions have also been observed in InCl ,¹³ GeTe ,¹⁴ and SnSe .¹⁵

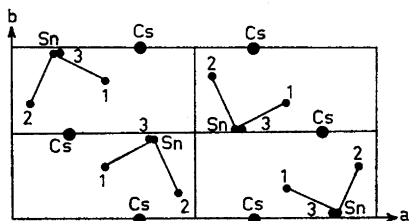


Fig. 1. The structure of CsSnCl_3 projected along the c -axis. The chlorine atoms are labelled as 1, 2, and 3.

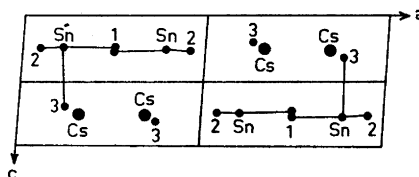


Fig. 2. The structure of CsSnCl_3 projected along the b -axis. Labelling as in Fig. 1.

The low temperature form of CsSnCl_3 is depicted in Figs. 1 and 2. The structure may be described as built from Cs^+ ions and pyramidal SnCl_3^- ions. The three distances $\text{Sn}-\text{Cl}$ (Table 3) are apparently not identical. It appears that the distance $\text{Sn}-\text{Cl}(3)=2.55_2 \text{ \AA}$ is longer than the other two. Similar distortions from a regular pyramid was found in $\text{KSnCl}_3 \cdot \text{H}_2\text{O}$.¹⁶ The $\text{Sn}-\text{Cl}$ distances in the SnCl_3^- ion are significantly shorter than those in SnCl_2 (2.67 \AA). In CsSnCl_3 the tin atom has a fourth chlorine neighbour at 3.21 \AA , a fifth at 3.45 \AA and a sixth at 3.77 \AA . The geometrical configuration around tin bears, however, no resemblance to that of a distorted octahedron. The surroundings of the cesium atom cannot be described as that of simple polyhedron. There are seven nearest chlorine neighbours with $\text{Cs}-\text{Cl}$ distances between 3.41 and 3.63 \AA . Three other chlorine atoms are found at 3.85 \AA , 3.94 \AA , and 4.14 \AA from the cesium atom. The projection along the b -axis (Fig. 1) shows clearly that the structure is a layer structure. Most of the atoms are found near the planes $z = \pm \frac{1}{4}$. In one SnCl_3^- ion the chlorine atom labelled No. 3

belongs to one layer whereas the rest of the group is located in a neighbouring layer. Thus chlorine atom No. 3 seems to be of special importance for the bonding between the layers. This chlorine atom is also the one which is 3.20 Å away from a tin atom in a neighbouring layer. This supports the conclusion that the Sn—Cl(3) bond length is longer than the other two Sn—Cl distances.

When a crystal is heated above 120°C it is transformed completely and a precession photograph taken at that temperature has the appearance of a powder photograph with some orientation effects. Guinier diagrams at 154°C and at 185°C exhibit two sets of lines. One set of eight lines can be indexed on the basis of a cubic unit cell with a cell constant of 3.92 Å, another set of six rather broad lines could be indexed as belonging to a cubic unit cell of cell constant 3.67 Å. Four other lines could not be assigned to any of the two sets. It seems therefore likely that the observed phase transition gives rise to more than one new compound. The phase transition is not reversible. The DTA diagram shows no sign of heat evolution when a sample is cooled immediately after having passed through the transition and powder photographs taken shortly after a transition are similar to photographs taken above the transition temperature. Powder photographs of a heated sample do, however, show that the low temperature phase is reestablished when the sample has been kept at room temperature for some weeks. From our X-ray data we conclude that one or more phases of CsSnCl₃ exist above ca. 120°C with a symmetry which is higher than that of the low temperature phase. We have not, however, information enough to suggest a structure for the high temperature form.

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