

The Crystal Structures of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$

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β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ is orthorhombic with space group $Pm\bar{c}n$. There are four formula units in a unit cell of dimensions $a=7.630$ (20), $b=13.079$ (3) and $c=18.663$ (4) Å. The structure has been determined by using the sign relations of reflexions and refined by the full-matrix least-squares method. The final R is 0.108 for 449 three-dimensional photographic intensities. The structure is formed by Cs and Cl atoms in nearly closest packing and Sb atoms in octahedral holes. The unit cell has six layers which are stacked along the c axis in the sequence . . . $ABACBCABACBC$. . . The structure contains two types of SbCl_3 molecules, one with the average distances $\text{Sb-Cl}=2.43$, $\text{Cl-Cl}=3.52$ Å and the other with $\text{Sb-Cl}=2.52$, $\text{Cl-Cl}=3.73$ Å. $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ is isostructural with β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and has a unit cell of dimensions $a=7.644$ (3), $b=13.227$ (3) and $c=18.684$ (4) Å. The final R is 0.16 for 253 two-dimensional photographic intensities. The structure also contains two types of BiCl_3 molecules, one with the average distances $\text{Bi-Cl}=2.50$, $\text{Cl-Cl}=3.57$ Å and the other with $\text{Bi-Cl}=2.53$, $\text{Cl-Cl}=3.69$ Å.

Introduction

There are many compounds with the formula $\text{R}_3\text{M}_2\text{Cl}_9$ ($\text{R}=\text{Cs}, \text{K}, \text{etc.}$, and $\text{M}=\text{Fe}, \text{As}, \text{Bi}, \text{W}, \text{Cr}, \text{Tl}, \text{etc.}$). Their structures are composed of Cl and R atoms in nearly closest packing and M atoms located in Cl octahedral holes. The structures can be classified into two groups: one has unit cells formed from three identical layers and the other six layers of RCl_3 .

The structures of $\text{Cs}_3\text{As}_2\text{Cl}_9$ (Hoard & Goldstein, 1935), α - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ (Yamatera & Nakatsu, 1954; Kihara & Sudo, 1971*b*) and $\text{Cs}_3\text{Fe}_2\text{Cl}_9$ (Yamatera & Nakatsu, 1954) are isostructural and have three-layered trigonal unit cells. The structures of $\text{K}_3\text{W}_2\text{Cl}_9$ (Watson & Waser, 1958), $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ (Wessel & IJdo, 1957) and $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ (Powell & Wells, 1935; Hoard & Goldstein, 1935) have six-layered hexagonal unit cells.

$\text{Cs}_3\text{Sb}_2\text{Cl}_9$ has two modifications, α - and β -types (Kihara & Sudo, 1971*a*). β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ are isostructural and crystallize in a new structure. It is the purpose of the present paper to give the results of the crystal structure examination of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ and to explain the structural relationship between the related structures.

Crystal data and intensity measurements

Single crystals of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ were obtained by slow and static recrystallization from dilute hydrochloric acid solutions of $\text{Cs}_3\text{Sb}_2\text{Cl}_9$. The structure is orthorhombic with the space group $Pm\bar{c}n$ or $P2_1cn$. Foster & Hargreaves's (1963) general moments tests were carried out to determine the space group. The results (weighted average values for all reflexions were used)

are shown in Table 1. The experimental moments were calculated from the intensities of 310 hkl reflexions in the range $\sin \theta=0.8$ – 1.0 . The experimental values indicate the centrosymmetric space group $Pm\bar{c}n$. The unit-cell dimensions were measured from Weissenberg and rotation photographs. The density (Kihara & Sudo, 1971*a*) corresponds to $4\text{Cs}_3\text{Sb}_2\text{Cl}_9$ in the unit cell. The crystallographic data of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ are summarized in Table 2 with those of three related structures.

Table 1. Comparison of experimental and theoretical moments of z for β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$

Moment	Experimental	Theoretical	
		$Pm\bar{c}n$	$P2_1cn$
$\langle z^2 \rangle$	3.1	3.03	2.04
$\langle z^3 \rangle$	15.0	14.73	6.33

The intensity data for β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ were obtained with $\text{Cu } K\alpha$ radiation on multiple-film integrated Weissenberg photographs for five layers along [100]. Since the crystals are readily affected by moisture, the specimens were coated with an adhesive material for long exposures. Three specimens with dimensions of about $0.15 \times 0.10 \times 0.5$ mm were used to complete the whole measurement. 449 independent reflexions were estimated by means of a microphotometer and corrected for absorption, Lorentz and polarization effects. The intensities of high-level reflexions on the Weissenberg photographs were corrected for extension using Phillips's (1954, 1956) equation. For $\text{Cs}_3\text{Bi}_2\text{Cl}_9$, 187 $0kl$ and 66 $hk0$ reflexions were measured by the same procedure as for β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$.

Structure determination

The structures of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ were solved by means of a systematic application of the sign

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relations. The procedures reported by Grant, Howells & Rogers (1957) were followed in detail. With the signs thus obtained, an electron density projection on (100) was calculated and interpreted based on packing relations. Successive Fourier syntheses reduced the R value to 0.35 for the $0kl$ reflexions of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$, and to 0.38 for those of $\text{Cs}_3\text{Bi}_2\text{Cl}_9$.

Refinement

The structures of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ were refined by the full-matrix least-squares method using the program *ORFLS* of Busing, Martin & Levy (1962), modified by Sakurai, Nakatsu & Iwasaki for the UNICS System (1967) of HITAC 5020 of Tokyo University. Scattering factors for non-ionized atoms and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962). Isotropic temperature factors and unit weights for reflexions were applied for the two structures. The centrosymmetric space group $Pm\bar{c}n$ was confirmed by the successful refinement of the structures.

The refinement of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ was started first in the centrosymmetric space group. Six iterations varying 41 parameters lowered the R value to 0.108 for 449 observed reflexions.* The refinement progressed somewhat slowly, but without oscillation of the parameter shifts. The maximum parameter shift in the final itera-

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30327 (2 pp.). Copies can be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

tion was in the z coordinate of Cl(1), and had a value of one-ninth of the corresponding estimated standard deviation. A structure refinement was also attempted on the basis of the non-centrosymmetric space group, but five iterations gave no convergence of the parameters.

Refinement for $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ was carried out with the $0kl$ and $hk0$ intensities. The atomic coordinates and isotropic temperature factors of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ described above were adopted as the initial parameters. The x coordinates of Cl(4), Cl(5) and Cl(6), and the temperature factors of all atoms were fixed because of overlapping of atoms in the (001) projection. Five iterations lowered R to 0.16 for the 253 reflexions. The atomic coordinates and the individual isotropic temperature factors are given in Table 3.

Discussion of the structures

Structure of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$

The structure of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ projected along [100] is shown in Fig. 1. The interatomic distances and angles were computed using Sakurai's program of the UNICS System (1967), *RSDA-4*, and are listed in Table 4 with those of $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ computed using *RSDA-4* modified by Kanazawa & Matsumoto for FACOM 230-35 of Kanazawa University.

The structure consists of a close-packed arrangement of large Cs and Cl atoms with Sb atoms in two-thirds of the octahedral holes of Cl atoms. The unit cell has six layers of CsCl_3 which are stacked along the c axis in a sequence $\dots ABACBCABACBC\dots$. The structure contains two crystallographically different

Table 2. Crystallographic data of $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$, $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ and other related structures

	$\text{Cs}_3\text{Fe}_2\text{Cl}_9$ Yamatera & Nakatsu (1954)	$\text{Cs}_3\text{As}_2\text{Cl}_9$ Hoard & Goldstein (1935)	$\alpha\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ Kihara & Sudo (1971)	$\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ Present study	$\text{Cs}_3\text{Bi}_2\text{Cl}_9$ Present study
Unit cell (Å)	$a = 7.28$	$a = 7.37$	$a = 7.633$	$a = 7.630$ (20) $b = 13.079$ (3) $c = 18.663$ (4)	$a = 7.644$ (3) $b = 13.227$ (3) $c = 18.684$ (4)
D_s	$c = 8.90$	$c = 8.91$	$c = 9.345$	3.43	3.99
Z	3.37	3.42	3.38	4	4
Space group	$P\bar{3}m1$ or $P321$	$P321$	$P321$	$Pm\bar{c}n$	$Pm\bar{c}n$

Table 3. Final atomic coordinates and isotropic temperature factors of (a) $\beta\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ and (b) $\text{Cs}_3\text{Bi}_2\text{Cl}_9$

	(a)			(b)				
	x	y	z	x	y	z		
Cs(1)	0.25	0.41690 (96)	0.08198 (59)	2.698	Cs(1)	0.25	0.41498 (159)	0.08636 (131)
Cs(2)	0.25	-0.24903 (84)	-0.24765 (65)	1.893	Cs(2)	0.25	-0.25083 (185)	-0.24888 (131)
Cs(3)	0.25	0.41430 (78)	0.40913 (46)	1.689	Cs(3)	0.25	0.41990 (160)	0.41093 (131)
Sb(1)	0.25	-0.23287 (49)	-0.00114 (47)	0.509	Bi(1)	0.25	-0.23861 (71)	-0.00124 (65)
Sb(2)	0.25	0.08239 (56)	0.31533 (34)	0.439	Bi(2)	0.25	0.08140 (79)	0.31632 (62)
Cl(1)	0.25	-0.41581 (365)	-0.08941 (225)	2.532	Cl(1)	0.25	-0.38597 (530)	-0.09354 (520)
Cl(2)	0.25	0.24366 (266)	0.24014 (166)	1.219	Cl(2)	0.25	0.22958 (389)	0.23534 (412)
Cl(3)	0.25	-0.41779 (307)	-0.42300 (196)	1.978	Cl(3)	0.25	-0.41915 (496)	-0.42254 (470)
Cl(4)	-0.01802 (590)	0.16273 (198)	0.07504 (134)	3.149	Cl(4)	-0.01802	0.16415 (368)	0.07798 (301)
Cl(5)	0.00369 (760)	-0.00127 (196)	0.24687 (137)	3.102	Cl(5)	0.00369	-0.00722 (405)	0.24759 (298)
Cl(6)	0.00435 (724)	0.17717 (236)	0.40550 (160)	4.160	Cl(6)	0.00435	0.17357 (427)	0.40931 (353)

Table 4. *Interatomic distances and angles of β -Cs₃Sb₂Cl₉ and Cs₃Bi₂Cl₉ (e.s.d.'s are given in parentheses)*

(1)	x	y	z	(i)	$\frac{1}{4}$	y	z
(2)	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(ii)	$\frac{3}{4}$	$-y$	$-z$
(3)	$\frac{1}{2}+x$	$-y$	$-z$	(iii)	$\frac{3}{4}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(4)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	(iv)	$\frac{1}{4}$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(5)	$-x$	$-y$	$-z$				
(6)	$\frac{1}{2}+x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$				
(7)	$\frac{1}{2}-x$	y	z				
(8)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$				

β -Cs₃Sb₂Cl₉
Distances (Å)

Sb(1) i		Sb(2) i		Cl(1) i	
Cl(3) iv	2.45 (4)	Cl(2) i	2.53 (4)	Cl(4) 3,5	3.76 (6)
Cl(4) 3,5	2.42 (4)	Cl(5) 1,7	2.52 (5)	Cl(6) 2,8	3.90 (6)
Cl(6) 4,6	2.89 (5)	Cl(6) 1,7	2.81 (5)	Cl(6) 4,6	4.12 (6)
Cl(1) i	2.90 (5)	Cl(1) iv	2.81 (5)	Cl(5) 2,8	3.75 (6)
Cl(2) i		Cl(3) i		Cs(1) i	
Cl(5) 4,6	3.87 (5)	Cl(6) 3,5	3.71 (6)	Cl(1) ii	3.82 (4)
Cl(4) 1,7	3.85 (5)	Cl(5) 2,8	3.84 (5)	Cl(4) 1,7	3.91 (4)
Cl(5) 1,7	3.72 (5)	Cl(4) 4,6	3.51 (5)	Cl(2) i	3.72 (4)
Cl(6) 1,7	3.71 (5)	Cl(4) 2,8	3.80 (5)	Cl(5) 4,6	3.88 (4)
				Cl(6) 4,6	3.93 (4)
				Cl(1) i	3.88 (4)
Cs(2) i		Cs(3) i		Cl(4) 1-Cl(4) 7	
Cl(2) ii	3.82 (4)	Cl(3) ii	3.83 (4)	Cl(4) 7-Cl(4) 1	3.55 (7)
Cl(5) 5,3	3.80 (4)	Cl(6) 1,7	3.62 (4)	Cl(5) 1-Cl(5) 7	3.76 (9)
Cl(6) 5,3	3.65 (4)	Cl(4) 2,8	3.84 (4)	Cl(5) 7-Cl(5) 1	3.87 (9)
Cl(3) i	3.95 (4)	Cl(3) i	3.83 (4)	Cl(6) 1-Cl(6) 7	3.75 (8)
Cl(5) 2,8	3.77 (3)	Cl(4) 4,6	3.71 (4)	Cl(6) 7-Cl(6) 1	3.88 (8)
Cl(1) i	3.67 (5)	Cl(5) 4,6	3.67 (4)		

Angles (°)

Sb(1) i			Sb(2) i		
Cl(4) 3 \wedge Cl(4) 5	93.9 (10)		Cl(5) 1 \wedge Cl(5) 7	96.4 (15)	
Cl(3) iv \wedge Cl(4) 3,5	92.0 (9)		Cl(2) i \wedge Cl(5) 1,7	94.6 (8)	
Cl(1) i \wedge Cl(4) 3,5	89.4 (9)		Cl(2) i \wedge Cl(6) 1,7	88.0 (9)	
Cl(1) i \wedge Cl(6) 4,6	90.8 (9)		Cl(1) iv \wedge Cl(6) 1,7	87.9 (9)	
Cl(3) iv \wedge Cl(6) 4,6	87.7 (9)		Cl(6) 1 \wedge Cl(6) 7	83.8 (13)	
Cl(6) 4 \wedge Cl(6) 6	84.5 (10)		Cl(1) iv \wedge Cl(5) 1,7	89.1 (9)	

Cs₃Bi₂Cl₉
Distances (Å)

Bi(1) i		Bi(2) i		Cl(1) i	
Cl(3) iv	2.55 (6)	Cl(2) i	2.47 (6)	Cl(4) 3,5	3.44 (7)
Cl(4) 3,5	2.48 (5)	Cl(5) 1,7	2.56 (5)	Cl(6) 2,8	4.24 (8)
Cl(6) 4,6	2.84 (5)	Cl(6) 1,7	2.83 (5)	Cl(6) 4,6	4.03 (9)
Cl(1) i	2.60 (8)	Cl(1) iv	3.08 (7)	Cl(5) 2,8	3.79 (9)
Cl(2) i		Cl(3) i		Cs(1) i	
Cl(5) 4,6	4.00 (6)	Cl(6) 3,5	3.79 (7)	Cl(1) ii	3.84 (1)
Cl(4) 1,7	3.68 (8)	Cl(5) 2,8	3.85 (8)	Cl(4) 1,7	3.90 (4)
Cl(5) 1,7	3.66 (6)	Cl(4) 4,6	3.57 (8)	Cl(2) i	3.71 (7)
Cl(6) 1,7	3.82 (8)	Cl(4) 2,8	3.83 (6)	Cl(5) 4,6	3.80 (6)
				Cl(6) 4,6	3.93 (6)
				Cl(1) i	4.27 (9)
Cs(2) i		Cs(3) i		Cl(4) 1-Cl(4) 7	
Cl(2) ii	3.84 (1)	Cl(3) ii	3.82 (1)	Cl(4) 7-Cl(4) 1	3.54 (6)
Cl(5) 5,3	3.92 (6)	Cl(6) 1,7	3.76 (6)	Cl(5) 1-Cl(5) 7	3.76 (8)
Cl(6) 5,3	3.72 (6)	Cl(4) 2,8	3.89 (6)	Cl(5) 7-Cl(5) 1	3.87 (8)
Cl(3) i	3.93 (7)	Cl(3) i	3.77 (7)	Cl(6) 1-Cl(6) 7	3.75 (8)
Cl(5) 2,8	3.71 (6)	Cl(4) 4,6	3.69 (5)	Cl(6) 7-Cl(6) 1	3.88 (8)
Cl(1) i	3.41 (9)	Cl(5) 4,6	3.67 (6)		

Angles (°)

Bi(1) i			Bi(2) i		
Cl(4) 3 \wedge Cl(4) 5	91.2 (20)		Cl(5) 1 \wedge Cl(5) 7	94.6 (20)	
Cl(3) iv \wedge Cl(4) 3,5	90.5 (20)		Cl(2) i \wedge Cl(5) 1,7	93.1 (20)	
Cl(1) i \wedge Cl(4) 3,5	85.1 (20)		Cl(2) i \wedge Cl(6) 1,7	92.0 (20)	
Cl(1) i \wedge Cl(6) 4,6	95.4 (20)		Cl(1) iv \wedge Cl(6) 1,7	91.5 (20)	
Cl(3) iv \wedge Cl(6) 4,6	89.2 (20)		Cl(6) 1 \wedge Cl(6) 7	83.3 (20)	
Cl(6) 4 \wedge Cl(6) 6	87.0 (20)		Cl(1) iv \wedge Cl(5) 1,7	83.6 (20)	

Sb atoms. Each Sb(1) atom is located at approximately 2.43 Å from three Cl atoms and at 2.89 Å from three opposite Cl atoms [Fig. 2(c)], and each Sb(2) atom at 2.52 Å from three Cl atoms and at 2.81 Å from opposite ones [Fig. 2(d)]. Thus the Sb atoms form pyramidal molecules with the three Cl atoms at the shorter distances. The apex angle Cl–Sb–Cl averages $93^{\circ}12'$ for Sb(1)Cl₃ and $95^{\circ}12'$ for Sb(2)Cl₃ molecule. The SbCl₃ molecules are represented by dotted lined triangles in Fig. 1.

SbCl₃ molecules

The two types of SbCl₃ molecule in the present structure are compared with those in other related structures in Fig. 2. The molecules in β -Cs₃Sb₂Cl₉ have only mirror symmetry while those in α -Cs₃Sb₂Cl₉ have trigonal symmetry. The differences 0.03 and 0.01 Å between the three bond lengths for Sb(1) and Sb(2) respectively are rather smaller than the corresponding estimated standard deviations. In the two independent molecules, however, there is no trigonal symmetry as far as bond angles are concerned. The two angles related by mirror symmetry are $92^{\circ}0'$ for Sb(1)Cl₃ and $94^{\circ}36'$ for Sb(2)Cl₃; the third angle is much greater: $93^{\circ}54'$ for Sb(1)Cl₃ and $96^{\circ}24'$ for Sb(2)Cl₃. It is notable that the difference, amounting to 0.10 Å between the mean bond lengths for the two independent molecules in

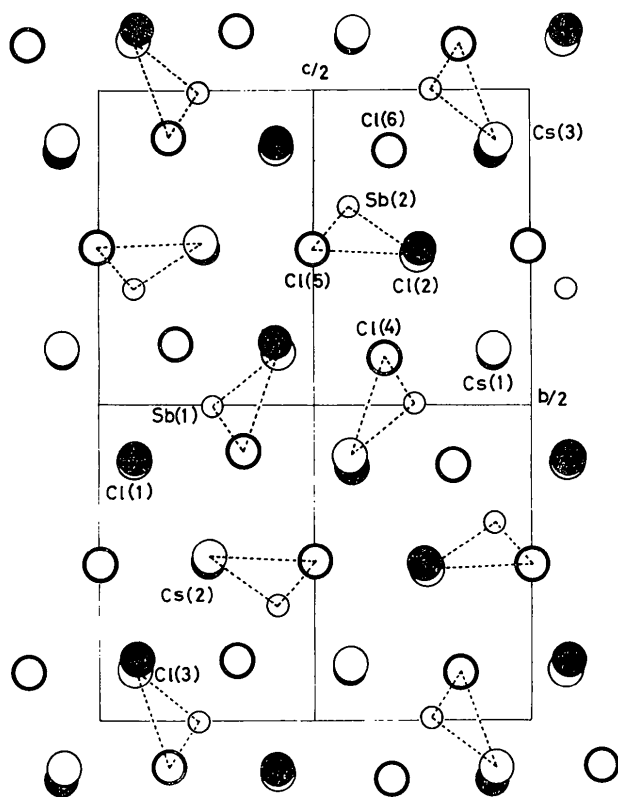


Fig. 1. The projection of β -Cs₃Sb₂Cl₉ along the *a* axis. The smaller open circles are Sb atoms, the larger ones are Cl atoms and the black ones, Cs atoms.

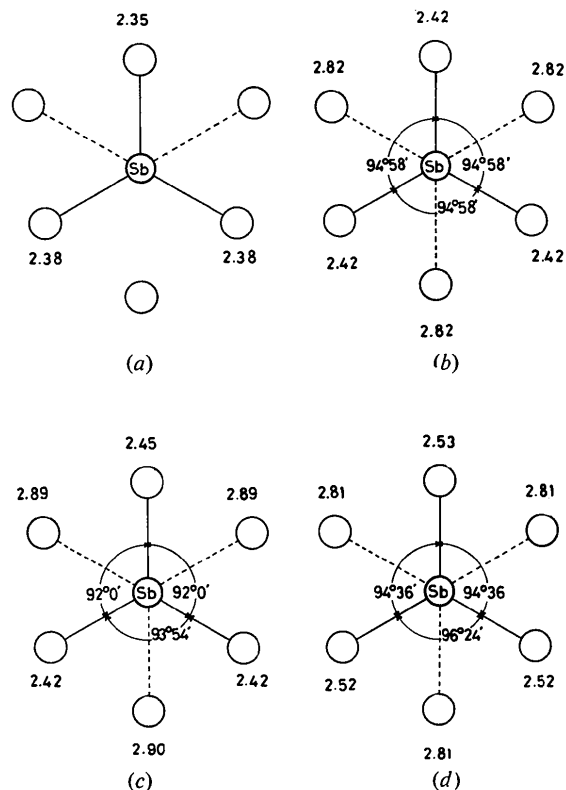


Fig. 2. Antimony trichloride molecules, showing interatomic distances and angles. (a) SbCl₃ (Lindqvist & Niggli, 1956), (b) SbCl₃ in α -Cs₃Sb₂Cl₉ (Kihara & Sudo, 1971), (c) Sb(1)Cl₃ in β -Cs₃Sb₂Cl₉ and (d) Sb(2)Cl₃ in β -Cs₃Sb₂Cl₉.

β -Cs₃Sb₂Cl₉, is more than twice the estimated standard deviation for the bond lengths. Since the normal covalent distance Sb–Cl is 2.40 Å (Pauling & Huggins, 1934), the mean bond length 2.52 Å between Sb(2) and three Cl atoms is considerably lengthened. Fig. 3 shows the arrangement of Cl and trivalent atoms in the structure of the As, Sb and Bi compounds. In the structure of β -Cs₃Sb₂Cl₉, octahedra occupied by Sb(1) atoms share corners with six, of which three are occupied by Sb(2) atoms and three are vacant, and those occupied by Sb(2) atoms share three corners with ones occupied by Sb(1) atoms and one face with a vacant octahedron. Each Sb(2)Cl₃ molecule shares its basal face with the vacant octahedron. The mean Cl–Cl distance of the Sb(2)Cl₃ molecule, 3.73 Å, is much longer than that of the Sb(1)Cl₃ molecule, 3.52 Å, and that of the SbCl₃ in α -Cs₃Sb₂Cl₉, 3.56 Å (Fig. 3). The longer Cl–Cl distance in the Sb(2)Cl₃ molecule, the larger angle of Cl–Sb(2)–Cl and the longer distance of Sb(2)–Cl can be considered to be caused by the sharing of the molecular basal face with a vacant octahedron.

The relationship between α and β types

The length of the *b* axis of β -Cs₃Sb₂Cl₉ is smaller than the length expected from α -Cs₃Sb₂Cl₉, as shown in Table 1. This can be explained by considering the ar-

arrangement and distortion of the anion octahedra. The octahedra occupied by Sb atoms are distorted as shown in Fig. 3 and the faces opposite the SbCl_3 molecules are considerably expanded compared with the others. In the structure of the α type, corners of the octahedra are shared and the octahedra occupied by Sb atoms are arranged so that the expanded faces are parallel to (001) [Fig. 3(b)]. Accordingly, the length of the a ($=b$) axis of the α type will be strongly affected by distortion of the octahedra occupied by Sb atoms. On the other hand, in the structure of the β type, the octahedra occupied by Sb(1) atoms do not arrange with the expanded faces parallel to (001) [Fig. 3(c)]. In this structure, accordingly, the length of the b axis

is smaller than $a_x/3$ (a_x : the a axis length of the α type). In addition to the above arguments, differences in volumes between vacant octahedra in the two structures should be noted. Vacant octahedra tend to expand in the α type, but do not expand in the β type since they share a face with an SbCl_3 molecule. It is apparent that the octahedral arrangement in the structure of the β type gives a more compact structure compared with that in the α type. Judging from the compactness of the structures, the β type is probably the low-temperature form and the α type the high-temperature form of $\text{Cs}_3\text{Sb}_2\text{Cl}_9$. This is supported by the fact that the β type transforms into the α type on heating to 300°C .

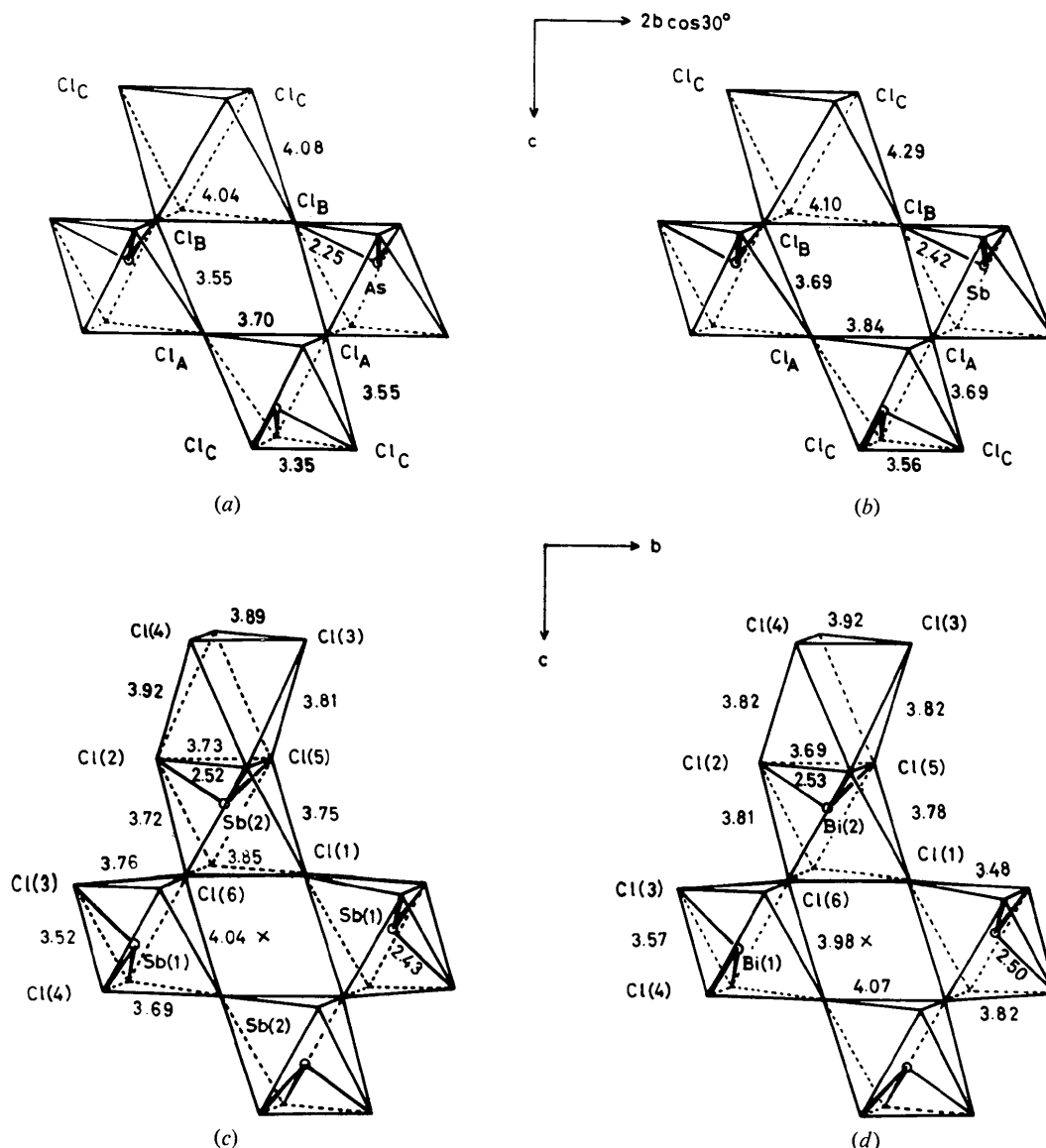
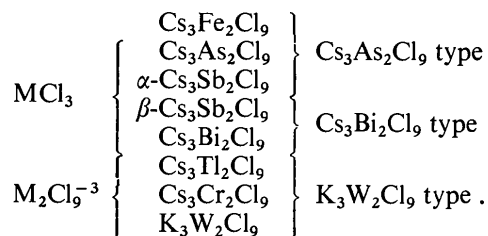


Fig. 3. Arrangements of Cl octahedra and of trichloride molecules. Numerals represent average values over three lengths. (a) $\text{Cs}_3\text{As}_2\text{Cl}_9$, (b) α - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, (c) β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and (d) $\text{Cs}_3\text{Bi}_2\text{Cl}_9$.

Bi compound and other related structures

The Bi compound gives only the structure analogous to β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$. Each Bi atom also forms a BiCl_3 pyramidal molecule. The interatomic distances in the molecules are 2.50 Å for $\text{Bi}(1)\text{-Cl}$, 2.53 Å for $\text{Bi}(2)\text{-Cl}$, 3.57 Å for Cl-Cl of $\text{Bi}(1)\text{Cl}_3$ and 3.69 Å for Cl-Cl of $\text{Bi}(2)\text{Cl}_3$. In this structure, the difference between the bond lengths and angles of the two crystallographically independent molecules is rather small and each molecule is less distorted.

The structural relationship between the Fe, As, Sb, Bi, Tl, Cr and W compounds is summarized as follows:



The structure of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ (or $\text{Cs}_3\text{Bi}_2\text{Cl}_9$) is comparable with, but not the same as, the structure of the $\text{K}_3\text{W}_2\text{Cl}_9$ type. The former is composed of Cs and Cl atoms and discrete MCl_3 molecules and the latter has the complex $\text{M}_2\text{Cl}_9^{3-}$ while both have a similar arrangement of Cs and Cl atoms. It is considered to be difficult for elements such as Fe, As, Sb and Bi, which do not appear to give stable complexes, to form the structure of the $\text{K}_3\text{W}_2\text{Cl}_9$ type, because of closer M-M separation in the structure of the $\text{K}_3\text{W}_2\text{Cl}_9$ type. The structure of the $\text{K}_3\text{W}_2\text{Cl}_9$ type is presumably shown only by elements such as Tl, Cr and W, which form stable complexes.

In the Fe, As, Sb and Bi compounds, with an increase in the size of the trivalent atoms, the structure of the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ type is preferentially formed. Fig. 3 shows that the vacant octahedra in the $\text{Cs}_3\text{As}_2\text{Cl}_9$ type are considerably larger than those in the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ type. With increase in the size of the trivalent atom, it becomes increasingly difficult to form a compact structure

of the $\text{Cs}_3\text{As}_2\text{Cl}_9$ type. On the other hand, each vacant octahedron in the structures of β - $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ slightly contracts because of sharing a face with an MCl_3 molecule [Fig. 3(c) and (d)]. The structure of the $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ type is stable for the compounds having large trivalent atoms, since they hardly require contraction of vacant octahedra. Only the Sb compound crystallizes in the two structural types, because of the intermediate size of the Sb atom between the As and the Bi atoms.

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