Simple Molecular-Orbital Model for the Correlation of Mössbauer Quadrupole Splitting with Stereochemistry in Organotin(IV) Compounds

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Mössbauer quadrupole splitting in organotin(IV) compounds is interpreted in terms of the additive approximation, in which the total electric field gradient at the ^{119}Sn nucleus is written as a sum of partial field gradient tensors. Localized orbitals are shown to provide the natural framework for discussion of additive electric field gradients, and it is conjectured that the existence of a suitable localization transformation is a necessary condition for additivity. It is shown that the partial field gradient associated with a given ligand is different for tetrahedral, trigonal-bipyramidal-apical, trigonal-bipyramidal-equatorial, and octahedral co-ordination positions. In particular, the partial field gradient for octahedral co-ordination is about 70% (experiment indicates 75%) of that for tetrahedral. Absolute numerical values for partial field gradient parameters cannot be obtained from experiment for any of the above co-ordination positions, but the evaluation of relative parameters is discussed, and working values are given for a variety of ligands in tetrahedral or octahedral structures. Quadrupole splittings calculated by use of these values agree with observed splittings to within 0·4 mm s^{-1} or better. Alternatively, disagreement may be used as evidence of large distortions or incorrect assignment of structure. It is shown that a literal ' point-charge ' treatment of the effect of distortions from idealized geometry cannot be justified in molecular-orbital terms. Illustrative calculations are performed for tetrahedral systems, but experimental data indicates that it is better to ignore small distortions in quantitative discussion of the magnitude of quadrupole splitting. Extension of the model to octahedral complexes of low-spin Fe(II) is briefly discussed.

MÖSSBAUER quadrupole-splitting data on diamagnetic compounds of tin(IV),[1-3] iron(II),[4-6] and iron(—II),[7] have established that in many cases the electric field gradient (e.f.g.) [8] at the metal nucleus is given, to a first approximation, by the sum of independent contributions, one for each ligand bound to the metal. A rudimentary rationalization of these observations is provided by the ' point-charge model '.[1,2,4] in which an effective point charge is associated with each ligand, the magnitudes of the charges being chosen to give the correct e.f.g. at the metal nucleus. A closely related molecular orbital model has been given [5] for the case of octahedral complexes of low-spin iron(II). It has been shown [9] that all such rationalizations are particular manifestations of special symmetry features which arise from the assumption that the e.f.g. at the metal nucleus is additive.

In this paper a simple, but general, molecular-orbital model for an additive e.f.g. is developed, and applied to the case of organotin(IV) compounds. The model is closely related to ideas commonly used in the interpretation of n.q.r. spectra.[10-12]

The electric field gradient at the tin nucleus in organotin(IV) compounds is considered [2,3,13] to arise mainly from aspherical distribution of the valence electrons involved in tin–ligand σ bonds. Thus the model is initially formulated for σ bonding alone, although the role of π bonding is briefly discussed in a section devoted to systems other than Sn^{IV}. The model is used to discuss the implications of changes in structural type, and of distortions from idealized co-ordination geometry. The relationship between theory and the experimental data for tin(IV) compounds is considered in some detail.

Outline of Model.—Consider a closed-shell molecule consisting of n ligands (A, B, ... N) bound to a central atom M by n σ bonds. Let the n valence molecular orbitals ψ_1, ψ, ... ψ_n contain $2n$ valence electrons. Then the total wavefunction Ψ is given by (1), where |) denotes a Slater determinant, and

$$\Psi = |\psi_1{}^{\alpha}\psi_1{}^{\beta}\psi_2{}^{\alpha}\psi_2{}^{\beta} \ldots \psi_n{}^{\alpha}\psi_n{}^{\beta}) \qquad (1)$$

α and β denote $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ respectively. Closed inner-shell orbitals are not included explicitly in equation (1) in order to avoid unnecessarily complicated notation.

The molecular orbitals ψ_i ($i = 1, 2, \ldots n$) have definite orbital energies, and form bases for irreducible representations of the point-symmetry group of the system. In general each ψ_i will be delocalized in the sense that it may have non-zero amplitude at many points in the molecule, not just in the region forming a particular metal–ligand bond.

The Slater determinant of equation (1) is unchanged by any unimodular linear transformation of its orbitals.

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

[2] R. V. Parish and R. H. Platt, *J. Chem. Soc.* (*A*), 1969, 2145; *Inorg. Chim. Acta*, 1970, **4**, 65.

[3] R. V. Parish and C. E. Johnson, *Chem. Phys. Letters*, 1970, **6**, 239; *J. Chem. Soc.* (*A*), 1971, 1906.

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[7] R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, 1969, **51**, 3220; J. P. Crow, W. R. Cullen, F. G. Herring, J. R. Sams, and R. L. Tapping, *Inorg. Chem.*, 1971, **10**, 1616.

[8] For the theory of e.f.g. tensors see M. H. Cohen and F. Reif, *Solid State Phys.*, 1957, **5**, 321, and M. G. Clark, *J. Chem. Phys.*, 1971, **54**, 697.

[9] M. G. Clark, *Mol. Phys.*, 1971, **20**, 257.

[10] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1949, **17**, 782; W. J. Orville-Thomas, *Quart. Rev.*, 1957, **11**, 162.

[11] E. A. C. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, London, 1969, ch. 7.

[12] E. Schempp and P. J. Bray in ' Physical Chemistry,' eds. H. Eyring, D. Henderson, and W. Jost, Academic Press, London, 1970, vol. 4, ch. 11.

[13] J. Phillip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, 1968, **7**, 1895; J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem. Soc.*, 1969, **91**, 1644.

In particular, the molecular orbitals ψ_i may be transformed [14,15] into a set of (orthonormal) localized orbitals ϕ_{L} (L = A, B, . . . N), chosen so that each ϕ_{L} is, as far as possible, localized in the region of a particular metal–ligand bond. The ϕ_{L} do not have well-defined orbital energies, and for this reason would not be appropriate for use in a discussion of, say, electronic spectra. However, the components V_{rs} of the e.f.g. tensor at M are given by diagonal matrix elements of the e.f.g. tensor operator, and these are unchanged by the transformation to localized orbitals. Further, V_{rs} may be written as a sum of one-electron matrix elements:

$$\begin{aligned} V_{rs} &= (\psi_1{}^{\alpha}\psi_1{}^{\beta} \ldots \psi_n{}^{\beta}|\sum_{\mathrm{el.}} \mathscr{V}_{rs}|\psi_1{}^{\alpha}\psi_1{}^{\beta} \ldots \psi_n{}^{\beta}) \\ &= (\phi_{\mathrm{A}}{}^{\alpha}\phi_{\mathrm{A}}{}^{\beta} \ldots \phi_{\mathrm{N}}{}^{\beta}|\sum_{\mathrm{el.}} \mathscr{V}_{rs}|\phi_{\mathrm{A}}{}^{\alpha}\phi_{\mathrm{A}}{}^{\beta} \ldots \phi_{\mathrm{N}}{}^{\beta}) \\ &= 2\sum_{\mathrm{L=A}}^{\mathrm{N}} (1 - R_{\mathrm{L}})(\phi_{\mathrm{L}}|\mathscr{V}_{rs}|\phi_{\mathrm{L}}) \\ &= \sum_{\mathrm{L=A}}^{\mathrm{N}} v_{rs}(\mathrm{L}), \qquad (2) \end{aligned}$$

where

$$\mathscr{V}_{rs} = -\mathrm{e}r^{-5}(3x_r x_s - r^2\delta_{rs}) \qquad (3)$$

In equations (2) and (3), $\sum_{\mathrm{el.}}$ denotes the sum over all electrons, e is the protonic charge, and R_{L} is the appropriate Sternheimer factor [16] to correct for distortion of the closed inner-shell orbitals of M.

Now if the orbital ϕ_{L} is well-localized into the region close to the M–L bond axis, it seems reasonable to suppose, as a first approximation, that ϕ_{L}, and hence $v_{rs}(\mathrm{L})$, depend mainly on the properties of that particular bond. Of course the other bonds will perturb the M–L bond to some extent, but when these perturbations are not too large the total field gradient is simply the tensor sum of approximately independent contributions, one for each ligand. It is convenient to write the tensor $v_{rs}(\mathrm{L})$ in terms of local axes defined in a standard way [9] with z directed along the M–L axis; in this form the tensor is termed the 'partial field gradient' due to L.

The above discussion leads to two conclusions. First, localized orbitals provide the natural framework for discussion of additive electric field gradients. Second, it is conjectured that the existence of a suitable localization transformation is a necessary condition for a field gradient to be additive. The first of these conclusions forms the basis of the present paper; the second, though not examined in detail here, is briefly discussed below.

It is convenient to require that the localized orbitals ϕ_{L} be equivalent orbitals.[14,15] The members of a set of equivalent orbitals are permuted among themselves by the operations of the molecular point-group or one of its subgroups. It is evident that each set of equivalent orbitals forms a basis for a permutation representation of the relevant point-group.[15,17]

The set $\{\phi_{\mathrm{L}}\}$ of localized orbitals may span one or more sets of equivalent orbitals.[15] In the former case the equivalent orbitals are unique, and the localized orbitals are completely defined by the equivalence relation. For example, in a tetrahedral molecule such as CH_4 the equivalent orbitals are familiar as the C–H σ bonds formed by use of carbon sp^3 hybrid orbitals. Cases below where the equivalent orbitals are not unique will be discussed as they arise.

The use of equivalent orbitals facilitates calculation because different members of the same set of equivalent orbitals give rise to the same partial field gradient.

Detailed Assumptions.—If the implications of the above model are to be elucidated without tedious numerical calculation, it is necessary to make simplifying assumptions. Our assumptions are essentially the same as those which have been found useful in the interpretation of n.q.r. spectra.[10–12]

We assume that the localized orbital ϕ_{L} can be written as a linear combination of a metal orbital h_{L} and a ligand orbital χ_{L} [equation (4)]. The orbitals

$$\phi_{\mathrm{L}} = c_1 h_{\mathrm{L}} + c_2\chi_{\mathrm{L}} \qquad (4)$$

ϕ_{L}, h_{L}, and χ_{L} may all be taken ∞ real, so that c_1 and c_2 are also real. The metal orbital is an appropriate equivalent orbital formed from the metal atomic orbitals, and is called a 'hybrid orbital'. Thus the matrix element in equation (2) may be written

$$(\phi_{\mathrm{L}}|\mathscr{V}_{rs}|\phi_{\mathrm{L}}) = c_1{}^2(h_{\mathrm{L}}|\mathscr{V}_{rs}|h_{\mathrm{L}}) + 2c_1c_2(h_{\mathrm{L}}|\mathscr{V}_{rs}|\chi_{\mathrm{L}}) + c_2{}^2(\chi_{\mathrm{L}}|\mathscr{V}_{rs}|\chi_{\mathrm{L}}) \qquad (5)$$

Provided that neither c_1 nor c_2 is close to zero, contributions to the e.f.g. from the second and third terms in equation (5) are each about an order of magnitude less than the contribution from the first term. (The r^{-3} dependence of $\mathscr{V}_{rs}$ causes the terms to fall off roughly as $1 : 10^{-1} : 10^{-2}$, but the third term will be enhanced by about an order of magnitude due to Sternheimer antishielding.) Thus contributions from the second and third terms will be neglected, as also will contributions to the e.f.g. from charges in more distant parts of the solid. This should be satisfactory provided the so-called 'valence terms' $(h_{\mathrm{L}}|\mathscr{V}_{rs}|h_{\mathrm{L}})$ do not cancel to give a small total valence contribution to the e.f.g.; certainly it is consistent with experimental studies of organotin(IV) compounds.[3] Also, the additivity assumption itself may not hold to a significantly higher degree of accuracy than that imposed by this assumption.

If local axes (x, y, z) are taken with z parallel to the M–L axes, then

$$v_{zz}(\mathrm{L}) = 2(1 - R_{\mathrm{L}})(h_{\mathrm{L}}|\mathscr{V}_{zz}|h_{\mathrm{L}})c_1{}^2 = 2\mathrm{e}[\mathrm{L}] \qquad (6)$$

The parameter [L] is sufficient to characterize the partial

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[14] J. Lennard-Jones, *Proc. Roy. Soc.*, 1949, *A*, **198**, 1, 14; G. G. Hall and J. Lennard-Jones, *ibid.*, 1950, *A*, **202**, 155; J. Lennard-Jones and J. A. Pople, *ibid.*, p. 166; J. A. Pople, *Quart. Rev.*, 1957, **11**, 273.

[15] G. G. Hall, *Proc. Roy. Soc.*, 1950, *A*, **202**, 337.

[16] A. J. Freeman and R. E. Watson in 'Magnetism,' eds. G. T. Rado and H. Suhl, Academic Press, London, 1965, vol. 2A, ch. 4, and references therein.

[17] W. Burnside, 'Theory of Groups of Finite Order,' Dover Publications, New York, 1955, ch. 12.

field gradient due to a bond with ' bond symmetry '[9] $C_{\infty v}$;* for C_{2v} bonds the additional parameter required is

$$\eta_{\mathrm{L}} = (h_{\mathrm{L}}|\mathscr{V}_{xx} - \mathscr{V}_{yy}|h_{\mathrm{L}})/(h_{\mathrm{L}}|\mathscr{V}_{zz}|h_{\mathrm{L}}) \qquad (7)$$

where x and y are chosen so as to diagonalize $\mathbf{v}$(L). (The condition[8] $|v_{xx}(\mathrm{L})| \leqslant |v_{yy}(\mathrm{L})| \leqslant |v_{zz}(\mathrm{L})|$ will be satisfied by appropriate choice of x and y in all but the most extreme cases.) We shall not consider cases in which none of the principal axes of the partial field gradient is directed along the bond.

Different Structural Types.—Symmetry arguments give no indication as to whether a given ligand should be assigned the same partial field gradient in compounds of different structural type. The molecular-orbital model, however, gives unambiguous predictions.

Tetrahedral, trigonal-bipyramidal, and octahedral structures are considered in this section. The partial field gradient due to a generic ligand L has been calculated for each case by use of equations (6) and (7) (Table 1). In the tetrahedral and octahedral systems the appropriate metal hybrids h_{L} (sp^3 and sp^3d^2, respectively) span a single set of equivalent orbitals. The sp^3d trigonal-bipyramidal hybrids span two sets (apical and equatorial) of orbitals equivalent under D_{3h}. The $5s$ and $5d_{z^2}$ orbitals may participate in both the apical and equatorial sets. This is allowed for by use[18] of a parameter θ ($0 \leqslant \theta \leqslant 2\pi$) describing the distribution of s and d_{z^2} between apical and equatorial hybrids.

TABLE 1

Calculation of partial field gradients in important structural types *

Tetrahedral

$$h_z^{\mathrm{tet}} = \tfrac{1}{2}s + \frac{\sqrt{3}}{2}p_z$$

$$[\mathrm{L}]^{\mathrm{tet}} = -\tfrac{3}{10}\langle r^{-3}\rangle_p \sigma_{\mathrm{L}}{}^{\mathrm{tet}}$$

Octahedral

$$h_z^{\mathrm{oct}} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_{z^2}$$

$$[\mathrm{L}]^{\mathrm{oct}} = \left(-\tfrac{1}{5}\langle r^{-3}\rangle_p - \tfrac{2}{21}\langle r^{-3}\rangle_d - \frac{\sqrt{2}}{3\sqrt{5}}\langle r^{-3}\rangle_{sd}\right)\sigma_{\mathrm{L}}{}^{\mathrm{oct}}$$

Trigonal bipyramidal

(*a*) apical

$$h_z^{\mathrm{tba}} = \left(\frac{1}{\sqrt{2}}\cos\theta\right)s + \frac{1}{\sqrt{2}}p_z + \left(\frac{1}{\sqrt{2}}\sin\theta\right)d_{z^2}$$

$$[\mathrm{L}]^{\mathrm{tba}} = \left(-\tfrac{1}{5}\langle r^{-3}\rangle_p - \tfrac{1}{7}\sin^2\theta\langle r^{-3}\rangle_d - \frac{1}{\sqrt{5}}\sin\theta\cos\theta\langle r^{-3}\rangle_{sd}\right)\sigma_{\mathrm{L}}{}^{\mathrm{tba}}$$

(*b*) equatorial

$$h_z^{\mathrm{tbe}} = \left(\frac{1}{\sqrt{3}}\sin\theta\right)s + \frac{\sqrt{2}}{\sqrt{3}}p_z + \left(\frac{1}{2\sqrt{3}}\cos\theta\right)d_{z^2} - (\tfrac{1}{2}\cos\theta)d_{x^2-y^2}$$

$$[\mathrm{L}]^{\mathrm{tbe}} = \left(-\tfrac{4}{15}\langle r^{-3}\rangle_p + \tfrac{1}{21}\cos^2\theta\langle r^{-3}\rangle_d - \frac{1}{3\sqrt{5}}\cos\theta\sin\theta\langle r^{-3}\rangle_{sd}\right)\sigma_{\mathrm{L}}{}^{\mathrm{tbe}}$$

$$\eta_{\mathrm{L}}{}^{\mathrm{tbe}} = \left|\frac{15\cos^2\theta\langle r^{-3}\rangle_d - 21\sqrt{5}\cos\theta\sin\theta\langle r^{-3}\rangle_{sd}}{28\langle r^{-3}\rangle_p - 5\cos^2\theta\langle r^{-3}\rangle_d + 7\sqrt{5}\cos\theta\sin\theta\langle r^{-3}\rangle_{sd}}\right|$$

* tet = tetrahedral, oct = octahedral, tba = trigonal-bipyramidal-apical, tbe = trigonal-bipyramidal-equatorial.

In Table 1 typical hybrids for each structural type are given in terms of local axes with z directed along the hybrid. The subscript z serves as a reminder of this choice of axes. The partial field gradient parameters given in Table 1 are obtained by inserting the tabulated expressions for h_z into equations (6) and (7). The radial averages $\langle r^{-3}\rangle_p$, $\langle r^{-3}\rangle_d$, and $\langle r^{-3}\rangle_{sd}$ are equal to the appropriate radial integrals corrected for distortion of inner shells by use of Sternheimer factors; for example:

$$\langle r^{-3}\rangle_{sd} = (1 - R_{sd})\int_0^\infty u_s(r)r^{-3}u_d(r)r^2\mathrm{d}r,$$

where $u_s(r)$ and $u_d(r)$ are the radial parts of the $5s$ and $5d$ wavefunctions. The empirical parameter σ_{L} is proportional to $2c_1{}^2$, but allows also for any systematic variation of the radial averages with structural type.

If it is assumed that the Sternheimer factors involved in $\langle r^{-3}\rangle_p$, $\langle r^{-3}\rangle_d$, and $\langle r^{-3}\rangle_{sd}$ are all of the same order of magnitude, then calculation[19] of the radial integrals by use of Herman–Skillman wavefunctions[20] indicates that the ratios $\langle r^{-3}\rangle_{sd} : \langle r^{-3}\rangle_p$ and $\langle r^{-3}\rangle_d : \langle r^{-3}\rangle_p$ are of order of magnitude 10^{-3} and 10^{-2} respectively. Thus terms in $\langle r^{-3}\rangle_{sd}$ and $\langle r^{-3}\rangle_d$ can be neglected. The partial field gradient parameters given in Table 1 then reduce to (8a—d).

$$[\mathrm{L}]^{\mathrm{tet}} = -\tfrac{3}{10}\langle r^{-3}\rangle_p\sigma_{\mathrm{L}}{}^{\mathrm{tet}} \qquad (8a)$$

$$[\mathrm{L}]^{\mathrm{oct}} = -\tfrac{1}{5}\langle r^{-3}\rangle_p\sigma_{\mathrm{L}}{}^{\mathrm{oct}} \qquad (8b)$$

$$[\mathrm{L}]^{\mathrm{tba}} = -\tfrac{1}{5}\langle r^{-3}\rangle_p\sigma_{\mathrm{L}}{}^{\mathrm{tba}} \qquad (8c)$$

$$[\mathrm{L}]^{\mathrm{tbe}} = -\tfrac{4}{15}\langle r^{-3}\rangle_p\sigma_{\mathrm{L}}{}^{\mathrm{tbe}},\ \eta_{\mathrm{L}}{}^{\mathrm{tbe}} = 0 \qquad (8d)$$

It is evident from equations (8) that an additive model may be used for the interpretation of $\mathrm{Sn^{IV}}$ quadrupole-splitting data only if different partial field gradient parameters are assigned to tetrahedral, octahedral, trigonal-bipyramidal-apical (tba), and trigonal-bipyramidal-equatorial (tbe) co-ordination sites. Further, it is predicted that an axially-symmetric partial field gradient is adequate for the trigonal-bipyramidal-equatorial site, although D_{3h} symmetry does not demand this.

Equations (8a) and (8b) imply that the ratio $[\mathrm{L}]^{\mathrm{oct}}/[\mathrm{L}]^{\mathrm{tet}}$ is equal to $0{\cdot}67(\sigma_{\mathrm{L}}{}^{\mathrm{oct}}/\sigma_{\mathrm{L}}{}^{\mathrm{tet}})$. Since $(\sigma_{\mathrm{L}}{}^{\mathrm{oct}}/\sigma_{\mathrm{L}}{}^{\mathrm{tet}})$ would not be expected to differ greatly from unity, it is predicted that the magnitude of $[\mathrm{L}]^{\mathrm{oct}}$ should be about 70% that of $[\mathrm{L}]^{\mathrm{tet}}$. Detailed analysis of experimental data (see below) confirms this prediction.

The electric field gradient in trigonal-bipyramidal $\mathrm{SnA_5}$ systems is predicted to be axially symmetric with zz component

$$V_{zz} = 4[\mathrm{A}]^{\mathrm{tba}} - 3[\mathrm{A}]^{\mathrm{tbe}} = \tfrac{4}{5}\langle r^{-3}\rangle_p(\sigma_{\mathrm{A}}{}^{\mathrm{tbe}} - \sigma_{\mathrm{A}}{}^{\mathrm{tba}}) \qquad (9)$$

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* Three-fold or higher effective symmetry about the M–L axis is sufficient to ensure that the bond symmetry in the sense of ref. 9 is $C_{\infty v}$.

[18] F. A. Cotton, ' Chemical Applications of Group Theory,' Interscience, London, 1963, p. 116.

[19] A. J. Stone, personal communication; programs written by B. S. Ing and A. J. Stone.

[20] F. Herman and S. Skillman, ' Atomic Structure Calculations,' Prentice–Hall, Englewood Cliffs, New Jersey, 1963.

The corresponding quadrupole splitting Δ is given by

$$\Delta = \tfrac{1}{2}e^2QV_{zz} = \Delta_0(\sigma_A{}^{\mathrm{tba}} - \sigma_A{}^{\mathrm{tbe}}), \quad (10a)$$

where

$$\Delta_0 = -\tfrac{2}{5}e^2Q\langle r^{-3}\rangle_p, \quad (10b)$$

and Q is the nuclear quadrupole moment of the 23·9 keV state of ^{119}Sn. Thus, in the additive approximation, the quadrupole splitting in SnA_5 arises solely from the difference $(\sigma_A{}^{\mathrm{tbe}} - \sigma_A{}^{\mathrm{tba}})$, and is, therefore, expected to be small. Experiment is in agreement with this; for example $SnCl_5{}^-$ gives a quadrupole splitting of about [2] 0·7 mm s^{-1}. If the value of Δ_0 is taken as 4·3 mm s^{-1},[21] then $|\Delta| = 0{\cdot}7$ mm s^{-1} corresponds to a value of 0·16 for $|\sigma_{\mathrm{Cl}}{}^{\mathrm{tbe}} - \sigma_{\mathrm{Cl}}{}^{\mathrm{tba}}|$.

Tabulation of $[L]^{\mathrm{tba}}$ and $[L]^{\mathrm{tbe}}$ for a range of ligands is completely equivalent to tabulation of the corresponding σ_L. But it is evident from equations (8c), (8d), and (9) that a constant quantity may be subtracted from all the σ_L without changing any e.f.g. calculated from such a table. Thus it is not possible to determine the absolute values of $[L]^{\mathrm{tba}}$ and $[L]^{\mathrm{tbe}}$ directly from experiment. The best that can be done is to evaluate $[L]^{\mathrm{tba}} - [X]^{\mathrm{tba}}$ and $[L]^{\mathrm{tbe}} - \tfrac{4}{3}[X]^{\mathrm{tba}}$, or alternatively $[L]^{\mathrm{tba}} - \tfrac{3}{4}[X]^{\mathrm{tbe}}$ and $[L]^{\mathrm{tbe}} - [X]^{\mathrm{tbe}}$, where X is a fixed reference ligand. Similarly, since symmetry demands that tetrahedral SnA_4 and octahedral SnA_6 should give zero quadrupole splittings, it is evident that only $[L]^{\mathrm{tet}} - [X]^{\mathrm{tet}}$ and $[L]^{\mathrm{oct}} - [X]^{\mathrm{oct}}$ can be evaluated directly from experiment.

The determination of partial field gradient parameters for tetrahedral and octahedral structures is discussed below.

Distortions from Idealized Geometry.—Several factors can lead to the actual co-ordination geometry of the tin atom being distorted from the idealized co-ordination polyhedron. Thus it is necessary to ask what effect such distortions might have on the e.f.g. at the tin nucleus. One approach [3,7,22,23] is to calculate the changes in e.f.g. arising from changes in relative orientation of the various partial field gradient tensors, while leaving the partial field gradient parameters unchanged. In effect this is a literal interpretation of the 'point-charge model'. On the other hand, it is clear that in any molecular-orbital model the expression for a given bond orbital ϕ_L may change as the bond is distorted from its idealized direction. This could lead to changes in the partial field gradient parameters in addition to changes in the orientation of the tensor.

In this section the changes caused by distortions are calculated on the basis that the metal hybrids continue to point directly at the ligands as the molecule is distorted. Attention is confined to tetrahedral systems which remains sp^3 hybridized on distortion, since the vector character of p orbitals means that our criterion is most easily applied in this case. Even then there are, in general, three disposable parameters,[24] so we shall consider only two special distortions involving a single disposable parameter in each case.

The distortions considered are illustrated in Figures 1 and 2. The distortion of SnA_3B (Figure 1) preserves C_{3v} symmetry, and that of SnA_2B_2 (Figure 2) preserves C_{2v} symmetry. In each case the angle α will be taken as the disposable parameter. In both systems the metal hybrids span two sets of equivalent orbitals, those pointing at A ligands and those pointing at B ligands. Expressions for the hybrids may be calculated by using the vector character of p orbitals.[25] Tables 2 and 3 list the linear combination coefficients obtained. After allowing for differences in notation, and correction

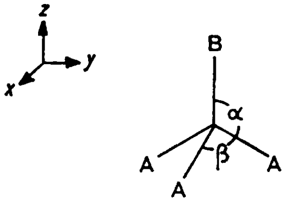

FIGURE 1 Distortion of SnA_3B considered in text

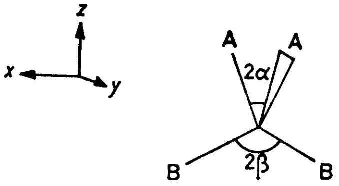

FIGURE 2 Distortion of SnA_2B_2 considered in text

TABLE 2

Metal hybrids in SnA_3B distorted as in Figure 1

	s	p_x	p_y	p_z
h_1	$-\sqrt{2}\cot\alpha$	0	0	$(1-2\cot^2\alpha)^{\frac{1}{2}}$
h_2	$\frac{1}{\sqrt{3}}(1-2\cot^2\alpha)^{\frac{1}{2}}$	$\frac{\sqrt{2}}{\sqrt{3}}$	0	$\frac{\sqrt{2}}{\sqrt{3}}\cot\alpha$
h_3	$\frac{1}{\sqrt{3}}(1-2\cot^2\alpha)^{\frac{1}{2}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{2}}{\sqrt{3}}\cot\alpha$
h_4	$\frac{1}{\sqrt{3}}(1-2\cot^2\alpha)^{\frac{1}{2}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{2}}$	$\frac{\sqrt{2}}{\sqrt{3}}\cot\alpha$

TABLE 3

Metal hybrids in SnA_2B_2 distorted as in Figure 2

	s	p_x	p_y	p_z
h_1	$\frac{1}{\sqrt{2}}(1-\cot^2\alpha)^{\frac{1}{2}}$	0	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}\cot\alpha$
h_2	$\frac{1}{\sqrt{2}}(1-\cot^2\alpha)^{\frac{1}{2}}$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}\cot\alpha$
h_3	$\frac{1}{\sqrt{2}}\cot\alpha$	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}(1-\cot^2\alpha)^{\frac{1}{2}}$
h_4	$\frac{1}{\sqrt{2}}\cot\alpha$	$-\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}(1-\cot^2\alpha)^{\frac{1}{2}}$

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[21] A. G. Maddock and R. H. Platt, *J. Chem. Phys.*, 1971, **55**, 1490.

[22] S. R. A. Bird, J. D. Donaldson, A. F. le C. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616.

[23] B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1868.

[24] W. Kauzmann, 'Quantum Chemistry,' Academic Press, New York, 1957, p. 415.

[25] C. A. Coulson, 'Valence,' Oxford University Press, London, 1961, section 8.3.

of a misprint, these agree with expressions given by Lucken.[26] The allowed ranges of α, and the expressions for β in terms of α, are

$$\mathrm{SnA_3B}: 2{\cdot}19 \geqslant \alpha \geqslant \tfrac{1}{2}\pi,\ \cos\beta = \tfrac{1}{2}(3\cos^2\alpha - 1) \qquad (11a)$$

$$\mathrm{SnA_2B_2}: \tfrac{1}{2}\pi \geqslant \alpha \geqslant \tfrac{1}{4}\pi,\ \cot^2\beta = 1 - \cot^2\alpha \qquad (11b)$$

Since the principal axes of the e.f.g. tensor at the Sn nucleus are determined by symmetry in both cases, it is convenient to calculate the total e.f.g. at the tin nucleus directly. If we assume that the σ^{tet} remain unchanged on distortion, then the quadrupole splittings are

$$\mathrm{SnA_3B}:\ \Delta_1(\alpha) = \tfrac{4}{3}(1 - 2\cot^2\alpha)e^2Q([\mathrm{B}]^{\mathrm{tet}} - [\mathrm{A}]^{\mathrm{tet}}) \qquad (12a)$$

$$\mathrm{SnA_2B_2}:\ \Delta_2(\alpha) = \varepsilon\tfrac{4}{3}(\cot^4\alpha - \cot^2\alpha + 1)^{\frac{1}{2}}e^2Q|[\mathrm{B}]^{\mathrm{tet}} - [\mathrm{A}]^{\mathrm{tet}}| \qquad (12b)$$

where

$$\varepsilon = \mathrm{sgn}\{[\mathrm{B}]^{\mathrm{tet}} - [\mathrm{A}]^{\mathrm{tet}}\}\mathrm{sgn}\{\alpha^{\mathrm{tet}} - \alpha\} \qquad (12c)$$

In equations (12) the superscript tet denotes idealized tetrahedral geometry, and sgn{} is equal to +1 or −1 according as the quantity in braces is positive or negative.

Equations (12) are conveniently written as

$$\Delta_1(\alpha) = f_1(\alpha)\Delta_1{}^{\mathrm{tet}} \qquad (13a)$$

$$\Delta_2(\alpha) = f_2(\alpha)|\Delta_2{}^{\mathrm{tet}}|\mathrm{sgn}\{Q\} \qquad (13b)$$

where

$$f_1 = \tfrac{4}{3}(1 - 2\cot^2\alpha) \qquad (13c)$$

$$f_2 = \varepsilon\frac{2}{\sqrt{3}}(\cot^4\alpha - \cot^2\alpha + 1)^{\frac{1}{2}} \qquad (13d)$$

and ε is defined in equation (12c). The functions $f_1(\alpha)$ and $f_2(\alpha)$ are plotted in Figures 3 and 4 respectively. Figure 4 is plotted on the assumption that $[\mathrm{B}]^{\mathrm{tet}} > [\mathrm{A}]^{\mathrm{tet}}$. Although the asymmetry parameter η is zero for all α in the case of $\mathrm{SnA_3B}$, for $\mathrm{SnA_2B_2}$ η varies with α, and is plotted on Figure 4 as a broken line. Note that in the case of $\mathrm{SnA_3B}$ Δ varies rapidly with distortion, while for $\mathrm{SnA_2B_2}$ $|\Delta|$ varies slowly and η varies rapidly.

It is apparent from equations (12a) and (12b) that in both cases the quadrupole splitting remains proportional to $([\mathrm{B}]^{\mathrm{tet}} - [\mathrm{A}]^{\mathrm{tet}})$ on distortion. This result does not hold for field gradients calculated on the basis of the point-charge model taken literally. It implies that if partial field gradient parameters are calculated from observed values of $|\Delta|$ on the basis of idealized tetrahedral geometry, the values obtained will be *apparent* values equal to $|f(\alpha)|$ times the value for exact tetrahedral geometry. The *true* partial field gradient parameters in the distorted system will be different from these apparent values. Expressions for the true parameters are:

$$\mathrm{SnA_3B}:\ [\mathrm{A}]^{\alpha} = \tfrac{8}{9}\,\mathrm{cosec}^2\alpha[\mathrm{A}]^{\mathrm{tet}}$$

$$[\mathrm{B}]^{\alpha} = \tfrac{4}{3}(1 - 2\cot^2\alpha)[\mathrm{B}]^{\mathrm{tet}}$$

$$\mathrm{SnA_2B_2}:\ [\mathrm{A}]^{\alpha} = \tfrac{2}{3}\,\mathrm{cosec}^2\alpha[\mathrm{A}]^{\mathrm{tet}}$$

$$[\mathrm{B}]^{\alpha} = \tfrac{2}{3}(2 - \cot^2\alpha)[\mathrm{B}]^{\mathrm{tet}}.$$

It was noted above that the point-charge model taken literally amounts to ignoring this variation of the true parameters with distortion.

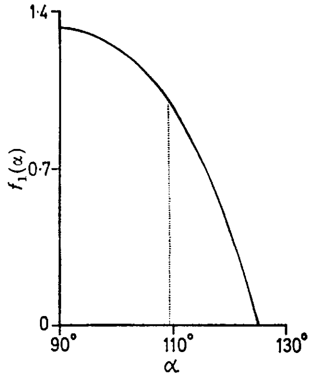

FIGURE 3 Plot of $f_1(\alpha)$ against α. Dotted line is $\alpha = \alpha^{\mathrm{tet}}$

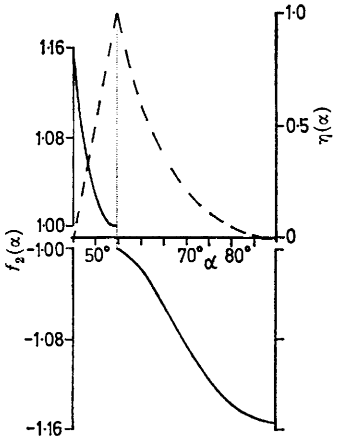

FIGURE 4 Plot of $f_2(\alpha)$ against α (full line) and $\eta(\alpha)$ against α (broken line). Dotted line is $\alpha = \alpha^{\mathrm{tet}}$

Quantitative assessment of the calculations described in this section is limited by lack of data. Table 4 lists a few suitable compounds for which both structural and Mössbauer data are known.

Consider first compounds (i)—(iii). The quadrupole-splitting ratios QS(ii) : QS(i) and QS(iii) : QS(i) calculated directly from the observed splittings have magnitudes of 0·77 and 0·68 respectively. If the quadrupole splittings are corrected to the 'tetrahedral' values by use of Figures 3 and 4, the ratios become 1·67 and 1·23, respectively. Since $[\mathrm{Cl}]^{\mathrm{tet}}$ and $[\mathrm{Br}]^{\mathrm{tet}}$ may be taken equal (see below), both ratios have a theoretical value [2,9] of $\frac{1}{2}\sqrt{3} = 0{\cdot}87$. Thus significantly better agreement between theory and experiment is obtained if corrections for distortion are ignored.

Similarly, if $\frac{1}{2}e^2|Q|([\mathrm{Me}]^{\mathrm{tet}} - [\mathrm{Cl}]^{\mathrm{tet}})$ is calculated from the data on compounds (iv) and (v) the value $-1{\cdot}13$ mm s^{-1} is obtained if corrections for distortion are ignored, whereas after correction the value obtained

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[26] Ref. 11, pp. 219 and 266; on p. 219 the coefficient of ψ_8 in ϕ_4 should read $\{(1 + 2\cos\alpha)/(1 - \cos\alpha)\}^{\frac{1}{2}}$, also the coefficients of ψ_8 in the other orbitals should bear the exponent $\frac{1}{2}$.

is −1·02 mm s^{-1}. The uncorrected value is closer to the 'working value' of −1·37 mm s^{-1} obtained below.

The precise implications of these results are not clear. The calculations embodied in Figures 3 and 4 are based on three assumptions: first, that the hybrids point directly at the ligands; second, that even in the distorted molecule the sp^3 basis is adequate; and third, that σ_L^{tet} does not vary with distortion. Any of these assumptions might break down. Some insight into the first two assumptions may be obtained by considering bond-angle data for SnA_2B_2 systems, where equation (11b) holds only if both are satisfied. Results for six compounds are listed in Table 5; bearing in mind that at θ = 50° a change in θ of 1° changes $\cot^2\theta$ by 0·05, it is seen that only $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn(NO_2)_2$, and possibly $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn(C_5H_5)_2$, can be considered as definite exceptions to equation (11b).

TABLE 4

Mössbauer quadrupole-splitting and structural data for certain tetrahedral compounds showing distortions from idealized geometry

Code	Compound *	α †	β †	Ref.	Obs. QS (mm s^{-1})	Ref.
(i)	$[CpFe(CO)_2]_2SnCl_2$	47·0°	64·3°	*a*	+2·37	*f, i*
(ii)	$[CpFe(CO)_2]SnCl_3$	119·2	98·3	*b*	+1·82	*f, i*
(iii)	$[CpFe(CO)_2]SnBr_3$	117·7	100·2	*c*	1·60	*f*
(iv)	$Me_3Sn[Mn(CO)_5]$	111·6	107·3	*d*	0·71	*g, j*
(v)	$[Mn(CO)_5]_3SnCl$	101·0	116·5	*e*	1·55	*h*

* Cp = π-cyclopentadienyl. † Average of nominally equal angles.

[a] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968. [b] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1970, 1696. [c] G. A. Melson, P. F. Stokley, and R. F. Bryan, *J. Chem. Soc.* (*A*), 1970, 2247. [d] R. F. Bryan, *J. Chem. Soc.* (*A*), 1968, 696. [e] J. H. Tsai, J. J. Flynn, and F. P. Boer, *Chem. Comm.*, 1967, 702. [f] Ref. 22. [g] C. Wynter and L. Chandler, *Bull. Chem. Soc. Japan*, 1970, **43**, 2115. [h] A. N. Karasyov, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. i eksp. Khim.*, 1966, **2**, 126. [i] Ref. 23. [j] S. Onaka, Y. Sasaki, and H. Sano, *Bull. Chem. Soc. Japan*, 1971, **44**, 726.

TABLE 5

Bond-angle data for some SnA_2B_2 systems

Compound *	Ref.	α †	β	$\cot^2\alpha + \cot^2\beta$
$[CpFe(CO)_2]_2SnCl_2$	*a*	64·3°	47·0°	1·10
$[CpFe(CO)_2]_2SnMe_2$	*b*	61·5	52	0·91
$[CpFe(CO)_2]_2Sn(NO_2)_2$	*c*	63	33·5	2·54
$[CpFe(CO)_2]_2Sn(C_5H_5)_2$	*d*	58	47·5	1·23
$Ph_2Sn[Mn(CO)_5]_2$	*e*	58·5	50	1·08
$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	*f*	57	53·7	0·96

* Cp = π-cyclopentadienyl. † 2α = M–Sn–M angle.

[a] J. E. O'Conner and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968. [b] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Comm.*, 1968, 159. [c] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Comm.*, 1967, 750. [d] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Comm.*, 1968, 1193. [e] B. T. Kilbourn and H. M. Powell, *Chem. Ind.*, 1964, 1578. [f] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharov, *Chem. Comm.*, 1967, 749.

Note also that the positive signs [23] of the quadrupole splittings observed in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnL_2$ (L = Cl, NCS) are correctly predicted by equations (12b) and (12c) on the basis that, in agreement with Table 5, it is the (metal)–Sn–(metal) angle which is greater than tetrahedral.

With regard to the point-charge model taken literally, it was noted above that it has no *a priori* justification in molecular-orbital terms. Further, since in this model the quadrupole splitting depends on both $[A]^{tet}$ and $[B]^{tet}$ independently, an extra disposable parameter is introduced, and it is difficult to see how the model is to be given any *a posteriori* justification except as a scheme for parameterizing results or as a vehicle for purely qualitative arguments.

Thus we feel on the basis of present evidence that in quantitative calculations the best course of action is to ignore small distortions from idealized geometry. The same suggestion has been made [12] in connexion with n.q.r. studies of other nuclei. Grossly distorted systems represent a separate problem which will not be considered here.

Analysis of Experimental Data.—Previous tables [2] of partial field gradient parameters are unsatisfactory [27] because no allowance was made for the variation of partial field gradient with structural type. In this section the evaluation of partial field gradient parameters from quadrupole-splitting data is discussed for tetrahedral and octahedral systems.

Table 6 summarizes the data used. Code numbers assigned to the compounds in Table 6 indicate their structural type: codes 1—99 are reserved for tetrahedral systems, and codes 101—199 for octahedral systems. Idealized geometry will be assumed in all cases. Reported errors for the experimental quadrupole splittings quoted in Table 6 vary upwards from ±0·02 mm s^{-1}. Splittings measured at or below 80 K have been averaged without adjustment, since any temperature dependence is within experimental error.

It was mentioned above that for a partial field gradient parameter [L] to be well-defined the particular Sn–L bond must be only slightly perturbed by other bonds. These perturbations will differ from compound to compound, with the result that values of [L] taken from a range of different compounds will form a distribution. The only essential condition on this distribution is that its width must not be so great that the concept of additivity breaks down. In particular, there is no obvious reason why the distribution should be adequately characterized by a single numerical value for [L]. Against this must be set the practical convenience of a table of numerical values.

A survey of the compounds listed in Table 6 reveals that certain ligands, namely the halogens, alkyl, and phenyl, appear with greater frequency than most. Further, it is found that differences between different alkyl ligands are not significant when compared with the overall level of accuracy of the additive model. Thus

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

TABLE 6

Analysis of experimental data

Data used to calculate parameters

Code no.†	Compound †	Refs.	Obs. QS ‡
(1)	Neo_3SnF	*a*	(−)2·79
(2)	Neo_3SnCl	*a*	(−)2·65
(3)	Neo_3SnBr	*a*	(−)2·65
(4)	Neo_3SnI	*a*	(−)2·40
(5)	$Neo_3Sn(MeCO_2)$	*a*	(−)2·45
(6)	$Me_3SnC_6F_5$	*d, u*	−1·35
(7)	$Me_3SnC_6Cl_5$	*d*	(−)1·09
(8)	Me_3SnCF_3	*d, y*	(−)1·48
(9)	$Me_3Sn(o\text{-}CF_3C_6H_4)$	*e*	(−)0·66
(10)	$(p\text{-}FC_6H_4)_3SnI$	*a*	(−)1·91
(11)	$Ph_3SnCo(CO)_4$	*f*	(−)1·00
(12)	$Cl_3SnMn(CO)_5$	*f, x, aa, dd*	+1·58
(13)	$ClSn[Re(CO)_5]_3$	*f*	(−)1·60
(14)	Ph_3SnCl	*b, c, cc*	−2·53
(15)	Ph_3SnBr	*b, c*	(−)2·50
(16)	$MeSn(C_6F_5)_3$	*q*	(+)1·14
(17)	$Ph_3SnC_6F_5$	*d, q, u*	−0·95
(18)	$[CpFe(CO)_2]SnCl_3$	*t, aa*	+1·82
(19)	$(C_6F_5)_3SnCl$	*r*	(−)1·55
(20)	$(C_6F_5)_3SnBr$	*r*	(−)1·60
(21)	$[CpFe(CO)_2]Sn(NCS)_3$	*t*	(+)2·24
(22)	$[CpFe(CO)_2]Sn(HCO_2)_3$	*t*	(+)1·45
(101)	$K_2[Me_2SnF_4]$	*b, u*	+4·12
(102)	$K_2[Et_2SnF_4]$	*b*	(+)4·44
(103)	$Cs_2[Me_2SnCl_4]$	*b, u*	+4·30
(104)	$(PyH)_2[Me_2SnCl_4]$	*h*	(+)4·32
(105)	$(Me_4N)_2[Et_2SnCl_4]$	*b*	(+)3·99
(106)	$Cs_2[Me_2SnBr_4]$	*b*	(+)4·22
(107)	$(PyH)_2[Ph_2SnCl_4]$	*h*	(+)3·80
(108)	Bu_2SnCl_2phen	*j*	(+)4·07
(109)	Me_2SnCl_2phen	*k*	(+)4·03
(110)	Me_2SnCl_2bipy	*k, gg*	(+)4·06
(111)	Bu_2SnCl_2bipy	*j*	(+)3·83
(112)	Bu_2SnI_2phen	*j*	(+)3·75
(113)	$Me_2SnCl_2(dmso)_2$	*g, ee*	(+)4·13
(114)	$Me_2SnCl_2(PyO)_2$	*g, bb*	+3·96
(115)	$Me_2SnCl_2Py_2$	*l, gg*	(+)3·92
(116)	$(edt)_2Sn(phen)$	*m, w*	(+)1·03
(117)	$(Me_4N)_2[(CH_2{:}CH)_2SnCl_4]$	*n*	(+)3·84
(118)	$Bu_2Sn(NCS)_2phen$	*i*	(+)4·18
(119)	$Et_2SnCl_2dipyam$	*o*	(+)3·78
(120)	$(Me_4N)_2[EtSnCl_5]$	*b, u*	+1·94
(121)	$(Et_4N)_2[BuSnCl_5]$	*p*	(+)1·86
(122)	$Bu_2Sn(pic)_2$	*z*	(+)4·35

Observed and predicted quadrupole splittings

Code no.†	Compound †	Refs.	QS ‡ Obs.	QS ‡ Calc.
(23)	Ph_3SnI	*b, c*	2·15	−2·18
(24)	$Ph_3SnC_6Cl_5$	*d*	0·84	−0·86
(25)	$(m\text{-}CF_3C_6H_4)_3SnBr$	*a*	1·94	−2·08 §
(26)	$(PhCH_2)_3SnCl$	*s*	2·80	−2·74 §
(27)	$PhSn[Co(CO)_4]_3$	*v*	1·28	+1·00
(28)	$Br_3SnMn(CO)_5$	*f, x, dd*	1·54	+1·58
(29)	$BrSn[Re(CO)_5]_3$	*f*	1·60	−1·60
(30)	$ClSn[Mn(CO)_5]_3$	*f*	1·55	−1·58
(31)	$Me_3SnMn(CO)_5$	*x, dd*	0·71	−1·16
(32)	$Me_2Sn[Mn(CO)_5]_2$	*x*	0·92	* 1·34
(33)	$MeSn[Mn(CO)_5]_3$	*x*	0·95	+1·16
(34)	$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	*f*	1·15	−1·12
(35)	$[Re(CO)_5][Mn(CO)_5]SnCl_2$	*f*	2·48	+1·84
(36)	$Ph_2Sn[Co(CO)_4]_2$	*f, v*	1·29	* 1·16
(37)	$Ph_2SnCl[Co(CO)_4]$	*f*	2·22	−2·38
(38)	$[CpFe(CO)_2]_2SnCl_2$	*t, aa*	+2·37	* 2·10
(39)	$[CpFe(CO)_2]_2SnBr_2$	*t*	2·42	* 2·10
(40)	$[CpFe(CO)_2]_2SnI_2$	*t*	2·25	* 1·71
(41)	$[CpFe(CO)_2]_2Sn(NCS)_2$	*t, aa*	+2·56	* 2·59
(42)	$[CpFe(CO)_2]_2Sn(HCO_2)_2$	*t*	2·19	* 1·69
(43)	$[CpFe(CO)_2]SnBr_3$	*t*	1·60	+1·82
(44)	$[CpFe(CO)_2]SnI_3$	*t*	1·50	+1·48
(45)	$[CpFe(CO)_2]Sn(MeCO_2)_3$	*t*	1·87	+1·52
(46)	$[CpFe(CO)_2]_2Sn(MeCO_2)_2$	*t*	2·60	* 1·76
(47)	$PhSn(C_6F_5)_3$	*q*	0·92	+1·12
(48)	$Ph_2Sn(C_6F_5)_2$	*q*	1·11	* 1·29
(49)	$Me_2Sn(C_6F_5)_2$	*q*	1·48	* 1·55
(50)	$Ph_2ISn(CH_2)_4SnIPh_2$	*n*	−2·37	−2·26
(123)	Me_2SnF_2	*g, ff*	4·38	+4·12 ‖
(124)	$(PyH)_2[PhSnCl_5]$	*h*	1·92	+1·90
(125)	Bu_2SnBr_2phen	*j*	3·94	+4·04 ‖
(126)	Bu_2SnBr_2bipy	*j*	3·95	+3·96 ‖
(127)	$Bu_2Sn(NCS)_2bipy$	*i*	4·04	+4·10 ‖
(128)	$Ph_2Sn(NCS)_2phen$	*i, u*	+2·35	−2·26 ¶
(129)	$Ph_2Sn(NCS)_2bipy$	*i*	2·13	See text
(130)	Ph_2SnCl_2bipy	*i, o*	3·45	+3·64 ‖
(131)	Ph_2SnBr_2bipy	*o*	3·52	+3·64 ‖
(132)	Ph_2SnI_2bipy	*o*	3·35	+3·36 ‖
(133)	$Ph_2SnCl_2dipyam$	*o*	3·58	+3·46 ‖
(134)	$Ph_2SnBr_2dipyam$	*o*	3·45	+3·46 ‖
(135)	$(edt)_2Sn(bipy)$	*m*	1·17	+0·96
(136)	$(edt)_2SnPy_2$	*m*	1·86	−1·84 ††
(137)	Ph_2SnCl_2phen	*i*	3·37	+3·72 ‖
(138)	Bu_2SnI_2bipy	*j*	3·82	+3·68 ‖
(139)	$Et_2SnBr_2dipyam$	*o*	3·64	+3·78 ‖
(140)	$Ph_2SnCl_2Py_2$	*o*	3·39	+3·61 ‖
(141)	$Ph_2SnBr_2Py_2$	*o*	3·49	+3·61 ‖
(142)	$(CH_2{:}CH)_2Sn(pic)_2$	*z*	4·02	+4·08 ‖
(143)	$Ph_2Sn(pic)_2$	*z*	1·94	−2·02 ‡‡
(144)	$Ph_2SnCl_2(dmso)_2$	*ee*	3·54	+3·82 ‖

† (1) to (50) tetrahedral; (101) to (144) octahedral; bipy = 2,2′-bipyridyl; Cp = π-cyclopentadienyl; dipyam = di-2-pyridylamine; dmso = dimethyl sulphoxide; pic = picolinate; Py = pyridine; PyH = pyridinium; PyO = pyridine *N*-oxide; Neo = 2-methyl-2-phenylpropyl; edt = 1,2-ethanedithio; phen = 1,10-phenanthroline. ‡ Units are mm s^{-1}. Observed values are unweighted averages, where appropriate, of measurements at or below 80 K. Predicted signs in parentheses, * indicates $\eta = 1$. See text for discussion of errors. § Assuming $[m\text{-}CF_3C_6H_4]^{tet} = [o\text{-}CF_3C_6H_4]^{tet}$ and $[PhCH_2]^{tet} = [Alkyl]^{tet}$. ‖ *trans*-(Hydrocarbon)$_2$. ¶ *cis*-Ph_2-*trans*-$(NCS)_2$. †† *trans*. ‡‡ *cis*.

[a] R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, 1965, **42**, 2447. [b] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65. [c] B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, 1969, **8**, 1120. [d] R. V. Parish and R. H. Platt, *J. Chem. Soc.* (*A*), 1969, 2145. [e] T. Chivers and J. R. Sams, *J. Chem. Soc.* (*A*), 1970, 577. [f] A. N. Karasyov, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. i eksp. Khim.*, 1966, **2**, 126. [g] A. G. Davies, L. Smith, and P. J. Smith, *J. Organometallic Chem.*, 1970, **23**, 135. [h] Ref. 1. [i] M. A. Mullins and C. Curran, *Inorg. Chem.*, 1968, **7**, 2584. [j] M. A. Mullins and C. Curran, *Inorg. Chem.*, 1967, **6**, 2017. [k] R. H. Herber, in ' Applications of the Mössbauer Effect in Chemistry and Solid-State Physics,' I.A.E.A., Vienna, 1966, 121. [l] K. M. Ali, D. Cunningham, M. J. Frazer, J. D. Donaldson, and B. J. Senior, *J. Chem. Soc.* (*A*), 1969, 2836. [m] R. C. Poller, J. N. R. Ruddick, and J. A. Spillman, *Chem. Comm.*, 1970, 680. [n] A. G. Maddock and R. H. Platt, *J. Chem. Soc.* (*A*), 1971, 1191; and unpublished data. [o] R. C. Poller, J. N. R. Ruddick, M. Thevarasa, and W. R. McWhinnie, *J. Chem. Soc.* (*A*), 1969, 2327. [p] N. W. S. Debye, E. Rosenberg, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 3234. [q] H. A. Stöckler and H. Sano, *Trans. Faraday Soc.*, 1968, **64**, 577. [r] M. Cordey-Hayes, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2306. [s] V. V. Khrapov, Candidate dissertation, Inst. of Chem. Phys., Acad. Sci. U.S.S.R., Moscow, 1965. [t] Ref. 22. [u] R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 1906. [v] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226. [w] L. M. Epstein and D. K. Straub, *Inorg. Chem.*, 1965, **4**, 1551. [x] C. Wynter and L. Chandler, *Bull. Chem. Soc. Japan*, 1970, **43**, 2115. [y] W. R. Cullen, J. R. Sams, and M. C. Waldman, *Inorg. Chem.*, 1970, **9**, 1682. [z] D. V. Naik and C. Curran, *Inorg. Chem.*, 1971, **10**, 1017. [aa] Ref. 23. [bb] B. W. Fitzsimmons, *J. Chem. Soc.* (*A*), 1970, 3235. [cc] B. A. Goodman and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1862. [dd] S. Onaka, Y. Sasaki, and H. Sano, *Bull. Chem. Soc. Japan*, 1971, **44**, 726. [ee] R. C. Poller, J. N. R. Ruddick, B. Taylor, and D. L. B. Toley, *J. Organometallic Chem.*, 1970, **24**, 341. [ff] R. H. Herber and S. Chandra, *J. Chem. Phys.*, 1970, **52**, 6045. [gg] M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1177.

all alkyl ligands may be assigned a single parameter, $[R]^{tet}$ or $[R]^{oct}$ according to structural type. For the same reason F, Cl, and Br may be assigned a single parameter, $[X]^{tet}$ or $[X]^{oct}$. Bearing these facts in mind, it was decided to concentrate on careful determinations of $[R]^{tet} - [X]^{tet}$, $[Ph]^{tet} - [X]^{tet}$, and $[R]^{oct} - [X]^{oct}$.

Values for these parameters have been calculated by taking unweighted averages of statistically independent estimates from several different sets of compounds believed to be relatively close to ideal geometry.*

TABLE 7

Calculation of partial field gradient parameters for key ligands

Parameter *	Estimator †	Estimate ‡	Mean value ‡
$[R]^{tet} - [X]^{tet}$	$+\frac{1}{2}QS(1)$	−1·40	−1·37 ± 0·06
	$+\frac{1}{2}QS(2)$	−1·33	
	$+\frac{1}{2}QS(3)$	−1·32	
	$+\frac{1}{2}[QS(6) + QS(19)]$	−1·45	
	$+\frac{1}{2}[-QS(16) + QS(20)]$	−1·37	
$[Ph]^{tet} - [X]^{tet}$	$+\frac{1}{2}QS(14)$	−1·27	−1·26 ± 0·01
	$+\frac{1}{2}QS(15)$	−1·25	
	$+\frac{1}{4}[2QS(17) + QS(19) + QS(20)]$	−1·26	
$[R]^{oct} - [X]^{oct}$	$-\frac{1}{4}QS(101)$	−1·03	−1·03 ± 0·06
	$-\frac{1}{4}QS(102)$	−1·11	
	$-\frac{1}{4}QS(103)$	−1·08	
	$-\frac{1}{4}QS(104)$	−1·08	
	$-\frac{1}{4}QS(105)$	−1·00	
	$-\frac{1}{4}QS(106)$	−1·05	
	$-\frac{1}{2}QS(120)$	−0·97	
	$-\frac{1}{2}QS(121)$	−0·93	

* R = alkyl; X = F, Cl, Br. † Code numbers refer to Table 6. ‡ Quantity tabulated is $\frac{1}{2}e^2|Q|([L] - [X])$ in units of mm s^{-1}.

The calculation is summarized in Table 7. Estimates listed in the third column of Table 7 are obtained by substituting values from Table 6 into the formulae given in the second column. Mean values and standard deviations[28] of the estimates are given in the fourth column.

Estimates of $[L] - [X]$ for the remaining ligands have been determined by the rather more subjective procedure of calculating a value from data on one or two compounds believed to be relatively close to ideal geometry. This is a compromise between the necessity to determine unbiased values at least for the key parameters which occur frequently, and the danger of using virtually all the data in the calculation of partial field gradient parameters, so that the analysis becomes no more than a slavish parameterization of the data.

The values for partial field gradient parameters obtained by these procedures are collected in Table 8. We use the term ' working values ' to indicate that the tabulated values are not in any sense the best possible values. Rather they are representative values, intended to facilitate semi-quantitative analysis of tin(IV) Mössbauer data. The uncertainty associated with these values is put on a numerical basis below.

TABLE 8

Working values for partial field gradient parameters in organotin(IV) compounds

Tetrahedral structures			Octahedral structures		
Ligand *	Data used †	Value ‡ (mm s^{-1})	Ligand *	Data used †	Value ‡ (mm s^{-1})
Alkyl	Table 7	−1·37	Alkyl	Table 7	−1·03
Ph	Table 7	−1·26	Ph	(107)	−0·95
I	(4)	−0·17	I	(112)	−0·14
NCS	(21)	+0·21	NCS	(118)	+0·07
$MeCO_2$	(5)	−0·15	½(phen)	(108), (109)	−0·04
C_6F_5	(6)	−0·70			
C_6Cl_5	(7)	−0·83	½(bipy)	(110), (111)	−0·08
CF_3	(8)	−0·63			
o-$CF_3C_6H_4$	(9)	−1·04	dmso	(113)	+0·01
p-FC_6H_4	(10)	−1·12	PyO	(114)	−0·08
$Co(CO)_4$	(11)	−0·76	Py	(115)	−0·10
$Mn(CO)_5$	(12)	−0·79	½(edt)	(116)	−0·56
$Re(CO)_5$	(13)	−0·80	$CH_2{:}CH$	(117)	−0·96
$CpFe(CO)_2$	(18)	−0·91	½(dipyam)	(119)	−0·17
HCO_2	(22)	−0·18	½(pic)	(122)	+0·06

* For ligand abbreviations see footnote to Table 6. † Code numbers refer to Table 6. ‡ Quantity tabulated is $\frac{1}{2}e^2|Q|([L] - [X])$, where X = F, Cl, Br.

Note that in Table 8, as in all *numerical* work in this paper, partial field gradients are measured in units of magnitude of quadrupole splitting, *i.e.* the tabulated quantities are actually $\frac{1}{2}e^2|Q|([L] - [X])$. It is important to bear this in mind when using algebraic equations in which Q appears explicitly. Note also[29] that the 23·9 keV state of ^{119}Sn has negative Q.

The compounds used in the calculations leading to Table 8 are listed on the left-hand side of Table 6. In many cases the sign of the quadrupole splitting has not been measured. Any ambiguities which arise from this may be resolved because the alternative partial field gradient parameter is either ridiculous or obviously fails to predict splittings in other compounds. The required choice of sign is noted in parentheses if no direct experimental confirmation is known to us.

The di-hydrocarbon octahedral compounds used in the calculation of parameters are all *trans*, as evidenced by their large quadrupole splittings. The parameter values obtained from $R_2SnCl_2L_2$ systems [(113), (114), and (115)] are independent of whether the *trans-trans-trans-* or the *trans-cis-cis-* isomer is involved, since $[L]^{oct} - [X]^{oct}$ is small in all three cases.

On the right-hand side of Table 6 quadrupole splittings

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* Recent suggestions [B. A. Goodman and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1862; J. Ensling, Ph. Gütlich, K. M. Hassellbach, and B. W. Fitzsimmons, *J. Chem. Soc.* (*A*), 1971, 1940] that Ph_3SnCl and Ph_3SnBr are trigonal-bipyramidal may be discounted. Goodman and Greenwood have apparently failed to note that both tetrahedral and trigonal-bipyramidal structures would give negative quadrupole splitting, and both papers underestimate the magnitude of the splitting predicted for tetrahedral Ph_3SnX. Tetrahedral co-ordination of Sn in Ph_3SnCl has been verified by *X*-ray crystallography (N. T. Bokii, G. N. Zakharova, and Yu. T. Struchkov, ***Zhur. strukt. Khim.***, 1970, **11**, 895).

[28] The standard deviations are calculated from the sample ranges; see D. V. Lindley and J. C. P. Miller, ' Cambridge Elementary Statistical Tables,' Cambridge University Press, 1961, Table 6.

[29] A. H. Muir, jun., K. J. Ando, and H. M. Coogan, ' Mössbauer Effect Data Index, 1958—1965,' Interscience, London, 1966, p. 126.

calculated from the parameters given in Table 8 are compared with observed splittings. The calculated magnitudes are unbiased in the sense that statistical testing[30] reveals no evidence that they systematically underestimate or overestimate the observed magnitudes. This confirms that representative values have been obtained at least for the parameters which occur most frequently.

The additive model is a satisfactory first approximation only if terms arising from non-additivity or distortions contribute no more than about 10—20% of the total field gradient. Thus we suggest that a discrepancy between observed and calculated quadrupole-splitting values should be considered exceptional if it exceeds about 0·4 mm s^{-1}. This figure corresponds to a numerical uncertainty in the partial field gradient parameters of about $\pm$0·2 mm s^{-1}, which, if interpreted as 3 standard deviations, is in agreement with Table 7.

Note that 0·4 mm s^{-1} is slightly more than three times the largest experimental errors (presumably standard deviations) reported in cases where spectra are not well-resolved. On the other hand it is often substantially less than the differences between the splittings predicted for different structures when the additive model is used to resolve questions of stereochemistry.

The proposed limit of $\pm$0·4 mm s^{-1} is intended as a maximum. If independent evidence of factors such as gross non-additivity or significant distortions from idealized geometry is available, more stringent limits might be appropriate.

Of the 28 tetrahedral compounds listed on the right-hand side of Table 6 only six [(31), (32), (35), (40), (42), and (46)] show a discrepancy between observed and calculated quadrupole splitting in excess of 0·4 mm s^{-1}. It is interesting to note that four of the six are SnA_2B_2 systems, and a fifth, (35), is quasi-SnA_2B_2. None of the 22 octahedral compounds listed shows a discrepancy greater than 0·4 mm s^{-1}, and only one, (137), shows a discrepancy greater than 0·3 mm s^{-1}.

The generally good agreement between observed and calculated splittings in Table 6 tends to support the notion that when serious disagreement is observed it is likely to arise from incorrect assignment of idealized geometry or distortions from that geometry. For example, in the trihalides $RSnX_3$ (R = Et, Ph; X = Cl, Br) the observed quadrupole splittings[2] are considerably less (0·7 mm s^{-1} or more) than the splittings calculated for tetrahedral structures, clearly indicating that these systems are not tetrahedral in the solid state.

For octahedral systems which have more than one geometrical isomer the calculated splitting listed in Table 6 is that of the structure which gives best agreement. Structures predicted in this way are recorded as footnotes to Table 6. These predictions should be considered in conjunction with the references cited in Table 6. In the present paper attention will be confined to operational points involved in application of the additive model to stereochemical problems; a detailed review will be given elsewhere.[31]

Compounds (128) and (129) illustrate two such points. First, if we consider only the magnitudes of the quadrupole splittings, (128) is clearly the *cis*-Ph_2-*trans*-$(NCS)_2$ isomer since a splitting of 1·94 mm s^{-1} is calculated for the *cis-cis-* isomer. However, in (129) the *cis-trans-* and *cis-cis-* isomers have calculated splittings of 2·34 mm s^{-1} and 1·91 mm s^{-1}, respectively. Since the observed splitting is 2·13 mm s^{-1} the additive model does not give an unambiguous prediction for the stereochemistry of (129). Second, it will be noted that the observed sign for the quadrupole splitting in (128) is positive, whereas the predicted sign is negative. This discrepancy has been observed[3,32] in several *cis*-(hydrocarbon)$_2$ octahedral systems, and is attributed to distortions from idealized geometry.[3,32] It has been argued[3] that the magnitude of the quadrupole splitting is only slightly affected by the distortion.

In the case of bidentate ligands with two different donor atoms, the partial field gradients associated with the two points of ligation might be different. However, if the two donor atoms are connected by a conjugated system then it is found that assigning the same partial field gradient parameter to both atoms is often a satisfactory empirical procedure. The picolinate complexes (122), (142), and (143) are cited as an example of this.

A simple perturbation calculation shows that η is relatively very sensitive to small low-symmetry terms in the electric field gradient. For this reason, even if experimental estimates of η were available they might not agree too well with the predictions of an additive model. This is particularly true for the predicted $\eta = 1$ in SnA_2B_2 systems (note the cusp in Figure 4).

The parameters listed in Table 8 may be used to test the prediction made above that $[L]^{oct}$ is about 70% of $[L]^{tet}$. From equations (8a) and (8b) it follows that

$$\frac{[L]^{oct} - [X]^{oct}}{[L]^{tet} - [X]^{tet}} = \frac{2}{3}\left(\frac{\sigma_L{}^{oct} - \sigma_X{}^{oct}}{\sigma_L{}^{tet} - \sigma_X{}^{tet}}\right) = r[L] \text{ (say)}$$

Values of $r[L]$ for L = alkyl, Ph, I, and NCS are 0·75 $\pm$ 0·06, 0·75 $\pm$ 0·07, 0·82 $\pm$ 0·51, and 0·33 $\pm$ 0·33, respectively. The errors cited are standard deviations calculated on the basis that an effective standard deviation of 0·067 mm s^{-1} can be assigned to all the parameters listed in Table 8. These values of $r[L]$ support our prediction, although $r[NCS]$ does seem curiously small.

Data from Table 8 may also be used to obtain a lower bound for Δ_0, the quadrupole splitting due to one electron in a $5p_z$ orbital. If the variation of $\langle r^{-3}\rangle_p$ with co-ordination number is ignored, then σ_L is equal to $2c_1{}^2$, and thus has a maximum value of 2. Hence, by equations (8a), (8b), and (10b),

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[30] N. Arley and K. R. Buch, 'Introduction to the Theory of Probability and Statistics,' J. Wiley, New York, 1950, section 11.14.

[31] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, to be published.

[32] B. A. Goodman, N. N. Greenwood, K. L. Jaura, and K. K. Sharma, *J. Chem. Soc.* (*A*), 1971, 1865.

$$\tfrac{1}{2}e^2Q[\max]^{\text{tet}} = -\tfrac{3}{10}e^2Q\langle r^{-3}\rangle_p = \tfrac{3}{4}\Delta_0 \qquad (14a)$$

and

$$\tfrac{1}{2}e^2Q[\max]^{\text{oct}} = -\tfrac{1}{5}e^2Q\langle r^{-3}\rangle_p = \tfrac{1}{2}\Delta_0, \qquad (14b)$$

where $|[\max]|$ is the maximum possible magnitude for a partial field gradient parameter ([L] is negative, of course). The range of values recorded in Table 8 for each structural type must be less than or equal to $|[\max]|$ for that structure. The range for tetrahedral structures is 1·58 mm s^{-1}, and that for octahedral structures 1·10 mm s^{-1}. These correspond to $\Delta_0 \geqslant$ 2·11 mm s^{-1} and $\Delta_0 \geqslant$ 2·20 mm s^{-1}, respectively. The equalities correspond to the unlikely situation in which the electrons in a Sn–alkyl bond are entirely on the tin, and those in a Sn–(NCS) bond entirely on the ligand. Thus we conclude that the quadrupole splitting due to one electron in a $5p_z$ orbital is greater than 2·20 mm s^{-1}.

Systems other than Tin(IV).—Additive models for the field gradient have also been used to interpret Mössbauer quadrupole-splitting data for octahedral complexes of low-spin Fe^{II} [4-6] (d^6), and tetrahedral complexes of Fe(−II) [7] (d^{10}). In this section the points involved in generalizing our model to systems other than Sn^{IV} will be illustrated briefly by a discussion of the Fe^{II} case.

The valence configuration of octahedral complexes of low-spin Fe^{II} is [33] $[a_{1g}(\sigma^b)]^2[t_{1u}(\sigma^b)]^6[e_g(\sigma^b)]^4[t_{2g}(\pi)]^6$. The σ molecular orbitals involve bonding between the metal $3d_\gamma + 4s + 4p$ orbitals and the ligand σ orbitals. They may be localized as a single set of equivalent orbitals based on d^2sp^3 metal hybrids. Thus the expression given in Table 1 for the partial field gradient in an octahedral structure applies directly, provided that the radial averages are interpreted as involving 3*d*, 4*s*, and 4*p* orbitals. If, as seems likely, $\langle r^{-3}\rangle_p$ and $\langle r^{-3}\rangle_{sd}$ are negligible compared with $\langle r^{-3}\rangle_d$, the contribution to the partial field gradient due to σ bonding is given by

$$[L]^\sigma = -\tfrac{2}{21}\langle r^{-3}\rangle_d \sigma_L^{\text{oct}}.$$

The parameter σ_L used by Bancroft *et al.*[5] is equal to $-\tfrac{3}{2}[L]^\sigma$.

Thus contributions to the total e.f.g. arising from σ molecular orbitals do not require any extension of our model. However, the $t_{2g}(\pi)$ molecular orbitals may involve bonding between the metal $3d_\epsilon$ orbitals and vacant π orbitals on the ligands. Therefore it is necessary to ask if it is possible to form π orbitals localized in the region of particular bonds.

In general a total of twelve (2 per M–L axis) localized π orbitals will be required. It may be shown that these twelve orbitals form a single equivalent set under the D_{3d} subgroup of O_h, and span the $T_{1g} + T_{1u} + T_{2g} + T_{2u}$ irreducible representations of O_h. Hence a suitable localization transformation exists only if the electronic configuration includes filled orbitals spanning all these representations. This condition is not satisfied in the case of low-spin Fe^{II} octahedrally co-ordinated by ligands with empty π orbitals. Thus it is not possible to write down localized π orbitals in a way which is general for the octahedral structure, and does not depend on the detailed stoicheiometry and stereochemistry of the particular complex.

The above argument does not preclude the possibility that contributions to the e.f.g. from $M \rightarrow L$ π bonds might be additive in special cases. It does mean that in the case of a π-acceptor ligand there is no obvious theoretical justification for writing the π-bonding contribution to the total e.f.g. as a partial field gradient parameter which is completely independent of the other ligands in the complex.

Note that the model of Bancroft *et al.*[5] gives no information on this point, because the additive approximation is implicit in the initial formulation of the model.

The situation for Fe^{II} should be contrasted with the case of a d^0 complex containing ligands with filled π orbitals. The filled π molecular orbitals span $T_{1g} + T_{1u} + T_{2g} + T_{2u}$ under O_h. Hence there exists a transformation to equivalent orbitals which yields a set of π orbitals, each localized mainly (though not entirely) in the region of a particular metal–ligand bond. Thus in the case of octahedral Sn^{IV}, even if the empty metal $5d_\epsilon$ orbitals were involved in π bonding with filled ligand orbitals it would still be possible to define partial field gradient parameters. However, the π contributions would involve $\langle r^{-3}\rangle_d$, which was calculated to be only about 1% of $\langle r^{-3}\rangle_p$ for tin (see above).

The considerations outlined in this section may be formalized in the conjecture, mentioned above, that the existence of a suitable localization transformation is a necessary condition for additivity.

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[33] Our notation is that of C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' W. A. Benjamin, New York, **1964**, ch. 8; see also Fig. 2 of H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **1963**, **85**, 2922, or Fig. 26-30 of F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Interscience, London, **1966**.