

Studies in Mössbauer Spectroscopy. Part IV.^{1,2} Signs of the Quadrupole Coupling Constants for Some Organotin(IV) Compounds

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Mössbauer spectra of some four-, five-, and six-co-ordinate organotin(IV) compounds, covering seven different structural types, have been measured in an applied magnetic field. From the signs of the quadrupole coupling constants, it is shown that the electric field gradient at the tin nucleus arises primarily from differences in the electron densities of the tin–ligand bonds (*i.e.* $|q_{val}| > |q_{lat}|$). The relative signs of the coupling constants agree with those predicted for regular structures by the point-charge model, except for the *cis*-R₂SnX₄ complexes. The apparently anomalous sign for the latter is probably due to deviations from strict octahedral geometry. It is deduced that the field gradient is largely determined by the disposition of the tin–carbon bonds.

QUADRUPOLE splitting in a Mössbauer spectrum indicates the presence at the Mössbauer nucleus of an electric field gradient which will be made up of contributions from (i) the electrons of the bonds between the Mössbauer atom and its ligands, (ii) charges on the ligands, and (iii) charges on the surrounding ions and molecules of the lattice. Contributions (ii) and (iii) are normally considered together as the lattice contribution, q_{lat} . The contribution to q_{lat} from atoms other than those in the first co-ordination sphere will generally be very small, owing to the inverse cubic dependence of the electric field gradient on the distance from the Mössbauer nucleus. Similarly, contribution (i) is termed the valence contribution, q_{val} , since electron density close to the Mössbauer nucleus (*i.e.* the valence shell) will be more effective than that close to the ligands.

In the interpretation of pure quadrupole resonance spectra it is usually assumed, on the basis of the inverse cube effect, that q_{val} is more important than q_{lat} .³ However, this is by no means certain because of the shielding and anti-shielding effects produced by the

polarisation of the inner electrons.⁴ The total electric field gradient ($-V_{zz}$) at the nucleus is given by:

$$V_{zz} = eq_{total} = e(1 - \gamma_{\infty})q_{lat} + e(1 - R)q_{val}$$

The (anti-)shielding factors γ_{∞} and R may differ greatly in value; in particular, γ_{∞} may assume large negative values, thus offsetting considerably the effect of the greater distance from the nucleus. Calculated estimates are $-7 > \gamma_{\infty} > -100$ and $0.2 > R > -0.2$.⁵ Since discussions of chemical bonding have been based on the assumption of the predominance of q_{val} ,⁶ it is essential that this be confirmed.

When the valence contribution is due to inequalities in the σ -bond framework, q_{val} will differ in sign from q_{lat} .⁷ Since the shielding factors $(1 - \gamma_{\infty})$ and $(1 - R)$ are both positive, a determination of the sign of the quadrupole coupling constant (e^2qQ), and hence that of q_{total} , will indicate which contribution is the greater. The sign of e^2qQ is not available from the normal Mössbauer spectrum of a randomly oriented powdered sample unless at least one of the nuclear states involved has a spin greater than 3/2. For the common case

¹ Preliminary communication, R. V. Parish and C. E. Johnson, *Chem. Phys. Letters*, 1970, **6**, 239.

² Part III, R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 589.

³ C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1952, **20**, 35; 1949, **17**, 782.

⁴ R. Sternheimer, *Phys. Rev.*, 1956, **102**, 73, and references therein.

⁵ R. E. Watson and A. J. Freeman in 'Hyperfine Interactions,' eds. A. J. Freeman and R. B. Frankel, Academic Press, London and New York, 1967, p. 71.

⁶ *E.g.*, M. Kubo and D. Nakamura, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 257.

⁷ Part II, R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65.

in which the spins of the ground and excited states are $1/2$ and $3/2$ (e.g. ^{57}Fe , ^{119}Sn , ^{197}Au), the spectrum consists of a simple doublet and the sign of e^2qQ can only be obtained by the application of a large magnetic field. This method has been applied widely to compounds containing ^{57}Fe , and is discussed in detail by Collins and Travis;⁸ the case of ^{119}Sn has been treated recently by Gibb.⁹

We have applied this technique to the determination of the sign of the electric field gradient in a range of organotin(IV) compounds, which has enabled confirmation of the predominance of q_{val} and also provides an opportunity to test the point-charge model, which is widely used to correlate quadrupole splitting with molecular structure.^{7,10,11} During the course of our work similar spectra for dimethyltin dichloride and molybdate¹² were reported but were interpreted incorrectly, the signs of eQ and of the m_I -substates being given wrongly. Subsequently the first of the errors was acknowledged,¹³ and communications giving correct treatments have appeared.^{1,14}

Magnetic Perturbation.—The energy levels for a ^{119}Sn nucleus in combined electric and magnetic fields are shown in Figure 1. The positions of the levels are functions of the magnetic moments, μ_g and μ_{ex} , of the ground and excited states, the quadrupole moment, eQ , of the excited state, the degree of mixing between levels of different m_I , and the orientation of the electric axis with respect to the magnetic field. The value of μ_g has been found by n.m.r. spectroscopy to be -1.0411 nuclear magnetons.¹⁵ The excited state can be examined only by the Mossbauer method, and a range of values has been reported for μ_{ex} ,¹⁶⁻²² the average value being $+0.73$ nuclear magnetons. These values differ both in magnitude and sign from those for ^{57}Fe . The quadrupole moment of the excited state has been determined as -0.08 b;²³ the signs of e^2qQ and V_{zz} are therefore opposite.

The averaging over the relative orientations of the electric and magnetic axes results in the σ -transitions appearing as a moderately well-resolved quartet and the π -transitions as a broadened doublet, both features having similar overall widths. The σ -transitions appear at lower energy than the π -transitions for e^2qQ positive (V_{zz} negative). The effect of mixing of the sublevels is to reduce the resolution of the quartet for large

quadrupole splittings. We have computed spectra for a range of values of e^2qQ and the magnetic field, which agree well in most cases with those of Gibb.⁹

RESULTS AND DISCUSSION

We have examined the spectra of powdered samples of a number of four-, five-, and six-co-ordinate organotin(IV) derivatives, covering seven different structure

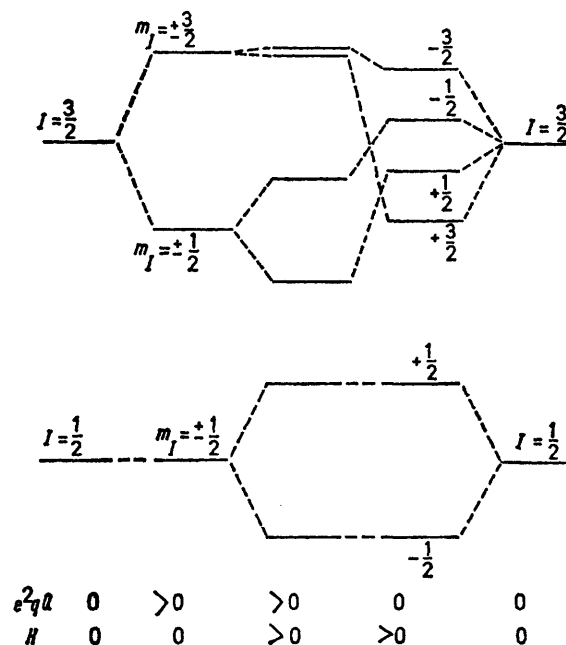


FIGURE 1 Energy levels for the ^{119}Sn nucleus in combined magnetic and electric fields for θ ca. 90°

types and stoichiometries, by use of an applied transverse magnetic field of 30 kOe. Representative spectra are shown in Figure 2, together with the computed spectra for random powders. Spectra for some of the other compounds are shown in ref. 1. Except for compounds with unresolved quadrupole splitting, the sign of e^2qQ is unambiguous, although it was necessary to powder the samples carefully to avoid preferential orientation which may lead to the appearance of additional absorption peaks. All the results are collected in Table 1. The data agree well with those reported

⁸ R. L. Collins and J. C. Travis in 'Mossbauer Effect Methodology', vol. 3, ed. E. I. Gruverman, Plenum Press, New York, p. 123.

⁹ T. C. Gibb, *J. Chem. Soc. (A)*, 1970, 2503.

¹⁰ B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc. (A)*, 1969, 143.

¹¹ R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, 1969, **51**, 3220.

¹² B. A. Goodman and N. N. Greenwood, *Chem. Comm.*, 1969, 1105.

¹³ T. C. Gibb, B. A. Goodman, and N. N. Greenwood, *Chem. Comm.*, 1970, 774.

¹⁴ N. E. Erickson, *Chem. Comm.*, 1970, 1349.

¹⁵ W. G. Proctor, *Phys. Rev.*, 1950, **79**, 35.

¹⁶ S. S. Hanna, L. Meyer-Schützmeister, R. S. Preston, and D. H. Vincent, *Phys. Rev.*, 1960, **120**, 2211.

¹⁷ O. C. Kistner, A. W. Sunyar, and J. B. Swan, *Phys. Rev.*, 1961, **123**, 179.

¹⁸ A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, *Proc. Phys. Soc.*, 1961, **77**, 1062.

¹⁹ V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel, *Soviet Phys. J.E.T.P.*, 1962, **15**, 818.

²⁰ J. Herberle, M. Schulhof, and S. S. Hanna, *Rev. Mod. Phys.*, 1964, **36**, 407.

²¹ V. I. Goldanskii, V. M. Trukhtanov, M. N. Devisheva, and V. F. Belov, *Phys. Letters*, 1965, **15**, 317.

²² D. Bosch, F. Pobell, and P. Keinle, *Phys. Letters*, 1966, **22**, 262.

²³ A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, *Proc. Phys. Soc.*, 1962, **79**, 416.

previously.^{7,24-26} The six-co-ordinate complexes all have positive quadrupole coupling constants, while the opposite sign is found for the four- and five-co-ordinate R_3Sn -derivatives. It has been shown that other *trans*- R_2SnX_4 systems also have positive quadrupole coupling constants [Me_2SnMoO_4 ,¹² Me_2SnF_2 ,¹⁴ $Me_2Sn(acetylacetonate)_2$ ¹⁴].

In order to interpret the signs of the electric field gradients thus obtained, it is necessary to have a means of assessing the effects of variations in structure and stoichiometry. The method usually adopted^{7,10,11} is the point-charge formalism, in which each ligand is regarded as a point charge situated at the centre of the

$SnX_4 : R_3SnX_2 : R_2SnX_4$, $+2 : +4 : -2 : -(3-4) : -2$. These ratios will apply strictly only if the groups R and X are constant along the series and if changes in co-ordination number have no effect (it has been

TABLE 1

Mössbauer parameters (mm/s, at 4.2 K unless otherwise indicated)			
Compound	δ^a	$\Delta = \frac{1}{3}e^2qQ$	Structure
$(Me_4N)_2[EtSnCl_6]$	0.96	+1.94	Octahedral
$Cs_2[Me_2SnCl_4]$	1.47	+4.28	
$K_2[Me_2SnF_4]$ (77 K) ^b	1.38	+4.12	
$Bu_3Sn(O_2CCH_2CHCO_2)_2$ (77 K) ^b	1.38	+3.74	
$Me_2Sn(oxin)_2$ (77 K)	0.81	+2.06	<i>trans</i> -Octahedral
$Ph_2Sn(oxin)_2$ (77 K)	0.88	+2.02	
$Ph_2Sn(oxin)_2$ (77 K)	0.70	+1.67	
$Ph_2Sn(S_2CNEt_2)_2$	0.68	1.69	
$Ph_2Sn(NCS)_2(phen)$	1.10	+1.72	<i>cis</i> -Octahedral
$Me_4N[Me_2SnCl_4]$	0.82	+2.36	
$Me_4N[Ph_2SnCl_4]$	1.27	-3.31	
$Ph_3PCH_2Ph[Et_3SnCl_2]$	1.42	-3.49	
$Me_4N[Ph_2SnCl_4]$	1.23	-3.02	Trigonal bipyramidal
$[Et_3SnCN]_n$	1.40	-3.17	
$Et_3N[Me_2SnBr_3]$	1.46	+3.39 ^c	
$(Bu_3Sn)_2O$	1.18	-1.64	
$Me_2SnC_6F_5$	1.23	-1.39	Tetrahedral
$Ph_2SnC_6F_5$	1.14	-0.97	
$Ph_3SnSnPh_3$	1.37	—	
Ph_3SnMe	1.23	—	
Me_2SnO	0.82	+2.13 ^c	

^a Relative to SnO_2 at room temperature. ^b R. H. Platt, Ph.D. Thesis, UMIST, 1969; sign determined at 4.2 K. ^c η ca. 0.8.

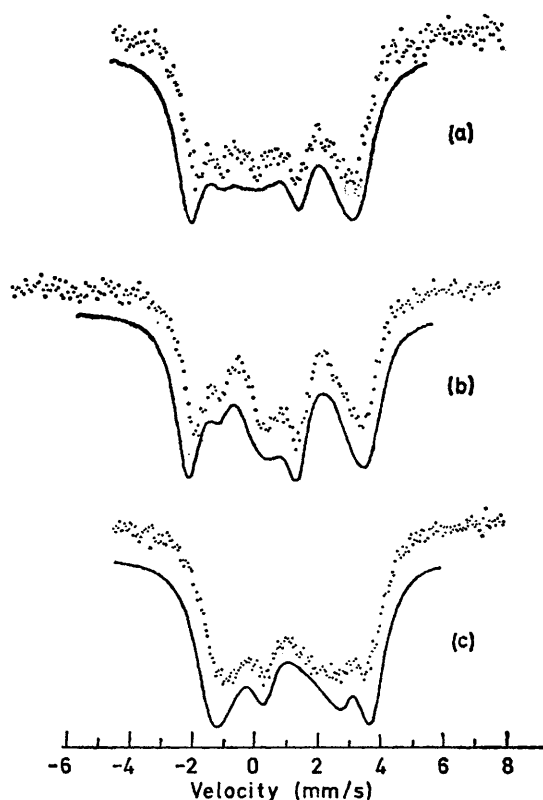


FIGURE 2 Observed and calculated Mössbauer spectra for (a) $Ph_2Sn(oxin)_2$ ($\Gamma = 1.0$ mm/s), (b) $Me_2Sn(oxin)_2$ ($\Gamma = 0.9$ mm/s), and (c) $Me_2SnC_6F_5$ ($\Gamma = 1.0$ mm/s) in transverse magnetic fields of 30 kOe

donor atom. Although this model is very artificial, the same results follow from a simple molecular orbital treatment²⁷ and from detailed symmetry considerations.²⁸ If regular structures are assumed, the relative magnitudes of e^2qQ expected for the species considered here are $RSnX_5 : trans-R_2SnX_4 : cis-R_2-$

suggested that the contribution of a ligand to the quadrupole splitting is dependent on the co-ordination number^{7,29}). However, provided that X is always considerably more electronegative than R, as is usually the case, the relative signs will be as shown.

The observed signs are in excellent agreement with the predictions of the model. The only exceptions are the *cis*-octahedral complexes, which are discussed in detail below. Positive quadrupole coupling constants are found when the organic groups are situated along the principal (z) axis. When the organic groups lie in the xy -plane, e^2qQ is negative. Owing to the negative value of Q , the signs for V_{zz} are the reverse of these. Thus, a structure in which the electronegative groups lie along the z -axis and the organic groups are in the xy -plane, e.g. R_3SnX_2 , has V_{zz} positive. Since quadrupole splitting is correlated with imbalances in the σ -bonding framework,²⁴ q_{val} would be positive (greater electron density in the xy -plane) and q_{lat} negative for such a structure. The results clearly indicate that q_{val} makes the major contribution to q_{total} for all the compounds studied. The recent observation¹³ that V_{zz} is negative for all of a range of stannous compounds is also consistent with our results, i.e. the contribution of the lone pair dominates the electric field gradient. A similar conclusion was reached from the study of some

²⁴ Part I, R. V. Parish and R. H. Platt, *J. Chem. Soc. (A)*, 1969, 2145.

²⁵ M. A. Mullins and C. Curran, *Inorg. Chem.*, 1968, **7**, 2584.

²⁶ B. W. Fitzsimmons, A. A. Owusu, N. J. Seeley, and A. W. Smith, *J. Chem. Soc. (A)*, 1970, 935.

²⁷ G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. (A)*, 1970, 956.

²⁸ M. G. Clark, *Mol. Phys.*, 1971, **20**, 257.

²⁹ A. G. Maddock and R. H. Platt, *J. Chem. Soc. (A)*, 1971, 1191.

iodine compounds³⁰ and, very recently, for a pair of low-spin ferrous complexes.³¹

The *cis* complexes require separate consideration. It is generally assumed, following the point-charge treatment, that the quadrupole coupling constants for *cis*- and *trans*- R_2SnX_4 structures lie in the ratio $-1:2$. The numerical values for a wide range of tin complexes agree well with this prediction.^{7,10,25,26} For the one pair of iron complexes investigated,³¹ the relative signs are also as predicted. The magnitude of the quadrupole splittings of the four complexes $R_2Sn(oxin)_2$ ($R = Me$ or Ph), $Ph_2Sn(S_2CNEt_2)_2$, and $Ph_2Sn(NCS)_2$ -(phen) (where oxin is 8-quinolinolato and phen is 1,10-phenanthroline) are consistent with *cis* configurations, but the signs are the same as those found for typical *trans* complexes. In view of the excellent agreement with the point-charge model found for the other complexes, this apparent anomaly is somewhat disturbing.

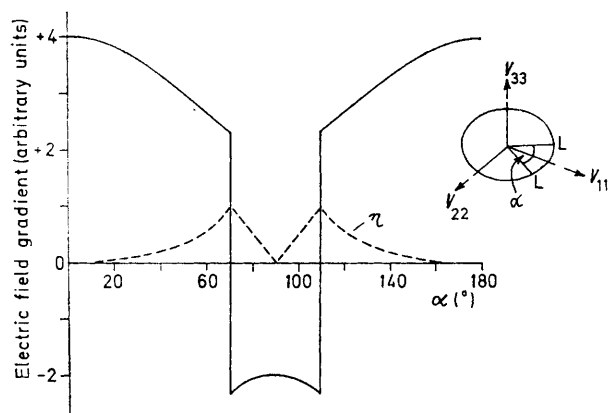


FIGURE 3 Relative magnitude of the electric field gradient for an $L-Sn-L$ system as a function of the bond angle (α). The principal component (V_{zz}) coincides with V_{11} for $0 < \alpha < 70.5^\circ$, with V_{33} for $70.5 < \alpha < 109.5^\circ$, and with V_{22} for $109.5 < \alpha < 180^\circ$.

The origin of the anomaly probably lies in distortion of the structures from the regular octahedral configurations previously assumed. The structure of $Me_2Sn(oxin)_2$ shows considerable distortion.³² In particular, the C-Sn-C bond angle is opened out to 111° and the N-Sn-N angle, which lies in the same plane, is closed to 76° . In the regular (90°) $C_2SnN_2O_2$ configuration, V_{zz} would be taken as lying along the O-Sn-O axis, but the observed distortions would not significantly affect the value of this component. The major component of the electric field gradient must therefore lie in the C_2SnN_2 plane. The contribution of one pair of ligands to the electric field gradient is shown in Figure 3 as a function of the L-Sn-L bond angle. Only for bond angles greater than the tetrahedral angle (109.5°) or less than its supplement does the major component lie in this plane, when the sign of the electric field

gradient is opposite to that for the 90° case. The apparent reversal of sign must therefore be due to the enlarged C-Sn-C bond angle, and V_{22} must be the principal component for the molecule. The magnitude of the electric field gradient is hardly affected by the distortion. It is noticeable, however, that the asymmetry parameter is not large.

Similar distortions presumably occur in the other *cis* complexes. It is noteworthy that all *cis*- R_2SnX_4 complexes reported to date involve at least one chelating ligand and the majority are diphenyltin compounds. By contrast, *trans* complexes are common, suggesting that this is the favoured form and that steric effects may be responsible for the *cis* configuration. Tobias has recently suggested³³ that the most stable configuration for an R_2SnX_4 system is that which maximises the contribution of the tin 5s-orbital in the tin-carbon bonds; this is supported by the isomer shift trends.² The distortion of the C-Sn-C bond angle from 90° in the *cis* complexes would be in keeping with this suggestion. Such effects would not be expected for the iron complexes, which presumably have regular structures.

Other R_2Sn -systems also give positive quadrupole coupling constants. The quadrupole splitting of the salt $Me_4N[Me_2SnBr_3]$ is consistent with the expected trigonal-bipyramidal structure with equatorial methyl groups and a C-Sn-C bond angle rather greater than 120° .⁷ A positive value is also reported for dimethyltin dichloride,¹² for which the relevant angle is 123.5° .³⁴ The spectrum of dimethyltin oxide shows that η is large but not unity. If the tin atom is four-co-ordinate²⁴ some distortion of the tetrahedron is therefore required, which would presumably be³⁵ by the opening of the C-Sn-C bond angle. For a polymeric structure³⁴ this angle would again be greater than 109.5° . Consistently, a positive quadrupole coupling constant is observed.

Insofar as it is reasonable to assign fixed contributions to the electric field gradient to individual ligands, the consistency of these results suggests that the gradient is determined to a large extent by the disposition of the organic groups. A similar conclusion was reached from a recent n.q.r. study of the compounds R_3MX_2 ($R = Me, PhCH_2$, or Ph ; $M = As, Sb$, or Bi ; $X = F, Cl$, or Br).³⁶ The numerical values of the quadrupole coupling constants of the central atoms, M , were found to be much more sensitive to change in R than to change in X , and decreased in the order of increasing electron withdrawal, $R = Me > PhCH_2 > Ph$. Since, as shown above, the electric field gradient arises mainly from the distribution of electrons in the metal-ligand bonds, these results are understandable. The inverse cubic dependence on distance implies that the most covalent

³⁰ M. Pasternak, A. Simopoulos, and Y. Hazony, *Phys. Rev.*, **1965**, **140**, A1892.

³¹ G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Comm.*, **1970**, 200.

³² E. O. Schlemper, *Inorg. Chem.*, **1967**, **6**, 2012.

³³ R. S. Tobias, *Inorg. Chem.*, **1970**, **9**, 1296.

³⁴ A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. (A)*, **1970**, 2862.

³⁵ H. A. Bent, *Chem. Rev.*, **1962**, **62**, 275.

³⁶ T. B. Brill and G. G. Long, *Inorg. Chem.*, **1970**, **9**, 1980.

bonds, which place most electron density close to the metal nucleus, will provide the greatest contribution to the electric field gradient. In organotin systems, quadrupole splitting increases with increase in the contribution from the organic groups: $\text{RSnX}_4 \sim \text{RSnX}_5 < \text{cis-R}_2\text{SnX}_4 < \text{R}_2\text{SnX}_3 \sim \text{R}_3\text{SnX}_2 < \text{trans-R}_2\text{SnX}_4$, and the nature of the X group has relatively little effect. This effect must be recognised in the setting up of partial quadrupole splitting scales. The isomer shifts are also dependent on the disposition of the organic groups.² These factors account for the observed insensitivity of the Mossbauer parameters of complexes of the type R_3SnClL to changes in L.³⁷ For the investigation of the Sn-L bond by the Mossbauer technique the tetrahalides would be more suitable acceptors.

In conclusion, it appears that the point-charge model provides an excellent method of correlating quadrupole splitting with structure. However, its name is somewhat misleading as it focusses attention on the charges borne by the ligands. Used in this way, the predicted signs for e^2qQ would be in error, *e.g.* for $\text{trans-(R}^{\delta+})_2\text{-Sn(X}^{\delta-})_4$ negative values would be expected. Since the electric field gradient arises mainly from differences in electron density in the bonding orbitals, and essentially within the valence shell of the tin atom, the name 'donated-charge' model is possibly more accurate.

³⁷ J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem. Soc.*, 1969, **91**, 1644; R. W. I. Wedd and J. R. Sams, *Canad. J. Chem.*, 1970, **48**, 71.

EXPERIMENTAL

Mossbauer spectra were determined by Dr. B. W. Dale and Mr. L. W. Becker, at the Physico-Chemical Measurements Unit, Harwell, with the support of the S.R.C. The sources (Pd/Sn , BaSnO_3) were at room temperature; the samples were cooled to liquid-helium temperature and a transverse magnetic field of 30 kOe was applied. The samples used have been described previously,^{7,24} except for the *cis* complexes which were prepared by literature methods.^{25,26,38} Analytical data for these are given in Table 2.

TABLE 2

Analytical data

	C(%)		H(%)		N(%)	
	Found	Calc.	Found	Calc.	Found	Calc.
$\text{Me}_2\text{Sn(oxin)}_2$	55.0	54.9	4.3	4.1	6.7	6.4
$\text{Ph}_2\text{Sn(oxin)}_2$	64.1	64.2	3.9	3.9	5.1	5.0
$\text{Ph}_2\text{Sn(S}_2\text{CNEt}_2)_2$	46.3	46.3	5.3	5.3	5.2	4.9
$\text{Ph}_2\text{Sn(NCS)}_2$ (phen)	54.2	54.9	3.6	3.2	9.3	9.8

The computations of the theoretical spectra were based on a programme supplied by Dr. D. St. P. Bunbury and Mr. A. P. Guimaraes (Department of Physics, University of Manchester), to whom we are most grateful. Powder spectra were approximated by summing over 5° ($\eta = 0$) or 10° ($\eta > 0$) increments in θ .

[0/2031 Received, November 30th, 1970]

³⁸ T. Tanaka, M. Komura, Y. Kawasaki, and R. Okamura, *J. Organometallic Chem.*, 1964, **1**, 484.