Mössbauer Spectra of Ternary Tin(IV) Sulphides in the Systems Na_2S–SnS_2, BaS–SnS_2, and PbS–SnS_2

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^{119}Sn Mössbauer spectra have been recorded for a number of ternary sulphides isolated from the systems Na_2S–SnS_2, BaS–SnS_2, and PbS–SnS_2. The series includes compounds of known crystal structure such as Na_4SnS_4, $Na_6Sn_2S_7$, the high- and low-temperature forms (HT and LT) of Ba_2SnS_4, and $Ba_3Sn_2S_7$, all of which contain tin tetrahedrally co-ordinated by sulphur atoms; Na_2SnS_3(LT) and $PbSnS_3$, in which the tin is octahedrally co-ordinated; and $Na_4Sn_3S_8$ which contains tin in both tetrahedral and trigonal bipyramidal sites. The measurements establish that the chemical isomer shift is sensitive to the co-ordination number of the central tin atom, and decreases by *ca.* 0.2 mm s^{-1} in going from tetrahedral, through trigonal bipyramidal, to octahedral co-ordination. The data for the compounds Na_2SnS_3(HT) and $BaSnS_3$, whose crystal structures are not known, are consistent with the presence of tin in distorted tetrahedral environments.

IN contrast to the many tin(II) and tin(IV) organometallic and co-ordination complexes that have been examined by Mössbauer spectroscopy,[1-3] relatively few tin sulphide compounds have been studied by this technique. To our knowledge the only compounds for which data were available when this study was commenced were the binary sulphides SnS, Sn_2S_3, Sn_3S_4, and SnS_2;[4] the ternary sulphide Cu_2SnS_3;[5] and a few naturally occurring minerals such as stannite (Cu_2FeSnS_4),[6-8] canfieldite (Ag_8SnS_6), cylindrite ($Pb_3Sn_4Sb_2S_{14}$), franckeite ($Pb_5Sn_3Sb_2S_{14}$), herzenbergite [(Sn,Pb)SnS_2], and teallite ($PbSnS_2$).[9] More recently, further work has been reported on SnS,[10a] Sn_2S_3,[10b] and SnSSe,[10c] and on glasses found in the system SnS–GeS–GeS_2.[10d]

During the course of a systematic synthetic and structural study of ternary chalcogenides of the group IVB elements we have isolated a number of compounds in the systems Na_2S–SnS,[11] BaS–SnS_2,[12] and PbS–SnS_2[13] which have been shown to feature a variety of stereochemical environments at the tin atom.[14-18] To complete this study Mössbauer parameters have now been determined and the data for those compounds of known structure have been used to diagnose structural features for the rest.

After the completion of this work we learned from Professor Negita and Dr. Ichiba of their studies on alkali and alkaline-earth thiostannates.[19] There is some overlap between their work and ours, and this is discussed where appropriate later in the paper.

EXPERIMENTAL

All the compounds were synthesized under vacuum, in sealed silica tubes, by reaction in the solid state of stoicheio-

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[1] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[2] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

[3] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

[4] P. P. Seregin, M. Sagatov, B. T. Melekh, V. P. Kostikov, and L. N. Vasil'ev, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1973, **9**, 134.

[5] K. Makariunas, A. Dragunas, and M. Adomynaite, *Liet. Fiz. Rinkinys*, 1972, **12**, 679; *Khim. Syvas krist. Poluprovodn. Polymet.*, 1973, 117.

[6] M. Eibschutz, E. Hermon, and S. Shtrikman, *J. Phys. and Chem. Solids*, 1967, **28**, 1633.

[7] U. Ganiel, E. Hermon, and S. Shtrikman, *J. Phys. and Chem. Solids*, 1972, **33**, 1873.

[8] N. N. Greenwood and H. J. Whitfield, *J. Chem. Soc. (A)*, 1968, 1697.

[9] D. L. Smith and J. J. Zuckerman, *J. Inorg. and Nuclear Chem.*, 1967, **29**, 1203.

[10] (*a*) V. Fano and I. Ortalli, *J. Chem. Phys.*, 1974, **61**, 5017; (*b*) S. Ichiba, M. Katada, and H. Negita, *Chem. Letters*, 1974, 979; (*c*) S. Ichiba, M. Katada, and H. Negita, *Chem. Letters*, 1974, 1061; (*d*) A. Feltz, E. Schelenzig, and D. Arnold, *Z. anorg. Chem.*, 1974, **403**, 243.

[11] F. Vermot-Daniel and J. C. Jumas, *Compt. rend.*, 1972, **275**, 741.

[12] J. C. Jumas, M. Ribes, E. Philippot, and M. Maurin, *Compt. rend.*, 1971, **272**, 1811.

[13] J. C. Jumas, M. Ribes, E. Philippot, and M. Maurin, *Compt. rend.*, 1972, **275**, 269.

[14] J. C. Jumas, E. Philippot, F. Vermot-Daniel, M. Ribes, and M. Maurin, *J. Solid State Chem.*, 1975, **14**, 379.

[15] J. C. Jumas, J. Olivier-Fourcade, F. Vermot-Daniel, M. Ribes, E. Philippot, and M. Maurin, *Rev. Chim. minérale.*, 1974, **11**, 13.

[16] W. Mark, O. Lindqvist, J. C. Jumas, and E. Philippot, *Acta Cryst.*, 1974, **B30**, 2620.

[17] J. C. Jumas, E. Philippot, and M. Maurin, *J. Solid State Chem.*, 1975, **14**, 152.

[18] K. Susa and H. Steinfink, *J. Solid State Chem.*, 1971, **3**, 75.

[19] S. Ichiba, M. Katada, and H. Negita, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2249.

metric proportions of tin disulphide and sodium, barium, or lead monosulphide. Specific details for the individual systems can be found in the literature as follows: Na_2S–SnS_2,[11] BaS–SnS_2,[12] and PbS–SnS_2.[13]

The Mössbauer spectra were recorded at 77 K either on powdered samples or, in the case of hygroscopic materials, on samples mixed with Apiezon grease; the tin concentration was 15 mg cm^{-2} in each case. The γ-ray source, which was kept at room temperature, was a nominal 15 mCi of ^{119m}Sn in a barium stannate matrix as supplied by the Radiochemical Centre, Amersham. The spectrometer was a Nuclear Science and Engineering Corporation instrument, model AM-1, used in conjunction with a 400-channel R.I.D.L. analyser, model 34-12B. The velocity scale was calibrated against the spectrum of an ^{57}Fe-enriched iron foil and the zero of velocity was defined by the spectrum of a barium stannate absorber at room temperature.

The data were analysed by computer programmes developed by Dr. T. C. Gibb.

RESULTS AND DISCUSSION

The System Na_2S–SnS_2.—Five compounds have been isolated in this system: Na_4SnS_4, $Na_6Sn_2S_7$, the high-temperature (HT) and low-temperature (LT) forms of Na_2SnS_3, and $Na_4Sn_3S_8$. With the exception of Na_2SnS_3(HT) the structures of these compounds are known in detail; the tin atom adopts various types of co-ordination and these are depicted in Figure 1. Further structural details are mentioned later, during the discussion of the Mössbauer data. The spectra for all the compounds in this system are shown in Figure 2 and the derived parameters listed in Table 1.

TABLE 1

Mössbauer data at 77 K for compounds in the system Na_2S–SnS_2

Compound	Ratio Na_2S/SnS_2	Co-ordination number	Chemical isomer shift [a] δ/mm s^{-1}	Quadrupole splitting [b] Δ/mm s^{-1}	Widths at half height [b] Γ/mm s^{-1}	Chi-squared/ (degrees of freedom)
Na_4SnS_4	2	4	1.23	0.34 [c]	1.08, 1.08 [d]	257/(194)
$Na_6Sn_2S_7$	3/2	4	1.28	0.82	0.89, 0.89 [d]	246/(239)
Na_2SnS_3(LT)	1	6	1.02	0.40 [c]	1.17, 1.17 [d]	279/(186)
Na_2SnS_3(HT)	1	(4)	1.31	1.14	1.04, 0.86	302/(242)
$Na_4Sn_3S_8$	2/3	5	1.19	0.54	0.84, 0.84 [d]	206/(182)
		4	1.30	1.40	0.84, 0.84 [d]	

[a] Relative to $BaSnO_3$ at 295 K, ±0.02 mm s^{-1}. [b] ±0.04 mm s^{-1}. [c] Visually unresolved. [d] Constrained to be equal.

The crystal structure of Na_4SnS_4 features sodium ions and discrete orthothiostannate tetrahedra, with D_{2d} point symmetry, in a tetragonal unit cell. The Sn–S bond lengths are all 2.388 Å, and the only deviations from perfect tetrahedral geometry are minor distortions in the bond angles; four are 107.5(1)° whereas the other two are 113.5(2)°.[14] The compound shows only a single peak in its Mössbauer spectrum (Figure 2), but when the spectrum is fitted with only a single Lorentzian line the chi-squared value is rather high (433 on 191 degrees of freedom) and the linewidth, $\Gamma = 1.20$ mm s^{-1}, is slightly greater than the natural value (*e.g.* 0.98 mm s^{-1} for $BaSnO_3$). The presence of an unresolved quadrupole splitting caused by the slight distortion of the SnS_4^{4-} tetrahedra is therefore probable, and the reduction in the value of chi-squared to 257 on 194 degrees of freedom when two peaks are fitted to the data is consistent with this interpretation. The chemical isomer shift for four co-ordinate tin in this compound is 1.23 mm s^{-1}. Ichiba *et al.* have also studied this compound and their value of δ agrees well with our own; however they did not attempt to fit the unresolved quadrupole splitting.[19]

Fourfold co-ordination is also present in the pyro-compound $Na_6Sn_2S_7$, which contains the $Sn_2S_7^{6-}$ anion. The latter comprises two highly distorted corner-sharing SnS_4 tetrahedra (Figure 1) in which three of the Sn–S bond lengths (Sn–$S_{terminal} = 2.36$ Å on average) are shorter than the fourth (Sn–$S_{bridge} = 2.43$ Å). The chemical isomer shift of 1.28 mm s^{-1} is very similar to that of the tetrahedral tin atom in Na_4SnS_4, but the greater distortion in the present compound is reflected in the quadrupole splitting, which is now well resolved ($\Delta = 0.82$ mm s^{-1}, see Figure 2). Ichiba *et al.* report a smaller quadrupole splitting for this species ($\Delta = 0.64$ mm s^{-1}) but their reported linewidth is rather larger than our own (1.25 compared with 0.89 mm s^{-1}) and the poorer resolution may have led to greater inaccuracies in the curve fitting.

In contrast to the preceding two compounds, Na_2SnS_3(LT) features six-co-ordinate tin atoms. The structure is a distorted NaCl-type, with ordered layers parallel to the *ab* plane but a disorder in the stacking sequence of successive layers. The SnS_6 octahedra are nearly perfect, each Sn–S bond length being 2.57 Å and the bond angles being close to 90 and 180°. The Na–S distances range from 2.73 to 2.98 Å.[16] The Mössbauer spectrum shows only a single line (Figure 2), but the linewidth again suggests an unresolved quadrupole splitting. A two-peak fit has therefore been attempted and the results obtained are listed in Table 1. The rather large value for the linewidth (1.17 mm s^{-1}) compared with those for the other sodium thiostannates probably reflects the order–disorder character of this structure. Of more general importance, however, is the observation that the chemical isomer shift in this example of octahedral co-ordination is significantly smaller than the values found for tin in the tetrahedral environment (1.02 compared with 1.23 and 1.28 mm s^{-1}).

The structure of Na_2SnS_3(HT) has not yet been determined by *X*-ray diffraction, but the Mössbauer data yield some clues. The spectrum (Figure 2) consists of a relatively large, resolved, quadrupole doublet ($\Delta = 1.14$ mm s^{-1}) with a chemical isomer shift of 1.31 mm s^{-1}. The linewidth is also reasonably narrow at 1.00 mm s^{-1}. On the basis of the earlier discussion, these features indicate that tin is in a grossly distorted tetrahedral environment. One possibility is that the compound contains discrete $Sn_2S_6{}^{4-}$ units with two terminal and two bridging sulphur atoms on each tin atom. It is also significant that the analogous copper compound Cu_2SnS_3, which crystallises with four-co-ordinate tin in a zinc-blende structure,[20] gives a well resolved quadrupole splitting of 1.07 mm s^{-1} and a chemical isomer shift of 1.25 mm s^{-1} relative to $BaSnO_3$.

$Na_4Sn_3S_8$ Is perhaps the most interesting compound of this series in that it contains tin in both four- and five-co-ordination.[17] The five-co-ordinate tin atoms are at the centres of trigonal bipyramids of sulphur atoms, and each bipyramid shares two edges with two other bipyramids to form continuous chains which in turn are linked to tin in four-fold co-ordination. For the five-co-ordinate tin the average equatorial bond length is 2.42 Å and the average axial bond length is 2.59 Å. For the four-co-ordinate tin the $Sn-S_{bridge}$ bond lengths (2.46 Å) are longer than the $Sn-S_{terminal}$ bond lengths (2.34 Å). There are twice as many five-co-ordinate tin atoms as four-co-ordinate and this aids the interpretation of the Mössbauer spectrum which is a complex envelope of overlapping lines. The spectrum can be fitted well (as shown in Figure 2) with two sets of doublets independently constrained to have equal halfwidths and intensities. The chi-squared value for the fit shown is 206 on 182 degrees of freedom. Although the halfwidths of the individual doublets were not constrained to be equal, it is gratifying that they emerge with identical values, which gives confidence in the chemical significance of the fit. The areas of the two doublets are in the ratio 1.6 : 1. The chemical isomer shift for the four-co-ordinate tin is 1.30 mm s^{-1}, which is comparable with the values found

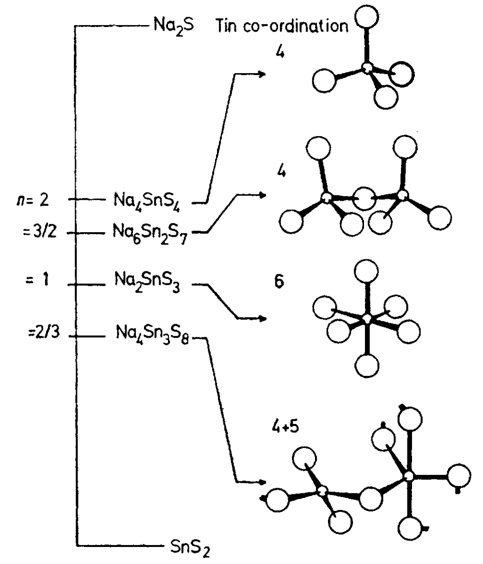

Figure 1 Different types of tin co-ordination in the system Na_2S-SnS_2 (*n* is the stoicheiometric ratio, Na_2S/SnS_2)

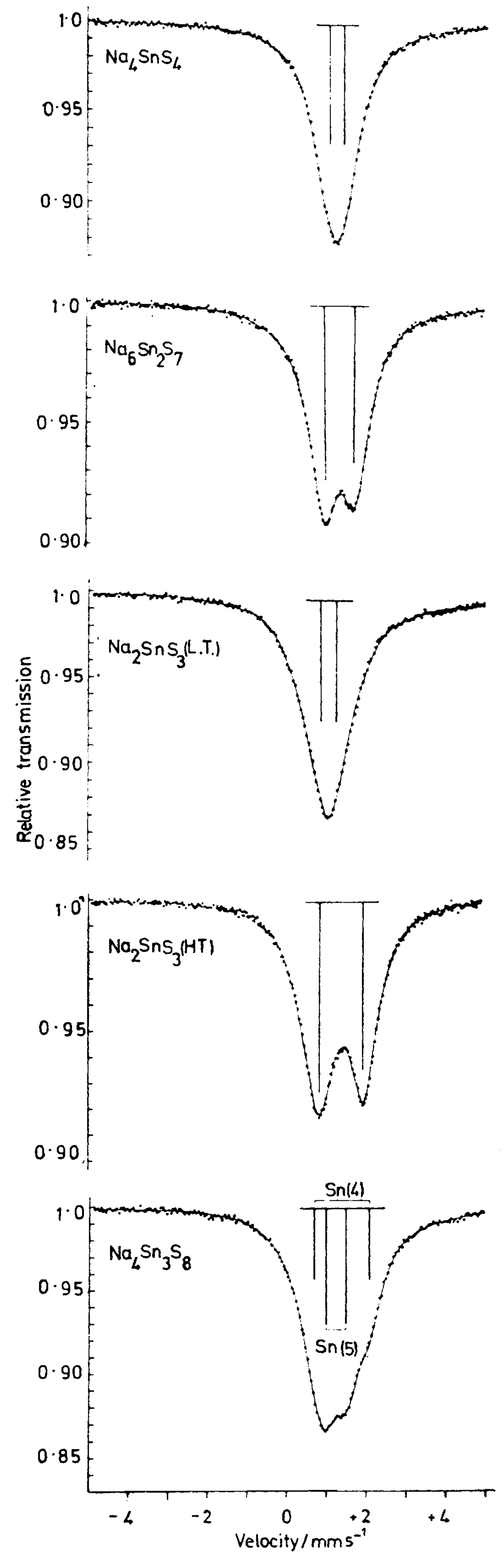

Figure 2 Mössbauer spectra at 77 K for compounds in the system Na_2S-SnS_2

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[20] J. Rivet, *Ann. Chim.*, 1965, **10**, 243.

for four-co-ordinate tin in the thiostannates already discussed. For the five-co-ordinate tin the observed value of 1.19 mm s^{-1} is intermediate between the values for four-co-ordinate and six-co-ordinate tin. An interesting feature of these results is the small quadrupole splitting of the five-co-ordinate tin atoms.

TABLE 2

Mössbauer data at 77 K for compounds in the systems BaS–SnS$_2$ and PbS–SnS$_2$

Compound	Co-ordination number	Chemical isomer shift [a] δ/mm s^{-1}	Quadrupole splitting [b] Δ/mm s^{-1}	Widths at half-height [b] Γ/mm s^{-1}	Chi-squared/(degrees of freedom)
Ba_2SnS_4(LT)	4	1.27	0.46 [c]	1.20, 1.20 [d]	272/(189)
Ba_2SnS_4(HT)	4	1.19	0.58 [c]	1.02, 1.02 [d]	326/(189)
$Ba_3Sn_2S_7$	4	1.29	0.74	1.19, 1.19 [d]	400/(239)
$BaSnS_3$	(4)	1.31	0.73	1.05, 1.05 [d]	222/(188)
	(4)	1.37	1.61	1.05, 1.05 [d]	
$PbSnS_3$	6	1.13	0.45	0.92, 0.92 [d]	231/(188)

[a,b,c,d] See footnotes to Table 1.

The System BaS–SnS$_2$.—The four compounds studied in this system are Ba_2SnS_4(LT), Ba_2SnS_4(HT), $Ba_3Sn_2S_7$, and $BaSnS_3$. Apart from $BaSnS_3$, which is of unknown structure, all these compounds contain tin in highly distorted SnS_4^{4-} tetrahedra. The Sn–S bond length varies from 2.34 to 2.43 Å for the monoclinic Ba_2SnS_4(LT)[14] and from 2.32 to 2.41 Å for the orthorhombic Ba_2SnS_4(HT) which has been shown to contain two types of distorted tetrahedra.[18] $Ba_3Sn_2S_7$ Is similar to $Na_6Sn_2S_7$ in containing discrete $Sn_2S_7^{6-}$ anions. The three Sn–S$_{\text{terminal}}$ bond lengths (2.36 Å on average) are the same as those in $Na_6Sn_2S_7$, whereas the Sn–S$_{\text{bridge}}$ bond length (2.43 Å) is slightly shorter than that in $Na_6Sn_2S_7$.[15]

The Mössbauer data for these compounds are summarized in Table 2. The two modifications of Ba_2SnS_4 both give broadened lines which can only be fitted satisfactorily as unresolved quadrupole doublets. The sample of Ba_2SnS_4 studied by Ichiba *et al.*,[19] which was prepared by dehydration of the hydrated material, has a chemical isomer shift which is very similar to that reported here for Ba_2SnS_4(LT), and probably corresponds to this modification. $Ba_3Sn_2S_7$ Gives a resolved quadrupole doublet and, apart from the slightly reduced value for the splitting, the data are similar to those for $Na_6Sn_2S_7$. The average chemical isomer shift for four-co-ordinate tin in these three compounds is 1.25 mm s^{-1}, compared with the value of 1.27 mm s^{-1} in the sodium thiostannates.

The spectrum for $BaSnS_3$ (Figure 3) consists of two relatively broad overlapping lines, with the low-velocity peak being more intense and narrower than its counterpart at higher velocity. If the spectrum is fitted as a doublet the resulting chemical isomer shift (1.31 mm s^{-1}) is in reasonable agreement with that found by Ichiba *et. al.*,[19] but the value for the quadrupole splitting (1.19 mm s^{-1}) is much greater than their value of 0.75 mm s^{-1}, possibly indicating that the material made by dehydrating the hydrate is structurally different from the compound which we have studied. However, the chi-squared value for the simple two-peak fit is unacceptably high (624 on 191 degrees of freedom), and the solid line through the data in Figure 3 is the result of fitting four lines of equal width. The chi-squared value for this fit is excellent (222 on 188 degrees of freedom) and the intensities are in the ratio 1.21 : 1.12 : 1.00 : 1.20. The data are therefore more consistent with the presence of two tin sites in $BaSnS_3$, and their chemical isomer shifts (1.31 and 1.37 mm s^{-1}) are indicative of tetrahedral co-ordination. The line-assignment 1,4 : 2,3 (see Figure 3) is preferred to the two other possibilities because these give chemical isomer shifts which fall well beyond the range of values observed for the other compounds in this study.

The System PbS–SnS$_2$.—The only compound isolated in this system, $PbSnS_3$, resembles the binary sulphide Sn_2S_3 in having the NH_4CdCl_3 structure.[13] This structure comprises bands of SnS_6 octahedra in which pairs of octahedra share edges. The octahedra are highly distorted and the Sn–S distances range from 2.47 to 2.60 Å. The Mössbauer data for this compound are listed in Table 2. The spectrum consists of an unresolved quadrupole doublet with a chemical isomer shift of 1.13 mm s^{-1}. This value confirms that the compound should be formulated as Pb$^{\text{II}}$Sn$^{\text{IV}}$S$_3$ (rather than as Pb$^{\text{IV}}$Sn$^{\text{II}}$S$_3$) as was expected from its mode of formation and the general chemistry of the elements.

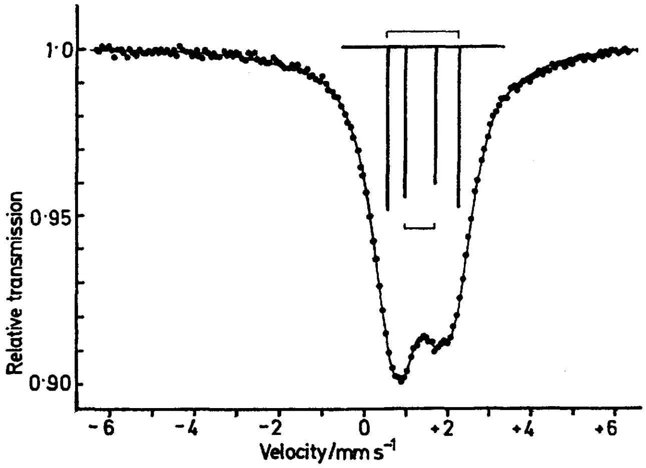

FIGURE 3 Mössbauer spectrum at 77 K for $BaSnS_3$, showing a possible four-peak fit

The only compound in this study with a more negative shift is the low-temperature modification of Na_2SnS_3, which also features octahedrally co-ordinated tin. This result therefore strengthens further the tentative correlation between the ^{119}Sn chemical isomer shift and tin co-ordination number in sulphide phases: δ (six-co-ordinate Sn) 1.02—1.13 mm s^{-1}; δ (five-co-ordinate Sn) 1.19 mm s^{-1}; δ (four-co-ordinate Sn) 1.19—1.35 mm s^{-1}. The trend is similar to that found in other tin systems, such as the halides where, for example, the shifts for SnX_6^{2-} are 0.2—0.3 mm s^{-1} less than those for the corresponding SnX_4 species, and intermediate values are found for the SnX_5^- anions.[1,21] In each case the results imply that the *s*-electron density at the tin nucleus increases with decreasing co-ordination number, and this is probably best interpreted in terms of a decrease in the occupation of tin 5*d* orbitals as the basis set for bonding changes from sp^3d^2, through sp^3d, to sp^3.

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[21] K. M. Harmon, L. L. Hessel, L. P. Kleman, C. W. Kolher, S. V. McKinley, and A. E. Young, *Inorg. Chem.*, 1969, **8**, 1054.