# Mössbauer Spectroscopic Studies of Trialkyl- and Triaryltin Complexes of Transition Metal Cyanides

Motomi KATADA,* Yoshio UCHIDA, Kumiko IWAI, Hirotoshi SANO,
Hiroshi SAKAI,† and Yutaka MAEDA†
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukasawa, Setagaya-ku, Tokyo 158
†Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-04
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The structural diagnosis and lattice dynamics of three complexes, $\{[R_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$ (R=Me, Bu(*n*-Bu), or Ph), $\{[R_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$ (R=Me, Bu, or Ph), and $\{[R_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$ (R=Bu or Ph) have been undertaken by means of $^{57}$Fe-, $^{119}$Sn-, and $^{197}$Au-Mössbauer spectroscopic techniques. The Mössbauer parameters for the complexes indicate that all the tin atoms are coordinated with three alkyl or aryl groups and two cyano groups having a trigonal-bipyramidal structure. The asymmetry of the quadrupole split-peak intensity observed in the $^{119}$Sn-Mössbauer spectra for the complexes was attributed to the anisotropic mean square vibrational amplitude with respect to a molecular symmetry axis. The temperature dependence of the recoil-free fraction of the $^{119}$Sn-Mössbauer atom shows that the mean-square vibrational amplitude of tin atoms in the complexes falls in the range of values found for a number of one-dimensional organotin polymers. In $^{57}$Fe-Mössbauer spectroscopy, the quadrupole splitting for $\{[Bu_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$ rapidly decreases with an increase in the temperature, reflecting small separations among the three $d_\varepsilon$ levels in energy. The very large $^{197}$Au-quadrupole splitting for $\{[R_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$ was explained by assuming strong $\sigma$-donating and $\pi$-accepting properties of the CN ligand.

Recently, Uson et al. synthesized various kinds of trialkyl- and triaryltin complexes of transition metal cyanides by treating the trialkyl- or triaryltin perchlorates with several cyano compounds of transition metals.[1] If the reaction with anionic dicyano compounds, such as $K[Au(CN)_2]$ and $Bu_4N[Ag(CN)_2]$, is carried out, the reaction products can be expected to have an infinite one-dimensional polymeric structure. On the other hand, the reaction with the square-planar coordinated palladium or platinum cyanides can be expected to give polymer complexes which are assumed to have an infinite two-dimensional structure. In the case of the reaction with $K_3[Fe(CN)_6]$, three-dimensional polymer products will be obtained.

On the basis of the IR spectra of those complexes, Uson et al. proposed that, in every case, the tin atoms are five-coordinated with three alkyl or aryl groups in the equatorial position and two cyano groups in the axial position of a trigonal-bipyramidal and that the tin and the transition metal are bridged by a cyano group.

Mössbauer spectroscopy can provide valuable information about the nature of chemical bonding and the structures of compounds containing "Mössbauer-active atoms," such as tin, iron, and gold, because Mössbauer parameters are very sensitive to the number and nature of ligands coordinated to the Mössbauer atoms.[2-4] Especially, $^{197}$Au-Mössbauer spectroscopy is one of the most powerful techniques in the structural diagnosis of the gold compounds. In the present study, $^{57}$Fe-, $^{119}$Sn-, and $^{197}$Au-Mössbauer spectroscopic studies have been undertaken in order to examine the coordination for the iron, tin, and gold atoms and to elucidate the lattice dynamical properties of tin and iron sites in the trialkyl- and triaryltin complexes of transition metal cyanides, such as $\{[R_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$ and $\{[R_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$ (R=Me, Bu, or Ph), and $\{[R_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$ (R=Bu or Ph).

## Experimental

**Materials.** All the complexes investigated were prepared by the following method, described in a reference.[1] Organotin perchlorates $R_3SnClO_4$ (R=Me, Bu, or Ph) were prepared in acetone by treating stoichiometric amounts of the corresponding organotin chloride, $R_3SnCl$, with $AgClO_4$. The filtrate was used for further reactions without any other treatment. The $\{[R_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$ complexes (R=Me, Bu, or Ph) were obtained by treating a solution of $K[Au(CN)_2]$ (3 mmol) in acetone with an equimolar amount of $R_3SnClO_4$. The precipitates were filtered off and washed with a mixture of water and acetone. The $\{[R_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$ (R=Me, Bu, or Ph) complexes were prepared by the same procedure using 3 mmol of $K_2[Pt(CN)_4]$ and 6 mmol of $R_3SnClO_4$. The precipitates were washed with acetone and then hexane. The $\{[R_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$ (R=Bu or Ph) complexes were also prepared as has been described above by treating 3 mmol of $K_3[Fe(CN)_6]$ with 9 mmol of $R_3SnClO_4$. The products were washed with acetone. The purity of the complexes was confirmed by elemental analyses for C, H, and N.

**Mössbauer Spectroscopic Measurements.** The temperature-dependent Mössbauer-effect measurements for $^{57}$Fe and $^{119}$Sn were carried out by using a constant-acceleration-type spectrometer over the temperature range of 78 K$\leq T\leq$300 K. Most of the $^{119}$Sn-Mössbauer spectroscopic measurements were carried out from 78 to about 200 K, since the recoil-free fraction of the complexes becomes too small to be measured at high temperatures. The temperature of the absorber was controlled within $\pm$0.5 K. $^{197}$Au-Mössbauer spectroscopic measurements were carried out with a source and an

absorber, both cooled to 16 K by using a constant-acceleration-type spectrometer in connection with a pure-Ge diode detector. The details of the $^{197}$Au-Mössbauer spectroscopy have been described elsewhere.[5]

The spectra observed were fitted with Lorentian-line shapes by using the least-squares fitting procedure. The velocity scale was calibrated by using a metallic iron-foil spectrum. The isomer shifts of the $^{57}$Fe and $^{119}$Sn spectra are reported with respect to $\alpha$-Fe and $BaSnO_3$ resonances respectively at room temperature. All the isomer shifts of the $^{197}$Au-Mössbauer spectra are referred to metallic gold at 16 K.

## Results and Discussion

**$^{119}$Sn-Mössbauer Spectra.** Some typical $^{119}$Sn-Mössbauer spectra obtained at 78 K are shown in Fig. 1 for $\{[R_3Sn](\mu\text{-CN})[Au(\mu\text{-CN})]\}_x$ (R=Me, Bu, or Ph), while the Mössbauer parameters, such as the isomer shift (*IS*), the quadrupole splitting (*QS*), and the half-width ($\Gamma_{exp}$), derived from the observed spectra are summarized in Table 1. The spectra observed consist of one doublet with relatively large *QS* values, as may be seen in Fig. 1.

In $^{119}$Sn-Mössbauer spectroscopy, the major variation in the *QS* values observed can be attributed to the difference in the structural change. The range of *QS* values for organotin compounds can be classified into the following four groups:[6] 1) tetrahedral $R_nSnX_{4-n}$ ($n$=1—3) [0.00—2.31 mm s$^{-1}$], 2) octahedral *cis*-$R_2SnX_4$ [1.63—2.34 mm s$^{-1}$], 3) trigonal-bipyramidal $R_3SnX_2$ (X axial) [2.76—3.86 mm s$^{-1}$], and 4) octahedral *trans*-$R_2SnX_4$ [3.37—4.32 mm s$^{-1}$]. On the basis of this criterion, the tin atoms in the complexes under discussion can be concluded to have a five-coordinated structure, in which the tin atom is bridged by a CN group. This result is in good agreement with the hypothetical conclusion proposed by Uson et al.[1] for the coordination state of tin atoms in the same compounds.

The *QS* values for $Ph_3Sn$ derivatives are smaller than those of the corresponding $Me_3Sn$ or $Bu_3Sn$ derivatives. The decrease in the *QS* values for the $Ph_3Sn$ derivatives can be explained by the greater partial *QS* value assigned to the phenyl group compared to that of the alkyl group. The same tendency was observed for various kinds of organotin compounds containing the phenyl group.[6]

The temperature dependence of the quadrupole splitting is negligible in every case, since the *QS* for organotin(IV) compounds arises from mainly an inequality in the nature of the tin-ligand bonds, which is temperature-independent. However, the intensity asymmetry of the quadrupole line and its temperature dependence were observed, as is shown in

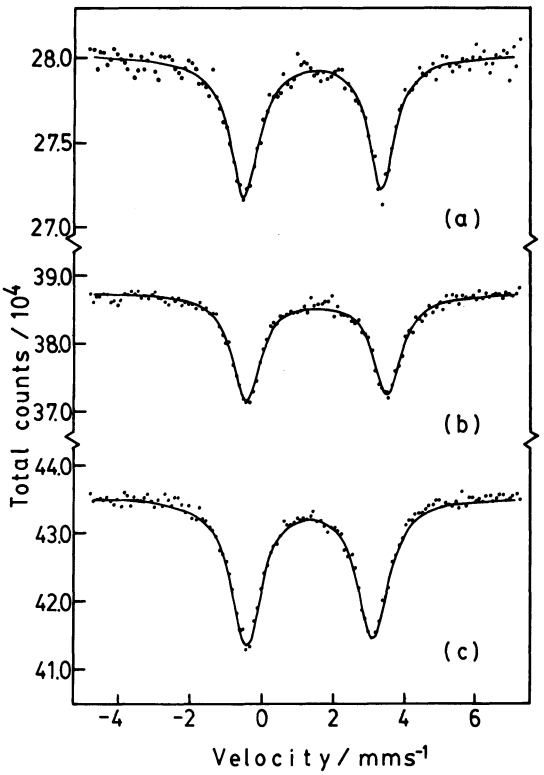


Fig. 1. $^{119}$Sn-Mössbauer spectra for (a) $\{[Me_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$, (b) $\{[Bu_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$, and (c) $\{[Ph_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ at 78 K.

Table 1. $^{119}$Sn-Mössbauer Parameters for Trialkyl- and Triaryltin Complexes of Transition Metal Cyanides

| Complex | *IS*[a] | *QS*[b] | $\Gamma_{exp}$[b] | | $\theta^2M$[c] |
|---|---|---|---|---|---|
| | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ | $10^6\times$deg$^2$ amu |
| $\{[Me_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 1.43 | 3.86 | 1.00 | 0.87 | 0.76 (78—157 K) |
| $\{[Bu_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 1.54 | 3.92 | 0.95 | 1.00 | 0.80 (78—133 K) |
| $\{[Ph_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 1.33 | 3.54 | 0.98 | 1.04 | 1.59 (78—219 K) |
| $\{[Me_3Sn]_2[(\mu\text{-NC})_4Pt]\}_x$ | 1.33 | 3.86 | 0.98 | 1.07 | 1.08 (78—179 K) |
| $\{[Bu_3Sn]_2[(\mu\text{-NC})_4Pt]\}_x$ | 1.58 | 4.18 | 1.07 | 1.13 | 1.00 (78—179 K) |
| $\{[Ph_3Sn]_2[(\mu\text{-NC})_4Pt]\}_x$ | 1.36 | 3.90 | 1.09 | 1.09 | 1.25 (78—179 K) |
| $\{[Bu_3Sn]_3[(\mu\text{-NC})_6Fe]\}_x$ | 1.49 | 3.86 | 0.98 | 1.16 | 1.00 (78—145 K) |
| $\{[Ph_3Sn]_3[(\mu\text{-NC})_6Fe]\}_x$ | 1.29 | 3.35 | 0.99 | 1.17 | 1.33 (78—195 K) |

a) Relative to $BaSnO_3$; $\pm$0.02 mm s$^{-1}$. b) $\pm$0.02 mm s$^{-1}$. c) $\pm$0.05 deg$^2$ amu.

Fig. 2 for $\{[Bu_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$. This asymmetry is commonly found in one- and two-dimensional polymeric compounds.[7] The temperature dependences of intensity asymmetry observed in other complexes are summarized graphically in Fig. 3, where $R$ is the ratio of the areal intensity, A+, of the resonance peak at the higher velocity to that, A−, of the peak at the lower velocity.

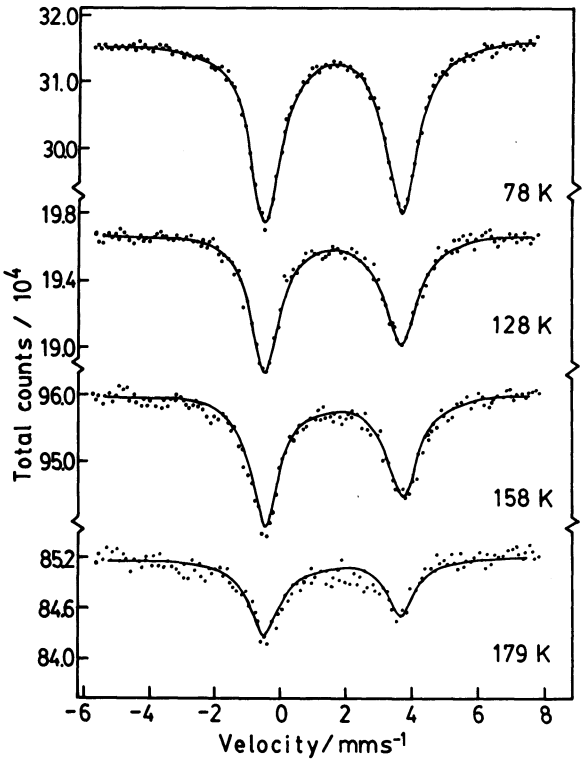


Fig. 2. $^{119}$Sn-Mössbauer spectra for $\{[Bu_3Sn]_2[(\mu\text{-}NC)_4\text{-}Pt]\}_x$ at various temperatures.

The intensity asymmetry has been theoretically expressed as a function of the difference in the mean-square vibrational amplitude parallel and perpendicular with respect to the principal axis of the electric-field gradient (EFG) tensor:[8]

$$R' = \frac{I(\pm 1/2 \leftrightarrow \pm 3/2)}{I(\pm 1/2 \leftrightarrow \pm 1/2)} = \frac{\int_0^{\pi} \exp\{-(1/\hbar^2)[\langle z^2\rangle - \langle x^2\rangle]\cos^2\theta\}(1+\cos^2\theta)\sin\theta d\theta}{\int_0^{\pi} \exp\{-(1/\hbar^2)[\langle z^2\rangle - \langle x^2\rangle]\cos^2\theta\}(5/3-\cos^2\theta)\sin\theta d\theta}, \quad (1)$$

where $\langle z^2\rangle$ and $\langle x^2\rangle$ are the mean square vibrational amplitudes parallel and perpendicular respectively to the principal axis of the EFG tensor.

The more intense line can be assigned to the $\pm 1/2 \leftrightarrow \pm 3/2$ transition by assuming that the difference in $[\langle z^2\rangle - \langle x^2\rangle]$ is negative, i.e., that the vibrational motion of the tin atom in the plane of $R_3Sn$ is larger than that along the molecular symmetry axis corresponding to the CN–Sn–NC chain. Thus, the observed intensity asymmetry suggests that the sign of the quadrupole coupling constant, $e^2qQ$, is negative; that is, the electric-charge distribution around a tin atom can be described as being oblate with respect to the polymer axis. This result is consistent with those for organotin compounds which have tin atoms five-coordinated in a one-dimensional chain structure in a solid.[7,9–11]

The observed intensity asymmetry $R$ shown in Fig.

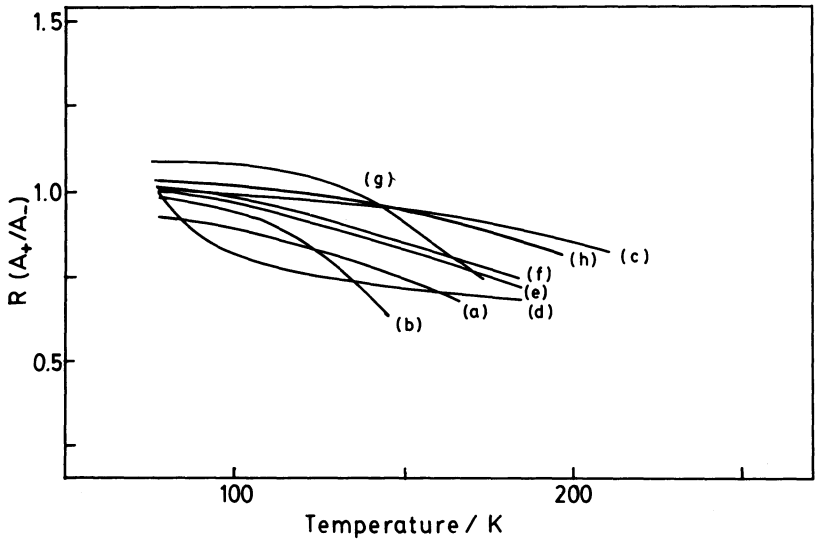


Fig. 3. Temperature dependences of peak intensity ratio for trialkyl- and triaryltin complexes of transition metal cyanides; (a) $\{[Me_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$, (b) $\{[Bu_3Sn](\mu\text{-}CN)[Au(\mu\text{-}CN)]\}_x$, (c) $\{[Ph_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$, (d) $\{[Me_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (e) $\{[Bu_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (f) $\{[Ph_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (g) $\{[Bu_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$, and (h) $\{[Ph_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$.

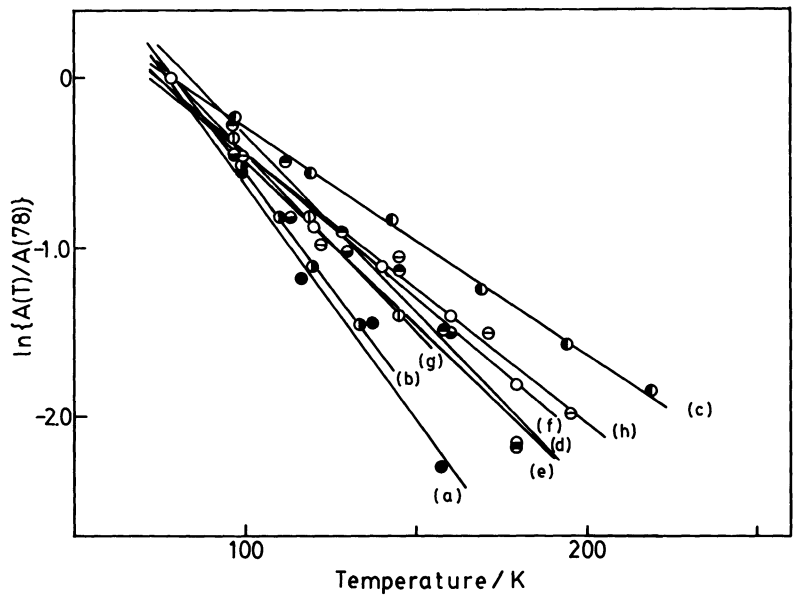


Fig. 4. Temperature dependences of the area under $^{119}$Sn-resonance line for (a) $\{[Me_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$, (b) $\{[Bu_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$, (c) $\{[Ph_3Sn](\mu\text{-}NC)[Au(\mu\text{-}CN)]\}_x$, (d) $\{[Me_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (e) $\{[Bu_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (f) $\{[Ph_3Sn]_2[(\mu\text{-}NC)_4Pt]\}_x$, (g) $\{[Bu_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$, and (h) $\{[Ph_3Sn]_3[(\mu\text{-}NC)_6Fe]\}_x$.

3 is inversely proportional to the ratio $R'$ in Eq. 1. All the $R$ values decrease with an increase in the temperature. This means that the mean-square vibrational amplitude in the direction perpendicular to the polymer axis depends significantly on the temperature. The temperature dependence of $R$ for $Ph_3Sn$ derivatives is smaller than those for $Me_3Sn$ and $Bu_3Sn$ derivatives. This result can be explained by assuming that the steric effect of the bulky phenyl group restricts the motion of the tin atom.

The recoil-free fraction, $f_a$, and its temperature dependence provide useful information about the lattice dynamical properties of a solid which are associated with the motion of Mössbauer atoms. The temperature dependences of the area under the resonance line are shown in Fig. 4 for the complexes studied in this work.

According to the Debye approximation at high temperatures, the "relative" values of the recoil-free fraction, $f_a$, are expressed as:

$$f_a = \exp\left(\frac{-3E_\gamma^2 T}{Mc^2k\theta^2}\right), \tag{2}$$

where $E_\gamma$ is the energy of the Mössbauer transition, $\theta$ is the Debye temperature, $M$ is the effective vibrating mass, and $k$ is the Boltzmann constant. The temperature dependence of the recoil-free fraction, $f_a$, is given by Eq. 3:

$$\frac{d\ln f_a}{dT} = \frac{-3E_\gamma^2}{Mc^2k\theta^2}. \tag{3}$$

Noting that $k\theta/h=\nu_{max}\propto(\alpha/M)^{1/2}$, the following equation is obtained for the parameter of the intermolecular force constant, $\alpha$:

$$\alpha \propto \theta^2M = \frac{-3E_\gamma^2}{kc^2}\left[\frac{d\ln f_a}{dT}\right]^{-1}, \tag{4}$$

where $\nu_{max}$ is the maximum lattice frequency, which is assumed to be equal to the Debye cut-off frequency, and where $h$ is the Planck constant. The coefficient of the temperature-dependent term, $d\ln f_a/dT$, in Eq. 4 can be replaced for a "thin" absorber by the observed temperature dependence of the areal intensity under the resonance line (normalized to 78 K point).

It was found in our previous study that there was a distribution of the $\theta^2M$ values with respect to the state of molecular association in a solid.[12] The values of $\theta^2M/10^6$ deg$^2$ amu are distributed around unity for a non-polymeric compound, while those of one-dimensional and two-dimensional polymeric compound are distributed around 1.3 and 1.7 respectively. The distribution of the $\theta^2M$ values for three-dimensional polymeric compounds may be beyond the value of the two-dimensional polymer. The distribution of the parameters can be used to determine the state of intermolecular association in a solid. Although much overlapping is observed between the non-polymeric compounds and one-dimensional polymeric compounds, and between the one-dimensional and two-dimensional polymers, the discrimination between the nonassociated and one-dimensional polymeric states and between two- and three-dimensional polymeric states can be done by detecting the asymmetric quadrupole split lines, as has been mentioned previously.

The values of $\theta^2M$, as estimated from the data of the

temperature dependence of the area for the complexes, are summarized in Table 1. Although the {[$R_3Sn$]$_2$[($\mu$-NC)$_4$Pt]} and {[$R_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ complexes are considered to be two- or three-dimensional polymer complexes, the values of $\theta^2M$ in Table 1 suggest that the state of molecular association for these complexes is close to that of non-polymeric compounds or one-dimensional polymers. The values of $\theta^2M$ for $Me_3Sn$ and $Bu_3Sn$ derivatives are smaller than those for $Ph_3Sn$ derivatives in each series. This means that the motion of tin atoms in these complexes depends mainly on the ligands in the first coordination sphere of tin atoms. A large temperature dependence of the mean-square vibrational amplitude perpendicular to the polymer axis strongly affects the values of $\theta^2M$. The relatively large values of $\theta^2M$ for $Ph_3Sn$ derivatives presumably reflect the restriction on the motion of tin atoms attributable to the bulky phenyl group, which is packed rigidly in a solid. The same tendency was observed for $R_4Sn$ compounds; e.g., the value of $\theta^2M$ for $Me_4Sn$ is $0.77\times10^6$, while that for $Ph_4Sn$ is $1.28\times10^6$.[12] Consequently, a comparison of the parameters of the intermolecular force constant, $\alpha \propto \theta^2M$, gives valuable information about the motion of tin atoms associated in a solid.

**$^{57}$Fe-Mössbauer Spectra.** The $^{57}$Fe-Mössbauer spectra and their temperature dependence for {[$Bu_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ are shown in Fig. 5, while the Mössbauer parameters derived from the observed spectra are listed in Table 2. The values of *IS* and *QS* and the temperature dependence of *QS* indicate that the iron atom in this complex is at an Fe(III) low-spin state. The temperature dependences of *QS* for {[$Bu_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ and {[$Ph_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ are shown in Fig. 6.

A low-spin Fe(III) atom has a nonspheric d shell. The contribution of this configuration to the EFG

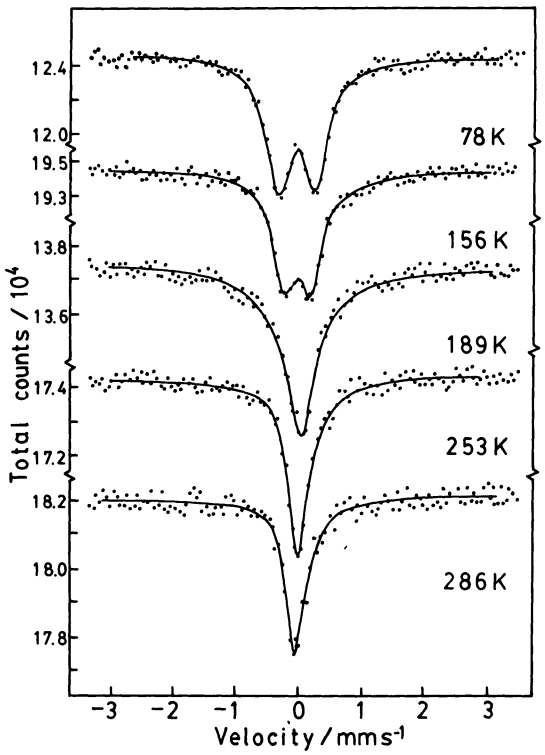


Fig. 5. $^{57}$Fe-Mössbauer spectra for {[$Bu_3Sn$]$_3$[($\mu$-NC)$_6$-Fe]}$_x$ at various temperatures.

Table 2. $^{57}$Fe-Mössbauer Parameters at 78 *K*

| Complex | *IS*[a] | *QS*[b] | $\Gamma_{exp}$[b] | |
|---|---|---|---|---|
| | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ |
| {[$Bu_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ | −0.05 | 0.55 | 0.42 | 0.47 |
| {[$Ph_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ | −0.07 | 1.19 | 0.43 | 0.45 |

a) Relative to $\alpha$-Fe foil; ±0.02 mm s$^{-1}$. b) ±0.02 mm s$^{-1}$.

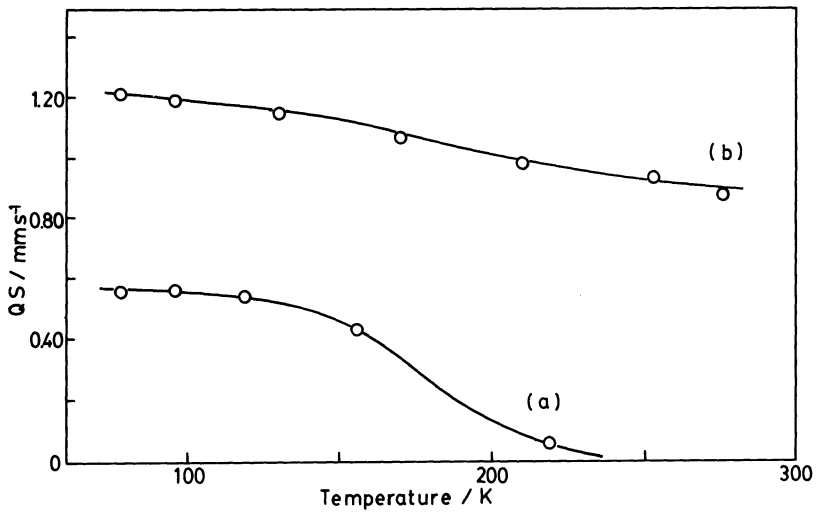


Fig. 6. Temperature dependences of the quadrupole splitting for (a) {[$Bu_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$ and (b) {[$Ph_3Sn$]$_3$[($\mu$-NC)$_6$Fe]}$_x$.

Table 3. $^{197}$Au-Mössbauer Parameters at 16 *K*

| Complex | *IS*[a] | *QS*[b] | $\Gamma_{exp}$[b] | |
|---|---|---|---|---|
| | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ | mm s$^{-1}$ |
| $\{[Me_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 4.51 | 10.45 | 2.00 | 2.00 |
| $\{[Bu_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 4.37 | 9.99 | 1.93 | 2.17 |
| $\{[Ph_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ | 4.45 | 10.08 | 2.01 | 2.01 |

a) Relative to Au foil; $\pm 0.04$ mm s$^{-1}$. b) $\pm 0.04$ mm s$^{-1}$.

depends on the symmetry of the external field and the temperature. A large temperature dependence of *QS* for the $Bu_3Sn$ derivative indicates that the three $d_\varepsilon$ levels are close to each other in energy. The environment around iron(III) atoms is assumed to be almost cubic. On the other hand, the decrease in the *QS* for the $Ph_3Sn$ derivative is slow. This can be explained by assuming that the three $d_\varepsilon$ levels are widely separated as a result of the distortion of $Fe(CN)_6$ octahedra caused by the steric hindrance of bulky phenyl groups.

The values of $\theta^2M/10^6$ for $^{57}$Fe estimated by using Eq. 4 are 0.97 and 1.63 for $Bu_3Sn$ and $Ph_3Sn$ derivatives respectively. These values are smaller than those expected for three-dimensional polymeric compounds. This result reflects the linkage of a long CN–Sn–NC chain, which probably reduces the motional rigidity of the iron atoms in these complexes. The fact that the value for the $Ph_3Sn$ derivative is larger than that for the $Bu_3Sn$ derivative can be explained by the same interpretation as has been proposed for the case of $^{119}$Sn, that is, the motion of the iron atom is restrained by the steric effect of bulky phenyl groups. The similarity between the values of $\theta^2M$ of $^{57}$Fe and those of $^{119}$Sn for $\{[Bu_3Sn]_3[(\mu\text{-NC})_6Fe]\}_x$ and $\{[Ph_3Sn]_3[(\mu\text{-NC})_6Fe]\}_x$ respectively suggests that the motion of iron atoms depends on that of tin atoms in these complexes.

**$^{197}$Au-Mössbauer Spectroscopy.** The $^{197}$Au-Mössbauer spectra for the $\{[R_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ complexes (R=Me, Bu, or Ph) consist of one doublet with quite large *QS* values. The Mössbauer parameters derived from the spectra are summarized in Table 3. The values of *IS* and *QS* for these complexes are very close to those of $K[Au(CN)_2]$.[13]

In linear gold(I) compounds, the $5d_{z^2}$, 6s, and $6p_z$ metal orbitals (the z axis being the molecular axis) are suitable for $\sigma$-bonding, while the $5d_{xz,yz}$ and $6p_{x,y}$ orbitals are used in $\pi$-bonding to the ligands. The $5d_{xy}$ and $5d_{x^2-y^2}$ orbitals are nonbonding. $\sigma$-Donation into the $5d_{z^2}$ and $6p_z$ orbitals is expected to contribute negatively to the quadrupole coupling constant, $e^2qQ$. The absolute value of $e^2qQ$ might be expected to increase the $\sigma$-donor strength of the ligands, assuming that the sign of $e^2qQ$ for the two coordinated gold(I) compounds is negative. The negative $e^2$qQ has been confirmed experimentally for $K[Au(CN)_2]$.[14] $\pi$-Bonding and $d_\pi$-back-bonding also affect the $e^2qQ$, but their contribution is estimated to be smaller than that of $\sigma$-donor bonding on the basis of theoretical considerations[15,16] and systematic $^{197}$Au-Mössbauer studies of many gold(I) compounds.[17–20] Thus, it is reasonable to conclude that the *QS* values mainly depend on the $\sigma$-donating ability of the ligands. On the other hand, it has been known that the *IS* value depends on the s electron density at the gold nucleus. The 6s population directly increases the electron density at the nucleus, while the $5d_{z^2}$ and $6p_z$ populations decrease the electron density because of their shielding effect. The shielding effect of 5d electrons is larger than that of 6p electrons. The $d_\pi$-back-bonding reduces the d electrons and then increases the electron density at the $^{197}$Au nucleus. Increases in the s electron density at the nucleus lead to the increase in the *IS* value because of the positive $\Delta R/R$ in $^{197}$Au-Mössbauer spectroscopy. Hence, both the *QS* and *IS* values depend on the $\sigma$-donating and $\pi$-accepting ability of the ligands. A linear relationship between the observed *IS* and *QS* values has been established for many gold(I) compounds.[18,20,21]

The values of *IS* and *QS* for the gold(I) compounds with a CN group are expected to be larger than those for other gold(I) compounds. This expectation is confirmed by the observed large *IS* and *QS* values for $\{[R_3Sn](\mu\text{-NC})[Au(\mu\text{-CN})]\}_x$ complexes. It can be concluded that the gold atom in these complexes is coordinated linearly with two cyano groups and forms an infinite one-dimensional polymeric structure.

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