Cluster Formation in $Cs_2Sn_6Br_3F_{11}$ *

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The crystal structure of $Cs_2Sn_6Br_3F_{11}$ has been determined using single-crystal X-ray diffraction and refined by full-matrix least-squares analysis to $R = 0.0736$, $R' = 0.0743$. The complex crystallises in the monoclinic space group $C2/m$ with $a = 22.856(7)$, $b = 4.370(3)$, $c = 10.229(4)$ Å, $\beta = 103.94(3)°$ and $Z = 2$. All atoms lie in planes perpendicular to the b axis with an interplanar separation of $b/2$, which is stabilised by interactions between Sn, Br and F. There are three distinct tin sites in the structure with tin forming strong bonds to fluorine atoms only. The tin(II) sites are novel in that they contain only one short and one long Sn–F bond with the additional bonding pattern being made up from Sn–F and cluster interactions involving Br atoms. ^{119}Sn Mössbauer data are presented and compared with those of other tin(II) halides.

Tin(II) compounds are often characterised by distorted geometries around the tin atoms caused by the presence of stereochemically active non-bonding electron pairs.[1,2] The most commonly observed distortion is a trigonal-pyramidal distribution, of three nearest-neighbour tin–ligand bonds and three longer, essentially non-bonding, contacts completing a distorted-octahedral geometry. The longer interactions arise because the close approach of ligands to the tin is prevented along the direction in which the non-bonding electron pairs point. Another tin(II) environment commonly found is the distorted square-pyramidal geometry, in which the tin atom usually has two short bonds to ligands and two bonds of greater length than those normally found in tin(II) compounds as nearest-neighbour contacts. Evidence has been found to suggest that the direction in which the non-bonding electron-pair orbitals point is important and that, in appropriate structures, this can lead to some delocalisation of the electron pairs into cluster orbitals.[3] A few structures have tin in high-symmetry regular octahedral sites;[4] such environments are usually found in compounds containing heavier halide and chalcogenide atoms, in which the distorting effects of the non-bonding electron pairs on the tin atoms are removed by population of solid-state bands arising from overlap of the empty halide or chalcogenide orbitals.

Although a great deal of evidence, including crystal-structure determinations,[5–7] is available on the nature of Sn^{II}–F interactions, much less is known about Sn^{II}–Br bonding in the absence of solid-state effects. We have determined the structure of $Cs_2Sn_6Br_3F_{11}$ and used the bond-length data, along with ^{119}Sn Mössbauer data, to assess the relative bonding characteristics of F and Br atoms towards Sn^{II}.

Experimental

The compound $Cs_2Sn_6Br_3F_{11}$ was prepared from solutions of CsBr and SnF_2 in the minimum amounts of boiling water and mixed in a 1:2 mole ratio. The SnF_2 solution contained a small piece of tin metal to minimise oxidation to Sn^{IV}. The resultant clear solution was evaporated and cooled to give white needles of the product. These were collected and dried *in vacuo*, over KOH pellets. The whole process was carried out in a nitrogen-filled glove-box to prevent oxidation of Sn^{II} to Sn^{IV}.

^{119}Sn *Mössbauer Spectrum.*—^{119}Sn Mössbauer data were recorded in constant-acceleration mode using a $CaSnO_3$ source on a Cryophysics MS-102 spectrometer with a multichannel analyser. Data were fitted to Lorentzian distributions. All measurements were recorded at 80 K and calibrated with SnO_2.

Crystallography.—Crystal data. $Cs_2Sn_6Br_3F_{11}$, $M = 1426.65$, monoclinic, space group $C2/m$, $a = 22.856(7)$, $b = 4.370(3)$, $c = 10.229(4)$ Å, $\beta = 103.94(3)°$, $U = 991.4$ Å^3, $T = 298$ K, $D_m = 4.48$ g cm^{-3}, $Z = 2$, $D = 4.78$ g cm^{-3}, white needles (darkening with time), $F(000) = 1228$, $\mu = 163.46$ cm^{-1}.

Data collection and processing. Intensity data were collected, at Queen Mary College, London on an Enraf–Nonius CAD 4 four-circle diffractometer in ω–2θ scan mode. Monochromatic Mo-Kα ($\lambda = 0.710\,69$ Å) radiation was used throughout. Data for 657 independent reflections, in monoclinic symmetry, with $I > 3\sigma(I)$ were used in subsequent calculations. They were corrected for Lorentz and polarisation factors.

Structure analysis and refinement. The only systematic absences in the intensity data were those for C-face centring giving three possible space groups, *viz.* C_2, Cm and $C2/m$ (nos. 5, 8 and 12 respectively).[8] Refinement was initially carried out in the non-centrosymmetric space group C_2. All calculations were performed using SHELX76[9] and MULTAN80.[10] Molecular plots were obtained using PLUTO[11] and ORTEP.[12]

The relative closeness of the atomic numbers of Sn and Cs made the Patterson vector density map difficult to interpret, and direct methods were employed for initial phasing of structure factors. From the resulting electron-density map the two highest peaks, at 0.11, 0, 0.08 and 0.78, 0, 0.18, were used in a Fourier synthesis with the y axis fixed at zero to define the origin. The lowest residuals were obtained with tin atoms in these sites. A third tin atom at 0.48, 0, 0.30 was located from the resulting electron-density map. The next highest peak was at the two-fold special position 0.5, 0, 0, with a closest contact distance to Sn of 3.3 Å. Although this distance is longer than the average tin to bromine bonding contact,[1] the lowest residual was obtained with a bromine refined in this position. Further Fourier refinement located a full site Br at 0.36, 0, 0.21, and a Cs at 0.34, 0, 0.52. The residual at this stage, with all the heavy atoms located, was 0.18.

From the atomic positions it was apparent that the structure would be better described in a centrosymmetric space group, with all atoms lying in special positions. Further refinement was therefore carried out in the centrosymmetric space group $C2/m$. A Fourier difference synthesis located six fluorine sites. If all

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

the fluorine sites were at full occupancy there would be an excess of half a negative charge per formula unit. Attempts to locate further positive ions failed and it was concluded that one or more of the halogen sites must be at less than full site occupancy. It was found that only the F(5) site (see Table 1) would accept less than full occupancy without adverse effects on the residual sum of squares.

Anisotropic thermal parameters were successfully applied to all the heavy atoms. Non-unitary weights were used in the final refinement, the weighting scheme used being $w = 1/[\sigma^2(F_o) + 0.060\,863\ F_o^2]$, with $\sigma(F_o)$ from counting statistics. Inter-layer scale factors were calculated and refined in *l* resulting in a final *R* factor of 0.0736 ($R' = 0.0743$). The maximum residual electron density in the final refinement was 1.8 e Å^{-3} with an average shift/e.s.d. = 0.016 for the refined parameters. The final atomic parameters are given in Table 1 with contact distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Discussion

A projection of the unit-cell contents of $Cs_2Sn_6Br_3F_{11}$ is shown in Fig. 1(*a*), and a plot illustrating thermal parameters in Fig. 1(*b*). The structure is layered with all atoms lying in planes perpendicular to the *b* axis with interplanar spacings of *b*/2. The layered structure is stabilised by Sn–Br, Sn–F and Br $\cdots$ Br interactions.

Three distinct tin sites are identifiable in the structure, all showing strong bonding interactions only with fluorine atoms. This is consistent with other known structures of tin(II) mixed halides containing Br and F.[13,14] The Sn(1) atoms are located in pairs at the same height in *b* and are linked by a pair of shared F(6) atoms at distances of 2.11 and 2.27 Å to form planar four-membered rings with alternating long and short bonds. These rings are linked to others in adjacent layers by bridging F(5) atoms at a distance of 2.30 Å. As a consequence of the half occupancy of the F(5) site, the average Sn(1) co-ordination number is three, making the average tin environment that of a distorted trigonal pyramid. The Sn $\cdots$ Sn distance across the ring of 3.587 Å is just within that normally considered for possible overlap of a filled non-bonding orbital on one tin with empty orbitals on a neighbouring tin atom. However, in this case no direct interaction is possible because, for stereochemical reasons, the non-bonding electron pairs must point out of the *a*/*c* plane, where they prevent the close approach of further atoms, and away from adjacent tin atoms. The partial occupancy of F(5) also means that two configurations for linking the planar Sn_2F_2 units are possible, *viz.* a stepped configuration, Fig. 2(*a*) and a closed configuration, Fig. 2(*b*). In both configurations the tin is co-ordinated to three fluorine atoms only. The stepped arrangement gives a polymeric cation, of general formula $[(Sn_2F_3)_n]^{n+}$, which runs perpendicular to the *a*/*c*-cell plane, whereas the closed configuration forms a discrete cation $[Sn_4F_6]^{2+}$. From the data it is impossible to distinguish between either of the two configurations or a disordered combination of the two. Three longer tin–halogen contacts complete the distorted six-co-ordinate geometry around Sn(1) with two Br(2) atoms at 3.620 Å and F(4) at 2.47 Å.

Table 1 Final atomic parameters for $Cs_2Sn_6Br_3F_{11}$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	Site	*X*/*a*	*Y*/*b*	*Z*/*c*	Occupancy
Cs	4i	0.345 59(6)	0.0(—)	0.538 9(1)	1.0(—)
Sn(1)	4i	0.988 01(6)	0.0(—)	0.320 2(1)	1.0(—)
Sn(2)	4i	0.108 20(6)	0.0(—)	0.072 5(1)	1.0(—)
Sn(3)	4i	0.755 66(7)	0.0(—)	0.161 5(1)	1.0(—)
Br(1)	2b	0.5(—)	0.0(—)	0.0(—)	1.0(—)
Br(2)	4i	0.360 4(1)	0.0(—)	0.195 8(2)	1.0(—)
F(1)	4i	0.792 2(8)	0.0(—)	0.819(2)	1.0(—)
F(2)	4i	0.346 9(6)	0.0(—)	0.842(1)	1.0(—)
F(3)	4i	0.228 4(5)	0.0(—)	0.640(1)	1.0(—)
F(4)	4i	0.585 8(5)	0.5(—)	0.257(1)	1.0(—)
F(5)	4i	0.485 7(8)	0.0(—)	0.627(2)	0.5(—)
F(6)	4i	0.555 3(5)	0.5(—)	0.502(1)	1.0(—)

The two remaining tin atoms have sites with similar co-ordinations: Sn(2) and Sn(3) have strong bonding contacts to two F atoms each, with one short Sn–F bond [2.07 and 1.98 Å to Sn(2) and Sn(3) respectively] and one longer Sn–F bond (2.28 and 2.34 Å respectively). These tin atoms also have weaker interactions to fluorine atoms in the adjacent layers [Sn(2)–F(2) 2.48, Sn(3)–F(1) 2.47 Å]. Since there are only two strong Sn–F interactions for Sn(2) and Sn(3) these atoms could be regarded as being in discrete angular SnF_2 units. Such an interpretation has to be questioned because the preferred co-ordination geometries for crystalline tin(II) fluorides are trigonal pyramidal or distorted square pyramidal.[15] An explanation of the stabilisation of these angular units could lie in Sn $\cdots$ Sn interactions and the Sn(2) $\cdots$ Sn(3) distance of 3.935 Å is just within that normally considered to permit direct interaction between tin atoms. Again in this case, the stereo-

Table 2 Selected contact distances (Å) and angles (°) in $Cs_2Sn_6Br_3F_{11}$ with e.s.d.s in parentheses

Cs $\cdots$ Br(2)	3.607(3)	Cs $\cdots$ F(4)	3.16(1) × 2
Cs $\cdots$ F(2)	3.09(1)	Cs $\cdots$ F(5)	3.11(2)
Cs $\cdots$ F(3)	3.09(1)	Cs $\cdots$ F(6)	3.25(1) × 2
Cs $\cdots$ F(3′)	3.08(1) × 2		
Sn(1)–F(4)	2.47(1)	Sn(1)–F(6)	2.11(1)
Sn(1)–F(5)	2.30(1)	Sn(1)–F(6′)	2.27(1)
Sn(2)–Br(1)	3.249(2) × 2	Sn(2)–F(2)	2.48(1) × 2
Sn(2)–Br(2)	3.710(3) × 2	Sn(2)–F(4)	2.07(1)
Sn(2)–F(1)	2.28(2)		
Sn(3)–Br(2)	3.198(2) × 2	Sn(3)–F(2)	2.34(1)
Sn(3)–F(1)	2.47(1) × 2	Sn(3)–F(3)	1.98(1)
Sn(1) $\cdots$ Sn(1)	3.587(3)	Sn(3) $\cdots$ Sn(3)	3.917(3) × 2
Sn(2) $\cdots$ Sn(3)	3.935(2)		
F(4)–Sn(1)–F(5)	82.0(5)	F(5)–Sn(1)–F(6)	72.4(4)
F(4)–Sn(1)–F(6)	73.7(4)	F(5)–Sn(1)–F(6′)	87.2(5)
F(4)–Sn(1)–F(6′)	143.7(4)	F(6)–Sn(1)–F(6′)	70.0(5)
Br(1)–Sn(2)–Br(1) (*y* = 1)	84.52(5)	Br(1)–Sn(2)–F(4)	82.3(2)
Br(1)–Sn(2)–F(1)	136.6(1)	F(1)–Sn(2)–F(4)	89.5(5)
Br(2)–Sn(3)–Br(2) (*y* = 1)	114.72(5)	Br(2)–Sn(3)–F(3)	86.6(3)
Br(2)–Sn(3)–F(2)	136.4(1)	F(2)–Sn(3)–F(3)	87.1(4)

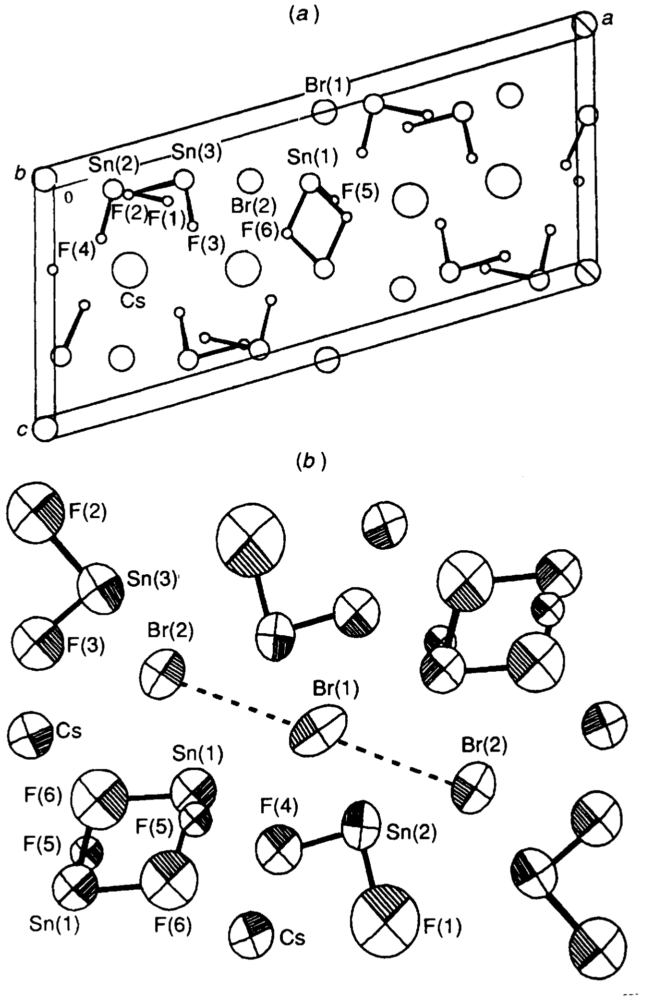

Fig. 1 (a) Unit-cell contents of $Cs_2Sn_6Br_3F_{11}$. (b) An ORTEP[12] plot of part of the $Cs_2Sn_6Br_3F_{11}$ structure

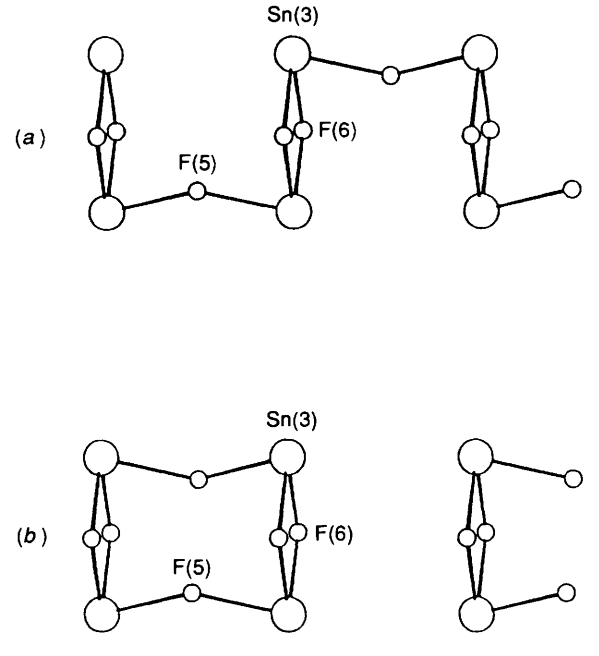

Fig. 2 Possible fluorine bridging configurations in $Cs_2Sn_6Br_3F_{11}$: (a) stepped configuration, (b) closed configuration

chemical requirements mean that the non-bonding pair must point away from adjacent tin atoms ruling out any direct interaction. Since Sn ··· Sn interactions are impossible, it is necessary to consider the effects of the Br atom positions and the potential interactions between the empty bromine orbitals and the tin non-bonding electron pairs. Bromine atoms are arranged in the layered structure in linear triplets with the outer Br(2) atoms equidistant (at 4.155 Å) from a central Br(1) atom. The triplets are arranged directly above each other in alternate atomic layers to give an intertriplet separation equivalent to the *b*-axis length of 4.370 Å; the resultant bromine ribbons run parallel to the *b*-axis. The Br ··· Br contact distances indicate that overlap of empty Br 4d orbitals is likely within the ribbons. The non-bonding pairs on Sn(2) and Sn(3) for stereochemical reasons must point away from the angular SnF_2 units towards the Br 4d orbitals in the ribbons (Fig. 3). The shortest distance between Sn(2) and the plane of the bromine ribbon is *ca.* 1.7 Å [Fig. 4(*a*)] suggesting that a limited stabilising overlap between the non-bonding orbital on the tin and the empty Br 4d orbitals is possible. The non-bonding orbital on Sn(3) lies parallel to the plane of the ribbon but stabilising overlap with empty Br 4d orbitals is still possible [Fig. 4(*b*)].

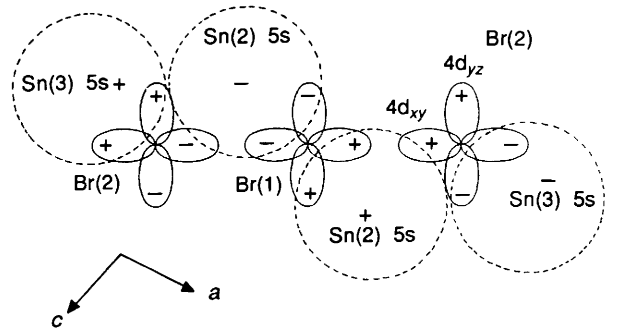

Fig. 3 Cluster interaction in $Cs_2Sn_6Br_3F_{11}$

The details of the delocalisation of tin non-bonding electron density into cluster orbitals in the structure of $Cs_2Sn_6Br_3F_{11}$ are unique, but the ability of Sn to become involved in this type of stabilising weak bond interaction is not. The interactions arising from delocalisation of the non-bonding tin orbitals into adjacent empty orbitals range from (*i*) dimer formation in $Sn[CH(SiMe_3)_2]_2$,[16] where the stability and structure of the material arises from interactions between the non-bonding pair on one tin atom with an empty orbital on a neighbouring tin atom, through (*ii*) cluster formation of tin atoms around halogens in $K_3Sn_2(SO_4)_3X$ (X = Br or Cl),[3] where the distorting effects of the non-bonding electron pairs pointing towards the halide ions are removed by delocalisation of the tin electron density into cluster orbitals, to (*iii*) the population of two- or three-dimensional solid-state bands by non-bonding electrons on Sn in compounds such as SnO and $CsSnBr_3$,[17,18] which accounts for their optical and electrical properties. Although the non-bonding electron orbital interactions with empty bromine orbitals in $RbSn_2Br_5$[19] differ from those in $Cs_2Sn_6Br_3F_{11}$, it is interesting that they are also responsible for stabilisation reactions within the $[(Sn_2Br_5)_n]^{n-}$ layers.

In $Cs_2Sn_6Br_3F_{11}$ the Cs atoms occupy nine-co-ordinate sites in the lattice, being surrounded by eight fluorine atoms at distances ranging between 3.08 to 3.25 Å and a single Br at 3.607 Å.

The Mössbauer spectrum of $Cs_2Sn_6Br_3F_{11}$ is shown in Fig. 5 and the fitted Mössbauer parameters are presented in Table 3 along with those of several other bromo- and fluoro-stannates(II). A single doublet was fitted to the data as attempts to fit individual overlapping doublets corresponding to the three tin sites proved unsuccessful. The final residual sum of squares for the fit was 273.3 for 493 degrees of freedom. The three tin sites in $Cs_2Sn_6Br_3F_{11}$ combine to give a single quadrupole-split doublet, reflecting similarity in the environments of the tin

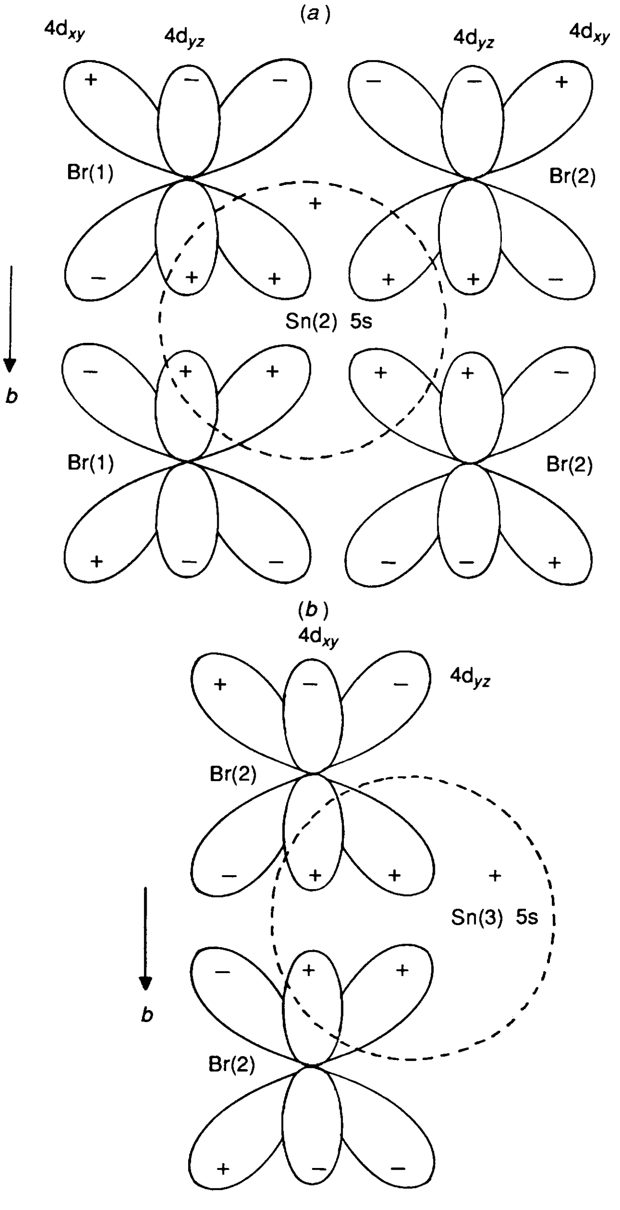

Fig. 4 Detail of (*a*) Sn(2)–Br cluster interaction and (*b*) Sn(3)–Br cluster interaction in $Cs_2Sn_6Br_3F_{11}$

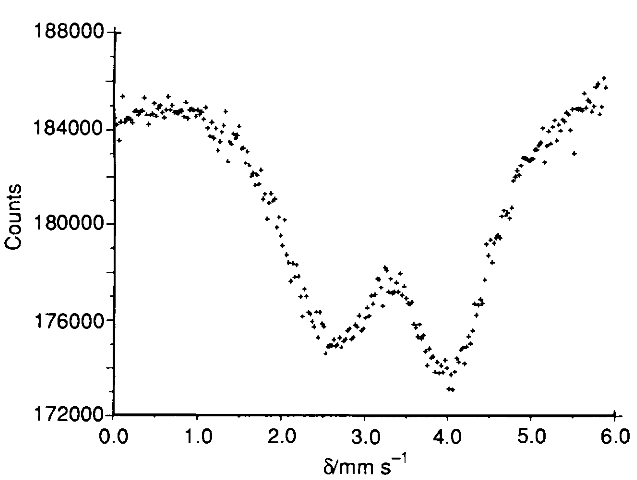

Fig. 5 Mössbauer spectrum of $Cs_2Sn_6Br_3F_{11}$

Table 3 Mössbauer data (mm s^{-1}) for $Cs_2Sn_6Br_3F_{11}$ and other tin(II) halides

Formula	δ	Δ	Γ	Ref.
$Cs_2Sn_6Br_3F_{11}$	3.50(1)	1.50(1)	1.16(2)	This work
SnF_2	3.62	1.77		20
$SnBr_2$	3.98	0		21
$CsSnF_3$	2.98	2.00		22
$NaSn_2F_5$	3.32	1.86		23
Sn_3BrF_5	3.69	1.18		21

atoms in these sites. The doublet is asymmetric with a slightly broadened linewidth of $\Gamma = 1.16(2)$ mm s^{-1} (full width at half maximum). The shift of 3.50 mm s^{-1} is significantly lower than that of $SnBr_2$, which is consistent with the absence of strong Sn–Br bonding interactions. The shift is also lower than those of SnF_2 and Sn_3BrF_5, which contain tin bonded only to F in a polymeric $[(Sn_3F_5)_n]^{n+}$ network with extensive fluoride bridging, but not as low as the shifts found for compounds that contain the discrete $[SnF_3]^-$ and $[Sn_2F_5]^-$ anions. The value of the chemical shift for tin(II) fluoride in the solid state arises because the co-ordination of the tin atoms is greater than two, owing to the presence of bridging F atoms. If $Cs_2Sn_6Br_3F_{11}$ contained discrete SnF_2 units, these would show a higher chemical isomer shift than tin(II) fluoride because of the absence of bridging F atoms. Since there is no evidence for a high shift component in the Mössbauer spectrum, the data are inconsistent with the presence of discrete SnF_2 units but are consistent with a lowering of the shift for the Sn(2) and Sn(3) atoms by delocalisation of some of their non-bonding electron density into empty cluster orbitals involving Br atoms. The shift and quadrupole splitting of $Cs_2Sn_6Br_3F_{11}$ therefore confirm that the Sn 5s-electron density remains to a large extent localised at the tin site despite the potential for electron delocalisation into the Br-4d network.

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