The Mössbauer Effect of ^{119}Sn in the Dimethylbis(8-quinolinolato)-tin(IV) Single Crystal

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Synopsis. The Mössbauer absorption spectrum of ^{119}Sn in the single crystal of dimethylbis(8-quinolinolato)tin(IV) was studied by an intensity-tensor method. The orientation of the principal axes of the electric-field gradient (EFG) was discussed from the point of view of point-charge formalism.

For the octahedral coordination, all the signs of V_{zz}, the principal component of EFG, are in good agreement with those to be expected from the point-charge formalism with the exception of the *cis* configuration.[1–4] From the magnetic perturbation study of a powder sample of dimethylbis(8-quinolinolato)tin(IV), $\mathrm{Sn(Me)_2(oxin)_2}$, which has a distorted *cis*-octahedral configuration, Parison and Johnson[4] have proposed that this inconsistency comes from a deviation from a regular octahedral geometry. The sign of V_{zz} as well as the orientation of the EFG axes can be inferred from the single crystal absorption spectra.[5–10] The purpose of the present study is to examine their proposition in more detail by means of Mössbauer experiments on the single crystal of $\mathrm{Sn(Me)_2(oxin)_2}$. The method employed here was first suggested by Zimmermann and applied by him to $\mathrm{FeCl_2 \cdot 4H_2O}$,[11] and recently it has also been applied to $\mathrm{Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$.[12] It is based on the fact that the quadrupole line intensities can be characterized by means of an intensity tensor.

Crystal Structure and Experimental

$\mathrm{Sn(Me)_2(oxin)_2}$ has monoclinic symmetry, and its space group is $P2_1/c$.[13] The dimensions of the unit cell are a=9.44, b=13.28, and c=15.67 Å, with β=110.0°. A unit cell consists of four $\mathrm{Sn(Me)_2(oxin)_2}$ molecules, as is shown in Fig. 1. These four molecules can be grouped into two sites, I and II, with different orientations of the EFG relative to the crystal axes. The symmetry relation between Site I and Site II is a 180° rotation about the b axis.

A single crystal of the complex was cut parallel to the 001 plane, and a crystal plate of *ca.* 13×8 mm^2 was polished to a thin plate, the surface density of which was 27.5 mg of Sn per cm^2. The Mössbauer spectra were obtained in the manner described in our previous paper,[10] except that the absorber was kept at 110 K and the source was $\mathrm{Ca^{119m}SnO_3}$.

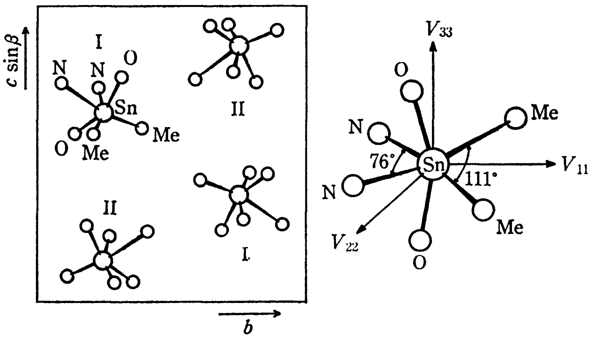

Fig. 1. The molecular geometry of the $\mathrm{SnMe_2N_2O_2}$ unit in dimethybis(8-quinolinolato)tin(IV) and the orientations in the unit cell.

Results and Discussion

A typical Mössbauer spectrum with computer-fitting Lorenzian curves is shown in Fig. 2. The parameters obtained from these spectra are presented in Table 1. In the table, the values of A^h/A^{tot}, the intensity of the higher energy peak line divided by the total intensity, were obtained from the observed spectra, whereas those of I^h/I^{tot} were calculated from Eq. 1 using a recoilless fraction of f'=0.11, estimated from powder samples:

$$\frac{A^h}{A^{tot}}-\frac{1}{2}=F\left(\frac{I^h}{I^{tot}}-\frac{1}{2}\right) \qquad (1)$$

where $F=[1+0.125T_a(1-4a^2)]^{-1}$, with $T_a=nf'\sigma_0$, the effective thickness of absorber, and $a=I^h/I^{tot}$.

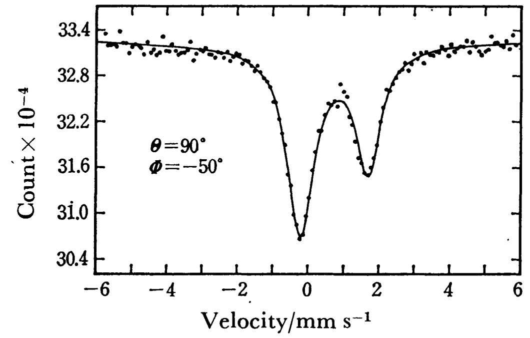

Fig. 2. Mössbauer absorption spectrum of dimethylbis-(8-quinolinolato)tin(IV) single crystal at 110 K. The γ-ray is in the pq plane and −50° from the p axis.

Table 1. Experimental parameters for $\mathrm{Sn(Me)_2(oxin)_2}$

$\Theta^{a)}$ / deg.	$\Phi^{a)}$ / deg.	A^h/A^{tot}	I^h/I^{tot}
90	−50	0.391±0.012	0.356±0.015
90	−40	0.390±0.011	0.360±0.014
90	−30	0.403±0.014	0.379±0.016
90	−20	0.426±0.015	0.409±0.018
90	−10	0.470±0.015	0.464±0.019
90	0	0.504±0.014	0.505±0.017
90	10	0.545±0.014	0.556±0.018
90	20	0.570±0.014	0.586±0.017
90	30	0.583±0.012	0.604±0.014
90	50	0.589±0.010	0.618±0.013

a) The polar angles of the γ-ray relative to $\mathrm{O_{pqr}}$.

Since the crystal axes, a, b, and c, are not orthogonal with each other, a orthogonal system, $\mathrm{O_{pqr}}$, is introduced. The base vectors, $\boldsymbol{p}$, $\boldsymbol{q}$, and $\boldsymbol{r}$, are parallel to $\boldsymbol{a}\times\boldsymbol{b}$, $\boldsymbol{a}$, and $\boldsymbol{b}$ respectively. The components of the

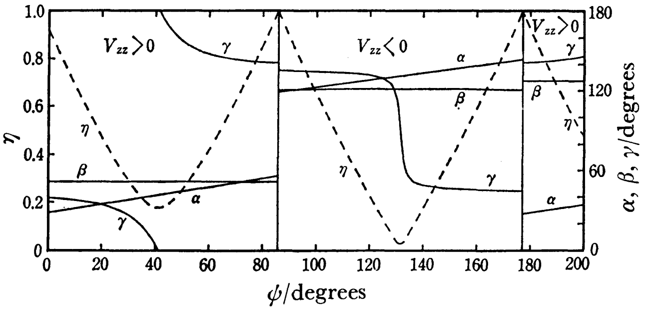

Fig. 3. Sign of V_{zz}, α, β, γ, and η as a function of the parameter ψ.

macroscopic-intensity tensor obtained by a least-squares analysis from the data of Table 1 are $I^{m}_{pp}=0.005\pm0.002$, $I^{m}_{qq}=-0.029\pm0.006$, $I^{m}_{rr}=0.024\pm0.006$, $I^{m}_{pq}=0.133\pm0.002$, and $I^{m}_{pr}=I^{m}_{qr}=0$. The observable tensor thus has monoclinic symmetry, and two components of the local site tensor are not recorded. However, the introduction of an unknown parameter, ψ (see Ref. 11 for the definition), makes it possible to represent the local intensity tensor. Figure 3 shows the values of the asymmetry parameter (η) and the Euler angles (α, β, γ), designating the orientation of the principal-axes system of EFG relative to O_{pqr}, as a function of the ψ angle. Although the values of ψ are restricted to $0°\leqslant\psi\leqslant200°$, the solutions for $\pi\leqslant\psi\leqslant2\pi$ are obtained by the following transformation from those for $0\leqslant\psi\leqslant\pi$:

$$\eta\rightarrow\eta,\ (\alpha,\beta,\gamma)\rightarrow(\alpha,\pi-\beta,\pi-\gamma)\ \text{for}\ \psi\rightarrow\pi+\psi.$$

From the point-charge model for *cis*-R_2SnX_4 structures, it is expected that, for bond angles of R–Sn–R greater than the tetrahedral angle (109.5°), V_{zz} lies on the R–Sn–R plane, and is normal for a bisector of the R–Sn–R, and has the sign opposite to that expected for a regular *cis* geometry, *i.e.*, a negative sign.[4)]

Although the 2Me, 2N, and Sn of the complex are not on a common plane, the local symmetry about the tin in $Sn(Me)_2(oxin)_2$ is approximately C_{2v}. We take an unweighted least-squares plane through the four ligand atoms (2Me and 2N) for the Sn atom as the Me_2SnN_2 plane and define V_{11} as the field gradient in the direction of the bisector of projection which two Sn–Me bonds form on the plane, and V_{33}, as that in the normal direction of the plane (see Fig. 1). The direction of V_{22} is normal with regard to V_{11} and V_{33}. The Me–Sn–Me angle is opened out to 111°, so that V_{zz} can be expected to coincide with V_{22}. However, the uncertainty as to the directions of V_{xx} and V_{yy} remains.

We shall refer only to the I site in the following discussion. Two possible cases are considered:

$$V_{xx}//V_{11},\ V_{yy}//V_{33},\ \text{and}\ V_{zz}//V_{22} \qquad \text{(i)}$$

$$V_{xx}//V_{33},\ V_{yy}//V_{11},\ \text{and}\ V_{zz}//V_{22} \qquad \text{(ii)}$$

The Euler angles for (i) and (ii) are $\alpha=93°$, $\beta=128°$, and $\gamma=135°$ and $\alpha=93°$, $\beta=128°$, and $\gamma=45°$ respectively (the corresponding values for the II site are obtained by the transformation of $(\alpha,\beta,\gamma)\rightarrow(\alpha,\pi-\beta,\pi-\gamma)$ in each case). Though the point symmetry of the tin sites imposes no restrictions on η, the value of η is expected to be large judging from the point-charge model (*cf.* Fig. 3 in Ref. 4). This value is seen, along with the values of α, β, and γ, in the $V_{zz}<0$ range in Fig. 3. The solutions for $86°\leqslant\psi\leqslant132°$ correspond to (i), and those for $132°\leqslant\psi<177°$, to (ii). The α values in the range of the former are closer to 93° than those of the latter. This suggests that the direction of the principal axes of the EFG may be as in Case (i). If η is found by an additional investigation, as in the case of $FeCl_2\cdot4H_2O$,[11)] the precise orientation of the EFG axes can be established.

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