Mössbauer Effect Study of the Electric Field Gradient Tensor at the Tin Atom in [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$]

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The asymmetry parameter, η, of the electric field gradient tensor at a tin atom has been determined for the first time: application of a 50 kG magnetic field at 4·2 K to the diamagnetic complex [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$] led to a value of $\eta = 0{\cdot}65 \pm 0{\cdot}05$. Use of an oriented matrix of single crystals in a zero-field experiment at 78 K then established that the direction of V_{zz} was at 48° to the *bc* plane of the crystal. The results imply that $\langle\psi|(3\cos^2\theta - 1)r^{-3}|\psi\rangle$ is greater for the Sn–Fe bonds than for the Sn–Cl bonds and that there is therefore less withdrawal of tin 5*p*-electron density into the Sn–Fe bonds than into the Sn–Cl bonds.

THE electric field gradient tensor at a Mössbauer nucleus can be studied *via* the nuclear quadrupole interaction. However, it is not possible to deduce all the parameters describing the tensor from line positions alone when the Mössbauer transition involves nuclear spin states of $\frac{1}{2}$ and $\frac{3}{2}$; in this instance the pure quadrupole spectrum consists of a simple doublet with separation $\Delta = \frac{1}{2}e^2qQ(1 + \frac{1}{3}\eta^2)^{\frac{1}{2}}$ where $-eq\ (= -V_{zz})$ is the principal value of the tensor, Q is the nuclear quadrupole moment, and η is the asymmetry parameter defined by equations (1) and (2). The electric field gradient tensor can,

$$\eta = (V_{xx} - V_{yy})/V_{zz} \qquad (1)$$

$$|V_{zz}| > |V_{yy}| > |V_{xx}| \qquad (2)$$

however, be studied in detail when the resonant nucleus shows combined magnetic–quadrupole hyperfine interactions,[1] or can be selectively oriented in a single crystal.[2] Unfortunately, the diamagnetism of all organotin compounds coupled with the paucity of detailed crystal structures and the general difficulty in producing even small single crystals, has militated against detailed electric field gradient tensor studies by use of the ^{119}Sn resonance. Comparatively recently a third method, which involves the application of a large external magnetic field to perturb the quadrupole interaction, has been used to determine the sign of V_{zz} in tin compounds,[3-5] and an increasing number of investigations are making use of this technique.[6-8] It was found that the magnetically perturbed spectra are often insensitive to small values of η,[5] and in the absence of *X*-ray structural data the possibility of distortion from a nominally regular geometry with zero η cannot be eliminated by this method. Consequently the quadrupole interaction alone is not a reliable guide to the stereochemistry. In an earlier paper we reported measurements of the sign of V_{zz} in a number of tin–transition metal compounds.[9] The magnetically perturbed ^{119}Sn spectra of two of these compounds, [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$] and [{Fe(π-$C_5H_5$)$(CO)_2$}$_2Sn(NCS)_2$], showed substantial deviations from prediction, which were thought to be due to a large asymmetry parameter. In this paper we report a more detailed study of [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$] to determine the asymmetry parameter, and discuss its significance in the light of the known crystal structure.[10]

RESULTS AND DISCUSSION

The spectrum of [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$] in a 50 kG field at 4·2 K was obtained by techniques described elsewhere,[9] and is shown in Figure 1 together with a number of computed spectra for different values

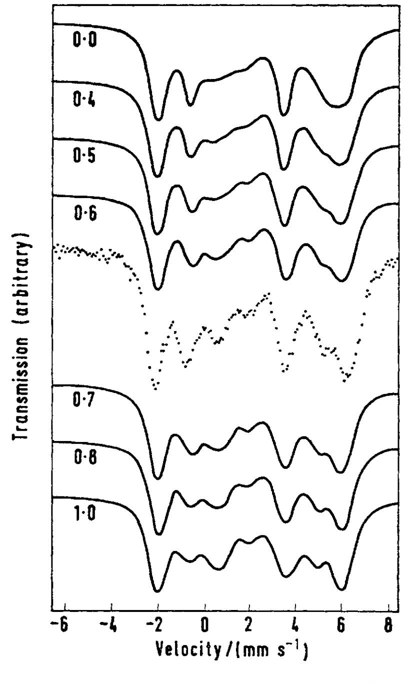

FIGURE 1 The Mössbauer spectrum of [{Fe(π-C_5H_5)$(CO)_2$}$_2$$SnCl_2$] at 4·2 K with a magnetic field of 50 kG applied perpendicular to the direction of observation. The solid curves are computed spectra for a range of values of the asymmetry parameter η. The experimentally determined value is $\eta = 0{\cdot}65 \pm 0{\cdot}05$

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of the asymmetry parameter.[5] The slight deviation from mirror symmetry about the centroid velocity for $\eta = 1{\cdot}0$ is a measure of the computational error in summing a large number of asymmetric spectra, and can only be reduced by a prohibitive increase in the total computing time. The zero-field spectrum at 4·2 K gave $\Delta = 2{\cdot}35$ mm s^{-1} and a chemical isomer shift of $+1{\cdot}98$ mm s^{-1} with respect to barium stannate.[9] The area ratio of the two peaks was 0·97, there being no substantial deviation due to the Karyagin effect or to preferential orientation.

Careful examination of Figure 1 gives an experimental value for η of $0{\cdot}65 \pm 0{\cdot}05$. We now combine this with the known molecular geometry for a detailed discussion of the electric field gradient tensor and the chemical bonding.

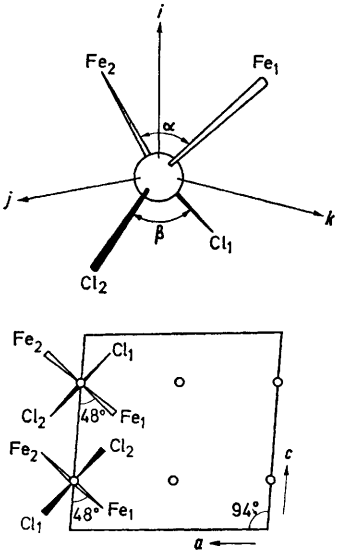

FIGURE 2 The molecular geometry of the $SnFe_2Cl_2$ unit in $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2SnCl_2]$ and the two possible orientations in the crystal unit cell

The method used to estimate the electric field gradient tensor has been outlined for iron by Mazak and Collins.[11] Their calculations for covalent, diamagnetic, pseudotetrahedral FeA_2B_2 compounds are directly applicable to the tin electric field gradient. Such an approach is usually referred to as a point-charge treatment, and has been widely used for covalently bonded compounds in a variety of geometries (*cf.* for iron [12] and for tin [13,14]). If we consider that the primary asymmetry in the tin electronic environment is caused by chemical bonding to the ligands, it is possible to represent the contribution of each σ-bonding electron pair to the electric field gradient tensor ($E_{zz} = -V_{zz}$) by an expectation value of the form $V_{zz} = -e\langle\psi|(3\cos^2\theta - 1)r^{-3}|\psi\rangle$, where z defines the axis of the bond. This representation is also adequate for axially symmetric π-bonding. For a $5p_z$ orbital the principal value V_{zz} is $-\frac{4}{5}e\langle r^{-3}\rangle$, and since the quadrupole moment of ^{119}Sn is negative in sign the quadrupole coupling constant e^2qQ is positive (in the following discussion we shall take e to be the charge on the proton so that V_{zz} is negative when e^2qQ is positive).

The molecular symmetry at the tin in $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2SnCl_2]$ is accurately C_2, and the geometry is illustrated in Figure 2. The FeSnFe plane is perpendicular to the ClSnCl plane, and consideration of the general electric field gradient tensor for this geometry confirms that two of the principal axes, arbitrarily labelled i and j, lie in these planes, the former bisecting the FeSnFe bond angle, α.

We denote the expectation value $-e\langle\psi|(3\cos^2\theta - 1)r^{-3}|\psi\rangle$ for the Sn–Fe bond as [Fe] and for the Sn–Cl bond as [Cl]. Note that both these quantities are negative in sign as they are defined on the individual bond axis.

The principal values of the electric field gradient tensor can now be evaluated and provide the relationships (3)—(5). These comprise V_{zz}, V_{yy}, and V_{xx}, but

$$V_{ii} = 2\left(3\cos^2\frac{\alpha}{2} - 1\right)[\mathrm{Fe}] + 2\left(3\cos^2\frac{\beta}{2} - 1\right)[\mathrm{Cl}] \qquad (3)$$

$$V_{jj} = -2[\mathrm{Fe}] + 2\left(3\sin^2\frac{\beta}{2} - 1\right)[\mathrm{Cl}] \qquad (4)$$

$$V_{kk} = 2\left(3\sin^2\frac{\alpha}{2} - 1\right)[\mathrm{Fe}] - 2[\mathrm{Cl}] \qquad (5)$$

not necessarily in that order. The detailed crystal structure of the compound gives $\alpha = 128{\cdot}6°$ and $\beta = 94{\cdot}1°$, whence we obtain equations (6)—(8). These

$$V_{ii} = -0{\cdot}8714[\mathrm{Fe}] + 0{\cdot}7858[\mathrm{Cl}] \qquad (6)$$

$$V_{jj} = -2[\mathrm{Fe}] + 1{\cdot}2142[\mathrm{Cl}] \qquad (7)$$

$$V_{kk} = +2{\cdot}8714[\mathrm{Fe}] - 2[\mathrm{Cl}] \qquad (8)$$

equations have been numerically evaluated in the range $0 < R < \infty$ where $R = [\mathrm{Fe}]/[\mathrm{Cl}]$ to determine the directions of the principal axes. The direction of V_{zz} proves to depend on the ratio R as given in the Table, and can adopt any of the three axes. The sign of V_{zz} also alters, and η shows a complex behaviour.

The dependence of the electric field gradient tensor on [Fe]/[Cl]

[Fe]/[Cl] = R	V_{zz}	V_{yy}	V_{xx}	Sign (V_{zz})
$0 < R < 0{\cdot}380$	k	j	i	+
$0{\cdot}380 < R < 0{\cdot}607$	k	i	j	+
$0{\cdot}607 < R < 0{\cdot}659$	i	k	j	−
$0{\cdot}659 < R < 0{\cdot}696$	i	j	k	−
$0{\cdot}696 < R < 0{\cdot}744$	j	i	k	+
$0{\cdot}744 < R < 0{\cdot}904$	j	k	i	+
$0{\cdot}904 < R$	k	j	i	−

To give an 'order of magnitude' to V_{zz} we have assumed that $|[\mathrm{Fe}] + [\mathrm{Cl}]| = 1$, and the resultant

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

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behaviour of ' V_{zz} ' and η is shown in Figure 3. It is rather unexpected to find no less than six values for [Fe]/[Cl] which will give $\eta = 0{\cdot}65$. The experimentally determined sign of e^2qQ is positive (*i.e.*, V_{zz} is negative), thereby eliminating three of the values and restricting the direction of V_{zz} to either the i or the k axis. The five values of R lying between 0·58 and 0·82 all correspond to small values of ' V_{zz} ', but in the absence of any comparative data on the magnitude it was deemed prudent to seek additional evidence to support the more likely value of $R = 1{\cdot}2$.

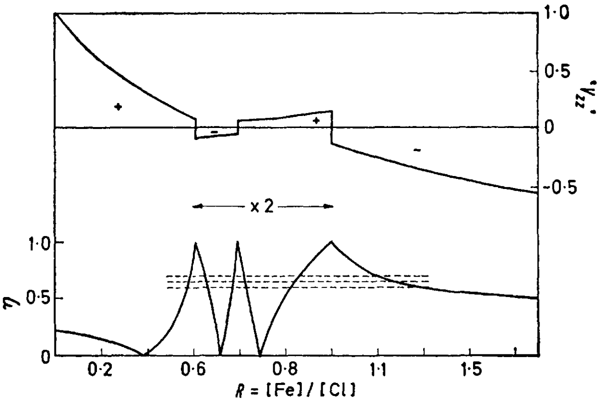

FIGURE 3 The dependence of the asymmetry parameter η and the arbitrarily normalised value of V_{zz} which is denoted by ' V_{zz} ' on R = [Fe]/[Cl]. Note the expanded horizontal scale in the centre

It was observed that $[\{Fe(\pi\text{-}C_5H_5)(CO)_2\}_2SnCl_2]$ could be crystallised from methanol in flat-sided needles several millimetres long. *X*-Ray diffraction confirmed that the crystals could be aligned on the ' *ab* ' plane. A Mössbauer absorber was made by hand-picking sufficient crystals to create a composite matrix with their ' *ab* ' planes in the plane of the absorber and the ' *b* ' axis at right angles to the γ-ray direction. A simplified projection of the crystal unit cell on the ' *ac* ' plane showing the two possible arrangements of the molecule is shown in Figure 2. They are related by a 180° rotation about the k axis.

In the event that the k axis is the major axis of the electric field gradient tensor, V_{zz} is at 44° to the direction of the γ-rays for all molecules. If the i axis is the major axis, then V_{zz} is at 90° to the γ-ray direction for all molecules. Single-crystal spectra for the cases (i)—(iii)

(i) $|V_{ii}| > |V_{kk}| > |V_{jj}|$
(ii) $|V_{ii}| > |V_{jj}| > |V_{kk}|$
(iii) $|V_{kk}| > |V_{jj}| > |V_{ii}|$

were calculated by use of the known values for e^2qQ and η and the appropriate Euler angles to give the correct orientation. Facility for making these calculations is included in the more general computer programme.[5] The ratios obtained for the intensity of the line at lower velocity to that at higher velocity were (i) 1·63, (ii) 1·59, and (iii) 0·89. Since any misorientation of crystallites was likely to have occurred on to the ' *bc* ' plane, these three possibilities were also calculated and gave (i) 1·67, (ii) 1·56, and (iii) 0·84. The values are similar because V_{zz} orients at 48 or 90° to the γ-ray direction in an analogous manner to the previous case, and misorientation was not considered to be a serious problem in this experiment.

The spectrum obtained with the oriented crystallite absorber at 78 K is shown in Figure 4. A computer fit of two Lorentzian lines gave a chi-squared value of 274 on 304 degrees of freedom, and the intensity ratio (by area) of the lines is 0·84 compared with 0·97 for the polycrystalline sample. There is therefore a clear differentiation between cases (i) and (ii) on the one hand and the experimentally verified case (iii). The result is a value for [Fe]/[Cl] of 1·2 ± 0·1, for $\eta = 0{\cdot}65 \pm 0{\cdot}05$, and a positive value of e^2qQ (V_{zz} negative). V_{zz} is oriented at 48° to the ' *bc* ' plane of the crystal.

The experimental results conclusively show that the value of $\langle r^{-3} \rangle$ is greater for the Sn–Fe bond than for the Sn–Cl bond. This is consistent with our interpretation of the Mössbauer spectra of a series of tin–transition metal compounds by a more empirical approach,[9] and shows that the more electronegative halogen atoms withdraw a greater proportion of 5p-electron density from the tin atom.

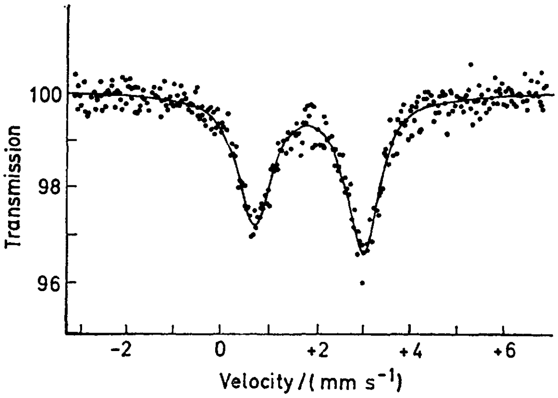

FIGURE 4 The Mössbauer spectrum at 78 K of an oriented crystallite absorber matrix with the direction of observation normal to the ' *ab* ' planes of the crystallites

We acknowledge financial support from the S.R.C.

[1/768 *Received, May* 14*th*, 1971]