^{35}Cl NQR of 1:2 Complexes of $SnCl_4$ with Several Nitriles

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^{35}Cl NQR spectra have been obtained for the complexes of $SnCl_4 \cdot 2RCN$ (R=CH_3, CD_3, t-C_4H_9, or C_6H_5). The NQR spectra reveal the existence of three crystal modifications in $SnCl_4 \cdot 2CH_3CN$, a stable phase (Form-1) and two metastable ones (Form-2 and Form-3). Form-3 was obtained as a mixture with Form-2. These modifications are suggested to be cis isomers. The complex, $SnCl_4 \cdot 2C_6H_5CN$, has likewise yielded three modifications, and the evidence for cis-trans isomerization in this complex has been found from NQR spectra. A Zeeman analysis on single crystals reveals that $SnCl_4 \cdot 2t$-C_4H_9CN has a cis form and that its molecular geometry is similar to Form-1 of $SnCl_4 \cdot 2CH_3CN$. In these complexes, the equatorial Cl atoms yield asymmetry parameters of 0.05 to 0.08 and the axial ones negligibly small values. The temperature dependence plot for the NQR frequencies in $SnCl_4 \cdot 2CH_3CN$ yields unusual curves. This is attributed to some interaction between the Cl atom and the methyl groups.

As to the stereochemistry of octahedral complexes of tin (IV) halides, spectral patterns of NQR have been interpreted mostly in terms of cis-trans isomerism.[1,2] Of a number of $SnCl_4 \cdot 2L$ (L=a monodentate ligand), complexes of nitriles do not always yield typical spectral patterns.[3] It has been suggested that the temperature coefficient of NQR frequency is one of significant criteria for deducing cis and trans forms of complexes.[3,4] This must be confirmed on the basis of unanimous assignment of ^{35}Cl lines. Zeeman studies on single crystals have advantages in permitting a consistent assignment of NQR lines for compounds of a known crystal structure. In addition, even when a crystal structure is unknown, information about molecular geometry can be obtained by using this technique. In most cases, however, because of the difficulty of preparing large single crystals a few complexes of $SnCl_4$ were examined by Zeeman analysis.[5,6]

Of numerous $SnCl_4$ complexes with nitriles, the available X-ray data are for only $SnCl_4 \cdot 2CH_3CN$.[7] This complex is cis-octahedral and yields four NQR lines consisting of a resonance line in the higher frequency region and three grouping lines in the lower one.[3] These lines were assigned on the basis of the Sn-Cl bond length.[3] The resonance frequency, however, depends not only on the bond length but on the position of the Cl atom in an octahedron and intermolecular interaction. Such a method of assignment does not always yield reasonable results.

The complexes $SnCl_4 \cdot 2CH_3CN$ and $SnCl_4 \cdot 2t$-C_4H_9CN were probed by means of the ^{35}Cl Zeeman effect, and information about the assignment of NQR lines, molecular shapes, and bond characters was obtained. In the course of preparing single crystals, the existence of three crystal modifications was found in $SnCl_4 \cdot 2CH_3CN$. Although single crystals of $SnCl_4 \cdot 2C_6H_5CN$ were successfully prepared, they were destroyed through phase transition to other modifications. This interfered with obtaining unambiguous information about the molecular shape of $SnCl_4 \cdot 2C_6H_5CN$ in the crystal. However, two new modifications of this complex were also found by NQR spectra. The structures of these modifications were discussed on the basis of spectral patterns and the temperature dependence of NQR frequencies.

Experimental

The nitrile complexes $SnCl_4 \cdot 2RCN$ (R=CH_3, t-C_4H_9, or C_6H_5) were prepared by the method described in the literature.[3,7,8] These complexes were purified by recrystallizing from carbon tetrachloride or vacuum sublimation and checked by measuring NQR frequencies.[3] Single crystals of these complexes were grown in evacuated sealed tubes by the Piper technique.[9]

^{35}Cl NQR spectra were obtained by means of a Dean-type externally-quenched superregenerative spectrometer. Resonance lines were displayed on an oscilloscope. Resonance frequencies were determined using a frequency counter. The Zeeman effect on resonance lines was examined by means of the zero-splitting cone method at room temperature. Zero-splitting loci were analyzed by the least squares method. Sample temperature was determined with a copper-constantan thermocouple inserted in the pit of a sample vial.

Results and Discussion

The sample of $SnCl_4 \cdot 2CH_3CN$ recrystallized from CCl_4 yielded four relatively broad resonance lines. This NQR spectrum was similar to that reported previously,[3] although the resonance frequencies differ somewhat from the literature values. The sample, sublimed above 360 K, likewise yielded a spectrum consisting of four NQR lines. This spectrum was different from that of the recrystallized sample, and the absorption lines were considerably narrow. These samples are referred to as Form-1 for the former and Form-2 for the latter.

The observed NQR spectra show that Form-1 and the crystal obtained by sublimation below 340 K are isomorphous. Under the preparative condition of

Table 1. ^{35}Cl NQR Parameters for Nitrile Complexes of $SnCl_4$

Compound		Frequency/MHz				η/%	e^2Qqh^{-1}/MHz
		77 K		295 K			
$SnCl_4 \cdot 2CH_3CN$							
(Form-1)	ν_1	19.214		19.207		4.9	38.40
	ν_2	19.600		19.513		5.3	39.01
	ν_3	19.846		19.752		2.5	39.45
	ν_4	20.644		20.466		3.1	40.93
(Form-2)			18.329		18.525		
			19.664		20.272		
(Form-3)			18.610		18.677		
			19.656		20.461		
$SnCl_4 \cdot 2CD_3CN$							
(Form-1)		19.214		19.216			
		19.610		19.525			
		19.867		19.770			
		20.665		20.484			
$SnCl_4 \cdot 2t\text{-}C_4H_9CN$							
	ν_1	19.439		18.859		8.1	37.68
	ν_2	19.583		18.981		7.8	37.92
	ν_3	19.700		19.426		1.3	38.85
	ν_4	20.334		20.039		2.8	40.07
$SnCl_4 \cdot 2C_6H_5CN$							
(Form-1)		19.805		19.363			
				19.884			
(From-2)		19.335		18.762			
		19.591		19.737			
		19.876		19.874			
		20.042		19.068			
(Form-3)		19.476[a]		19.294			
		19.536[a]		19.362			

a) The values at 214 K.

Form-2, another modification (referred to as Form-3) was incidentally obtained as a mixture with Form-2. Form-3 gave much broader resonance lines than Form-2. Both Form-2 and Form-3 were metastable, and these modifications transformed to Form-1 with the passage of time or through physical stimulation. The resonance frequencies were listed in Table 1. Inferring from the spectral patterns, both Form-2 and Form-3 are cis isomers.[1]

The ^{35}Cl NQR frequencies for Form-1 of $SnCl_4 \cdot 2CH_3CN$, over the temperature range of 77 K to nearly the melting point, are plotted in Fig. 1. The literature values[3] are also plotted for comparison. The resonance lines are designated as ν_1, ν_2, ν_3, and ν_4 from the lower to the higher frequency. The plot of the ν_1 line yields a convex curve with a maximum near 200 K. By contrast, the ν_3 curve possesses a less negative temperature coefficient above near 200 K than below it. Such a tendency, though not so remarkable, can be found in the ν_4 curve. The ν_2 curve is seemingly normal.

Figure 2 shows the temperature dependence of ^{35}Cl resonance frequencies of $SnCl_4 \cdot 2t\text{-}C_4H_9CN$ in the range of 77 K to the melting point (353 K). The spectrum at low temperature resembles very closely that of Form-1 of $SnCl_4 \cdot 2CH_3CN$ in pattern, the lower three lines being more closely spaced. The resonance lines fall gradually into two distinct

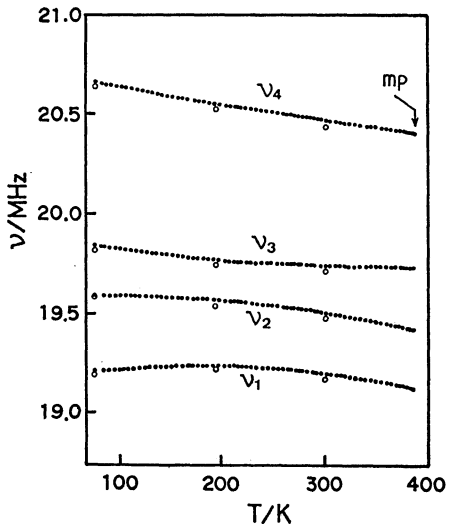

Fig. 1. Temperature dependence of ^{35}Cl DQR frequencies in Form-1 of $SnCl_4 \cdot 2CH_3CN$. The open circles indicate the plot of the literature values (Ref. 5).

groups, characteristic of a cis structure, with increasing temperature.

The existence of three modifications of $SnCl_4 \cdot 2C_6H_5CN$ was verified from NQR spectra. The sample crystallized from CCl_4 (referred to as Form-1) gave the same spectrum as that reported previously,[3] except

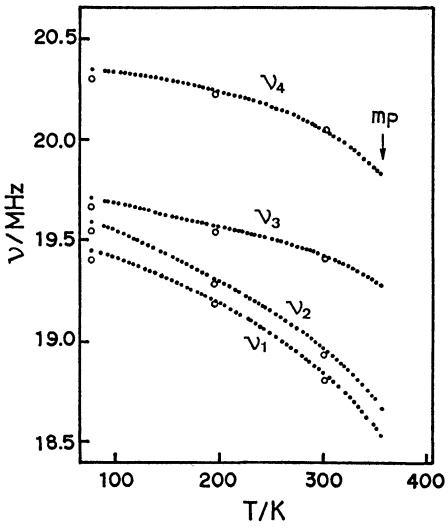

Fig. 2. Temperature dependence of ^{35}Cl NQR frequencies in $SnCl_4 \cdot 2t\text{-}C_4H_9CN$. The open circles indicate the plot of the literature values (Ref. 5).

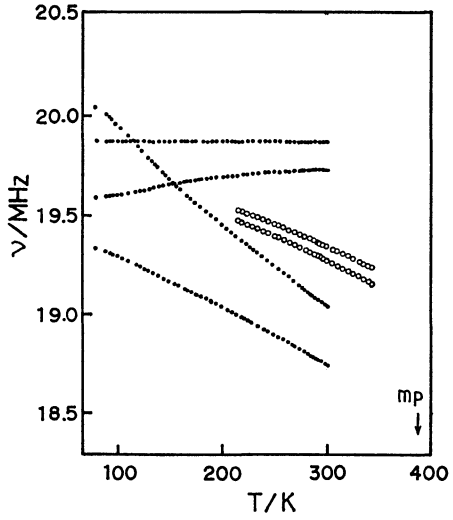

Fig. 3. Temperature dependence of ^{35}Cl NQR frequencies in Form-2 (●) and Form-3 (○) of $SnCl_4 \cdot 2C_6H_5CN$.

for some differences in frequency. Huggett et al.[3] ascribed this modification to a cis form on the basis of temperature coefficients of the resonance lines. The crystal grown from melt and the one obtained by subliming at ca. 350 K in an evacuated vial were isomorphous, yielding four NQR lines. This phase is referred to as Form-2. Complete transformation of Form-2 into Form-1 occurred on standing at room temperature for two days. On the contrary, the sample of Form-1 maintained at 335 K for two days gave the NQR spectrum of Form-2 at room temperature or below it. This phase transition is physically reversible, so that Form-1 is regarded as the lower-temperature phase and Form-2, as the higher-temperature one. The NQR frequencies in Form-2 are plotted against temperature in Fig. 3. The spectrum at 77 K

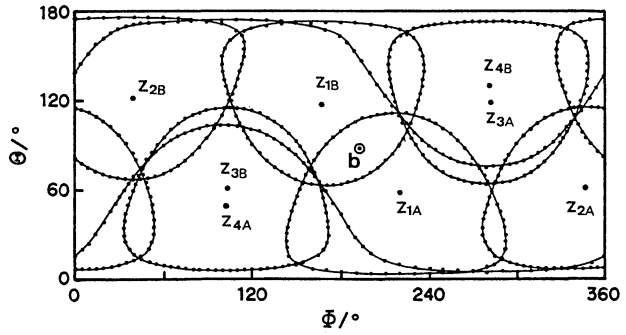

Fig. 4. Zero-splitting patterns of ^{35}Cl Zeeman lines in Form-1 of $SnCl_4 \cdot 2CH_3CN$.

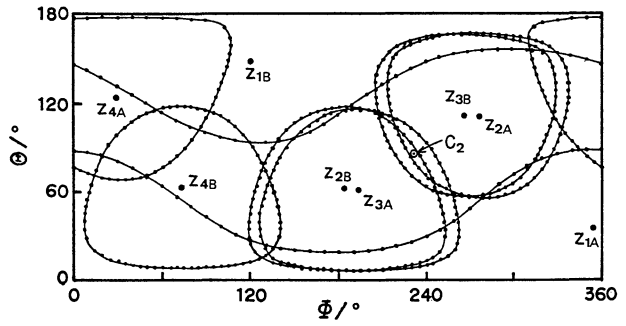

Fig. 5. Zero-splitting patterns of ^{35}Cl Zeeman lines in $SnCl_4 \cdot 2t\text{-}C_4H_9CN$.

is complicated, whereas that at room temperature is characteristic of a cis complex. This is a good illustration supporting the previous suggestion that temperature dependence of NQR frequencies is important for attempting structure assignment.[3,4]

Another modification (referred to as Form-3) was obtained when the crystal was sublimed at 315 K in an evacuated tube. This modification gave two closely spaced resonance lines. The temperature dependence plot for these lines is shown in Fig. 3. Judging from the type of the spectrum[1] and the temperature coefficients of the NQR frequencies,[3,4] Form-3 is a trans isomer. Form-3 was metastable and was converted gradually into Form-1 on standing at room temperature and rapidly into Form-2 at 77 K. This cis-trans isomerization is similar to the case of $SnCl_4 \cdot 2(CH_3)_2O$.[6] Attempts to examine direct conversion of Form-1 and Form-2 into Form-3 were unsuccessful. The NQR frequencies for these modifications are summarized in Table 1. The NQR lines faded out near 341 K in Form-1, near 298 K in Form-2, and near 343 K in Form-3.

The zero-splitting patterns on the ^{35}Cl Zeeman lines in Form-1 of $SnCl_4 \cdot 2CH_3CN$ are shown in Fig. 4, where z_i indicates the direction of the z axis for the ith resonance line. From these loci, the asymmetry parameter (η) and the orientations of the efg axes were determined. The asymmetry parameters and the calculated quadrupole coupling constants (e^2Qqh^{-1}) are

Table 2. Angles/° between the Sn-Cl Bonds in Form-1 of $SnCl_4 \cdot 2CH_3CN$[a]

Bond	Sn-Cl(1)[b]	Sn-Cl(2)[b]	Sn-Cl(3)	Sn-Cl(4)
Sn-Cl(2)	102.9 (102.6)[c]			
Sn-Cl(3)	94.5 (94.6)	94.0 (94.9)		
Sn-Cl(4)	93.5 (94.0)	92.5 (93.9)	163.8 (166.1)	
Sn-Cl(1')[d]	104.4 [104.2][c]			
Sn-Cl(2')	2.4 [2.7]	101.3 [100.8]		
Sn-Cl(3')	92.1 [92.5]	96.3 [96.9]	3.8 [2.6]	
Sn-Cl(4')	94.3 [95.8]	91.7 [92.0]	168.3 [165.9]	1.0 [2.4]
b-axis	37.8 [37.9]	140.6 [140.4]	91.5 [91.3]	89.5 [88.8]

a) Estimated error in the angle between the z axes ±0.1°. b) x_1 and x_2 orient at angles of 14±2° and 9±2°, respectively, to the Cl(1)SnCl(2) plane. c) The values in parentheses are based on X-ray analysis and those in brackets were calculated from atomic positions (Ref. 9). d) The Cl atoms marked with primed numbers belong to another lattice site.

Table 3. Angles/° between the efg z Axes in $SnCl_4 \cdot 2t\text{-}C_4H_9CN$[a]

z-axis	z_1[b]	z_2[b]	z_3	z_4
z_2	101.1			
z_3	95.3	93.9		
z_4	93.5	95.0	166.1	
z_1'[c]	29.1			
z_2'	82.9	101.7		
z_3'	74.1	8.5	86.4	
z_4'	62.3	21.9	73.1	
C_2-axis	75.4	50.8	43.2	36.6

a) Estimated error ±0.05°. b) x_1 and x_2 orient at angles of 5.3±1.9° and 9.2±0.6°, respectively, to the z_1z_2 plane. c) The z axes marked with primed numbers belong to another lattice site.

listed in Table 1. All the resonance lines are broad and not so intense, and in addition, each of the ν_3 and ν_4 Zeeman lines yielded overlapped patterns. These precluded accurate estimation of the η-values and the orientations of the efg axes for the ν_3 and ν_4 lines. Each of the resonance lines gave a pair of loci, in conformity with the crystal structure.[7] The direction of the b-axis was determined from the distribution of the zero-splitting loci.

The bond angles in Form-1 of $SnCl_4 \cdot 2CH_3CN$ are listed in Table 2. The assignment of the NQR lines was based on a comparison of orientation of the efg z axis with the corresponding Sn-Cl bond axis, assuming that the efg z axis is parallel to the Sn-Cl bond direction. The results of NQR are in fair agreement with those of X-ray analysis.[7] The axial Cl atoms contribute to the two higher resonance lines and the equatorial ones to the lower lines. The distinction between the Cl(4) and Cl(4') atoms in Table 2 is not always beyond question because their z axes orient very closely to each other. The assignment of the z_4 axis to the Cl(4) atom at a particular crystal site was made by choosing the angles closer to those determined by X-ray analysis.[7] The Sn-Cl lengths corresponding to Cl(1), Cl(2), Cl(3), and Cl(4) are 235.6, 234.1, 235.5, and 233.9 pm, respectively. The NQR lines for the Cl(2) and Cl(4) atoms were reversely assigned on the basis of the bond lengths.[3] The results of this study indicate that in the type of complexes $SnCl_4 \cdot 2L$ a trans effect of the ligand molecule is regarded as more important in assigning NQR lines.

Figure 5 reproduces the zero-splitting patterns in $SnCl_4 \cdot 2t\text{-}C_4H_9CN$. Each NOR line yields a pair of cones, which indicates that the crystal belongs to the monoclinic system.[10] The NQR parameters are listed in Table 1 and the angles between the z axes are given in Table 3. An examination of Table 3 reveals that this complex also has a cis configuration, as expected from its NQR spectra. Figure 6 shows the molecular shapes of $SnCl_4 \cdot 2t\text{-}C_4H_9CN$ and Form-1 of $SnCl_4 \cdot 2CH_3CN$ as deduced from Zeeman analysis.

Despite bulky ligands, the bond angles in $SnCl_4 \cdot 2t\text{-}C_4H_9CN$ are similar to those in $SnCl_4 \cdot 2CH_3CN$, $SnCl_4 \cdot 2POCl_3$,[5,11] and $SnCl_4 \cdot 2SeOCl_2$.[5,12] The ligands in these complexes, in common, possess 'pointed'[13] coordinating groups such as C≡N, P=O, and Se=O. It has been suggested that the pointed ligands prefer a distorted cis-octahedron to minimize steric repulsions of the Cl atoms and that ligands favoring a transconfiguration are bulky.[13] The occurrence of the cis-trans isomerism in $SnCl_4 \cdot 2C_6H_5CN$ and $SnCl_4 \cdot 2(CH_3)_2O$[6] suggests that the ligands in these complexes may be bulky rather than pointed. In case in the cis form of $SnCl_4 \cdot 2C_6H_5CN$ the ring planes of the ligands are perpendicular to the equatorial plane, the ligands are not sterically hindered and can be regarded as pointed. In case the ring planes lie in the equatorial plane, the ligands are sterically hindered and the complex is expected to prefer a trans form to a cis one. In cis complexes

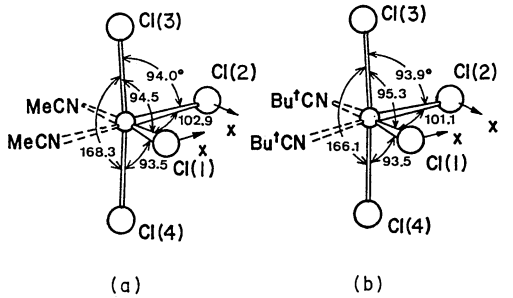

Fig. 6. Molecular shapes of (a) $SnCl_4 \cdot 2CH_3CN$ and (b) $SnCl_4 \cdot 2t\text{-}C_4H_9CN$ as determined by Zeeman analysis.

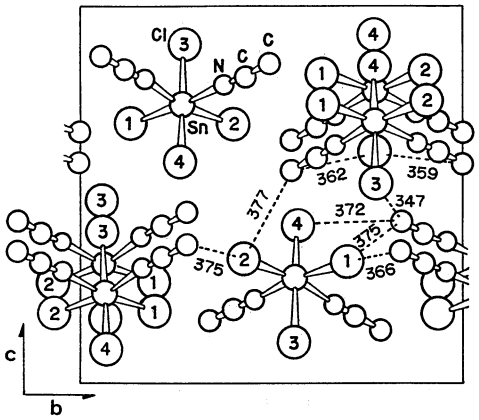

Fig. 7. Arrangement of $SnCl_4 \cdot 2CH_3CN$ molecules (Form-1) in the (100) projection. Intermolecular distances (in pm) are calculated from the atomic positions of the X-ray data (Ref. 5).

with less pointed ligands the octahedral environment around the tin atom is expected to be less distorted. This is supported by the geometry in *cis*-$SnCl_4 \cdot 2(CH_3)_2O$, where the $Cl_{eq}SnC_{eq}$ and $Cl_{ax}SnCl_{ax}$ angles are, respectively, 92.2° and 173.4°.[6]

The anomalous temperature variations of the resonance frequencies suggest some intermolecular interaction between the Cl and neighboring atoms. Since all the NQR lines have been assigned, intermolecular interaction associated with the Cl atoms can be examined. No data fitting our purpose, however, could be found in the literature. The distances between the Cl atoms and their neighbors were calculated from the atomic positions of X-ray data.[7] It was found that the Cl atoms make short contacts with the methyl groups. The significant distances are written in Fig. 7. The Cl(3) atom is in contact with the three methyl groups with the distances considerably less than the sum of van der Waals radii (380 pm).[14] The next significant contacts are associated with the Cl(1) and Cl(4) atoms. It is presumed that there are some approaches of the Cl atoms to the methyl hydrogens. The Cl(2) atom appears not to interact so strongly with the methyl groups. The distance between the Cl atom and the nearest neighbor is related to the anomalous temperature dependence.

The NQR frequencies for Form-1 of $SnCl_4 \cdot 2CD_3CN$ were recorded at various temperatures, and the values at 77 and 295 K are tabulated in Table 1. Each of the resonance lines in the CD_3CN complex shifted to the higher frequency with regard to the corresponding lines in the protonated complex. The frequency shifts of the ν_3 and ν_4 lines are ca. 20 KHz, and those of the ν_1 and ν_2 ca. 10 KHz. The magnitudes of the shifts are comparable to those in the case of 2,2′-dichloropropane[15] and the chloroform complex.[16] This suggests that these Cl atoms may be involved in hydrogen bonding.[17] Despite the shortness of the Cl(1)···CH_3 contact, the shift in the ν_1 line is small. This may result from that an H atom is situated at the position unfavorable to hydrogen bonding, which has as yet not fully been understood. No further details of hydrogen bonding can be discussed at this stage because of the unknown atomic positions of the H atoms.

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