Tin-119 Mössbauer Spectra of Organotin Oxines in Applied Magnetic Fields

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Signs of the ^{119}Sn quadrupole coupling constants and magnitudes of the asymmetry parameters for several mono-, di-, and tri-organotin oxines and two organotin Schiff base complexes have been determined from magnetically perturbed Mössbauer spectra. These results are used to deduce the probable structures of the compounds. Two of the triphenyltin derivatives are shown to be examples of less common structural types.

THE ability of organotin moieties to react with potentially chelating ligands to form stable complexes with high co-ordinations is well established. The 8-hydroxyquinoline (Hox) derivatives are classical examples,[1-4] with five-, six-, and seven-co-ordinate organotin oxines being reported. Although most of the conventional techniques, namely Mössbauer,[1,5] i.r.,[1,2] absorption,[6] and n.m.r.[2,7] spectroscopies, have been employed as aids in structural investigations, the geometry of certain of these oxines is still in doubt. The present work examines several organotin oxines and some related compounds formed by the potentially terdentate Schiff base *N*-(2-hydroxyphenyl)salicylaldimine [Hsal-*N*-(2-HOC$_6$H$_4$)] (I), by use of magnetically perturbed ^{119}Sn Mössbauer spectra. It was hoped that this technique, from which one can deduce the sign of the quadrupole coupling constant, e^2qQ, and magnitude of the asymmetry parameter, η, would provide useful information on the structures of these complexes.

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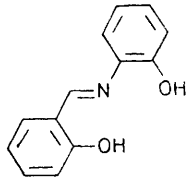
In the usual ^{119}Sn Mössbauer studies the spectrum consists of a simple doublet with lines of equal intensity. When the sample is subjected to a large magnetic field, the degeneracy of the m_I sub-levels is removed and a six-line pattern observed. More detailed treatments[8-10] have shown that the signs of e^2qQ and V_{zz} (the principal component of the electric field gradient; e.f.g.) are opposite, and that for a positive e^2qQ the four σ transitions appear at lower energy than the two π transitions. We have computed spectra for selected e^2qQ and η (the asymmetry parameter) in magnetic fields perpendicular and parallel to the γ-ray axis, and these agree with those reported by Gibb.[10]



(I)

RESULTS AND DISCUSSION

Three types of compound have been investigated, containing one, two, or three organic groups bonded to the central tin atom. Within each type examples with different co-ordinations and geometry are to be found. All the Mössbauer data are given in the Table, while some representative spectra are shown in Figure 1, together with the corresponding computed spectra. With one exception the sign of e^2qQ could be determined unambiguously by a visual inspection.

Complexes with One Tin–Carbon Bond.—Earlier it was suggested that $BuSnCl(ox)_2$ and $PhSnCl(ox)_2$ are six-co-ordinate. The quadrupole interaction of the monobutyl adduct is certainly similar to those observed[11] for the 2,2′-bipyridyl and phenanthroline complexes of $BuSnCl_3$. The small isomer shift is also consistent with a six-co-ordinate structure, while the stronger electron-withdrawing power of the oxygen than of chlorine appears to remove primarily more '*s*'-electron density from the tin atom. This may be shown since the quadrupole interactions of $BuSnCl_3$(2,2′-bipyridyl) and $BuSnCl(ox)_2$ are identical while the isomer shift (δ) of the latter is smaller. Since δ is proportional to the effective *s*-electron density at the tin nucleus, the lower δ corresponds to a reduction in the effective *s*-electron density. The somewhat smaller $|\Delta E_Q|$ and δ values observed for the phenyl derivative are not unexpected, and similar differences between corresponding alkyl- and aryl-tin compounds have been reported in a number of cases.[12]

In applied longitudinal magnetic fields of 40—50 kG (1 G = 10^{-4}T), both $RSnCl(ox)_2$ derivatives are found to have positive quadrupole coupling constants and moderate asymmetry parameters [η = *ca.* 0·5—0·6, see Figure 1(a)]. The positive e^2qQ indicates an excess of electron density at the tin nucleus along the z-axis (Sn–R bond direction) as expected. If, as in the usual additive field gradient model,[13,14] we treat these compounds as $RSnXY_4$ systems [$Y = \frac{1}{2}$(ox)] then there are two possible structures corresponding to either *cis*- or *trans*-R and -X groups. A simple point-charge calculation[8,14] predicts $e^2qQ > 0$ for both structures, but $\eta \neq 0$ only for the *cis*-RSnX arrangement. The experimental results therefore seem more compatible with a *cis*-octahedral structure for these derivatives, since it is unlikely that distortions of the bond angles in a *trans*-$RSnXY_4$ structure would produce η values as large as those observed.

The other mono-organotin complex studied here is $BuSn(ox)_3$ [Figure 1(b)]. On the basis of i.r. data, which indicate that all three oxines are equivalent and appear to have the same bonding as in $Me_2Sn(ox)_2$, it has been suggested[1,3] that in this compound the tin atom is seven-co-ordinate. The decrease in isomer shift from $BuSnCl(ox)_2$ to $BuSn(ox)_3$ is consistent with an increase in *d*-electron screening which would be expected to accompany an increase in the co-ordination number at tin.

It is interesting to consider the ΔE_Q and η values expected for a seven-co-ordinate tin species. To do this we have made approximate point-charge calculations, choosing a partial quadrupole splitting (p.q.s.) value for the butyl group of [Bu] = $-1{\cdot}0$ mm s^{-1} as suggested by Clark *et al.*[13] for an alkyl group in octahedral co-ordination. We have also assumed that the p.q.s. value for $\frac{1}{2}$(ox) lies in the range $0{\cdot}0 \pm 0{\cdot}1$ mm s^{-1}, consistent with values tabulated[14] for similar ligands (*e.g.*, $\frac{1}{2}$[2,2′-bipyridyl] = $-0{\cdot}08$ mm s^{-1} and $\frac{1}{2}$[picolinate] = $+0{\cdot}06$ mm s^{-1}). There are two well-established geometries for seven-co-ordination.[15] An *X*-ray crystallographic study of $MeSn(NO_3)_3$ has shown that this molecule has a distorted pentagonal bipyramidal structure.[16] The diagonal elements of the e.f.g. tensor for a pentagonal bipyramidal $RSnX_6$ species with R and one X in apical positions are given by equations

$$V_{xx} = 2{\cdot}60[X]^{PBE} - [X]^{PBA} - [R]^{PBA} \qquad (1)$$

$$V_{yy} = 2{\cdot}40[X]^{PBE} - [X]^{PBA} - [R]^{PBA} \qquad (2)$$

$$V_{zz} = 2[R]^{PBA} + 2[X]^{PBA} - 5[X]^{PBE} \qquad (3)$$

(1)—(3) where PBA and PBE specify apical and equatorial ligands, respectively, in the pentagonal bipyramid.

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From these expressions and the above p.q.s. values for (Bu) and $\frac{1}{2}$(ox) (with the assumption that $[ox]^{PBE} = [ox]^{PBA}$), we find that ΔE_Q for BuSn(ox)$_3$ based on this structure is predicted to be in the range $+2{\cdot}0 \pm 0{\cdot}3$ mm s^{-1} with η in the range 0·00—0·01. Of course distortions from ideal geometry would be expected to render η somewhat larger.

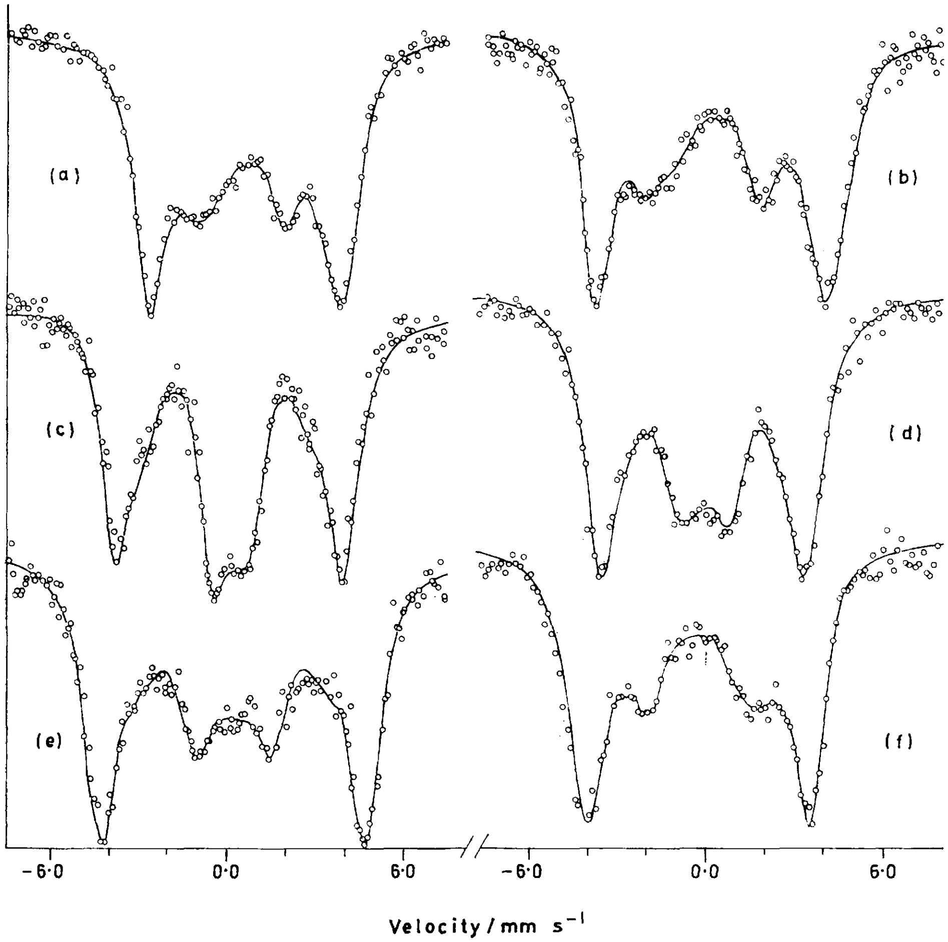

FIGURE 1 Representative ^{119}Sn Mössbauer spectra in longitudinal applied magnetic fields at 4·2 K. The solid lines are theoretically computed spectra. (a) BnSnCl(ox)$_2$: $H_{app} = 50$ kG, $\Delta E_Q = +1{\cdot}67$ mm s^{-1}, $\eta = 0{\cdot}5$; (b) BuSn(ox)$_3$: $H_{app} = 50$ kG, $\Delta E_Q = +1{\cdot}82$ mm s^{-1}, $\eta = 0{\cdot}2$; (c) Me$_2$SnCl(ox): $H_{app} = 40$ kG, $\Delta E_Q = -3{\cdot}12$ mm s^{-1}, $\eta = 0{\cdot}7$; (d) Ph$_2$SnCl(ox): $H_{app} = 40$ kG, $\Delta E_Q = +2{\cdot}40$ mm s^{-1}, $\eta = 0{\cdot}8$; (e) Ph$_3$Sn(sal-*N*-2-HOC$_6$H$_4$): $H_{app} = 50$ kG, $\Delta E_Q = -2{\cdot}88$ mm s^{-1}, $\eta = 0{\cdot}9$; (f) Ph$_3$Sn(ox): $H_{app} = 50$ kG, $\Delta E_Q = -1{\cdot}75$ mm s^{-1}, $\eta = 0{\cdot}7$

The other seven-co-ordinate structure is of the TaF$_7^{2-}$ type, derived from a trigonal prism by the addition of a seventh ligand along the normal to one face.[15] In this case we have taken R to occupy the unique position. The appropriate bond angles and p.q.s. values were read into a computer programme which then diagonalised the e.f.g. tensor to yield the predicted values $\Delta E_Q = +2{\cdot}0 \pm 0{\cdot}2$ mm s^{-1} and $\eta = 0{\cdot}0$—$0{\cdot}2$. Thus both seven-co-ordinate structures would be expected to give ΔE_Q and η values similar to those observed (Table). We feel this lends further support to the assignment of such a structure to BuSn(ox)$_3$, but on the other hand it is clear that Mössbauer spectroscopy is unlikely to be capable of distinguishing between different seven-co-ordinate geometries.

Complexes with Two Tin–Carbon Bonds.—The diorganotin complexes 4—6 (Table) have been assigned five-co-ordinate structures in previous studies.[1,17] The lack of definitive crystallographic work in this area of organotin chemistry is a severe handicap. The sole structure known is that of the Me$_2$SnCl$_3^-$ anion [18] where the methyl groups occupy equatorial positions of a trigonal bipyramid, and it seems likely that most five-co-ordinate diorganotin compounds will possess this basic geometry.

As for Me$_2$SnBr$_3^-$,[19] positive e^2qQ and large η values are observed for Me$_2$SnCl$_3^-$, Me$_2$Sn(sal-*N*-2-OC$_6$H$_4$), and Ph$_2$SnCl(ox). However, for Me$_2$SnCl(ox) e^2qQ is negative [see Figure 1(c), (d)]. This is reminiscent of the

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[18] F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc.* (*A*), 1968, 3019.

[19] R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 1906.

situation with the *cis*-octahedral [20] compound $Me_2Sn(ox)_2$, where the observed [19] positive coupling constant is opposite in sign to that expected on the basis of point-charge calculations. This was rationalised in terms of variations in the C–Sn–C bond angle by Parish and Johnson,[19] who showed that a negative e^2qQ should only be observed if ∠C–Sn–C lay between the tetrahedral angle and its supplement. The large asymmetry parameters for compounds 4—7 suggest that the structures of these derivatives are such that fairly small variations in ∠C–Sn–C would be sufficient to cause a reversal in the sign of e^2qQ. However, in view of the fact that ∠C–Sn–C is *ca.* 140° in $Me_2SnCl_3^-$ [18] it seemed unlikely that this angle would be less than 109·5° in $Me_2SnCl(ox)$. In their calculations Parish and Johnson[19] considered only the R_2Sn fragment, but the nature of the remaining groups in the compound would be expected to exert some influence on the precise value of ∠C–Sn–C at which the z-axis of the e.f.g. tensor flips direction.

^{119}Sn Mössbauer data

Compound [a]	δ/ mm s^{-1} [b]	ΔE_Q/ mm s^{-1} [c]	η
1. $BuSnCl(ox)_2$	0·85	+1·67	0·5
2. $PhSnCl(ox)_2$	0·64	+1·48	0·6
3. $BuSn(ox)_3$	0·70	+1·82	0·2
4. $Me_2SnCl(ox)$	1·22	−3·12	0·7
5. $Ph_2SnCl(ox)$	1·07	+2·40	0·8
6. $Me_2Sn(sal\text{-}N\text{-}2\text{-}OC_6H_4)$	1·13	+3·04	0·7
7. $(Et_4N)^+(Me_2SnCl_3)^-$	1·44	+3·76	0·6
8. $Me_3SnOCOMe$	1·30	−3·68	0·0
9. $Ph_3Sn(sal\text{-}N\text{-}2\text{-}HOC_6H_4)$	1·21	−2·88	0·9
10. $Ph_3Sn(ox)$	1·04	−1·75	0·7

[a] Hox = 8-Hydroxyquinoline; $Hsal\text{-}N\text{-}2\text{-}HOC_6H_4$ = N-(2-hydroxyphenyl)salicylaldimine. [b] Isomer shift relative to $BaSnO_3$. [c] The sign given is that of the quadrupole coupling constant e^2qQ.

To show that this is indeed the case, we have performed a simple point-charge treatment on $Me_2SnCl_3^-$. It has been pointed out [13,14] that in trigonal bipyramidal co-ordination, different p.q.s. values should be used for a given ligand X depending upon whether the ligand occupies an apical ($[X]^{TBA}$) or equatorial ($[X]^{TBE}$) position. To obtain the necessary p.q.s. values we have chosen the $Me_3SnCl_2^-$ anion as a model compound. Both Mössbauer [19,21] and far i.r.[22] data are consistent with a trigonal bipyramidal structure with axial chlorines and a planar Me_3Sn moiety. We follow the method of Clark *et al.*[13] for tetrahedral and octahedral complexes of tin, and arbitrarily assign $[Cl]^{TBA} = 0{\cdot}0$ mm s^{-1}. From the reported quadrupole splitting in $Me_3SnCl_2^-$ ($\Delta E_Q = -3{\cdot}31$ mm s^{-1}, $\eta = 0$) [19] we then obtain $[Me]^{TBE} = -1{\cdot}10$ mm s^{-1}. From these two p.q.s. values ΔE_Q and η for $Me_2SnCl_3^-$ were calculated for a range of $[Cl]^{TBE}$ values from the known crystallographic bond angles.[18] Satisfactory agreement with the data in the Table was obtained for $[Cl]^{TBE} = ca.\ -0{\cdot}30$ mm s^{-1}. We have then calculated ΔE_Q and η for $Me_2SnCl_3^-$ as a function of C–Sn–C angle, all other angles about tin being constrained to their strict trigonal bipyramidal values.

The results are shown in Figure 2, from which one sees that a sign reversal in e^2qQ is predicted for ∠C–Sn–C of *ca.* 120—125°, well above the tetrahedral angle. It can also be seen from Figure 2 that an increase in the effective electronegativity of the axial substituents (*i.e.*, a more positive $[X]^{TBA}$) also leads to an increase in ∠C–Sn–C for which the sign change occurs. Thus it appears that the negative e^2qQ found for $Me_2SnCl(ox)$ most probably results from a somewhat smaller ∠C–Sn–C than those in the other diorganotin compounds studied here rather than from a different basic structure, but it is still possible that this angle is greater than 120°.

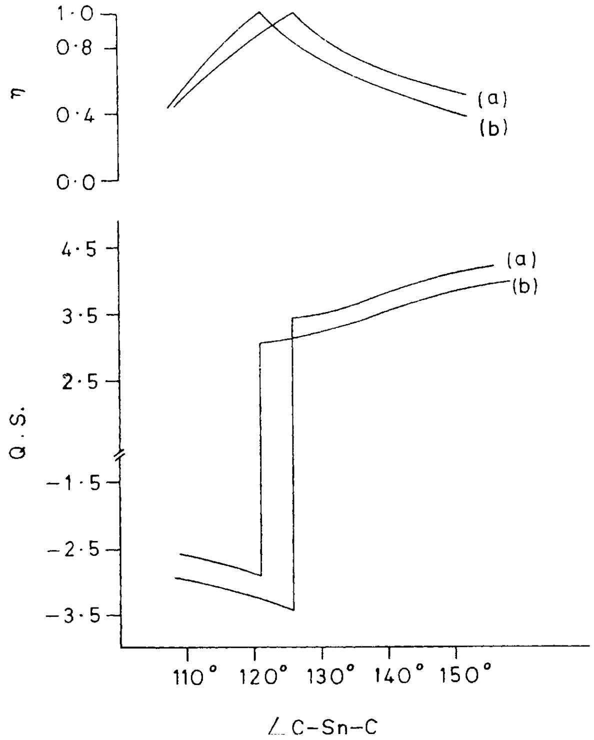

FIGURE 2 Variations in quadrupole splitting (Q.S.) and asymmetry parameter (η), for a trigonal bipyramidal R_2SnX_2Y species as a function of C–Sn–C bond angle: (a) $R = -1{\cdot}1$, $X = 0{\cdot}0$, $Y = -0{\cdot}3$; (b) $R = -1{\cdot}1$, $X = +0{\cdot}1$, $Y = -0{\cdot}3$

Complexes with Three Tin–Carbon Bonds.—A number of triorganotin compounds have already been studied *via* magnetic perturbation Mössbauer spectroscopy,[19,23,24] all of which have large negative quadrupole splittings and small or zero asymmetry parameters. Typical of this type of compound is $Me_3SnOCOMe$ (Table). A recent X-ray study has shown this compound to be polymeric with bridging bidentate acetate groups.[25] The C_3Sn fragment is essentially planar and the O–Sn–O

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bond angle is 172°, so that there are only small departures from ideal trigonal bipyramidal geometry. The negative e^2qQ and zero η are just as expected for such a structure.

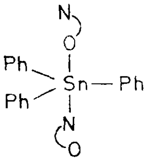
$Ph_3Sn(sal\text{-}N\text{-}2\text{-}HOC_6H_4)$ represents a more interesting case. The quadrupole splitting of $-2{\cdot}88$ mm s^{-1} is fully consistent with the usual trigonal bipyramidal co-ordination, and the magnitude compares well with those of Ph_3SnCl(pyridine) ($|\Delta E_Q| = 3{\cdot}15$ mm s^{-1})[26] and $Ph_3Sn(OC_6H_3Cl_2)$(pyridine) ($|\Delta E_Q| = 2{\cdot}90$ mm s^{-1}).[27] However the asymmetry parameter close to unity [see Figure 1(e)] is unexpected, and indeed rules out such a structure. Similarly, a tetrahedral structure with the Schiff base ligand being unidentate can be eliminated since here too η should be close to zero. Since this ligand appears to have a strong tendency to be terdentate,[17] it seemed likely that it might adopt a *mer*-octahedral configuration.* For a *mer*-R_3SnX_3 structure the e.f.g. tensor elements are[8,14] given by equations (4) and (5). The p.q.s. value for a phenyl

$$V_{zz} = -V_{yy} = 3[R] - 3[X] \qquad (4)$$

$$V_{xx} = 0 \qquad (5)$$

group in octahedral co-ordination suggested by Clark *et al.*[13] is $[Ph] = -0{\cdot}95$ mm s^{-1}. If we make the reasonable assumption that $\frac{1}{3}[sal\text{-}N\text{-}2\text{-}HOC_6H_4] = 0{\cdot}0 \pm 0{\cdot}1$ mm s^{-1}, *i.e.*, that the Schiff base ligand is similar to oxine, then one predicts $\Delta E_Q = \pm 3{\cdot}28 \pm 0{\cdot}35$ mm s^{-1} and $\eta = 1$. Although both $|\Delta E_Q|$ and η are somewhat larger than the observed values, it should be pointed out that any distortions from regular geometry will serve to reduce the magnitudes of both quantities. Note that the sign of the e.f.g. is not predicted by a point-charge calculation and will depend upon fine details of the electronic structure of the complex and the precise values of the bond angles at tin. However, it seems very likely that $Ph_3Sn(sal\text{-}N\text{-}2\text{-}HOC_6H_4)$ does indeed have a *mer*-octahedral configuration. This is the first time that Mössbauer studies have indicated this geometry, although similar structures have been suggested[28] for some $MeSnCl_3$ and Me_3SnCl adducts with *NN'*-ethylenebis(2-hydroxyacetophenoneimine) on the basis of complex i.r. spectra.

There has been some disagreement concerning the structure of $Ph_3Sn(ox)$, both four-[29] and five-co-ordinate[26] structures having been assigned from the magnitude of the quadrupole splitting. There are four possible structures for $Ph_3Sn(ox)$, if we ignore permutations of O and N, as shown in structures (II)—(V). The magnitude of ΔE_Q eliminates (II) and (V), since much larger splittings are expected for these cases ($|\Delta E_Q| > 2{\cdot}6$ mm s^{-1}).[21,24] Both (III) and (IV) are expected to have a negative e^2qQ as observed [Table and Figure 1(f)], but the large asymmetry parameter is inconsistent with the tetrahedral structure (III) for which η should be nearly zero. Thus we conclude that $Ph_3Sn(ox)$ is five-co-ordinate with a chelating oxine group, and has a structure based on (IV).[26] Triphenyltin *N*-benzoyl-*N*-phenylhydroxamate has recently been shown[30] to have this geometry, and has a quadrupole splitting $|\Delta E_Q| = 1{\cdot}94$ mm s^{-1}.[31]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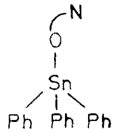
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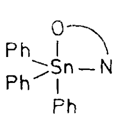
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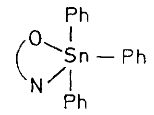
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EXPERIMENTAL

The compounds were prepared by reported methods: $RSnCl(ox)_2$,[1,2] $R_2Sn(Cl)(ox)$,[1,2] $Me_2Sn(sal\text{-}N\text{-}2OC_6H_4)$,[32] $Ph_3Sn(Hsal\text{-}N\text{-}2\text{-}HOC_6H_4)$,[32] and $Ph_3Sn(ox)$.[1] The Mössbauer spectra were determined from carefully ground samples to eliminate packing of the crystallites, which would lead to anomalous magnetically perturbed spectra. The source (10 mCi $BaSnO_3$) and absorbers were cooled to 4·2 K. The samples were located at the centre of the field of a Westinghouse superconducting solenoid mounted in a Janis Dewar vessel. The field axis was parallel to the γ-ray axis. The source was mounted on the end of a long stainless steel drive rod, and vibrated by an Austin Science Associates model K3 linear motor. The drive unit was mounted vertically in an evacuated chamber located at the top of the cryostat. By having a common vacuum space the need for a bellows connection to the Dewar vessel was eliminated. The linearity of the velocity scale was checked by use of an iron foil. Care was taken to ensure that the source was outside the fringing field of the magnet, and fields of 40—50 kG were applied to the samples. Theoretical spectra were computed from a programme supplied by G. Lang[33] which allowed the applied field, linewidth, and asymmetry parameter to be varied independently for any e^2qQ. Determination of the best fit between theoretical and observed spectra was by visual inspection. For the parallel fields used in these experiments, the error in the asymmetry parameter η for the range $0 < \eta < 0{\cdot}6$ is quite large; *ca.* $\pm 0{\cdot}2$ due to the small changes in the simulated spectra. For $\eta > 0{\cdot}6$, the error is $\pm 0{\cdot}1$.

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* A *fac*-octahedral structure can be ruled out since in this case ΔE_Q should be approximately zero.[8,14]

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