Effects of the Presence of Valence-shell Non-bonding Electron Pairs on the Properties and Structures of Caesium Tin(II) Bromides and of Related Antimony and Tellurium Compounds

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The ideal perovskite structure of $CsSn^{II}Br_3$ at room temperature has been confirmed by a single-crystal *X*-ray diffraction study. It is proposed that the high-symmetry environment for the Sn^{II} in this compound arises because the distorting effect of the non-bonding electrons is reduced by their populating an empty low-energy band in the solid, thus giving rise to the black colour and metallic-conducting properties. The high-temperature phases of $CsSn_2^{II}Br_5$, $Cs_4Sn^{II}Br_6$, and of compositions from the $CsSn^{II}_2Br_5$–$CsSn^{II}_2Cl_5$ system show similar properties. Colour can be introduced into the $Cs_2Sn^{IV}Br_6$ system by formation of mixed phases with $CsSn^{II}Br_3$ which has a closely related structure. The colour and electrical properties of the mixed Sn^{II}–Sn^{IV} material can be explained by population of the low-energy delocalised solid-state bands by the Sn^{II} non-bonding electrons without recourse to intervalence-transfer-absorption ideas. Comparison of the complex bromides and chlorides of Sn^{II} and Te^{IV} with the mixed-valence Sb^{III}–Sb^{V} compounds suggests that direct population of bands rather than intervalence charge transfer may also be the dominant process in determining the properties of the antimony derivatives. I.r. data for the mixed-valence antimony compounds are consistent with the direct-population explanation.

THREE caesium tin bromides are known, dicaesium hexabromostannate(IV) and two tin(II) derivatives, $CsSnBr_3$ and $CsSn_2Br_5$. We have previously described the preparation of $CsSnBr_3$ and of mixed phases based on it.[1,2] Caesium tin(II) tribromide is a black solid with metallic lustre which acts as a metallic conductor over a wide temperature range.[1-3] *X*-Ray diffraction powder and ^{119}Sn Mossbauer and vibrational spectroscopic data were all consistent with $CsSnBr_3$ having an undistorted cubic perovskite structure,[1,4] but there is some evidence from ^{81}Br n.q.r. spectra for slight tetragonal distortion below 19 °C.[3] We have suggested that the Mössbauer data and metallic-conducting properties of this, and related compounds, can be explained by population of conduction bands in the solids by the tin $5s^2$ non-bonding electrons, the conduction bands being formed by mutual overlap of empty bromine t_2 d orbitals. Maximum overlap of these orbitals would occur in the undistorted perovskite lattice and we now confirm this structure for $CsSnBr_3$ at room temperature by a single-crystal *X*-ray diffraction study. Dicaesium hexabromostannate(IV), which is white and is said to contain discrete $[SnBr_6]^{2-}$ ions, has a closely related face-centred cubic structure.[5,6] The existence of caesium pentabromodistannate(II) has been reported,[7] but little is known about this compound.

We now report on the relation between the structures of these caesium tin bromides and of a new compound, $Cs_4Sn^{II}Br_6$, and their colours and conducting behaviour. We also discuss the relevance of this work to similar structures and properties found in compounds of other *p*-block elements in their lower oxidation states.

RESULTS AND DISCUSSION

The Crystal Structure of $CsSn^{II}Br_3$.—A thin acicular slice (maximum cross section 0·0071 cm) of $CsSnBr_3$ was cut from a larger crystal pulled from molten solution.[8] The cubic unit-cell size, refined on *X*-ray powder diffractometer data (Cu-K_α), is 5·795 ± 0·002 Å, $D_m = ca.$ 4·2 g cm^{-3} (by displacement of benzene), $Z = 1$, and $D_c =$ 4·19 g cm^{-3}. Space group *Pm3m* (no. 221); there were no systematic absences of *X*-ray reflection. Integrated Weissenberg film-intensity data (Mo-K_α) for layers 0—5 were collected and measured on a Nonius microdensitometer. There was no evidence from the intensity data for symmetry lower than cubic and this gave 97 independent measured (averaged) reflections which were corrected for Lorentz and polarisation factors but not for extinction or absorption (optimum thickness of the compound for Mo-K_α radiation, 0·0085 cm; maximum cross section of crystal, 0·0071 cm). The data were refined on the basis of the atomic positions in the ideal perovskite lattice to *R* 0·12. The isotropic temperature factors at this stage were 7·1 (Cs), 1·7 (Sn), and 7·5 (Br). The high temperature factor for Cs is not surprising in view of the large space available (radius *ca.* 2·1 Å) for this ion compared with its ionic radius for twelve-co-ordination (1·84 Å). No ^{137}Cs Mössbauer spectrum can be obtained from $CsSnBr_3$ at 4·2 K suggesting a low *f* fraction which would be consistent with a caesium ion vibrating in a large hole. The electron-density map for $CsSnBr_3$ indicated that the bromine atoms could vibrate more easily towards Cs than Sn. When Br was given anisotropic temperature factors with b_{12}, b_{13}, and b_{23} constrained to 0 the structure refined to a final *R* of 0·11. The small temperature factor for the tin atom shows that these are the most firmly held in the structure. There is no evidence for any distortion of the tin environment from a regular octahedral site in agreement with the Mössbauer data for this and related compounds.[1] High temperature factors for Cs and Cl compared with those for germanium have been observed [9] for

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the high-temperature perovskite phase of $CsGeCl_3$. Movement of the atoms in $CsSnBr_3$ from their ideal locations in larger cells did not lead to an improved residual. The relatively high residual for $CsSnBr_3$ reflects: (*i*) the restricted data available for the cubic system; (*ii*) the crystal, although small, was not ideally shaped and the colour made accurate indexing of the faces difficult; and (*iii*) the fact that Cs could not be given anisotropic temperature factors although its vibration pattern was unlikely to be simple. The atomic positions, temperature factors, and structure-factor data are in Table 1.

TABLE 1

Atomic positions, temperature factors, and structure factors for $CsSnBr_3$

	x	y	z	$B/Å^2$	10^4b_{11}	10^4b_{22}	10^4b_{33}
Cs	0	0	0	7·1 (4)			
Sn	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1·7 (2)			
Br	0	$\frac{1}{2}$	$\frac{1}{2}$		32 (5)	52 (16)	99 (23)

h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	149·6	145·0	5	2	5	13·2	11·6
4	0	0	65·1	69·6	7	2	5	8·7	7·0
6	0	0	29·4	29·5	4	3	3	21·4	20·5
8	0	0	15·5	12·4	5	3	3	6·4	−7·3
1	1	0	58·6	58·4	6	3	3	12·3	13·0
2	1	0	24·7	−26·2	7	3	3	5·9	−7·0
3	1	0	32·5	37·1	8	3	3	10·2	7·2
4	1	0	20·3	−23·5	4	3	4	11·5	−13·5
5	1	0	17·0	20·0	5	3	4	13·8	13·1
6	1	0	15·8	17·1	6	3	4	9·2	−9·7
8	1	0	15·4	10·0	7	3	4	7·2	7·8
2	2	0	111·9	108·7	5	5	0	11·0	11·8
3	2	0	13·1	−16·6	6	5	0	10·8	−9·3
4	2	0	54·0	55·8	1	1	1	83·1	73·6
5	2	0	14·2	−11·5	2	1	1	49·7	52·2
6	2	0	22·2	24·9	3	1	1	28·6	29·0
8	2	0	14·6	10·9	4	1	1	36·2	37·3
3	3	0	27·6	27·0	6	1	1	13·3	21·4
4	3	0	15·9	−17·1	2	1	2	20·5	−25·1
5	3	0	17·6	16·6	3	1	2	35·2	34·9
6	3	0	11·7	−13·3	4	1	2	19·4	−21·7
7	3	0	6·8	9·7	5	1	2	16·3	19·3
8	3	0	10·1	−8·2	6	1	2	10·8	−15·5
4	4	0	28·3	32·0	3	1	3	9·7	8·8
5	4	0	9·0	−11·7	4	1	3	21·0	26·9
6	4	0	17·2	16·1	5	1	3	7·8	−4·6
7	4	0	9·2	−7·9	6	1	3	18·0	16·3
8	4	0	9·5	7·9	7	1	3	5·9	−7·0
7	1	4	8·5	9·0	8	1	3	7·8	−8·7
8	1	4	9·3	−7·3	4	1	4	14·5	−17·3
5	1	5	10·3	−7·6	5	1	4	13·7	16·0
6	1	5	11·7	−10·6	6	1	4	12·9	−11·9
2	2	2	85·6	84·3	8	3	4	8·9	−6·0
3	2	2	15·9	−17·1	5	3	5	7·5	−7·8
4	2	2	42·6	45·4	6	3	5	5·7	8·8
5	2	2	12·9	11·3	7	3	5	8·9	−6·0
6	2	2	19·3	21·1	6	3	6	10·7	−6·8
3	2	3	25·6	25·8	4	4	4	15·8	17·3
4	2	3	15·2	−16·2	5	4	4	9·5	−9·7
5	2	3	13·7	16·1	6	4	4	9·4	10·0
6	2	3	10·1	−12·2	7	4	4	6·1	−6·4
7	2	3	8·2	9·3	8	4	4	9·2	5·5
8	2	3	10·7	−7·5	5	4	5	10·8	9·2
4	2	4	28·5	26·9	6	4	5	7·8	−7·1
5	2	4	9·3	−11·2	7	4	5	4·5	5·8
6	2	4	13·8	14·0	8	4	5	6·7	−4·4
7	2	4	8·4	−7·6	6	4	6	9·7	6·4
8	2	4	7·0	7·1	6	4	7	3·3	−4·7

All other reflections were of zero intensity.

One very weak reflection (**333**) was removed from the final refinement because $F_o > 2F_c$.

High-symmetry Tin(II) *Environments and Physical Properties.*—The compound $CsSnBr_3$ is the only alkali-metal tribromostannate(II) that is black and that shows metallic conduction. It differs from other $MSnBr_3$ derivatives (M = Na, K, Rb, and NH_4), which are white, in that it has a high-symmetry environment shown by a narrow Mössbauer resonance line [1,4] and confirmed by the present structural study. None of the white tribromostannates(II) are of known structure but their Mössbauer data do suggest [7] the presence of Sn^{II} in distorted environments. The Mössbauer chemical shift for $CsSnBr_3$ is, however, surprisingly low for a compound containing Sn^{II} in an undistorted octahedral environment and we have explained this observation by suggesting [1,4] that some tin 5*s*-electron density is lost by delocalisation in a band formed by bromine orbitals. The colours and electrical properties of $CsSnBr_3$ and of related materials are certainly consistent with this explanation. The variation of Mössbauer chemical shift and linewidth data with temperature (chemical shift 2·09, 1·92, and 1·84 mm s^{-1}; linewidth 1·00, 0·84, and 0·77 mm s^{-1} respectively at 4·2, 78, and 293 K) for $CsSnBr_3$ does suggest an increasing population of such a conductance band with tin *s* electrons as the temperature increases over the range. If this behaviour is of general importance in the development of colour and conducting properties in compounds containing both Sn^{II} in a highly symmetrical environment and empty low-energy conduction bands, it should be possible to (*i*) obtain high-temperature coloured phases for other caesium tin(II) bromides and (*ii*) introduce colour to materials containing empty conduction bands by doping them with Sn^{II}. We now show that both of these properties can be observed and discuss the implications of this to the general chemistry of elements with ns^2 outer-electronic configurations.

High-temperature Phases of $CsSn^{II}{}_2Br_5$ *and* $Cs_4Sn^{II}Br_6$.—The products obtained on cooling molten mixtures of $SnBr_2$ and CsBr in the ratios of 2 : 1 and 1 : 4 are not highly coloured but both undergo phase transitions to black compounds at higher temperatures.

$CsSn^{II}{}_2Br_5$. When $CsSn_2Br_5$ was prepared from aqueous solution the product in hot solutions was black. The colour faded as the temperature was reduced to give a grey non-cubic form which was also the product from cooled 1 : 2 melts of CsBr and $SnBr_2$. When the grey material was heated it underwent a phase change at *ca.* 200 °C to a black cubic form with $a = 5·81$ Å. This modification decomposed slowly at *ca.* 240 °C to give $SnBr_2$, which evaporates off, and CsBr. *X*-Ray data for the cubic form of $CsSn_2Br_5$ (Table 2) were very similar to those of cubic $CsSn^{II}Br_3$. When the black form was heated rapidly to *ca.* 300 °C, decomposition was suppressed and a black to red colour change was observed. This could be associated with a reduction in the population of conduction bands in the material and a similar effect is noted in $CsSnBr_3$.[1] *X*-Ray diffraction powder data (to 2 Å) for the non-cubic phase are in Table 3. These data can be indexed on the tetragonal cell given down to 1·266 Å, apart from one line (5·82 Å) which arises from the presence of cubic $CsSn_2Br_5$ as an impurity.

TABLE 2

High-temperature X-ray data of the cubic $CsSn^{II}_2Cl_{5-n}Br_n$ system

Compound:	$CsSn^{II}_2Cl_5$		$CsSn^{II}_2Br_3Cl_2$		$CsSn^{II}_2Br_5$	
a (±0·01 Å):	5·56		5·80		5·81	
Transition temperature (θ_c/°C)	94		166		201	
	d/Å		d/Å		d/Å	
hkl	obs.	calc.	obs.	calc.	obs.	calc.
(100)	5·57vvw	5·56	5·79w	5·80	5·81vw	5·81
(110)	3·93vs	3·916	4·11s	4·10	4·13m	4·110
(111)	3·21w	3·205	3·34m	3·35	3·35w	3·356
(200)	2·78vs	2·780	2·90s	2·90	2·90s	2·905
(210)	2·48w	2·483	2·60vw	2·60	2·59w	2·599
(211)	2·28vs	2·266	2·36m	2·37	2·37m	2·373
(220)	1·964vs	1·962	2·05m	2·05	2·06m	2·055
(300) (221)	1·854vw	1·853	1·93vvw	1·933	1·937vw	1·937
(310)	1·758m	1·756	1·84w	1·834	1·837m	1·837
(222)	1·603w	1·603	1·68w	1·674		
(321)	1·484m	1·483	1·551vw	1·550		
(400)			1·452w	1·450		

High-temperature, coloured, cubic phases have been found in the $CsSnBr_3$–$CsSnCl_3$ system [1] and we now show that similar high-temperature phases exist in the $CsSn_2Br_5$–$CsSn_2Cl_5$ system.

TABLE 3

Tetragonal X-ray data for the $CsSn^{II}_2Cl_{5-n}Br_n$ system

$CsSn^{II}_2Cl_5$			$CsSn^{II}_2Br_5$		
$a = b = 11{\cdot}497 \pm 0{\cdot}005$ Å			$a = b = 12{\cdot}05 \pm 0{\cdot}01$ Å		
$c = 14{\cdot}28 \pm 0{\cdot}01$ Å			$c = 15{\cdot}40 \pm 0{\cdot}01$ Å		
	d/Å			d/Å	
hkl	obs.	calc.	hkl	obs.	calc.
(002)	7·44vs	7·414	(002)	7·70vs	7·70
(020)	5·75m	5·748	(020)	6·03m	6·03
(022)	4·55vs	4·543		5·82m *	
(013)		4·541	(022)	4·75vs	4·75
(220)	4·07wm	4·065	(220)	4·26m	4·26
(030)	3·80wm	3·833	(221)	4·12vs *	4·11
(031)	3·71ms	3·710	(130)	3·83m	3·81
(123)	3·56vvs	3·563	(004)		3·83
(032)	3·39vvw	3·404	(123)	3·72vvs	3·72
(231)	3·12s	3·118	(230)	3·36ms *	3·34
(204)		3·115	(204)	3·23ws	3·24
(133)	2·93vvs	2·929	(400)	3·01ms	3·01
(232)		2·929	(015)		2·98
(040)	2·87s	2·874	(140)	2·83vvw	2·92
(015)		2·872	(115)	2·90vs *	2·90
(141)	2·74wm	2·741	(330)	2·85m	2·84
(224)		2·739	(125)	2·68vvs	2·67
(330)	2·72w	2·710	(241)	2·64w	2·65
(332)	2·54vvs	2·545	(043)	2·60w *	2·60
(006)	2·47vw	2·471	(016)	2·51vw	2·511
(225)	2·40vw	2·396	(051)	2·38s	2·381
(050)	2·31vs	2·300	(243)		2·386
(135)		2·298	(044)	2·372vs *	2·373
(051)	2·276m	2·272	(026)	2·356w	2·362
(431)		2·272	(126)	2·310w	2·317
(151)	2·230w	2·229	(007)	2·199w	2·200
(144)		2·228	(226)		2·199
(126)		2·227	(053)	2·187w	2·182
(007)	2·117vs	2·118	(343)		2·183
			(531)	2·049vs *	2·049
			(442)		2·053
			(253)		2·051
			(060)	2·004m	2·008
			(352)		1·996

* Reflections from high-temperature-phase impurity.

$CsSn^{II}_2Cl_5$. When this material was prepared from aqueous solutions, the product obtained in the hot solution was yellow and crystalline. The colour faded as the temperature was reduced to give the white tetragonal form, which was also the product from a cooled 1 : 2 melt of CsCl and $SnCl_2$. X-Ray diffraction powder data for tetragonal $CsSn_2Cl_5$ are given to 2 Å in Table 2, although data to 1·39 Å have been indexed on the cell given. When the tetragonal material was heated it underwent a phase change at *ca.* 94 °C to a yellow cubic form with $a = 5{\cdot}56$ Å. This cubic modification decomposed at *ca.* 280 °C to give $SnCl_2$, which evaporates off, and CsCl. X-Ray data for the cubic form of $CsSn_2Cl_5$ (Table 2) were very similar to those of cubic $CsSnCl_3$.

The $CsSn^{II}_2Cl_5$–$CsSn^{II}_2Br_5$ *system.* The materials first precipitated from hot solutions containing both chloride and bromide were highly coloured. These products have cubic unit cells (*e.g.* $CsSn^{II}_2Br_3Cl_2$ in Table 2) and their colours resemble those found in the $CsSnCl_{3-n}Br_n$ (n = 0—3) [1] system:

$CsSn^{II}_2Cl_5$	Yellow
$CsSn^{II}_2Cl_4Br$	Yellow-orange
$CsSn^{II}_2Cl_3Br_2$	Orange-red
$CsSn^{II}_2Cl_2Br_3$	Red
$CsSn^{II}_2ClBr_4$	Dark red
$CsSn^{II}_2Br_5$	Black

These results suggest that a series of cubic compositions similar to those formed in the $CsSnCl_3$–$CsSnBr_3$ system [1] exist. As the solutions containing the coloured products cooled, the crystals lost their colour and off-white tetragonal phases were formed. The X-ray diffraction powder data for the phases with the following compositions index on the basis of the tetragonal cells shown:

	$a = b$ ±0·01 Å	c ±0·01 Å
$CsSn^{II}_2Cl_4Br$	11·61	14·87
$CsSn^{II}_2Cl_3Br_2$	11·70	15·00
$CsSn^{II}_2Cl_2Br_3$	11·74	15·19
$CsSn^{II}_2ClBr_4$	11·88	15·35

In many systems the coloured and white products coexist for a period of time. The precipitation of cubic materials first, and their subsequent transformation to lower-symmetry phases, means that a continuous variation in composition of the white tetragonal $MSn^{II}_2X_5$ compounds can be achieved and for this reason analytical data are of little value, since all the cubic phases must be based on packing requirements rather than on any complex species present. It was, however, found that distinct white phases could be obtained as the first precipitate from aqueous solution provided that the temperature was kept below *ca.* 40 °C. These white crystalline products were identified by chemical analysis and by their *X*-ray diffraction powder data. The first materials precipitated were found to be distinct phases rather than mixtures. The phases $CsSn^{II}_2Cl_4Br$, $CsSn^{II}_2Cl_2Br_3$, and $CsSn^{II}_2ClBr_4$ were, for example, obtained as the first products from solutions containing the correct molar proportions of the starting materials. These phases were also the first products obtained from solutions with composition around the correct molar compositions. Analytical data for these products are in Table 4. The precipitation of distinct compositions from these lower-temperature aqueous systems is consistent with the existence of mixed polynuclear Sn^{II} halide ions in solution. When the white materials were heated they underwent transformations to coloured phases. These changes were followed by high-temperature *X*-ray powder photography and coincide with tetragonal to cubic phase transformations. For example, the phase transformations of $CsSn^{II}_2Cl_5$ (white to yellow), $CsSn^{II}_2Cl_2Br_3$ (white to red), and $CsSn^{II}_2Br_5$ (grey to black) were found to occur at *ca.* 94, 166, and 201 °C respectively. When the phase changes were followed visually on a heating microscope the transformation was seen to begin as colour centres. For $CsSn^{II}_2Cl_2Br_3$ the transformation began at 160 °C with the appearance of coloured (orange-red) centres that gradually grew in size until the phase change was complete at 180 °C. The transformation temperature for most of the tetragonal compositions were higher than can be obtained in boiling aqueous solutions; the coloured products from the aqueous system are therefore being produced in temperature ranges in which they are metastable.

TABLE 4

Analyses (%) of $CsSn_2Cl_{5-n}Br_n$ (n = 0—5) compounds *

	Sn	Br	Cl
$CsSn_2Cl_4Br$	39·8 (40·1)	13·5 (13·5)	24·5 (24·0)
$CsSn_2Cl_2Br_3$	33·7 (34·9)	34·0 (35·2)	9·5 (10·4)
$CsSn_2ClBr_4$	32·3 (32·7)	43·1 (44·1)	4·9 (4·8)

* Calculated values are given in parentheses.

The materials obtained when molten systems containing $CsSn^{II}_2Cl_5$ and $CsSn^{II}_2Br_5$ solidified were coloured and cubic, again undergoing phase transformations to white tetragonal products on cooling. The final tetragonal products were not mixtures and gave distinct *X*-ray diffraction powder patterns. It is therefore possible to obtain a range of compositions for both the cubic and tetragonal phases. These compositions must form part of a range of solid solutions in which packing requirements are the dominant feature. The products were identified by their high-temperature colours (which change with % Br) and by their low-temperature *X*-ray data.

^{119}Sn Mössbauer parameters for the low-temperature $CsSn^{II}_2X_5$ phases obtained at 80 K are in Table 5. The Mössbauer spectra for the coloured high-temperature phases could not be obtained at room temperature and above because of poor *f* fractions. The chemical isomer shifts (δ) for the low-temperature phases were very similar although there was some tendency to increase with increasing Br content. All the materials had quadrupole splittings and these decreased with increasing Br content. The electronic environment of the tin atoms in the materials therefore becomes symmetrical with increasing Br content. Mössbauer data for the low-temperature phases suggest [10] that the Sn atom is in a distorted rather than a regular octahedral environment. This could be due either to the existence of discrete $[Sn^{II}_2X_5]^-$ ions such as $[Sn^{II}_2F_5]^-$ (refs. 9 and 11) or to distortion of the Sn atoms away from the centre of octahedral sites in a structure such as that proposed for MPb_2X_5 (M = K, Rb, and NH_4).[12]

TABLE 5

Mössbauer data for the tetragonal materials.

Composition	T/K	δ ±0·003 mm s⁻¹	Δ ±0·03 mm s⁻¹
$CsSn^{II}_2Cl_5$	80	1·72	1·00
$CsSn^{II}_2Cl_4Br$	80	1·73	1·07
$CsSn^{II}_2Cl_3Br_2$	80	1·74	0·96
$CsSn^{II}_2Cl_2Br_3$	80	1·74	0·93
$CsSn^{II}_2ClBr_4$	80	1·76	0·92
$CsSn^{II}_2Br_5$	80	1·77	0·82
$CsSn^{II}Br_3$	4·2	2·09	0
$Cs_4Sn^{II}Br_6$	4·2	2·30	0

$Cs_4Sn^{II}Br_6$. This compound was black when prepared from the molten CsBr–$SnBr_2$ system. Over a long period of time it loses colour to give a white form. *X*-Ray powder data for the black form suggest that it is isostructural with hexagonal Cs_4PbBr_6.[13] The lead compound, which is said to contain discrete $[PbBr_6]^{4-}$, has Pb–Br bond lengths (3·10 Å) longer than those in $CsPbBr_3$ (2·94 Å). The ^{119}Sn Mössbauer data for the tin compound are consistent with the presence of similar species in Cs_4SnBr_6. The Mössbauer resonance line at 4·2 K was very narrow suggesting the high-symmetry environment expected for a discrete ion $[Sn^{II}Br_6]^{4-}$ and its chemical shift is consistent with the presence of longer Sn–Br bonds in the hexagonal structure compared with the perovskite $CsSn^{II}Br_3$. The lack of colour in the room-temperature form of Cs_4SnBr_6 is presumably due to the effects, on formation of delocalised bands and their population, of the increase in the Cs : Br and the decrease in the Sn : Br ratios in Cs_4SnBr_6 compared with $CsSnBr_3$.

It thus seems significant that $Cs_4Sn^{II}Br_6$, $CsSn^{II}_2Br_5$, and the phases from the $CsSn^{II}_2Br_5$–$CsSn^{II}_2Cl_5$ system do become coloured at high temperatures.

Addition of Sn^{II} *to* $Cs_2Sn^{IV}Br_6$.—The compound $Cs_2Sn^{IV}Br_6$ is a white material which has a cubic structure closely related to that of $CsSn^{IV}Br_3$. The cubic cell of the

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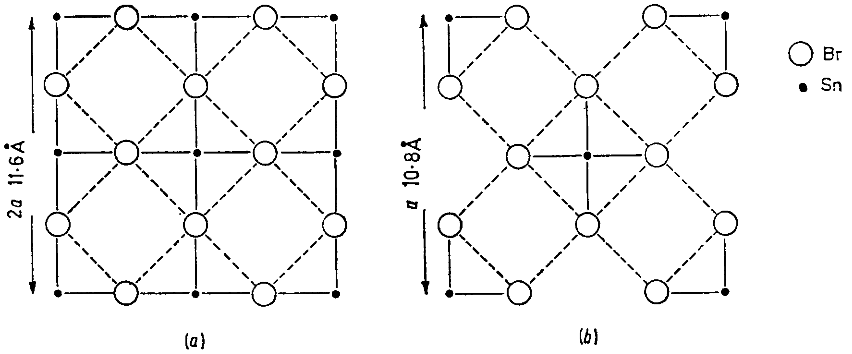
[11] J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*), 1968, 946.

[12] H. M. Powell and H. S. Tasker, *J. Chem. Soc.*, 1937, 119.

[13] C. K. Moeller, *Kgl. Danske. Videnskab. Selskab. Mat., Fys Medd*, 1960, **32**, 3.

Sn^{IV} compound ($a = 10{\cdot}8$ Å) contains the same number of Cs and Br atoms but only half as many Sn atoms as a cell ($a = 11{\cdot}6$ Å) containing eight formula units of $CsSn^{II}Br_3$. Projections of the positions of the Sn and Br atoms show (Figure) the close relation between these structures. There are no high-energy non-bonding electrons in $Cs_2Sn^{IV}Br_6$ to populate the empty bands which must be present in this structure. The Sn^{IV} compound does, however, form a mixed-lattice compound with $CsSn^{II}Br_3$ which effectively introduces Sn^{II} into $Cs_2Sn^{IV}Br_6$ without destroying its cubic unit cell. The materials obtained were coloured and showed increased conductivity. Mössbauer spectra for the Sn^{II} sites ($\delta = 1{\cdot}13$, $\Delta = 1{\cdot}63$ mm s^{-1}) show that the Sn^{II} is in a distorted environment, which would be expected because of the shorter Sn^{II}–Br bonding that must be present in doped $Cs_2Sn^{IV}Br_6$. There must, however, be a large enough population of the empty $Cs_2Sn^{IV}Br_6$ bands to produce colour in the doped material. Colours of this type can be explained in terms of intervalence-transfer absorption, but this seems less likely than direct population of conductance bands by ns^2 electrons in view of the colours of caesium tin(II) halides in the absence of Sn^{IV} and the fact that other halide perovskite lattices such as $CsCdBr_3$, $CsHgBr_3$, and $CsPbBr_3$ also developed colour when doped with Sn^{II}.



Direction of t_2 orbital overlap in (*a*) $CsSnBr_3$ ($2a = 11{\cdot}6$ Å), (*b*) Cs_2SnBr_6 ($a = 10{\cdot}8$ Å). (— — —), Direction of overlap of t_2 orbitals

Comparison with Compounds of Other Elements with ns^2 *Lower Oxidation States*.—Compounds of the type M_2EX_6 (M = K, Rb, Cs, and NH_4; E = Se, Te, and Po; X = Cl and Br) are intensely coloured and isostructural with the corresponding white hexahalogenostannates(IV). The difference between the Sn^{IV} and the Group 6 metal(IV) compounds is the presence of ns^2 non-bonding lone-pair orbitals in the Group 6 elements. The colours and electrical properties of the Se^{IV}, Te^{IV}, and Po^{IV} compounds can therefore be explained, like those of $CsSn^{II}Br_3$, by population of bands by the ns^2 non-bonding electrons. Intervalence charge-transfer absorption has been used to explain[14] colours in the mixed-valence $M_4Sb^{III}Sb^{V}X_{12}$ compounds (X = Cl and Br). Many of these Sb compounds are, however, isostructural with the corresponding hexahalogeno-stannates(IV) and -tellurates(IV) and it, therefore, seems more likely that population of bands by the Sb^{III} $5s^2$ electrons is largely responsible for their colours and conducting properties.[14] It is significant that mixed-oxidation-state compounds such as Sb_2O_4[15] and Sn_3F_8,[16] in which the anion orbitals cannot form low-energy bands, are white and do not show visible-region absorptions attributable to intervalence charge transfer. High-symmetry environments in compounds of the lower oxidation states of most *p*-block elements are found only in their heavier halide and chalcogenide derivatives where these anions are in close contact. Regular octahedral Sn^{II} environments associated with colour and conducting properties are, for example, found in SnSe,[17] SnTe,[17] and SnI_2[10] as well as in $CsSnBr_3$ and related halides. Compounds of these elements with oxygen or fluorine environments, in which the anions have no *d* orbitals available for formation of low-energy conduction bands, have distorted sites for the element. The oxide and fluoride derivatives are usually white unless, as in SnO and PbO, the metal–metal contacts are short enough to permit formation of a delocalised band using their empty *d* orbitals.

Studies on the i.r. spectra of some of the hexahalogenometal(IV) compounds do in fact provide some evidence for halogen–halogen interactions when elements with ns^2-outer-electronic configurations are present in the solid state. We studied the i.r. spectra of some compounds of $M^{I}_2Sn^{IV}X_6$, $M^{I}_4Sb^{III}Sb^{V}X_{12}$, and $M^{I}_4Sn^{IV}Sb^{III}_{0{\cdot}5}Sb^{V}_{0{\cdot}5}X_{12}$ (X = Cl or Br). The hexahalogenostannates(IV) studied have the $K_2[PtCl_6]$ structure, which is cubic, space group $O_h^5(Fm3m)$ with $Z = 4$, and has Pt, K, and Cl on O_h, T_d, and C_{4v} sites respectively. This means that, in the absence of distortion, the selection rules imposed by the anion site symmetry are the same as those for the free ion. Factor-group analysis shows that for the primitive unit cell there are 3 F_{1u} i.r.-active modes, ($1A_{1g} + 1E_g + 2F_{2g}$) Raman-active modes, and ($1F_{1g} + 1F_{2u}$) inactive modes. There is also 1 F_{1u} acoustic mode.

The hexahalogenoantimonates may be formally considered to have the $K_2[PtCl_6]$ structure, but, since we have Sb in two different oxidation states, we can say that there is a primitive unit cell around each O_h site. The number of vibrations should then be doubled, since there are

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[14] L. Atkinson and P. Day, *J. Chem. Soc.* (*A*), 1969, 2423, 2432.

[15] D. Rogers and A. C. Skapski, *Chem. Comm.*, 1965, 611.

[16] M. F. A. Dove, R. King, and T. J. King, *J.C.S. Chem. Comm.*, 1973, 944.

[17] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

primitive unit cells containing two different co-ordination polyhedra. The spectrum should be further enriched if half the antimony is replaced by Sn^{IV}; the system now formally contains Sb^{III}, Sb^{V}, and Sn^{IV} and should show vibrations characteristic of each. When half the antimony was replaced by Sn^{IV}, the spectra obtained contained additional bands characteristic of M_2SnX_6; these are in Table 6, together with previously reported data on hexahalogeno-antimonates(III)(IV) and -stannates(IV). Comparison of these two sets of data shows that, at room temperature, none of the spectra of the chloro-complexes which we have studied display the strong band in the region 300—320 cm^{-1} characteristic of the $[SbCl_6]^{3-}$ grouping; all the observed bands can be interpreted as being due to $[SbCl_6]^-$ and $[SnCl_6]^{2-}$.

TABLE 6

Vibrational spectra of some solid octahedral hexahalogeno-stannates and -antimonates

Compound	Method	Observed wavenumber/cm^{-1}											Ref.
K_2SnCl_6	I.r.		324					174			84		*a*
$(NH_4)_2SnCl_6$	I.r.		320					182		126			*a*
K_2SnBr_6	I.r.					220				117	94		*b*
$(NH_4)_2SnBr_6$	I.r.					217				122	97		*b*
$CsSbCl_6$	I.r.		324					188				57	*c*
$(Cl_4As)SbCl_6$	I.r., Raman	350	333	291				180	174				*d*
$(Cl_4P)SbCl_5Br$	Raman	332	308	290		222		175	157				*e*
$(Et_4N)SbCl_5Br$	Raman	332	308	289		223		173	158				*e*
$Rb_4Sb^{III}Sb^{V}Cl_{12}$	I.r.	354				242(sh)		188vb				64	*a*
$Cs_4Sb^{III}Sb^{V}Cl_{12}$	I.r.	350				248		190				60	*a*
$Rb_4Sb^{III}Sb^{V}Br_{12}$	I.r.					242		188	160	124		62	*a*
$Cs_4Sb^{III}Sb^{V}Br_{12}$	I.r.					238		180	156	128		56	*a*
$Cs_4Sn^{IV}Sb^{III}{}_{0\cdot5}Sb^{V}{}_{0\cdot5}Cl_{12}$	I.r.	352	316					196	178			70	*a*
$Rb_4Sn^{IV}Sb^{III}{}_{0\cdot5}Sb^{V}{}_{0\cdot5}Br_{12}$	I.r.					224vb		194	164	118		60	*a*
$Cs_4Sn^{IV}Sb^{III}{}_{0\cdot5}Sb^{V}{}_{0\cdot5}Br_{12}$	I.r.					238	220	188	158	118		58	*a*
K_3SbCl_6	Raman		319	295	266	229			135	109		67	*f*
$(NH_4)_3SbCl_6$	Raman		317	296	262	226			136	103			*f*
Rb_3SbCl_6	Raman		316	298	256	224			140			73	*f*
Cs_3SbCl_6	Raman		318	277	245				143	114		63	*f*
$[Co(NH_3)_6][SbCl_6]$	Raman			299	266	215				114		80	*f*
	I.r.				268	218	215		124	113			*g*
$[Co(NH_3)_6][SbBr_6]$	I.r.								141			69	*g*
	Raman								159	137		81, 67	*g*

[a] This work. [b] Ref. 19. [c] L. Atkinson and P. Day, *J. Chem. Soc.* (*A*), 1969, 2423. [d] I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1967, 712. [e] Ref. 18. [f] E. Martineau and J. B. Milne, *J. Chem. Soc.* (*A*), 1970, 2971. [g] C. J. Adams and A. J. Downs, *Chem. Comm.*, 1970, 1699.

The situation with regard to the bromo-complexes is less clear-cut, as there is little information available and what there is suggests that the spectra of $[SbBr_6]^-$ and $[SbBr_6]^{3-}$ are difficult to distinguish from each other. Bentley *et al.*[18] stated that a strong Raman band at 194 cm^{-1} (presumably the A_{1g} stretching mode) is characteristic of $[SbBr_6]^-$; the i.r. bands which we observed at frequencies well above this are also, presumably, due to this species. As with the chloro-complexes, the stretching mode for the $[SnX_6]^{2-}$ grouping lies near or just below that for $[SbX_6]^-$. However, it can be argued that those compounds do display at least one band (near 160 cm^{-1}) which is assignable to $[SbBr_6]^{3-}$. Our reason for believing this interpretation to be incorrect arise from the spectra obtained at liquid-nitrogen temperature.

The results of work described elsewhere in this paper lead to the conclusion that, in the mixed-valence antimony complexes studied here, some of the ns^2 electronic character of Sb^{III} is delocalised into a band. If this is true, one would expect depopulation of the band at lower temperatures and possibly the appearance of absorptions characteristic of $[SbX_6]^{3-}$; if any absorption due to such species were present already their intensities would increase. We found that absorption bands already present at room temperature did not significantly change their relative intensities, but that new bands appeared in the spectra of all seven compounds at liquid-nitrogen temperature. In $M_4Sb^{III}Sb^{V}Cl_{12}$ bands appeared at 308 and 280 cm^{-1} ($M = Cs$) and 300 and 268 cm^{-1} (Rb); in $Cs_4Sn^{IV}Sb^{III}{}_{0\cdot5}Sb^{V}{}_{0\cdot5}Cl_{12}$ a new band appeared at 266 cm^{-1} but the broad absorption due to the $[SnCl_6]^{2-}$ grouping, at 316 cm^{-1}, obscured any possible new feature in this region. In $M_4Sb^{III}Sb^{V}Br_{12}$, new bands appeared at 136 and 84 cm^{-1} (Cs) and 142 and 86 cm^{-1} (Rb) and the higher-frequency band also appeared, at exactly the same frequency, in the respective $M_4Sn^{IV}Sb^{III}{}_{0\cdot5}Sb^{V}{}_{0\cdot5}Br_{12}$ compounds. This is very close to the 141 cm^{-1} band observed for $[Co(NH_3)_6][SbBr_6]$.

We, therefore, conclude that, at room temperature, all the antimony in these materials is effectively present as Sb^{V}, due to delocalisation of the Sb^{III} ns^2 electrons into a conduction band, and that, at liquid-nitrogen temperatures, depopulation of this band causes the appearance of absorptions due to $[SbX_6]^{3-}$ groupings to appear in the i.r. spectra. I.r. spectra of the hexachlorostannates(IV) consist of the three bands predicted by the factor-group selection rules,[19] but the hexahalogenoantimonate spectra contain additional bands. The relative intensities of the bands, and comparison with the observations of other workers (see Table 6), strongly suggest that the three fundamental modes are near 350, 190, and 60 cm^{-1} for the

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[19] N. N. Greenwood and B. P. Straughan, *J. Chem. Soc.* (*A*), 1966, 1962.

$[SbCl_6]^-$ grouping and near 240, 160, and 60 cm^{-1} for the $[SbBr_6]^-$ grouping. Additional bands might well be combinations, but, as the colours of these materials preclude observation of the Raman spectra, and any i.r.-active binary combination must involve one i.r.- and one Raman-active mode, it is not possible to interpret these features.

EXPERIMENTAL

The *X*-ray data were obtained with Phillips 11·64 cm and focussing Guinier cameras at the appropriate temperatures, using Cu-K_α radiation. Mossbauer spectra were obtained with a $BaSnO_3$ source and the absorber at 80 or 4·2 K. The chemical shift for the reference material from the source was 2·10 mm s^{-1} at 80 K. The Mössbauer apparatus has been described previously.[20] I.r. data were obtained on a Beckman RIIC FS-720 spectrometer.

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