Molecular Geometry of SnCl$_4$ DME Based on ^{35}Cl NQR Zeeman Effect

(NQR / Zeeman Effect / SnCl$_4$-complex)

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^{35}Cl NQR spectra in SnCl$_4$.DME have been observed in the range of 77 K to 420 K. Two NQR lines have been detected at the temperatures above 96 K and a single line at 77 K. Three crystal modifications of SnCl$_4$.DME have been found. A *trans* geometry is suggested for one of them. The Zeeman effect on a single crystal of SnCl$_4$.DME has been studied at room temperature. It is revealed on the basis of the orientations of the z axes of the electric field gradient that the molecule of SnCl$_4$.DME has a *cis* geometry at room temperature. The higher-frequency line is assigned to the axial Cl atoms and the lower-frequency one to the equatorial Cl atoms. The asymmetry parameters for the Cl atoms contributing to the higher- and lower-frequency lines are 0.038 and 0.099, respectively.

Introduction

1,2-Dimethoxyethane (DME), the bidentate Lewis base, yields a 1:1 octahedral complex with SnCl$_4$. There are conflicting reports on stereochemistry of SnCl$_4$ DME. It has been proposed on the basis of the IR spectra at room temperature and the spectrum of nuclear quadrupole resonance (NQR) at 77 K that SnCl$_4$ DME has a *trans* geometry,[1-3] whereas a *cis* geometry has been proposed on the basis of the IR and Raman spectra.[4,5] Ruzicka and Merbach has reported that the absence of a *trans* complex is confirmed in a solution by means of NMR spectra.[6] However, the results of NQR at 77 K cannot be compared with those of the vibrational spectra at room temperature, because temperature appears one of significant factors determining a molecular geometry. It is interesting in whether SnCl$_4$ DME has a *cis* geometry or a *trans* one in a solid state.

The purpose of the present work is to throw light on a geometry of SnCl$_4$ DME. NQR serves as a powerful tool for determining geometries of SnCl$_4$ complexes[7,8] The Zeeman effect on a single crystal of SnCl$_4$ DME is examined in order to obtain information on the orientations of Sn Cl bonds and bond character.

Experimental

Crystals of SnCl$_4$ DME were obtained by adding a

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slight excess of DME dropwise to SnCl$_4$ in CH$_2$Cl$_2$. A single crystal was grown by subliming in a sealed glass tube with 13.5 mm inner diameter at *ca.* 330 K in a similar manner to the Piper method.[9]

The ^{35}Cl NQR spectra were recorded on a home-made super-regenerative spectrometer through a lock-in amplifier followed by a pen-recorder below *ca.* 180 K, whereas those were observed on a display above 180 K. Temperature was determined with a Yokogawa 5763 thermometer by use of a copper-constantan thermocouple. The Zeeman effect was examined by means of the zero-splitting cone method. The Zeeman field supplied by Helmholtz coil was about 20 mT. The magnetic field orientation for the zero-splitting was determined in polar coordinates (Θ, Φ), where Θ and Φ are polar and azimuthal angles, respectively, in the coordinate fixed to the sample.

Results and Discussion

The ^{35}Cl NQR frequencies for SnCl$_4$ DME are given in Table 1, while a graphical presentation of the complete experimental data is provided in Fig. 1. Only a weak line, the frequency of which was in good agreement with the literature value,[3,4] was detected at 77 K. Unfortunately the resonance lines could not be observed near 80 K, because the desired temperature was difficult to be kept constant for a definite period of time required for phase sensitive detection. Although no resonances were detected at 90 K, two closely spaced lines appeared at 96 K. The difference in frequency between these lines increased with an

Table 1. NQR frequencies and asymmetry parameters

T/K	Frequency/MHz		η	e^2Qqh^{-1}/MHz
	$\nu_L\ (\nu_L{}')$	$\nu_H\ (\nu_H{}')$		
77	19.620[a]			
96	19.618	19.640		
160	19.539	19.617		
196	19.460	19.540		
298	19.273		0.099 ± 0.003	38.50
		19.444	0.038 ± 0.002	38.89
423	18.894	19.265		

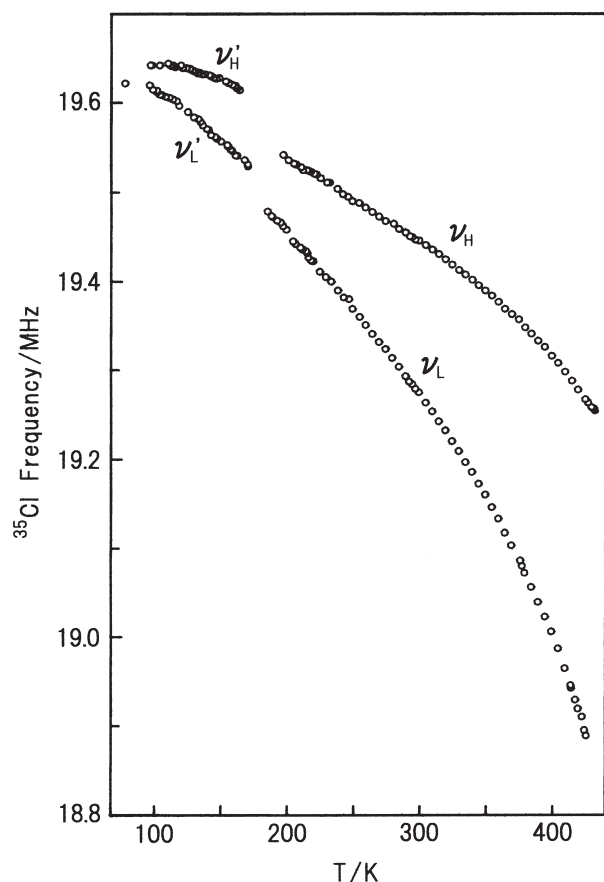a) The frequency at 77 K is in agreement with the literature value (Ref. 2).

Fig. 1. Temperature dependence of the NQR frequencies of SnCl$_4$ DME.

increase in temperature, and the higher- and lower-frequency lines faded out at 169 and 164 K, respectively. No resonance could be detected over the range of 170 to 184 K.

The complex SnCl$_4$ DME gave two fairly intense NQR lines at room temperature. The frequencies of these lines increased monotonously with a decrease in temperature and the higher-frequency line faded out at *ca.* 195 K and the lower-frequency line at *ca.* 184 K, whereas the NQR frequencies of these lines decreased steeply and the difference in frequency between the two lines increased with an increase in temperature. These lines faded out at *ca.* 420 K. As seen in Fig. 1, there are discontinuities of the frequency curves in the ranges 77 96 K and 169 184 K, suggesting that there exist three crystal modifications of SnCl$_4$ DME above 77 K. These modifications are tentatively termed Phase-I, Phase-II, and Phase-III in order of temperature, respectively.

The zero-splitting patterns of Phase-III of SnCl$_4$.DME obtained from the Zeeman effect of the ^{35}Cl lines at room temperature are reproduced in Figs 2 and 3. Eight loci were obtained from each line. From the distributions of these Zeeman patterns, one four-fold and four two-fold axes were obtained, suggesting that there are four physically equivalent sites in the crystal and the crystal of
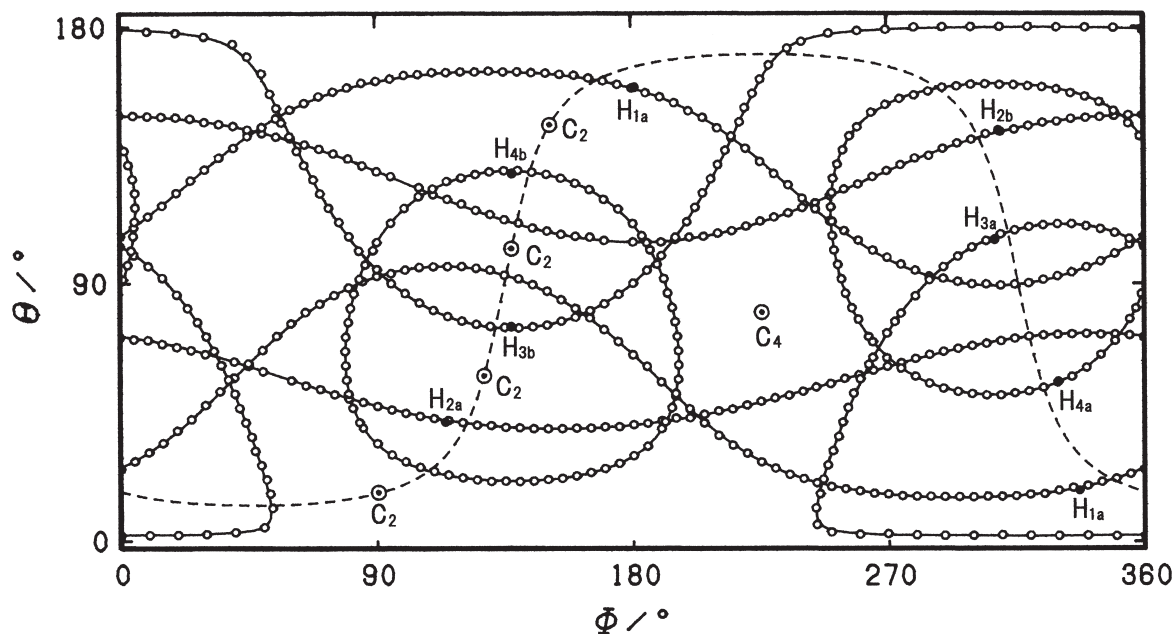
Fig. 2. Zero-splitting patterns for a ^{35}Cl higher-frequency (i_H) line in Phase-III of SnCl₄ DME. The H_{ia} and H_{ib} represent the efg z axes belonging to the molecule at the ith site and the dashed line represents the plane perpendicular to the four-fold axis C₄.

Fig. 3. Zero-splitting patterns for a ^{35}Cl lower-frequency line (i_L) in Phase-III of SnCl₄ DME. The L_{ia} and L_{ib} represent the efg z axes belonging to the molecule at the ith site and the dashed line represents the plane perpendicular to the four-fold axis C₄.
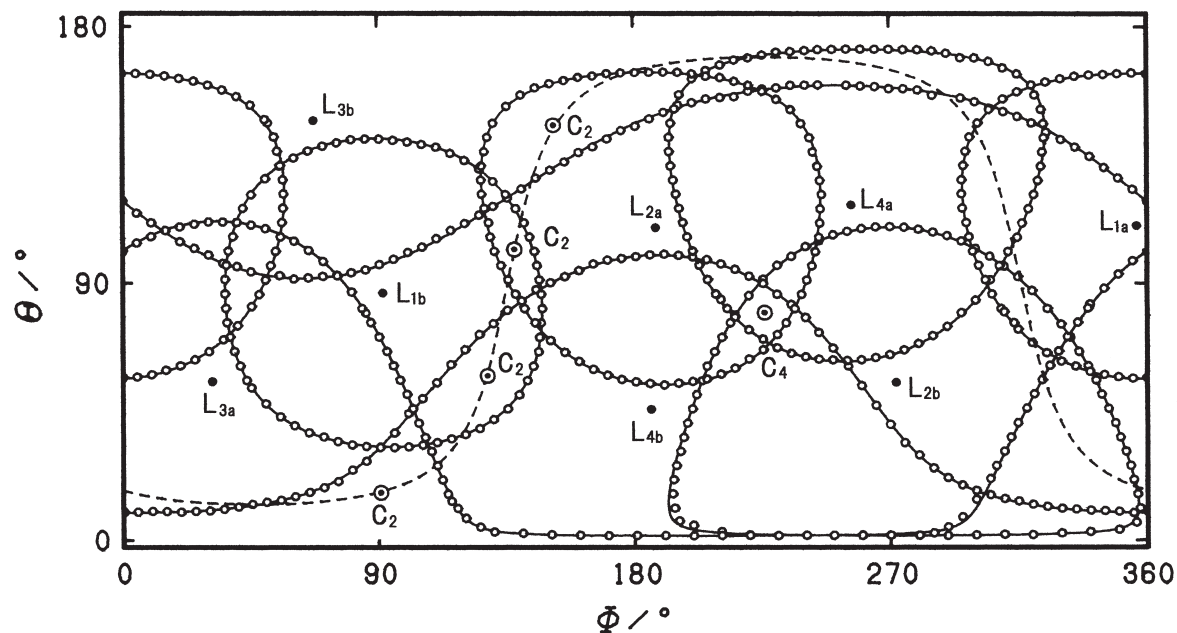
Phase-III belongs to tetragonal system.[10] All of the two-fold axes lies in the plane perpendicular to the four-fold axis and the two-fold axes orient at an angle of 45 to the adjacent two-fold axes. The crystal of Phase-III, therefore, belongs to one of the symmetry classes V_d, C_4^h, D_4, and D_4^h in the Wyckoff's notation.[11] Four equivalent crystal sites are arbitrarily numbered as 1, 2, 3, and 4 in Figs.

2 and 3.

The asymmetry parameter (η) and the axes of the electric field gradient (efg) can be determined by transforming the zero-splitting locus in the coordinate system (Θ, Φ) to the principal coordinate system (θ, ϕ), in which the locus is expressed by I=3/2 as follow[12]:

$$\sin^2\theta = 2/(3 - \eta\cos 2\phi), \qquad (1)$$

Table 2. Angles (/degree) between the efg axes and significant planes in SnCl₄.DME.

	x_{La}	y_{La}	z_{La}	z_{Lb}	z_{Ha}	z_{Hb}
x_{Lb}	84.9 ±0.2	81.3 ±1.3	10.2 ±1.0			
y_{Lb}	82.3 ±0.9	11.2 ±1.0	82.0 ±1.3			
z_{Lb}	9.3 ±0.6	83.2 ±0.8	**96.17 ±0.03**			
z_{Ha}	79.2 ±0.9	11.3 ±0.8	**92.86 ±0.06**	**93.66 ±0.05**		
z_{Hb}	86.4 ±0.8	5.2 ±0.6	**93.66 ±0.05**	**92.86 ±0.06**	**170.26 ±0.06**	
z_{La}-z_{Lb}[a] plane	6.9 ±0.8	83.1 ±0.8	0	0	85.14 ±0.06	85.05 ±0.12
z_{Ha}-z_{Hb}[b] plane	48.5 ±0.2	5.2 ±0.5	48.02 ±0.09	48.14 ±0.11	0	0

a) The subscripts H and L represent that the efg x, y and z axes arise from the higher- and lower-frequency lines, respectively.
b) The z_{ia}-z_{ib} plane (i = L or H) represents the plane made up of the z_{ia} and z_{ib} axes.

where θ and ϕ are polar and azimuthal angles, respectively. The loci were also analyzed by the method of the least squares. The coupling constant (e^2Qqh^{-1}) is related to the resonance frequency (ν) as follows:

$$2\nu = e^2Qqh^{-1}(1 + \eta^2/3)^{1/2}. \qquad (2)$$

The calculated NQR parameters are listed in Table 1, together with the NQR frequencies.

Only the average angles between the efg axes are listed in Table 2, because there are thirty-two significant efg axes in all. The angles between the Sn–Cl bond can be deduced, assuming that the efg z axis is parallel to the Sn–Cl, as is generally the case. The angle between the z axes on the higher-frequency line is 170.3 and that between the z axes on the lower-frequency lines 96.2. These angles reveal that SnCl₄ DME has a cis geometry. The molecule of SnCl₄ DME has a two-fold axis which is coincident in direction to the four-fold axis of the crystal. The higher- and lower-frequency lines are assigned to the axial (Cl$_{ax}$) and equatorial (Cl$_{eq}$) chlorine atoms in SnCl₄ DME, respectively. The arrangement of the chlorine atoms around the tin atom are shown together with the bond angles in Fig. 4. The complex SnCl₄ DME resembles the cis-complex SnCl₄ 2Me₂O closely in molecular geometry.[13] In SnCl₄ 2Me₂O the Cl$_{eq}$-Sn-Cl$_{eq}$ angle and the Cl$_{ax}$-Sn-Cl$_{ax}$ angle are 92.2 and 173.4, respectively. In other cis-complexes of SnCl₄ studied by Zeeman analysis, the Cl$_{eq}$-Sn-Cl$_{eq}$ angles range from 99.6 to 102.9 and the Cl$_{ax}$-Sn-Cl$_{ax}$ angles from 161.9 to 168.3.[13-15] The shape of SnCl₄ DME is therefore relatively less distorted. It comes in question whether the molecule of SnCl₄ DME is discrete or polymeric. Unfortunately the Cl-Sn-Cl angles are incompetent for solving this problem. The molecule of
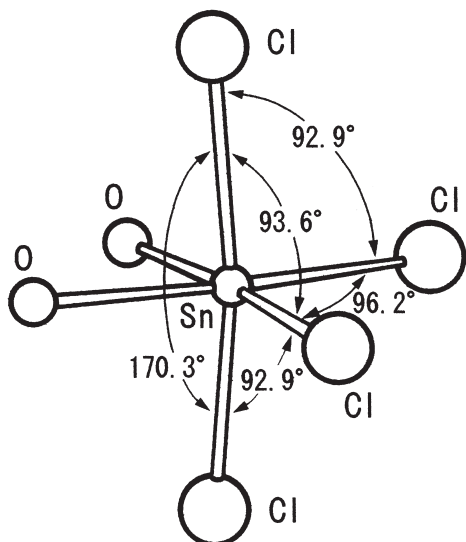
Fig. 4. Molecular shape of the SnCl₄ DME molecule in Phase-III. The two O atoms are the ones from DME.

SnCl₄ DME is, however, presumed to be discrete, taking into account that the complex is a *cis* form in a solution[4-6] and a single crystal of the complex could be obtained by sublimation at relatively low temperature.

The η-value for the equatorial chlorine atom is *ca.* 0.10, whereas that for the axial chlorine atom is very small. As can be seen in Table 2, the efg x axes on the equatorial chlorine atoms are nearly parallel to the $Cl_{eq}SnCl_{eq}$ plane and the y axes nearly perpendicular to the $Cl_{ax}SnCl_{ax}$ plane, suggesting that there is very weak π bonding in the plane containing the two Cl_{eq}, two O and Sn atoms. Using the atomic coupling constant for ^{35}Cl, 109.74 MHz,[16] the π bond character for the Sn Cl_{eq} bond is calculated to be at most 2.3 percent, whereas the that for the Sn Cl_{ax} bond is less than 1 percent. The ionic characters for the Sn Cl_{eq} and Sn Cl_{ax} bonds are calculated to be 57.3 and 58.3 percent, respectively. The difference in ionic character between the Sn Cl_{eq} and Sn Cl_{ax} bonds is very small. On the contrary, in other *cis*-complexes of SnCl₄ with oxygen donors, the ionic character for the Sn Cl_{eq} bond is greater by 3-6 percent than for the Sn Cl_{ax} bond.[13,14] This may result from a weak *trans* effect of the DME molecule.

The NQR spectrum of Phase-I consisting of a single line reveals that all of the Sn Cl bonds is equivalent and hence at 77 K the complex is concluded to be a *trans* isomer in agreement with the structure previously proposed.[2] There is no saying whether the complex of Phase- has a *cis* or *trans* geometry, though the two resonance lines are closely spaced. When the curves of frequency *vs.* temperature for Phase- are shifted about 35 kHz to the low-frequency side without changing temperatures, the shifted curves look like the prolonged parts of the corresponding curves for Phase- . The molecule of Phase-II may therefore be a *cis*-form. The transformation from a *trans* form to a *cis* one appears to cause the phase transition in the temperature range between 77 K and 96 K or between 170 K and 184 K. Such *cis-trans* isomerism in a solid state was found in SnCl₄ 2Me₂O and SnCl₄ 2C₆H₅CN.[13,15] In these complexes, however, the formation of modifications depends on the method of preparation and the phase transitions at particular temperature were not observed, contrary to the case in SnCl₄ DME.

The difference in frequency between the higher- and lower-frequency lines is at most 170 KHz at room temperature and 370 KHz even at 420 K, though in other *cis*-complexes the difference between the corresponding frequencies ranges from 1.4 to 2.4 MHz.[13,15] At 420 K, however, the absolute value of the temperature coefficient of the lower-frequency line is about 2.5 times that for the higher-frequency line. This appears to be a good illustration supporting the previous suggestion that the coefficient of the NQR frequency is significant criteria for deducing a geometry of the hexacoordinated SnCl₄-complex.[7,8]

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