

# The InSnCl<sub>3</sub>-Type Arrangement

## I. A New ABX<sub>3</sub> Structure Type with Close Cation–Cation Contacts

H. P. Beck, H. Tratzky, V. Kallmayer, and K. Stöwe

*Institute of Inorganic and Analytical Chemistry and Radiochemistry, Saarland University, Saarbrücken, Germany*

Received January 6, 1999; in revised form April 21, 1999; accepted May 7, 1999

**We report on the synthesis and structure of InSnCl<sub>3</sub> and InSnBr<sub>3</sub>. Their structure represents a new ABX<sub>3</sub> structure type which will only be found for compounds with large cations *A* and *B* having an *ns*<sup>2</sup> electron configuration. The cations have high coordination numbers and therefore their coordination polyhedra are connected mainly by common edges and even faces. This leads to fairly short cation–cation distances. However, the electrostatic repulsion may be decreased by a shielding effect of the *s*-electrons. The distribution of the cations on different sites, which cannot be determined by routine X-ray investigations, is discussed on the basis of crystal chemical considerations. Low temperature diffraction measurements on InSnCl<sub>3</sub> show that the high symmetry of the arrangement is mimicked by a polydomain configuration, which can be dealt with by a split atom refinement.** © 1999 Academic Press

### INTRODUCTION

In the course of our studies on the crystal chemistry of cations with *ns*<sup>2</sup> configuration we have examined a variety of ternary halides containing such species. We found many new compounds of this type as a result of our thermo-analytical investigations on quasi-binary systems *AX* – *BX*<sub>2</sub>, where *A* = K, Rb, In, Tl, *B* = Sn, Pb, and *X* = Cl, Br, I. We have reported on the corresponding phase diagrams (1–5) and on X-ray structure determinations of compounds with the formulas *AB*<sub>2</sub>*X*<sub>5</sub> (6, 7), *A*<sub>4</sub>*BX*<sub>6</sub> (8–10), and *A*<sub>3</sub>*BX*<sub>5</sub> (11), which are often encountered in such systems. The structures show some peculiar features which can be attributed to geometrical and electronic effects of the *ns*<sup>2</sup> cations. Such cations are even a prerequisite for these structures (10); a substitution by cations with noble gas configuration will always lead to a destabilization. The compound will either not exist or crystallize in a different structure. However, this sensitivity toward substitution is only seen for special sites of the structures, e.g., the *B* site in the *AB*<sub>2</sub>*X*<sub>5</sub> compounds and the *A* site in the *A*<sub>4</sub>*BX*<sub>6</sub> compounds, in any way, sites where the corresponding *ns*<sup>2</sup> cations are found with fairly close distances in neighboring polyhedra having

common faces. To understand the interaction of *ns*<sup>2</sup> cations, compounds with a high concentration of them are therefore of special interest.

In this paper, we report on the structure of the isotopic ternary halides InSnCl<sub>3</sub> and InSnBr<sub>3</sub>. In these compounds the size relations do not allow a perovskite-type arrangement; the high coordination numbers of these large cations lead to a new structure where the coordination polyhedra share many corners, edges, and even faces. Their centers are therefore quite close, and such arrangements, too, will only be stabilized by the special effects of *ns*<sup>2</sup> cations which are again a prerequisite for their existence. However, not all combinations of the elements given above form such *ABX*<sub>3</sub> compounds. A comparable ternary halide has not been found in the systems In–Pb–Cl (12, 13), In–Pb–Br (14), Tl–Pb–Cl (15), and Tl–Pb–Br (16), and its existence is questionable in the system Tl–Sn–Br. InSnCl<sub>3</sub> is a congruently melting phase (2), InSnBr<sub>3</sub> exists only in a narrow range of temperatures and decomposes at lower temperatures (5), and TIPbCl<sub>3</sub>, nonexistent at normal conditions, can be synthesized under high pressure conditions as we will show in a forthcoming paper (17). The existence of *ABX*<sub>3</sub> compounds of this type evidently depends on a delicate interplay of several geometric and electronic factors.

### EXPERIMENTAL

#### Synthesis

InSnCl<sub>3</sub> can be synthesized by slowly cooling a melt containing InCl and SnCl<sub>2</sub> in a 1:1 ratio. It is, however, favorable to make the compound by solid state reaction of the binary educts because redox reactions may lead to unwanted by-products (2). It seems to be stable at all temperatures below the melting point. InSnBr<sub>3</sub> can only be synthesized by equilibrating an InBr–SnBr<sub>2</sub> mixture in the temperature range between 200 and 223°C for several days. Good crystals will only be obtained after weeks. After quenching, the products should be kept in the dark and handled under inert atmospheres. Traces of water will



TABLE 1  
Details of the Data Collection

Compound	InSnCl <sub>3</sub>	InSnCl <sub>3</sub>	InSnBr <sub>3</sub>
Sample temperature	293 K	203 K	293 K
Scan	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan range	0.7° 2 $\theta$	0.7° 2 $\theta$	0.7° 2 $\theta$
Scan speed	2–10°/min	2–10°/min	2–10°/min
Range of data collection	3–30°/60° (see text); $hkl, \bar{h}\bar{k}\bar{l}$	30–60°, $hkl, \bar{h}\bar{k}\bar{l}$	3–32°; $hkl, \bar{h}\bar{k}\bar{l}$
Radiation	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$
Residual of merging (%)	2.0/3.2 (see text)	4.2	1.7
Number of reflections	144/928 (see text)	918	652
Absorption correction	yes	yes	yes
HABITUS/ABSPSI (19)			
$R/R_w$	4.4/14.8 (see text)	4.0/8.3	7.4

accelerate the decomposition of the compound which can be stored only a short time. Above 223°C there is a peritectic decomposition to InSn<sub>2</sub>Br<sub>5</sub>, and below 206°C the compound slowly decomposes to form InSn<sub>2</sub>Br<sub>5</sub> and In<sub>3</sub>SnBr<sub>5</sub> (5).

#### Structure Determination

For X-ray investigations, the substances were sealed in glass capillaries under argon. Powder diagrams were taken with a Guinier-type diffractometer (Huber, Rimsting, FRG). Diffraction intensities of single crystals of InSnCl<sub>3</sub> and InSnBr<sub>3</sub> were collected on a Siemens P4 diffractometer (see Table 1). SHELXL93 (18) was used for the determination and refinement of the structures. The results are presented in Tables 2, 3, 4, and 5.

## RESULTS AND DISCUSSION

#### Structure Model and Refinement

The structure of these compounds was first determined from single crystal data taken at ambient temperatures. Extinction rules and intensity statistics clearly pointed to the space group *I4/mcm*. Direct methods only gave parts of the structure; unfavorable relations of electron numbers made a solution by Patterson methods quite difficult. The structure presented here was developed in several steps by Fourier maps and refinement procedures.

Even though the data could be corrected for absorption very well with excellent  $R$ -values for merging, the residual  $R$ -values of refinement are fairly high, and they differ for data sets with different  $2\Theta_{\max}$ . Furthermore there are large and in some cases extremely anisotropic thermal parameters. This is true for the chloride as well as for the bromide.

This could indicate that the symmetry is lower than assumed. We have therefore reduced the symmetry in minimal steps and have used all reasonable subgroups of

*I4/mcm* down to *P4* as a model in the refinements with quite different results. Even though the number of refinable parameters increases during symmetry reduction  $R$ -values do not decrease correspondingly in many of the models used.

TABLE 2  
Crystallographic Parameters at Room Temperature

		InSnCl <sub>3</sub>	InSnBr <sub>3</sub>	
Lattice parameters				
$a$	(pm)	1199.5(1)	12.497(2)	
$c$	(pm)	1594.3(1)	16.411(3)	
$V$	(10 <sup>6</sup> pm <sup>3</sup> )	2293.9	2563.0	
$Z$		16	16	
Density				
$\rho_{\text{calc}}$	g/cm <sup>3</sup>	3.94	4.91	
Formula weight				
$M$	g/mol	340.0	473.2	
Positional parameters				
Atom	Site			
M(1)	16l	$x$	0.1633(2)	0.1642(2)
		$y$	0.6633(2)	0.6642(2)
		$z$	0.1781(2)	0.1812(2)
M(2)	8h	$x$	0.6379(2)	0.6372(4)
		$y$	0.1379(2)	0.1372(4)
		$z$	0	0
M(3)	4a	$x$	0	0
		$y$	0	0
		$z$	$\frac{1}{4}$	$\frac{1}{4}$
M(4)	4c	$x$	0	0
		$y$	0	0
		$z$	0	0
Cl(1)	32m	$x$	0.0669(5)	0.0673(2)
		$y$	0.2065(5)	0.2051(2)
		$z$	0.1383(3)	0.1406(2)
Cl(2)	8h	$x$	0.1785(7)	0.1773(4)
		$y$	0.6785(7)	0.6773(4)
		$z$	0	0
Cl(3)	8g	$x$	0	0
		$y$	$\frac{1}{2}$	$\frac{1}{2}$
		$z$	0.1307(8)	0.1322(6)

**TABLE 3**  
Thermal Parameters ( $\text{pm}^2$ ) for  $\text{InSnCl}_3$  at Room Temperature

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{\text{eq.}}$
M(1)	1080(16)	1080(16)	942(24)	-412(19)	-91(13)	91(13)	1034(12)
M(2)	691(19)	691(19)	2043(47)	91(22)	0.0	0.0	1142(18)
M(3)	1374(32)	1374(32)	610(35)	0.0	0.0	0.0	1119(22)
M(4)	1067(28)	1067(28)	709(36)	0.0	0.0	0.0	948(20)
X(1)	671(44)	549(45)	814(39)	-24(37)	31(37)	-99(37)	678(20)
X(2)	921(62)	921(62)	616(83)	-291(84)	0.0	0.0	820(45)
X(3)	515(49)	515(49)	1290(12)	65(78)	0.0	0.0	773(43)

Furthermore in many cases split atom positions seem advisable and some thermal parameter sets are nonpositive definite. In all cases cutting down  $2\Theta_{\text{max}}$ , i.e., reducing the resolution of the experiment, “seemingly improves” the  $R$ -values more than we would usually expect on an estimate of the parameter/reflection-ratios and  $|F_o - F_c|$ -sums. For  $\text{InSnCl}_3$  the “best” residuals ( $R1 = 3.9\%$ ) result from a refinement using the space group  $I4/mcm$  with a reduced data set ( $2\Theta_{\text{max}} = 30^\circ$ , 144 unique reflections), a data set with  $2\Theta_{\text{max}} = 60^\circ$  (928 unique reflections) will only yield  $R1 = 14.8\%$ . Refinement in  $P4$  using a large data set ( $2\Theta_{\text{max}} = 60^\circ$ ) measured as  $P$  lattice and containing all Friedel pairs results in  $R1 = 19.5\%$  (but  $11.1\%$  using only  $F_o > 4\sigma$ ). Other “good tries” are  $I\bar{4}c2$  ( $R1 = 12.6\%$ ) and  $I\bar{4}2m$  ( $R1 = 14.0\%$ ). The inclusion of many weak reflections of course worsens the picture. One would expect that scrutinizing the data sets with respect to the extinction rules and the symmetry in the distribution of intensities should settle the matter. However the statistics of merging clearly confirm the crystal class  $4/mmm$  and the extinction rules seem no more “violated” than in “normal” data sets.

During the refinement in lower symmetric models there is a slight shift away from the atomic positions of the  $I4/mcm$  parameter set. However, many of the structure factors calculated for reflections which would be extinct in the

**TABLE 4**  
Positional Parameters for  $\text{InSnCl}_3$  at 203 K<sup>a</sup>

	Wyckoff position	$x$	$y$	$z$
M11	32m	0.1413(2)	0.6874(2)	0.16484(9)
M12	16l	0.1633(1)	0.6633(1)	0.1898(1)
M2	16l	0.63712(6)	0.13712(6)	0.02089(5)
M3	16i	0.0206(1)	0.0206(1)	1/4
M4	4c	0	0	0
Cl1	32m	0.06550(9)	0.20584(9)	0.13823(8)
Cl2	8h	0.1792(2)	0.6792(2)	0
Cl31	8g	0	1/2	0.1455(6)
Cl32	8g	0	1/2	0.1198(5)

<sup>a</sup> $a = 1194.21(1)$  pm;  $c = 1588.3(1)$  pm.

**TABLE 5**  
Thermal Parameters ( $\text{pm}^2$ ) for  $\text{InSnCl}_3$  at 203 K

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{\text{eq.}}$
M11	372(85)	736(107)	2918(92)	69(67)	-3(61)	-55(69)	467(45)
M12	498(52)	498(52)	361(85)	-13(54)	-81(44)	-81(44)	440(34)
M2	549(35)	549(35)	536(74)	127(39)	-103(29)	-103(29)	545(33)
M3	580(14)	580(14)	413(62)	-31(87)	-128(18)	128(18)	525(94)
M4	761(49)	761(49)	489(55)	0	0	0	670(35)
Cl1	442(57)	370(52)	728(8)	-15(41)	6(50)	-65(50)	513(31)
Cl2	690(98)	690(98)	290(92)	-143(12)	0	0	557(6)
Cl31	488(25)	488(25)	779(76)	67(27)	0	0	586(3)
Cl32	274(15)	274(15)	471(42)	1(16)	0	0	340(2)

highest symmetry are by far too large compared with the few very small detectable intensities. The parameter shifts have evidently been induced by a minimization of  $|F_o - F_c|$  of the normal reflections with high intensity, resulting in a secondary minimum in the hypersurface during the refinement.

Another approach would be to assume disordering or polydomain configurations. As to the latter consideration calculations assuming different ways of twinning (inversion, plane, axis) do not seem to improve the residuals more than by the usual effect of increased parameter numbers, and systematic checking of the data sets following the procedures proposed by Britton (20) or Yeates (21) gave no definite clues for twinning.

One may then conjecture that the size of domains containing distortions in different orientations is very small leading to a broadening of reflections—especially of the weak originally “extinct” ones—and seemingly lower intensities, but the very few reflections violating the extinction rules show the same FWHM as the normal ones. It seemed therefore that the problem would not be solved within the kinematical theory of a polydomain configuration.

Low temperature diffraction measurements on  $\text{InSnCl}_3$  finally yielded a data set which behaved quite different in the refinement procedures. Reasonable  $R$ -values were achieved by assuming split atom positions and the high symmetry space group  $I4/mcm$ . A detailed crystal chemical analysis of these mathematical findings is given below. It furnishes an insight into a complex polydomain situation which is evidently due to local distortions brought about by the special electronic configuration of the cations. The aspect of disordering, however, proved to be important.

In view of these findings we prefer to describe the new structure in the space group with highest symmetry, and after that we will give a model for the distortion in small domains.

### The Structure

The structure of  $\text{InSnCl}_3$  and the isotypic compounds constitutes a new  $ABX_3$  type which is only found for

compounds with  $ns^2$  cations which are evidently a prerequisite for the formation of this specific structure. The other structures such as the perovskite type and the NH<sub>4</sub>CdCl<sub>3</sub> type together with their deformation variants have  $BX_6$  octahedra sharing corners or corners and edges, respectively, as a main structural principle and  $A$  cations in voids of different size according to the special arrangement in the three dimensional  $BX_{6/2}$  sublattice. The same is in principle true for the TIPbI<sub>3</sub> structure. In a structure field map of  $ABX_3$  compounds on the basis of  $A/X$  vs  $B/X$  ratios, one will find the InSnCl<sub>3</sub> structure at fairly small to medium  $A/X$  and at the largest  $B/X$  size-ratios. This leads to different  $BX_n$  polyhedra and a completely new type of linking. We will give a picture of the InSnCl<sub>3</sub>-type arrangement by describing the different coordination polyhedra and the way they are linked to form the complete structure. Element combinations such as In/Sn will always make trouble in X-ray structure determinations because there is hardly a difference in atomic form factors. The assignment of the cations to the different sites can only be based on crystal chemical considerations. We therefore first describe the structure without distinguishing between the different elements in the cation sublattice, and we first refer to the picture derived from the room temperature data.

The coordination around M(1) shows a geometry rarely found (22). We find eight anions (medium cation–anion distance 324 pm) in the form of a polyhedron, which may be described by the abbreviation 1:5:2 when counting the ligands in three planes (see Fig. 1). It is a special feature of this structure that two such polyhedra are connected by

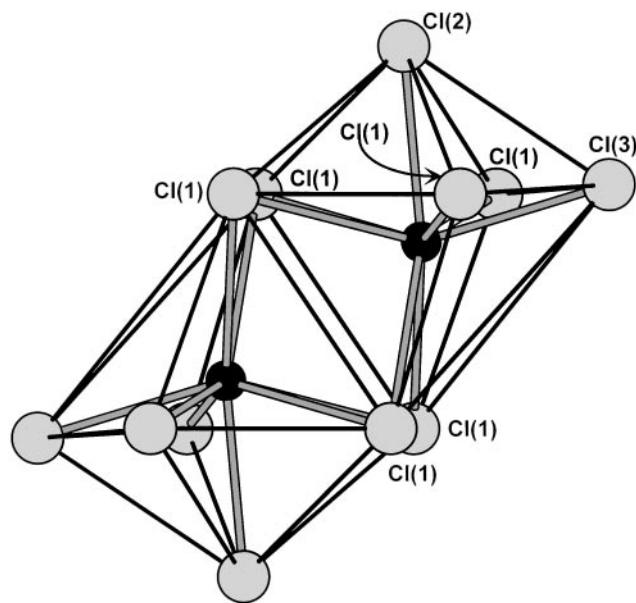


FIG. 1. Two 1:5:2 polyhedra sharing a square face. Light gray spheres, Cl; black spheres, M(1).

sharing a square face (Fig. 1). This leads to a fairly short distance between the central M(1) atoms. We believe that this structural feature is a “sore point” in the whole arrangement and the thermal parameters of the central cation also give a hint to that. This double polyhedron may be compared with the fourfold capped double prisms which are encountered in the  $AB_2X_5$ ,  $A_4BX_6$  and  $A_3BX_5$  structures mentioned above, and indeed, it may easily be converted to such a double prism by a slight deformation. This structural unit will only exist if  $ns^2$  cations make up the centers so that the  $s$  electron density will at least partially shield the repulsive charge (see discussion in (10)). This is why a substitution by  $s^0$  cations will destabilize the structure, and even in the case of the compounds with  $ns^2$  cations described here the repulsive forces remaining will evidently lead to the polydomain configuration described below.

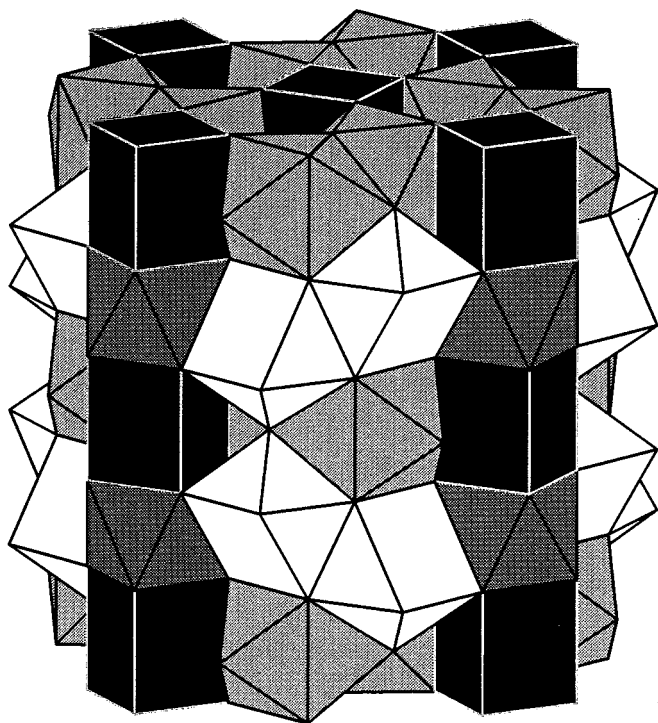
M(2) is surrounded by nine anions (medium cation–anion distance 324 pm) in the form of a tricapped trigonal prism. M(3) is at the center of a square antiprism (medium cation–anion distance 314 pm), and around M(4), there is a slightly elongated cube of eight anions (medium cation–anion distance 339 pm). The latter two polyhedra are piled on top of each other sharing square faces to form rods along [001] in a centered arrangement.

Between these rods and sharing common atoms we see the other building units. The tricapped trigonal prisms form pairs sharing one prism edge and two caps. They are therefore different from the double prisms in the other structures mentioned above. These units connect the rods in two heights in  $c$ . Due to symmetry, the orientation of them is complementary. The  $M(1)_2Cl_{12}$  double polyhedra are dispersed into the framework. Figure 2 shows the packing of these different polyhedra in the complete structure at a viewing angle which shows all the details mentioned.

#### The Distribution of the Cations

As mentioned above the assignment of the cations to the different sites can only be based on crystal chemical considerations. Distances around M(4) fit nicely with the sum of radii for In<sup>+</sup> and Cl<sup>-</sup>, and those around M(3) imply that the position is occupied by Sn<sup>2+</sup>. Distances around M(1) and M(2) are in between these two. We must therefore envisage a statistical occupancy of In<sup>+</sup> and Sn<sup>2+</sup> at these positions. Table 6 shows several possibilities of distributing In<sup>+</sup> and Sn<sup>2+</sup> on the different cation sites preserving electroneutrality.

The last possibility distributes all different cations on different sites. However, as mentioned above it seems little probable because of the observed cation–anion distances. Apart from the distances there is another feature that makes this arrangement unfavorable. According to Pauling’s electrostatic valence rule the cationic charge contributions to the three crystallographically different anions would be



**FIG. 2.** The  $\text{InSnCl}_3$  structure type ( $c$  axis points upward, the intensity of shading of the different polyhedra around the cations increases in the sequence M(1), M(2), M(3), M(4)).

extremely unbalanced. It is surprising, however, that the Madelung part of lattice energy (MAPLE) is very high with such a distribution of cations.

The third line in the table seems to describe the best choice. It has the highest MAPLE value, a fairly balanced valence sum, and complies with the distances when keeping in mind that the M(2) position has six very short cation-anion distances and two very long ones. We cannot exclude, however, that other local distributions play a certain role.

#### *Distortion in Small Domains*

It is characteristic of  $ns^2$  cations that they tend to distort a higher symmetric environment due to the lone pair

**TABLE 6**  
**Comparison of Cation Distributions**

M(1) (16l)	M(2) (8h)	M(3) (4a)	M(4) (4c)	Pauling's valence sums			MAPLE KJ/mol (for $\text{InSnBr}_3$ )
				Cl(1)	Cl(2)	Cl(3)	
8 In/8 Sn	4 In/4 Sn	4 Sn	4 In	1.10	0.88	0.71	2843
10 In/6 Sn	2 In/6 Sn	4 Sn	4 In	1.09	0.93	0.73	2876
12 In/4 Sn	8 Sn	4 Sn	4 In	1.06	0.98	0.76	2929
4 In/12Sn	8 In	4 Sn	4 In	1.14	0.77	0.66	2837
16 In	8 Sn	4 Sn	4 Sn	1.10	0.92	0.69	2933

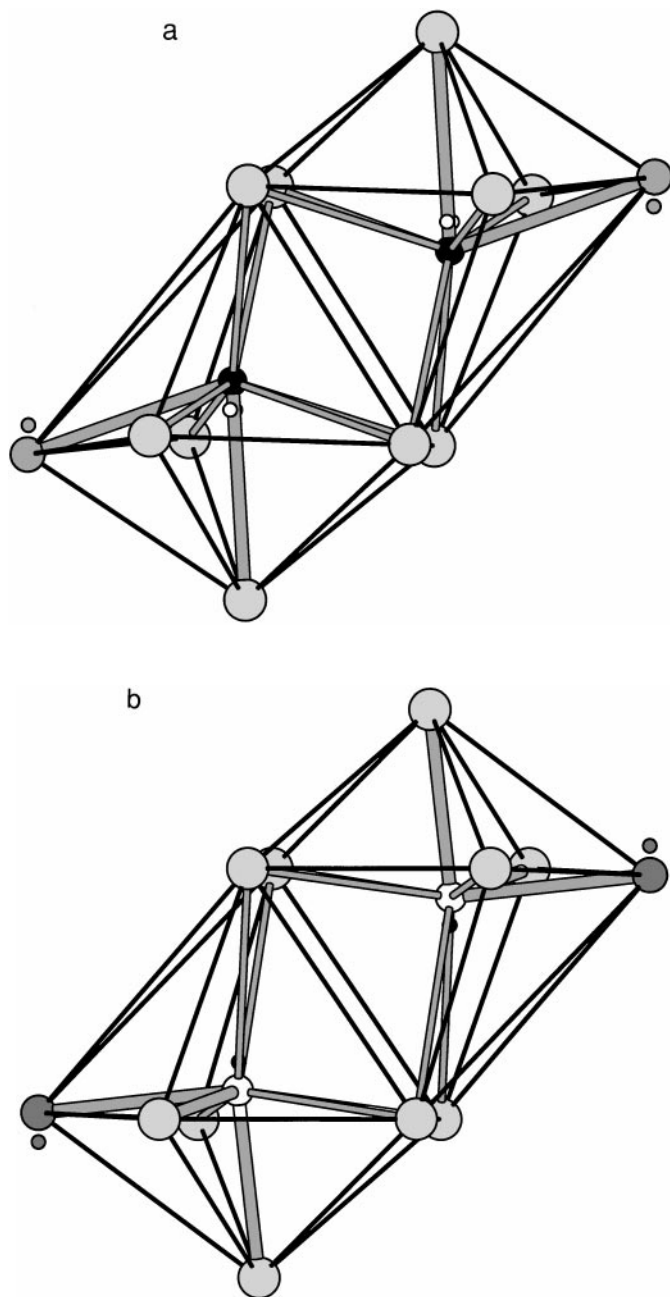
activity, i.e., more or less  $p$  character of the atomic orbital containing the free electron pair. In all polyhedra described above the cations have a fairly high site symmetry. One may assume that there is a statistical distribution of displacements from these positions which mimic the higher symmetry seen in X-ray diffraction. In an attempt to force at least some ordering we have equilibrated a single crystal of  $\text{InSnCl}_3$  for fairly long times at  $-70^\circ\text{C}$ . The data set which has been taken at that temperature could be refined differently from all the others. When introducing specific split atom positions the refinement converged quickly to low residuals which prove the statistical relevance of the model. The following discussion and the parameters and distances given refer to this data set.

In the "coarse picture" M(1) lies on a mirror plane parallel (110). Refinement of the low temperature data set shows up the electron density on this plane and to both sides of it. The model of the cation distribution that we favor expects In as well as Sn on this site. These elements differ in their tendency to develop an eccentric electron distribution. We find three positions for the cations in the double 1:5:2 polyhedra. The central ones, still on the mirror plane, have slightly moved away from the original position in opposite directions along [001]. They come closer by this movement, and it is obvious that this can only happen when the lower charged  $\text{In}^+$  occupies this position.

In the coarse model Cl(3) also has large anisotropic thermal parameters. It can be refined as a split atom position too. Which of the two positions is occupied depends on whether there is  $\text{In}^+$  or  $\text{Sn}^{2+}$  in the polyhedron. Figure 3a shows the situation where  $\text{In}^+$  lies on the mirror plane and the Cl(3) position with the larger distance to it is occupied. (The empty positions are given as small spheres.) There are now two fairly short In-Cl distances (297 and 303 pm) and eight longer ones ( $2 \times 325$  pm,  $2 \times 336$  pm,  $2 \times 338$  pm). The In-In distance (374 pm) is almost as short as in  $\text{InCl}$ .

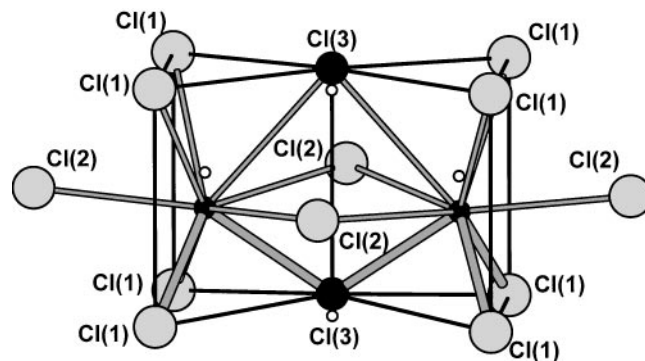
Figure 3b shows the situation where positions off the mirror plane are occupied and the other Cl(3) site is chosen. The distance between adjacent cations can be maximized when placing the cations on different sides of the original mirror plane (404 pm). The mean cation-anion distances indicate that this is a  $\text{Sn}^{2+}$  position, and we find a typical bonding situation for  $\text{Sn}^{2+}$ , i.e., three shorter Sn-Cl distances (266 pm,  $2 \times 282$  pm) and five longer ones in the range from 308 to 320 pm. The eccentricity of the lone pair of  $\text{Sn}^{2+}$  is distinctly larger than that of  $\text{In}^+$ . By this choice of positions the lone pairs do not point toward each other and repulsion is minimized.

Figure 4 shows the split atom positions of the M(2) in the double prisms which we assume to contain  $\text{Sn}^{2+}$ . The common central edge of the prisms is formed by Cl(3) ions for which the split atom positions have been discussed above. Choosing one of them together with one of the cations positions as shown in the figure again gives the typical



**FIG. 3.** Split atom positions for M(1) (white and black spheres). Alternative positions for Cl(1) are shown as small dark spheres and short distances are represented by thick sticks. Light gray spheres, nonsplit Cl (for atom assignments see Fig. 1). (a) M(12) and Cl(32) occupied; (b) M(11) and Cl(31) occupied.

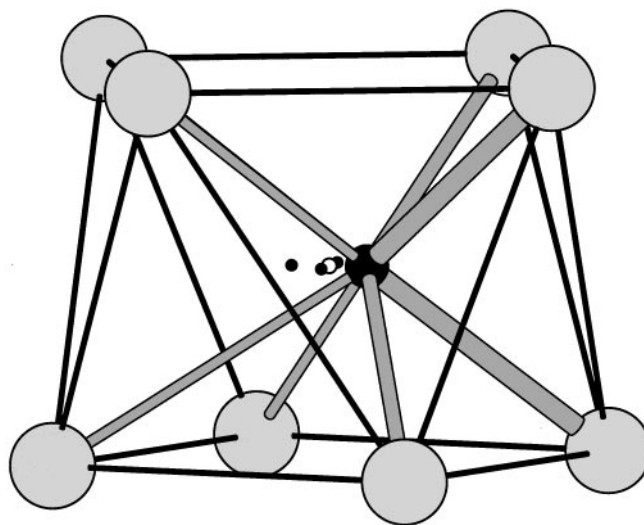
bonding situation with three fairly short Sn-Cl distances ( $2 \times 278$  pm, 280 pm) and six long ones (312 pm,  $2 \times 326$  pm,  $2 \times 383$  pm, 351 pm). In this picture the cations would move away from their original position on a mirror plane along [001] and both Cl(3) anions would do the same but in the opposite direction. The situation where the two cations



**FIG. 4.** Tricapped trigonal prisms around M(2). Either black or white positions are occupied (the black positions are shown). Short distance represented by thick lines. Light gray spheres: nonsplit Cl.

move to different sides of the mirror plane would have the consequence that both Cl(3) positions closer to the plane should be occupied, both would move in, and no split atom configuration would result.

In the coarse model the thermal ellipsoid of M(3) is a flat disk. It can be shown by calculating so-called hindrance parameters (7) that geometric restraints are not the cause for such an anisotropic movement. The refinement of the low temperature data set shows maxima of electron density in a ring about 35 pm away from the fourfold axis where the cation was placed originally. Figure 5 shows a situation



**FIG. 5.** A tetragonal antiprism around M(3). Black sphere, M(3) split positions lying on twofold axes (see text). Alternative positions are shown as small spheres and thick sticks refer to shorter distances. The white sphere shows the "crude position" with fourfold symmetry. Light gray spheres, Cl(1).

where the cation positions are assumed to be away from the fourfold axis but still on the twofold axis perpendicular to it. This leads to a similar situation resulting in groups of shorter and longer Sn–Cl bonds. However, the exact position could not be determined reliably.

All the “movements” in the different polyhedra are evidently caused by the different sizes of the substituting cations and/or by the different eccentricity of the lone pair. The different local distortions may not be correlated by a symmetry element or be cooperative on a larger scale and this would result in larger domains whose existence could be proven by twin refinements or even by new extinction rules, i.e., another space group.

The cooperativity of distortions in the different polyhedra will strongly depend on the movement of Cl(3) which is common to the polyhedra around M(1) and M(2). Substitution or movement in one polyhedron will force a corresponding change in the other one. This structural peculiarity may be responsible for the reduced stability of all phases having this structure.

It may well be that the *I4/mcm* structure “exists” at high temperatures where larger atomic motions blur the fine distortions caused by aliovalent substitution and the different eccentricity of lone pairs and that there is a phase transition at lower temperatures resulting either in a decomposition of the phase (as with InSnBr<sub>3</sub>) or in a situation where the symmetry is reduced by local distortion without ordering on a larger scale. InSnCl<sub>3</sub>—seemingly stable down to lower temperatures—could be an example for the latter case. On the basis of our X-ray data we assume that the crystals have a polydomain configuration with small domain sizes and more or less random orientations.

Refinement models with some symmetry correlation or with split atom positions will seemingly correspond with the data only if specific local situations are repeated to have a sufficient statistical weight, and this is evidently not the case here. This is why we prefer to describe the new structure in the high symmetric space group. Refinement of models with even lower symmetry does not seem to make sense in view of the symmetry of intensity distribution in reciprocal space.

## CONCLUSION

The *ABX<sub>3</sub>* structure described here is a new structure type which will only be encountered for larger cations *A* and *B*. It seems essential for the stability and structure of these compounds that the cations have a *ns<sup>2</sup>* electron configuration. A substitution by others having a rare gas electron configuration will destabilize the structure. The compounds

described here all show a disorder of *A* and *B* cations on some of the crystallographically different sites.

InSnCl<sub>3</sub> is the most stable of these compounds with respect to the temperature range of existence and its melting characteristics. InSnBr<sub>3</sub> only exists at higher temperatures where possibly entropy effects stabilize an otherwise energetically unfavorable situation. It may well be, however, that InSnCl<sub>3</sub> undergoes a phase transition from a *I4/mcm*-type arrangement stable at higher temperatures to a low temperature form with lower symmetry. The crystals used in our single crystal X-ray measurements could then be polydomain configurations with merohedral twinning where classical refinement procedures will fail.

We are currently preparing for exact thermoanalytical investigations to elucidate the problem of a phase transition and for synchrotron diffraction experiments at varying wavelengths to get clues for the distribution of the different cations.

Our results on the synthesis of the corresponding thallium lead compounds will be reported in a forthcoming paper.

## REFERENCES

1. H. P. Beck and H. Nau, *Z. Anorg. Allg. Chem.* **554**, 43 (1987).
2. H. P. Beck and D. Wilhelm, and A. Hartl-Gunselmann, *Z. Anorg. Allg. Chem.* **602**, 65 (1991).
3. K. Stöwe and H. P. Beck, *Z. Anorg. Allg. Chem.* **608**, 115 (1992).
4. K. Stöwe and H. P. Beck, *Z. Anorg. Allg. Chem.* **608**, 119 (1992).
5. H. P. Beck and H. Glaser, *Z. Anorg. Allg. Chem.* **621**, 550 (1995).
6. H. P. Beck, G. Clicqué, and H. Nau, *Z. Anorg. Allg. Chem.* **536**, 35 (1986).
7. H. P. Beck, *Z. Anorg. Allg. Chem.* **536**, 45 (1986).
8. H. P. Beck and W. Milius, *Z. Anorg. Allg. Chem.* **539**, 7 (1986).
9. H. P. Beck and W. Milius, *Z. Anorg. Allg. Chem.* **562**, 102 (1988).
10. H. P. Beck and W. Milius, *Z. Anorg. Allg. Chem.* **562**, 105 (1988).
11. K. Stöwe and H. P. Beck, *Z. Krist.* **209**, 36 (1994).
12. Yu. P. Afinogenov, L. I. Shumeiko, and T. N. Larionova, *Russ. J. Inorg. Chem.* **17**, 916 (1972).
13. D. Wilhelm, PhD thesis, University of Saarland, Germany, 1993.
14. H. Tratzky, PhD thesis, University of Saarland, Germany, 1995.
15. H.-L. Keller, *J. Solid State Chem.* **48**, 346 (1983).
16. H.-L. Keller, *Rev. Chim. Miner.* **10**, 178 (1981).
17. H. P. Beck and M. Schramm, *J. Solid State Chem.* **146**, 351 (1999).
18. G. M. Sheldrick, SHELXL93, FORTRAN 77, Program for the Refinement of Crystal Structure from Diffraction Data, Göttingen 1994; G. M. Sheldrick, *Acta Crystallogr. A* **46**, 467 (1990).
19. (a) W. Herrendorf, HABITUS, Programm zur Optimierung der Kristallbeschreibung für numerische Absorptionskorrektur anhand geeigneter Psi-abgetasteter Reflexe, Universität Karlsruhe, 1992; (b) N. W. Alcock, P. J. Marks, and K.-G. Adams, “ABSPSI, Absorption Correction and Refinement of the Crystal Habitus.” Karlsruhe, Germany, 1994.
20. D. Britton, *Acta Cryst. A* **28**, 296 (1972).
21. T. O. Yeates, *Acta Cryst. A* **44**, 142 (1988).
22. H. P. Beck, M. Schramm, R. Haberkorn, R. Dinnebie, and P. W. Stephens, *Z. Anorg. Allg. Chem.* **624**, 393 (1998).