

are coupled to form dimers by means of hydrogen bonding. This kind of coupling was also observed in KHSO_4 (Loopstra & MacGillavry, 1958).

Confirmation of the significant difference of one S—O distance in the HSO_4^- tetrahedron with respect to the remaining S—O distances was obtained from the Hamilton significance test (Hamilton, 1965): the hypothesis that all four S—O distances are equal must be rejected at the significance level $\alpha = 0.01$.

The difference between the structures of the α and β -phases becomes clear, if both structures are described in terms of cations and anions. Then the structure of β - NaHSO_4 can be regarded as a distorted CsCl structure while the structure of α - NaHSO_4 (determination in progress) can be described as a distorted NaCl structure. According to this approach one should expect the β - NaHSO_4 structure to be more loosely packed. This is in accordance with the difference in

unit-cell volume of about 3% (Table 1), and also with the greater stability of the α -phase.

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$\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ with the Hexagonal $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ Structure Type

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Abstract. $\text{Cs}_3\text{Sb}_2\text{I}_9$: FW 1748, hexagonal, $P6_3/mmc$, $a = 8.349$ (2), $c = 20.936$ (9) Å, $Z = 2$, $D_x = 4.68$ g cm^{-3} , $R = 0.062$, $\mu(\text{Mo } K\alpha) = 178$ cm^{-1} , $F(000) = 1488$; $\text{Cs}_3\text{Bi}_2\text{I}_9$: FW 1959, $P6_3/mmc$, $a = 8.404$ (2), $c = 21.183$ (19) Å, $D_x = 5.02$ g cm^{-3} , $R = 0.092$, $\mu(\text{Mo } K\alpha) = 245$ cm^{-1} , $F(000) = 1616$. The investigation involved single-crystal diffractometry, absorption correction and least-squares refinement. The structures are isotypic with $\text{Cs}_3\text{Cr}_2\text{Cl}_9$. The $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ type is compared with six other structure types having the same composition and similar construction principles. It is shown by a unit-cell shift that the $\text{K}_3\text{W}_2\text{Cl}_9$ and $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ structures are lower-symmetry versions of the $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ type.

Introduction. $\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ have been synthesized by Dr F. Lévy using counter diffusion of liquid reagents slowed down by silicate gel (CsI in H_2O and SbCl_3 or BiCl_3 in HCl). Originally the composition of the red crystals formed was unknown. However, the structure determination led us to the chemical formula

given, which also agreed with the results of the chemical analysis. Preliminary diffraction experiments indicated that the two compounds are isotypic and that their Laue symmetry is $6/mmm$. A crystal of $\text{Cs}_3\text{Sb}_2\text{I}_9$ was ground in a compressed-air mill to an ellipsoid ($190 \times 128 \times 128$ μm) while a $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystal was available in the form of a platelet ($23 \times 64 \times 80$ μm). Lattice constants and intensities were measured on an automatic four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation and a graphite monochromator in the θ - 2θ scan mode. Data collection for $\text{Cs}_3\text{Sb}_2\text{I}_9$ ($\text{Cs}_3\text{Bi}_2\text{I}_9$) was carried out to a limit of 0.7 Å $^{-1}$ in $\sin \theta/\lambda$, yielding 727 (757) independent reflections, of which 707 (588) with $|F|$ greater than $3\sigma_F$ were used for the structure refinement. In both cases, the *CAMEL JOCKEY* experimental method for absorption correction (Flack, 1975, 1977) was used. Examination of the systematic absences indicated that $P6_3mc$, $P6_2c$ and $P6_3/mmc$ were possible space groups. The structure was solved by the Patterson method. Relativistic Hartree-Fock scattering factors (Cromer & Mann,

Table 1. Positional parameters for Cs₃Sb₂I₉ and Cs₃Bi₂I₉

E.s.d.'s are given in parentheses.

Equipoint	x	y	z
Cs ₃ Sb ₂ I ₉			
Cs(1)	0	0	$\frac{1}{4}$
Cs(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.0833 (2)
Sb	$\frac{1}{2}$	$\frac{1}{2}$	0.8447 (1)
I(1)	0.4931 (2)	0.9862 (2)	$\frac{1}{4}$
I(2)	0.8336 (1)	0.6672 (1)	0.0811 (1)
Cs ₃ Bi ₂ I ₉			
Cs(1)	0	0	$\frac{1}{4}$
Cs(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.0819 (2)
Bi	$\frac{1}{2}$	$\frac{1}{2}$	0.8454 (1)
I(1)	0.4929 (2)	0.9858 (2)	$\frac{1}{4}$
I(2)	0.8369 (2)	0.6738 (2)	0.0805 (1)

Table 2. Survey of A₃B₂X₉ compounds with the Cs₃Cr₂Cl₉ type or its lower-symmetry versions, all characterized by B₂X₉³⁻ ions

	a	c	c/a	d'/d''	Reference
Compounds with P6 ₃ /mmc symmetry					
Cs ₃ Tl ₂ Cl ₉	7.32	17.97	2.45		(a)
Cs ₃ V ₂ Cl ₉	7.24	17.94	2.48		(a)
Cs ₃ Cr ₂ Cl ₉	7.22 (1)	17.93 (2)	2.48	1.23	(a)
Cs ₃ Mo ₂ Cl ₉	7.357 (5)	17.545 (12)	2.38 ₄	0.98	(b)
α-Cs ₃ Fe ₂ Cl ₉	7.28*	17.8*			(c)
Cs ₃ Cr ₂ Br ₉	7.507 (6)	18.680 (15)	2.48 ₈	1.28	(b)
Cs ₃ Mo ₂ Br ₉	7.648 (3)	18.339 (16)	2.39 ₇	0.97	(b)
Cs ₃ Mo ₂ Br ₈ †	7.757 (3)	17.804 (7)	2.29 ₅	0.84	(d)
Cs ₃ Sb ₂ I ₉	8.349 (2)	20.936 (8)	2.50 ₇	1.21	(e)
Cs ₃ Bi ₂ I ₉	8.404 (2)	21.183 (19)	2.52 ₀	1.29	(e)
	8.411 (6)	21.18 (2)	2.51 ₈	1.29	(f)
Compounds with P6 ₃ /m symmetry					
K ₃ W ₂ Cl ₉	7.17	16.25	2.26 ₆	0.90	(g)
Cs ₃ W ₂ Cl ₉	7.36	18.09	2.45 ₇		(h)
(NH ₄) ₃ W ₂ Cl ₉	7.17	16.20	2.25 ₀		(h)
Rb ₃ W ₂ Cl ₉	7.25	16.98	2.34		(h)
Tl ₃ W ₂ Cl ₉	7.16	16.36	2.28		(h)
Compounds with P6̄2c symmetry					
Rb ₃ Mo ₂ Cl ₈ †	7.190 (5)	16.662 (10)	2.31 ₇	0.89	(i)
Cs ₃ Mo ₂ Cl ₈ †					(i)

References: (a) Wessel & Ijdo (1957). (b) Saillant, Jackson, Streib, Foltling & Wentworth (1971). (c) Ginsberg & Robin (1963). (d) Cotton, Frenz & Mester (1973). (e) This work. (f) Lindqvist (1968). (g) Watson & Waser (1958). (h) Brosset (1935). (i) Bennett, Brenčić & Cotton (1969).

* Appropriate values of the lattice constants of α-Cs₃Fe₂Cl₉ were calculated by comparing the list of d values given by Ginsberg & Robin (1963) with simulated powder patterns obtained with the *LAZY PULVERIX* program (Yvon, Jeitschko & Parthé, 1977). β-Cs₃Fe₂Cl₉ has, according to Yamatera & Nakatsu (1954), the Cs₃As₂Cl₉ type of structure.

† The composition of these compounds is A₃Mo₂X₈, because one third of the bridging halogen atoms are missing.

1968) were used for the least-squares refinement (XRAY system, 1976) which gave the final atomic positions listed in Table 1. The final value of *R* ($= \sum |\Delta F| / \sum |F_o|$) was 0.062 (or 0.048 weighted with $w = 1/\sigma_r^2$) for Cs₃Sb₂I₉, and 0.092 (or 0.034 weighted) for Cs₃Bi₂I₉.*

Discussion. The structures of Cs₃Sb₂I₉ and Cs₃Bi₂I₉ are isotopic and virtually identical to the structure of Cs₃Cr₂Cl₉ (Wessel & Ijdo, 1957). That Cs₃Sb₂I₉ and Cs₃Bi₂I₉ might be isotopic had been suggested by Cavalca, Nardelli & Braibanti (1955) from a comparison of powder diffraction patterns. The structure of Cs₃Sb₂I₉ has been determined by Lindqvist (1968) but the relationship to the Cs₃Cr₂Cl₉ structure was not recognized at that time. It is possible by a shift of origin

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33053 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

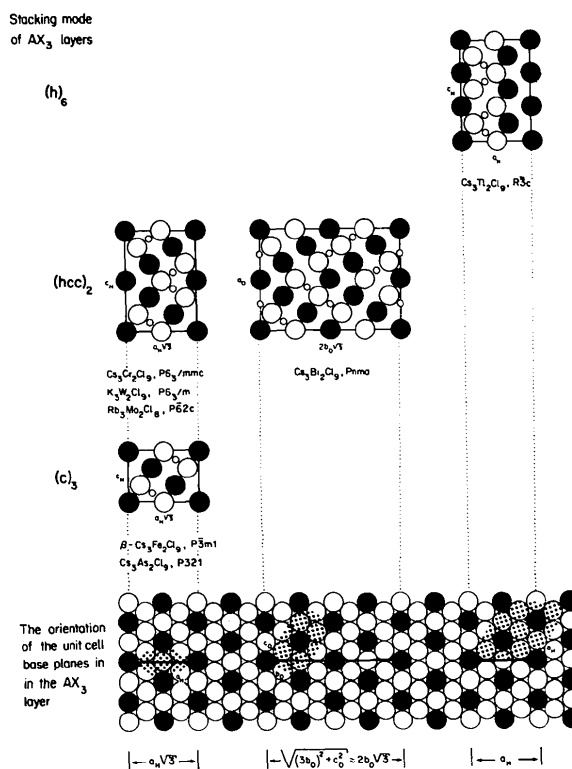


Fig. 1. The different A₃B₂X₉ crystal structure types presented by the atom arrangement in a plane perpendicular to the AX₃ layers. The position of this plane in the AX₃ layer is indicated by bold lines in the drawing at the bottom which presents a direct view of one AX₃ layer. A atoms are represented by large filled circles, B atoms by small open circles and X atoms by large open circles. The drawings represent idealized structures where the B atoms are placed exactly at the centres of the X₆ octahedra.

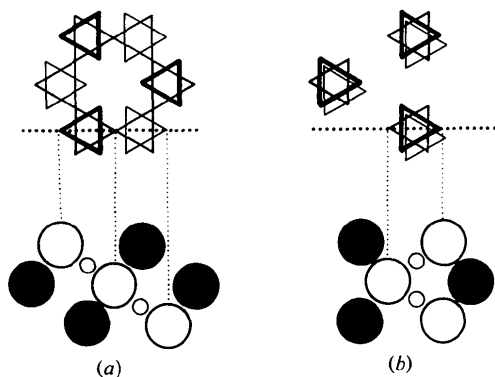


Fig. 2. Schematic representation of the two kinds of BX_6 groupings found in $A_3B_2X_9$ structures. The upper part of the figure represents the stacking of three AX_3 layers. The bold, medium thickness and fine lines correspond to the three levels (respectively upper, intermediate and lower) of these AX_3 layers. (a) The first type of BX_6 grouping where the layers are stacked in the 'c' manner and the octahedra are connected by vertices. (b) The second type of BX_6 grouping where the layers are stacked in the 'h' manner and in which 'double octahedra', i.e. two octahedra with a common face, are formed. The lower part of this figure shows the elevation of two of these octahedra with respect to the upper part. The representation is the same as in Fig. 1.

of $0,0,\frac{1}{2}$ to show the correspondence between the two structure descriptions. Applying the same shift of origin to $K_3W_2Cl_9$ (space group $P6_3/m$) and to $Rb_3Mo_2Cl_8$ (space group $P62c$) one finds that both structures are lower-symmetry versions of the $Cs_3Cr_2Cl_9$ type. The only difference from $Cs_3Cr_2Cl_9$ is found in the point positions which correspond to $6(h)$ and $12(k)$ where the numerical values for y are near but not quite the double of x . Further, in $Rb_3Mo_2Cl_8$ the point position corresponding to $6(h)$ is only two-thirds occupied. A list of all compounds with the $Cs_3Cr_2Cl_9$ type and its lower-symmetry versions is given in Table 2.

The $Cs_3Cr_2Cl_9$ structure type belongs to the set of $A_3B_2X_9$ structures which consist of a stacking of hexagonal AX_3 layers, as shown in the lower part of Fig. 1. The stacking is in a close-packed fashion such that every A atom has 12 X nearest-neighbours, but no A nearest-neighbours. The B atoms occupy octahedral interstices in the close-packed structure where they are always surrounded by six X atoms (in most cases with three closer and three further away). Only two-thirds of the available X_6 octahedra are filled by B atoms. The arrangement of these octahedra in the structure depends on the stacking sequence. Experimentally, three different stackings of AX_3 layers are known. Using the Jagodzinski-Wyckoff symbols (Jagodzinski, 1954) these stacking modes are h , hcc and c . Fig. 1 shows that with the hcc stacking two different arrangements of the filled X_6 octahedra are possible. The figure also indicates (on the left-hand side) that low-symmetry variants of a given stacking and octahedral arrangement are known. The particular plane we have chosen

Table 3. Distances and angles in the $Sb_2I_9^{3-}$ and $Bi_2I_9^{3-}$ double octahedra in $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$

For the notation see Fig. 3.

	$Sb_2I_9^{3-}$	$Bi_2I_9^{3-}$
$B-B, D$	3.962 (4) Å	4.046 (4) Å
$B-X_{br}^*, r'$	3.198 (2)	3.244 (2)
$B-X_r^*, r''$	2.870 (2)	2.920 (2)
$X_{br}-X_{br}, R'$	4.347 (2)	4.391 (2)
X_r-X_r, R''	4.180 (1)	4.270 (3)
$X_{br}-B-X_{br}, \alpha'$	85.65 (6)°	85.21 (8)°
X_r-B-X_r, α''	93.46 (7)	93.9 (1)
$X_{br}-B-X_r, \alpha'''$	90.32 (3)	90.25 (6)
$B-X_{br}-B, \beta$	76.56 (6)	77.17 (6)
$B-X_{br}$ plane, d'	1.878 Å	2.023 Å
$B-X_r$ plane, d''	1.553	1.565
d'/d''	1.209	1.292
$90^\circ - \alpha'$	4.35°	4.79°
$\beta - 70.53^\circ$	6.03	6.64

* X_{br} denotes bridging X atoms and X_r denotes terminal X atoms.

for Fig. 1 allows all the different octahedral sites found in the four structure types to be presented in a single figure. In these structures, one always finds either BX_6 octahedra which are joined to other BX_6 octahedra by single X atoms in common, or double octahedra with a face in common. These two kinds of BX_6 groupings can be easily recognized in Fig. 1 by referring to Fig. 2. The upper part of Fig. 2 represents two schematic projections of three AX_3 layers (as defined in Fig. 1) onto a plane parallel to the AX_3 layers. In both cases, X atoms are attached to the corners of the equilateral triangles and the stacking of two rotated triangles corresponds to an octahedron which contains a B atom at its centre. In the case of Fig. 2(a) the layers are stacked in the 'c' manner so that the octahedra are connected by vertices, while in Fig. 2(b) the layers are stacked in the 'h' manner so that the octahedra are connected by a common face. The lower part of Fig. 2 shows the elevation of two of these octahedra with respect to the upper part. The A atoms (filled large circles) have been added on this drawing in order that the two particular kinds of octahedron groupings with the representations shown in Fig. 1 can be easily recognized. According to this, only double octahedra with a face in common are possible with $(h)_6$ stacking, as demonstrated in the rhombohedral structure of $Cs_3Ti_2Cl_9$ (Powell & Wells, 1935; Hoard & Goldstein, 1935b). If the AX_3 layers are stacked in the $(c)_3$ mode, only octahedra joined by single X atoms in common are possible, as shown with trigonal $Cs_3As_2Cl_9$ (Hoard & Goldstein, 1935a). For the case of $(hcc)_2$ stacking the presence of both kinds of octahedron netting would be possible in principle, but

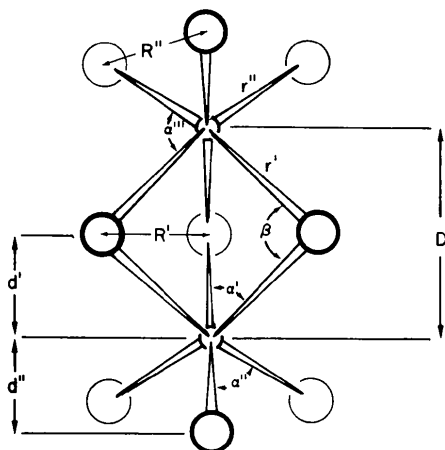


Fig. 3. Notation of distances and angles in the $B_2X_9^{3-}$ double octahedra after Cotton & Ucko (1972).

this has not yet been found experimentally. For example, in hexagonal Cs₃Cr₂Cl₉ (Wessel & IJdo, 1957) there are only double octahedra with a face in common, while in orthorhombic Cs₃Bi₂Cl₉ (Kihara & Sudo, 1974) only octahedra joined by single X atoms in common are observed.

The presence of double octahedra in Cs₃Sb₂I₉ and Cs₃Bi₂I₉ may be interpreted as a tendency to form stable Sb₂I₉³⁻ or Bi₂I₉³⁻ ionic groups. One might expect that the stability of these ionic groups is due to covalent interactions between the Sb or Bi atoms across the shared octahedron face. Interestingly, the geometrical interaction criterion of Cotton & Ucko (1972) does not indicate an attractive interaction between Sb or Bi atoms. In Table 3, the interatomic distances and angles in the Sb₂I₉³⁻ and Bi₂I₉³⁻ double octahedra are given using the notation of Cotton & Ucko. Fig. 3 illustrates this notation in detail. In the ideal case the filled double octahedra are built up of two regular octahedra with B atoms at their centres, and consequently: $d'/d'' = 1$, $90^\circ - \alpha' = 0^\circ$, and $\beta - 70.53^\circ = 0^\circ$. In Cs₃Sb₂I₉ and Cs₃Bi₂I₉, the Sb₂I₉³⁻ and Bi₂I₉³⁻ ions are geometrically alike: the d'/d'' ratio is greater than one (1.209 and 1.292 respectively) and the angular deviations with respect to the undistorted double octahedra are positive (4.35 and 4.79° for $90^\circ - \alpha'$, and 6.03 and 6.64° for $\beta - 70.53^\circ$).

$A_3B_2X_9$ compounds having such characteristic $B_2X_9^{3-}$ groups are listed in Table 2. In this table, c/a and d'/d'' ratios are listed together, whenever available, in order to point out that these two values are to a first

approximation linearly related. Compounds with a c/a ratio less than ~ 2.4 have a d'/d'' ratio of less than one. Consequently, the readily available c/a ratio may be used as a criterion (in place of d'/d'') for characterizing the nature of the B–B interactions in these structures.

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