

# Evidence for Cluster Orbital Formation in $\text{CsSn}_2\text{X}_5$ Compounds ( $\text{X}=\text{Cl}, \text{Br}$ )

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The formation of cluster orbitals in  $\text{CsSn}_2\text{Br}_5$  is discussed and related more generally to tetragonal compounds of the type  $\text{AB}_2\text{X}_5$  ( $A$  = monovalent cation;  $B$  = Sn, Pb;  $X$  = Cl, Br, I). The crystal structures of  $\text{CsSn}_2\text{Cl}_5$  and  $\text{CsSn}_2\text{Br}_5$  have been solved by single-crystal X-ray diffraction. These compounds are isostructural with each other and a range of  $\text{AB}_2\text{X}_5$  structural analogues. In many  $\text{AB}_2\text{X}_5$  compounds where  $B$  is a subvalent main group metal a tetragonal cell is observed with space group  $I4/mcm$ . The structures of  $\text{CsSn}_2\text{Br}_5$  and  $\text{CsSn}_2\text{Cl}_5$  are layered with polymeric sheets of  $[\text{Sn}_2\text{X}_5]_n^{n-}$  separated by the  $\text{Cs}^+$  cations. Stereochemical considerations suggest that stabilization of this structural form, rather than the more ionic  $\text{NH}_4\text{Pb}_2\text{Cl}_5$  or  $\text{NaSn}_2\text{Cl}_5$  structures, is through interaction of the “nonbonding” valence electron pairs on tin with low-lying empty  $d$ -orbitals on neighboring  $X$  atoms. Electronic structure calculations based on the structural data confirm the likelihood of cluster orbital formation. Crystal data:  $\text{CsSn}_2\text{Cl}_5$ , tetragonal,  $I4/mcm$ ,  $a = 8.153(1)$  Å,  $c = 14.882(4)$  Å,  $Z = 4$ ,  $R_1 = 0.0215$ ,  $wR_2 = 0.0503$  [ $I > 2\sigma(I)$ ],  $R_1 = 0.0393$ ,  $wR_2 = 0.0536$  (all data);  $\text{CsSn}_2\text{Br}_5$ , tetragonal,  $I4/mcm$ ,  $a = 8.483(6)$  Å,  $c = 15.28(2)$  Å,  $Z = 4$ ,  $R_1 = 0.0607$ ,  $wR_2 = 0.1411$  [ $I > 2\sigma(I)$ ],  $R_1 = 0.1579$ ,  $wR_2 = 0.1677$  (all data).

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## INTRODUCTION

The structural chemistry of subvalent main group metal compounds is often characterized by stereochemical distortion caused by the “nonbonding” valence electrons on the metal atom. Trigonal pyramidal and square pyramidal coordination environments often result. In these systems the highly directional “nonbonding” valence electron pair (lone pair) on the metal prevents the close approach of further anions required to complete more regular coordination geometries. There are several examples of structures which are stabilized by interactions utilizing the “nonbonding” electron pair on the metal atom. These interactions usually involve overlap of the lone-pair orbital with neighboring

vacant orbitals. An important example of this is the structure of  $\text{CsSnBr}_3$  where the Sn- $5s$  orbital overlaps with empty Br- $4d$  orbitals resulting in a black conducting solid, where the stereochemical activity of the Sn- $5s^2$  pair is completely removed (1).

In a previous study on  $\text{RbSn}_2\text{Br}_5$  we suggested that the observed layered tetragonal structure was stabilized by interactions between the nonbonding electrons on Sn and low-lying empty Br  $d$ -orbitals (2). The relative stability of the  $[\text{SnX}_3]^-$  anion in solution makes isolation of pure compounds containing the  $[\text{Sn}_2\text{X}_5]^-$  anion difficult. In the case of a mixed solution of CsBr and  $\text{SnBr}_2$  the isolated product is invariably contaminated with  $\text{CsSnBr}_3$  even in large excesses of  $\text{SnBr}_2$ . Stoichiometric molten salt routes also yield mixtures of  $M\text{Sn}_2\text{X}_5$  and  $M\text{SnX}_3$  due to the relatively high volatility of  $\text{SnX}_2$ . Nevertheless, even from multiphasic samples it is possible to obtain detailed structural information on the principal phase. Here we present a detailed study of the structures of  $\text{CsSn}_2\text{Br}_5$  and  $\text{CsSn}_2\text{Cl}_5$  which have been obtained from multiphasic samples. These compounds are not only isostructural with each other, but also with a range of tetragonal analogues of the type  $\text{AB}_2\text{X}_5$  ( $A$  = monovalent cation;  $B$  = Sn, Pb;  $X$  = Br, Cl, I) (3).

## EXPERIMENTAL

### Preparations

Single-crystal samples were prepared from acidic solutions containing CsX (CsBr, BDH, 99%; CsCl Aldrich, 99%) and  $\text{SnX}_2$  ( $X$  = Br or Cl) in a 1:2.5 mole ratio. A 3 cm<sup>3</sup> amount of concentrated HX was added to a hot aqueous solution of either  $\text{SnBr}_2$  ( $\text{SnBr}_2$  was synthesized as described previously (4)) or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (BDH, 98%). The solution was heated under a stream of flowing nitrogen and contained a small piece of granulated tin metal to prevent oxidation of the dissolved Sn. To the hot solution was added a solution of CsX dissolved in the minimum amount of distilled water. The mixture was further heated until a clear solution was obtained. The solution was cooled in ice and the resultant crystalline precipitate was collected by vacuum

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filtration and dried over silica gel *in vacuo*. Both samples contained significant CsSnX<sub>3</sub> impurities; however, crystals of CsSn<sub>2</sub>X<sub>5</sub> were easily distinguished using an optical microscope.

### Crystallography

Single-crystal X-ray diffraction data were collected on crystals of CsSn<sub>2</sub>Br<sub>5</sub> and CsSn<sub>2</sub>Cl<sub>5</sub>. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\omega$ - $2\theta$  scans at 293(2) K. Data were initially corrected for absorption by empirical methods ( $\Psi$ -scan) (5). The structures were solved by Patterson methods using the SHELXS-97 program (6) and developed by difference Fourier techniques with subsequent refinement on  $F^2$  by full-matrix least squares using SHELXL-97 (6). In the final stages of refinement, data were corrected for absorption against a refined isotropic model with the program DIFABS (7). Anisotropic thermal parameters were refined for all atoms. Graphics were obtained using PLUTON (8). WINGX (9) was used to prepare material for publication. Crystal and refinement parameters for CsSn<sub>2</sub>Cl<sub>5</sub> and CsSn<sub>2</sub>Br<sub>5</sub> are summarized in Table 1.

### Electronic Structure Calculations

Molecular orbital calculations were performed at the Hartree-Fock (HF) level as well as employing density functional theory (DFT). For the DFT calculations the Becke3-Lee-Yang-Parr (B3LYP) functional (10,11) was

used. Two basis sets were used at these levels of theory. Ahlrichs's valence double-zeta coulomb fitting basis (12, 13) included the following contractions: Sn [4s3p3d1f1g], Br [6s4p2d1f1g], B [7s3p3d1f], and H [3s2p1d]. A basis set containing shape-consistent electric core potentials (ECPs) (14-17) was employed with the following primitives: Sn (3s,3p,4d), Br (3s,3p,4d), B (4s,4p), and H (4s). The Gaussian98 quantum chemical software (18) was used. Calculations were performed on two different molecular fragments with cores corresponding to parts of the CsSn<sub>2</sub>Br<sub>5</sub> crystal structure. The first fragment (Sn<sub>4</sub>Br<sub>12</sub>B<sub>8</sub>H<sub>16</sub>) comprised a Sn<sub>4</sub>Br<sub>4</sub> ring with two out-of-plane bromine atoms attached to each ring Sn and two BH<sub>2</sub> groups bonded to each ring Br atom to terminate the fragment. The total charge of this fragment was +4. The second fragment (Sn<sub>12</sub>Br<sub>36</sub>H<sub>8</sub>) was larger in size: the BH<sub>2</sub> groups were replaced by SnBr<sub>3</sub> fragments representing the adjacent ring structures, and H atoms were added in place of the Cs atoms in the crystal structure. The hydrogens thus provided the positive charges due to the Cs atoms at lower computational cost. The total charge of the second fragment was -4.

## RESULTS AND DISCUSSION

### Crystal Structures

The refined atomic parameters and selected bond lengths, contact distances, and angles are given in Tables 2 and 3, respectively.

CsSn<sub>2</sub>Cl<sub>5</sub> and CsSn<sub>2</sub>Br<sub>5</sub> are isostructural with each other. Their structures are layered and consist of sheets of the polymeric anion [Sn<sub>2</sub>X<sub>5</sub>]<sub>n</sub><sup>-</sup> separated by layers of the alkali metal cation, Fig. 1. The polymeric anion is constructed from planar four-sided, eight-membered rings containing four Sn and four X atoms. Each side is shared with a neighboring ring to give the two-dimensional framework. Tin is in a distorted square pyramidal environment with two short terminal halide bonds (Sn-Cl(2), 2.567(2) Å; Sn-Br(2), 2.737(5) Å) which point above and below the plane, and two longer bridging halide bonds (Sn-Cl(1), 2.997(1) Å; Sn-Br(1), 3.112(4) Å) in the rings.

Within each ring in the polymeric anion, the "nonbonding" valence electron pairs on two of the Sn atoms on opposite sides of the ring point toward each other. The metal nucleus to inert pair distance has been calculated as 0.95 Å for Sn<sup>2+</sup> (19). Clearly this does not allow for direct overlap of these orbitals between neighboring Sn atoms, which show Sn...Sn distances of 4.124 and 4.340 Å across the ring for the chloride and bromide, respectively. However, as we have previously indicated for the structural analogue RbSn<sub>2</sub>Br<sub>5</sub> (2), it is possible that empty *d*-orbitals on the terminal halide atoms form a bridge between the

**TABLE 1**  
Crystal and Refinement Parameters for CsSn<sub>2</sub>Cl<sub>5</sub> and CsSn<sub>2</sub>Br<sub>5</sub>

Name	Cesium pentachlorodistannate(II)	Cesium pentabromodistannate(II)
Chemical formula	CsSn <sub>2</sub> Cl <sub>5</sub>	CsSn <sub>2</sub> Br <sub>5</sub>
Formula weight	547.55	769.81
Crystal system	Tetragonal	Tetragonal
Space group	<i>I4/mcm</i>	<i>I4/mcm</i>
Unit cell dimensions	<i>a</i> = 8.153(1), <i>c</i> = 14.882(4) Å	<i>a</i> = 8.483(6), <i>c</i> = 15.28(2) Å
Volume	989.2(3) Å <sup>3</sup>	1099.9(16) Å <sup>3</sup>
<i>Z</i>	4	4
Density (calculated)	3.676(2) g cm <sup>-3</sup>	4.649(8) g cm <sup>-3</sup>
$\mu$	9.943 mm <sup>-1</sup>	25.894 mm <sup>-1</sup>
<i>F</i> (000)	960	1320
Sample description	Colorless plates	Colorless plates
Crystal dimensions	0.15 × 0.12 × 0.07 mm	0.15 × 0.12 × 0.02 mm
Temperature	293(2) K	293(2) K
$\theta$ range collected	3.53-24.89°	3.40-24.99°
Reflections collected	542	598
Unique reflections	254 [ <i>R</i> (Int) = 0.0649]	254 [ <i>R</i> (Int) = 0.3066]
Final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0215, [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <i>wR</i> <sub>2</sub> = 0.0503	<i>R</i> <sub>1</sub> = 0.0607, <i>wR</i> <sub>2</sub> = 0.1411
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0393, <i>wR</i> <sub>2</sub> = 0.0536	<i>R</i> <sub>1</sub> = 0.1579, <i>wR</i> <sub>2</sub> = 0.1677

**TABLE 2**  
**Atomic Coordinates and Thermal Parameters for (a)**  
**CsSn<sub>2</sub>Cl<sub>5</sub> and (b) CsSn<sub>2</sub>Br<sub>5</sub> with Estimated Standard Deviations**  
**in Parentheses**

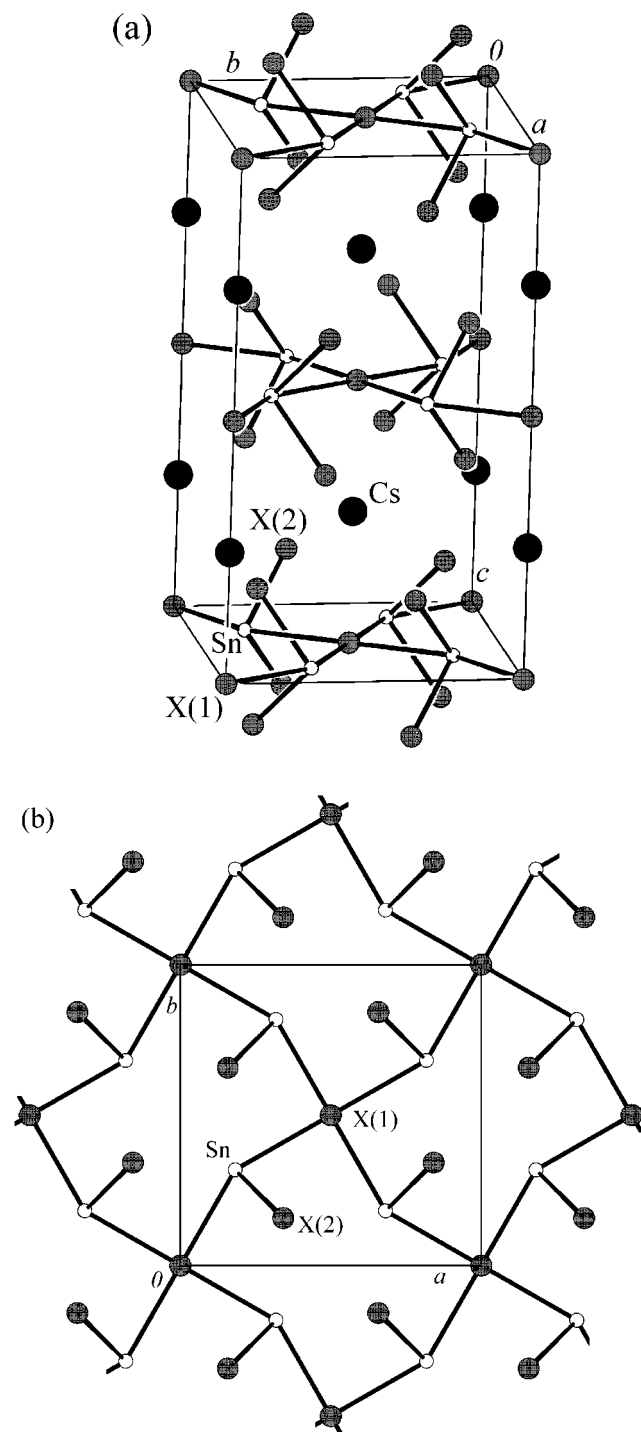
(a)						
Atom	Site	x	y	z	Occ.	$U_{\text{eqv}} (\text{\AA}^2)^a$
Cs	4a	0.5(-)	0.5(-)	0.25(-)	1.0(-)	0.0312(3)
Sn	8h	0.32116(7)	0.82116(7)	0.0(-)	1.0(-)	0.0331(3)
Cl(1)	4c	0.5(-)	0.5(-)	0.0(-)	1.0(-)	0.0273(8)
Cl(2)	16m	0.1665(2)	0.6665(2)	0.1241(1)	1.0(-)	0.0334(5)
Anisotropic Thermal Parameters						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cs	0.0334(4)	0.0334(4)	0.0268(5)	0.0	0.0	0.0
Sn	0.0334(4)	0.0334(4)	0.0325(5)	0.0	0.0	-0.0060(4)
Br(1)	0.024(1)	0.024(1)	0.035(2)	0.0	0.0	0.0
Br(2)	0.0352(7)	0.0352(7)	0.030(1)	0.0043(7)	0.0043(7)	0.0045(9)
(b)						
Atom	Site	x	y	z	Occ.	$U_{\text{eqv}} (\text{\AA}^2)^a$
Cs	4a	0.5(-)	0.5(-)	0.25(-)	1.00(-)	0.042(1)
Sn	8h	0.3191(4)	0.8191(4)	0.0(-)	1.00(-)	0.049(1)
Br(1)	4c	0.5(-)	0.5(-)	0.0(-)	1.00(-)	0.033(2)
Br(2)	16m	0.1602(3)	0.6602(3)	0.1284(3)	1.00(-)	0.042(1)
Anisotropic Thermal Parameters						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cs	0.027(2)	0.027(2)	0.072(3)	0.0	0.0	0.0
Sn	0.030(2)	0.030(2)	0.086(3)	0.0	0.0	-0.013(2)
Br(1)	0.013(2)	0.013(2)	0.074(5)	0.0	0.0	0.0
Br(2)	0.027(1)	0.027(1)	0.073(2)	0.009(2)	0.009(2)	0.002(2)

$$^a U_{\text{eqv}} = (U_{11} + U_{22} + U_{33})/3.$$

neighboring tin orbitals to produce a localized cluster orbital.

Beck *et al.* (3) have shown that compounds of the type  $AB_2X_5$  ( $A = \text{Cs, Rb, K, In, NH}_4, \text{Tl}$ ;  $B = \text{Sr, Ba, Eu, Sm, Sn, Pb}$ ; and  $X = \text{Cl, Br, I}$ ) generally adopt one of two known structure types, the monoclinic  $\text{NH}_4\text{Pb}_2\text{Cl}_5$  structure (20, 21) with space group  $P2_1/c$  and the tetragonal  $\text{NH}_4\text{Pb}_2\text{Br}_5$  structure (22) with space group  $I4/mcm$ . They suggest that the particular structure type adopted is governed by the size relationships between the ion radius ratios  $A/X$  and  $B/X$ . Although the resulting structure field diagram presented by these authors divides the two structure-forming regions, it is worth noting that the difference in  $A$  and  $B$  coordination numbers between the two structure types invariably results in different  $A/X$  and  $B/X$  ratios for the same ion pairs. Due to this ambiguity this method cannot be used to predict the particular structure type adopted. In addition this explanation fails to take into account the degree of covalency clearly exhibited in the tetragonal compounds. These authors also

comment that more polarizable  $B$  atoms, in particular the lone pair metals, seem to favor the tetragonal structure. While some Sn and Pb compounds can exhibit both monoclinic and tetragonal structural types, compounds with



**FIG. 1.** Structure of  $\text{CsSn}_2\text{X}_5$  ( $X = \text{Cl, Br}$ ): (a) unit cell contents and (b) projection onto the  $a/b$  cell plane of a single  $[\text{Sn}_2\text{Br}_5]^{n-}$  layer. Black, open, and shaded circles represent Cs, Sn, and X atoms, respectively.

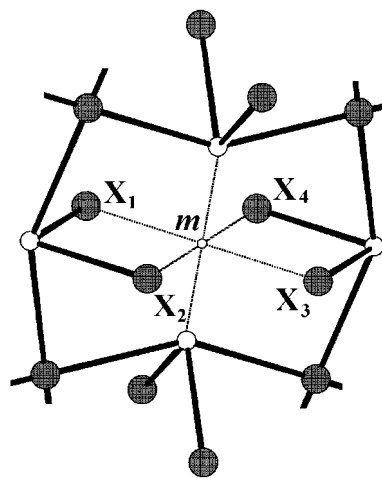
**TABLE 3**  
Selected Bond Lengths and Contact Distances (Å) and Angles (°) for CsSn<sub>2</sub>Cl<sub>5</sub> and CsSn<sub>2</sub>Br<sub>5</sub> with Estimated Standard Deviations in Parentheses

	X = Cl	X = Br
Cs–X(1)	3.721(1) × 2	3.821(4) × 2
Cs–X(2)	3.570(1) × 8	3.689(4) × 8
Sn–X(1)	2.997(1) × 2	3.112(4) × 2
Sn–X(2)	2.567(2) × 2	2.737(5) × 2
Sn...X(2) <sup>a</sup>	3.369(2) × 4	3.500(5) × 4
Sn...Sn <sup>b</sup>	4.124(1)	4.340(7)
Sn...Sn <sup>a</sup>	4.238(1) × 4	4.401(5) × 4
X(2)...X(2) <sup>d</sup>	3.840(3)	3.843(6)
X(2)...X(2) <sup>c</sup>	3.694(4)	3.925(9)
X(1)–Sn–X(1) <sup>e</sup>	148.22(2)	149.1(1)
X(1)–Sn–X(2)	79.04(4)	79.3(1)
X(2)–Sn–X(2) <sup>f</sup>	92.01(8)	91.7(2)
Sn–X(1) <sup>g</sup> –Sn <sup>a</sup>	90.00(–)	90.00(–)

Symmetry relations:  $a = 0.5 - x, 0.5 + y, z; b = 1 - x, 2 - y, z; c = x, y, -z; d = -x, 1 - y, z.$

other polarizable cations in the *B* position such as Eu, Sm, Sr, and Ba all show the monoclinic form only. This suggests that it is not just the polarizability of the *B* atom that allows for stabilization of the tetragonal structure, but the presence of “nonbonding” valence electron pairs, and supports the cluster orbital explanation outlined in the present study. More recently a third structure type has been characterized in NaSn<sub>2</sub>Cl<sub>5</sub> (23) which adopts a distorted Rh<sub>5</sub>Ge<sub>3</sub>-type structure related to NH<sub>4</sub>Pb<sub>2</sub>Cl<sub>5</sub>. In addition to the two tetragonal crystal structures presented in this study, crystal structure data for another five structural analogues are available from the literature (2, 22, 24).

It is possible to define a point at the center of the rings in the layers, which is halfway between the two Sn/Pb atoms on opposite sides of the ring (Fig. 2). This “midpoint” (*m*), with coordinates 0.5, 0, 0, has six contacts to neighboring atoms in an octahedral coordination. Table 4 shows a comparison of distances and angles around the midpoints for the known structural analogues where crystal structure data



**FIG. 2.** Definition of midpoint *m* in [Sn<sub>2</sub>X<sub>5</sub>]<sub>n</sub><sup>–</sup> layers in CsSn<sub>2</sub>X<sub>5</sub> (X = Cl, Br).

are available. On comparison of the data for the bromide structures, it is clear that *m*–Sn/Pb and the *m*–*X* distances are relatively unaffected by the size of the counterions in the *A* site between the layers. However, significant differences are seen between Sn and Pb structures, which reflect the difference in metal nucleus to lone pair (lp) distances in Sn and Pb (Sn–lp, 0.95 Å; Pb–lp, 0.86 Å (19)). Interestingly, the parameters for InSn<sub>2</sub>Br<sub>5</sub>, which nominally has In<sup>+</sup> occupying the *A* site, lie between those of Pb and Sn. The present study allows us to compare the midpoint parameters for InSn<sub>2</sub>Br<sub>5</sub> with other isostructural bromides. Since In<sup>+</sup> and Sn<sup>2+</sup> are isoelectronic, conventional X-ray methods, as were used in the structure determination of InSn<sub>2</sub>Br<sub>5</sub> (24), are unable to distinguish between them. The structural chemistry of In<sup>+</sup>, like that of Sn<sup>2+</sup>, is dominated by stereochemical distortions involving its lone pair. If one considers the possibility that In<sup>+</sup> occupies the intralayer *B* site rather than the interlayer *A* site, the *B* site could be shared equally between randomly distributed Sn and In, with the remaining Sn fully occupying the *A* site. In<sup>+</sup> has a metal to lone pair distance equal to that of Pb<sup>2+</sup> (19). If the assumption is made that the midpoint parameters of [Pb<sub>2</sub>Br<sub>5</sub>]<sub>n</sub><sup>–</sup> layers

**TABLE 4**  
Comparison of Environments for Ring Midpoints (*m*) in Layered AB<sub>2</sub>X<sub>5</sub> Analogues

Compound	<i>m</i> –Sn/Pb × 2 (Å)	<i>m</i> –X × 4 (Å)	X <sub>1</sub> – <i>m</i> –X <sub>4</sub> × 2 (°)	X <sub>1</sub> – <i>m</i> –X <sub>2</sub> × 2 (°)	Struct. ref.
CsSn <sub>2</sub> Cl <sub>5</sub>	2.062	2.664	92.21	87.79	This work
RbSn <sub>2</sub> Br <sub>5</sub>	2.131	2.759	88.34	91.66	52
CsSn <sub>2</sub> Br <sub>5</sub>	2.170	2.747	88.79	91.21	This work
InSn <sub>2</sub> Br <sub>5</sub>	2.033	2.738	86.43	93.57	24
NH <sub>4</sub> Pb <sub>2</sub> Br <sub>5</sub>	1.875	2.757	89.10	90.90	22
RbPb <sub>2</sub> Br <sub>5</sub>	1.879	2.755	89.45	90.55	22
InSn <sub>2</sub> I <sub>5</sub>	2.124	2.912	85.07	94.93	24

are close to those expected for  $[\text{In}_2\text{Br}_5]_n^{3n-}$  layers, then for a layer of composition  $[\text{InSnBr}_5]_n^{2n-}$ , one would predict midpoint parameters halfway between those of  $[\text{Pb}_2\text{Br}_5]_n^{n-}$  and  $[\text{Sn}_2\text{Br}_5]_n^{n-}$ . This is indeed close to the situation observed. Similarly, it is possible that *B*-site sharing by In and Sn also occurs in the isostructural analogue  $\text{InSn}_2\text{I}_5$  (24).

### Electronic Structure Calculations

In order to investigate the possibility of interactions involving valence Sn-*s*/Br-*d* filled molecular orbitals (MOs), quantum chemical calculations were performed on two molecular fragments, viz.,  $\text{Sn}_4\text{Br}_{12}\text{B}_8\text{H}_{16}$  and  $\text{Sn}_{12}\text{Br}_{36}\text{H}_8$ . In both of these fragments the positions of the core atoms Sn and Br atoms corresponded exactly to those in the crystal structure of  $\text{CsSn}_2\text{Br}_5$ . For both molecules the calculations indicated the presence of a valence Sn-*s*/Br-*d* filled molecular orbital (MO).

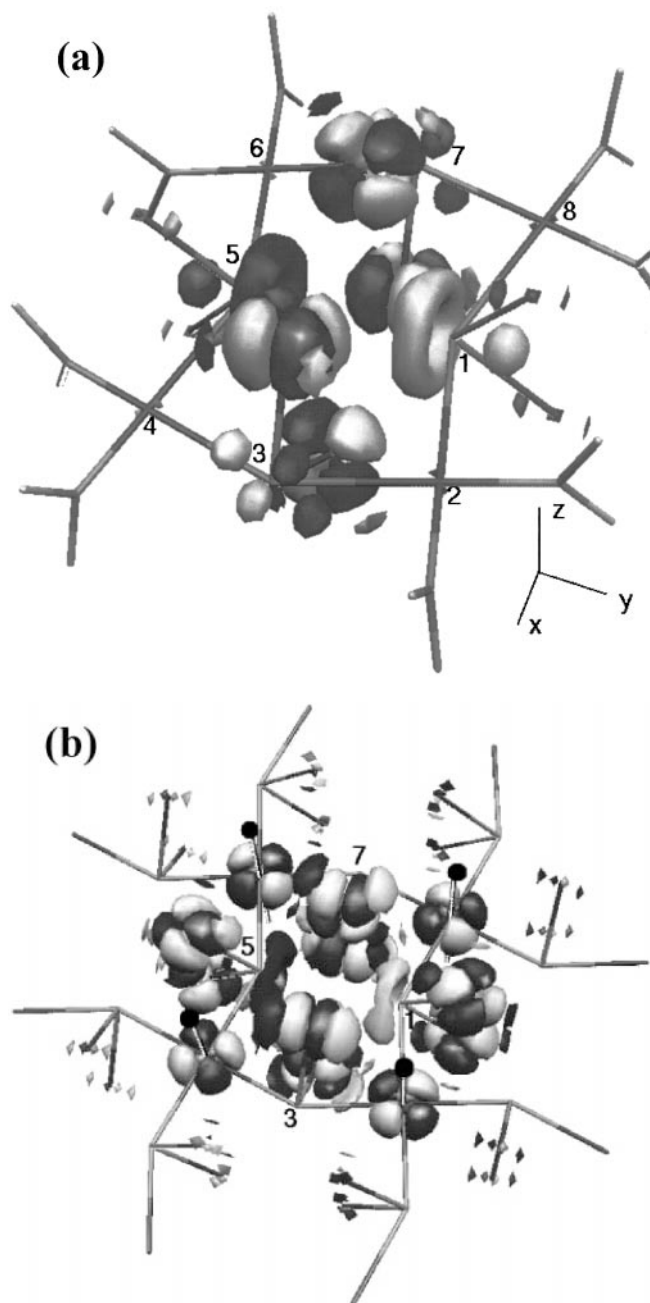
The corresponding MOs at the HF level of theory are shown in Fig. 3a. The DFT results were very similar to those from the HF calculations. In the case of  $\text{Sn}_4\text{Br}_{12}\text{B}_8\text{H}_{16}$  the MO consists mainly of  $d_{yz}$  atomic orbitals (AOs) on the bromine atoms pointing toward each other and valence *s* atomic orbitals located on the neighboring Sn atoms. This MO also contains contributions from the valence  $p_y$  AOs on these Sn atoms; therefore, the *s* AOs appear to be slightly distorted along the *y*-axis.

For the  $\text{Sn}_{12}\text{Br}_{36}\text{H}_8$  molecular fragment, we were also able to detect a filled MO with major contributions from valence Sn-*s* and Br-*d* atomic orbitals (Fig. 3b). Again, the Sn-*s* AOs are polarized by valence  $p_y$  atomic orbitals. For this molecule the ring Br atoms also contribute  $d_{xy}$  atomic orbitals to the MO. This may be related to the fact that during the calculations the overall charge of the  $\text{Sn}_{12}\text{Br}_{36}\text{H}_8$  molecule was taken to be  $-4$ , whereas for the  $\text{Sn}_4\text{Br}_{12}\text{B}_8\text{H}_{16}$  fragment the net charge was  $+4$ . However, despite the two different net charges, the character of the corresponding MOs in both molecules remained the same.

While it can be argued that for network structures of this type, periodic boundary calculations represent a better description of the total crystal structure, the fact that two different-sized model molecular fragments with different net charges and overall composition gave similar results suggests that, in this case, use of an isolated fragment approach is justified. This gives considerable savings in computational time with respect to periodic boundary calculations.

### CONCLUSIONS

The MO calculations appear to support the proposed interaction involving the lone pairs on Sn atoms with empty *d*-orbitals on neighboring Br atoms in  $\text{CsSn}_2\text{Br}_5$ . It is also



**FIG. 3** Occupied molecular orbitals of molecular fragments with cores corresponding to part of the  $\text{CsSn}_2\text{Br}_5$  crystal structure. (a) Filled molecular orbital for a  $\text{Sn}_4\text{Br}_{12}\text{B}_8\text{H}_{16}$  molecule. Numbers 1, 3, 5, and 7 indicate the Sn atoms of the SnBr plane. Each of the bromine atoms 2, 4, and 6, and 8 is “capped” by a  $\text{BH}_2$  group. Atoms 1 and 5 lie on the *y*-axis; atoms 3 and 7 on the *x*-axis of a Cartesian coordinate system (shown next to the molecule). (b) Corresponding molecular orbital for a  $\text{Sn}_{12}\text{Br}_{36}\text{H}_8$  fragment. Each of the bromine atoms 2, 4, 6, and 8 is “capped” by  $\text{SnBr}_3$ . Hydrogen atoms replacing the Cs atoms in the crystals are marked with ● and are located above and below Br, 2, 4, 6, and 8 atoms.

likely that this type of interaction also occurs in  $\text{RbSn}_2\text{Br}_5$  since the data in Table 4 suggest that there is little structural difference in the  $[\text{Sn}_2\text{Br}_5]_n^{n-}$  layers compared to  $\text{CsSn}_2\text{Br}_5$ .

In addition, since Cl and I also have available *d*-orbitals, it is therefore reasonable to suppose that this type of interaction is also seen in the other isostructural AB<sub>2</sub>X<sub>5</sub> compounds. This appears to be a more realistic explanation of the stabilization of the tetragonal structures over the monoclinic form. It is also interesting to note that the calculations appear to confirm directionality of the Sn-5s orbital with incorporation of a Sn-*p*<sub>y</sub> component. It is clear that a quantum chemical approach to rationalization of the solid state structures adopted by lone pair compounds can lead to a more realistic picture of bonding and electronic structure in these systems.

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