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^{35}Cl NQR in $SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$

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^{35}Cl NQR spectra in $SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$ have been observed. Three crystal modifications of $SnCl_4 \cdot 2Me_2O$ have been found. A cis geometry is suggested for one of them, and a trans geometry for the remainder. A transformation between the cis and trans isomers in the solid state is indicated. The Zeeman effect on single crystals of *cis*-$SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$ has provided detailed information on bond angles and bond character. It is confirmed that the molecular geometry of *cis*-$SnCl_4 \cdot 2Me_2O$ belongs to the C_2 group and that $SnCl_4 \cdot 2Et_2O$ has a trans geometry. The η values of the Cl atoms in *cis*-$SnCl_4 \cdot 2Me_2O$ are negligibly small and those of the Cl atoms in $SnCl_4 \cdot 2Et_2O$ are 0.11. The relatively small η values for the latter are ascribed to π bonding between the Sn and Cl atoms.

Raman and Mössbauer spectroscopies revealed that several octahedral complexes of $SnX_4 \cdot 2L$ (X=Cl, Br; L=Lewis bases) exist in a cis or trans form in the solid state, depending on the conditions of preparation and purification.[1,2] It was demonstrated by Raman[1] and NMR[3–5] measurements that a number of SnX_4 complexes are at cis–trans equilibrium in solution. On the other hand, Davanzo and Gushikem[6] obtained evidence for the cis–trans transformation in the solid state through studies of vibrational spectroscopy, thermal analysis, and X-ray powder diffraction, and reported the transition temperature. For the solid $SnCl_4 \cdot 2Me_2O$, however, the cis geometry was proposed on the basis of Raman spectra.[1]

NQR is a useful method for examining configurations of $SnCl_4$ complexes.[7–9] We examined $SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$ by means of NQR in order to determine their molecular geometries. Furthermore, the Zeeman effect of ^{35}Cl on single crystals of *cis*-$SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$ was examined to obtain information on bond angles and bond characters.

Experimental

The complex $SnCl_4 \cdot 2Me_2O$ was prepared by bubbling a gas of dimethyl ether into a dichloromethane solution of tin(IV) chloride. The crystalline solid was filtered and purified by recrystallization from dichloromethane or chloroform and sublimation. The contents of tin and chlorine were determined gravimetrically.[10] (Found: Sn, 33.8; Cl, 40.4. Calcd: Sn, 33.7; Cl, 40.2%). The complex $SnCl_4 \cdot 2Et_2O$ was prepared by the method described in the literature[11] and identified by measuring its melting point[10,12] and NQR frequencies.[13] Single crystals of the complexes were grown in evacuated sealed tubes by sublimation.

The NQR spectrometer used was a Dean-type superregenerative spectrometer with frequency modulation. The Zeeman effect was examined by means of the zero-splitting cone method. A magnetic field was supplied by means of a Helmholtz coil. Temperature was determined by the use of a copper–constantan thermocouple. Temperature below room temperature in the Zeeman study was controlled by varying the flow of the nitrogen gas from liquid nitrogen.

Results and Discussion

The NQR spectrum for $SnCl_4 \cdot 2Me_2O$ obtained by recrystallization differed from that for the sample obtained by sublimation above 50 °C. The ^{35}Cl resonance frequencies are shown as a function of temperature in Fig. 1. The recrystallized sample gave two NQR lines and the sublimed one only one line. The former is tentatively termed Form-1 and the latter Form-2. The NQR spectrum of Form-2 suggests that the four Sn–Cl bonds of the complex are equivalent. Therefore, the molecule in Form-2 has a trans configuration.[7] Form-1 is assumed to be a cis isomer, judging from the magnitude of the splitting between adjacent NQR lines. This was confirmed by the Zeeman study on a single crystal. In Form-1 the

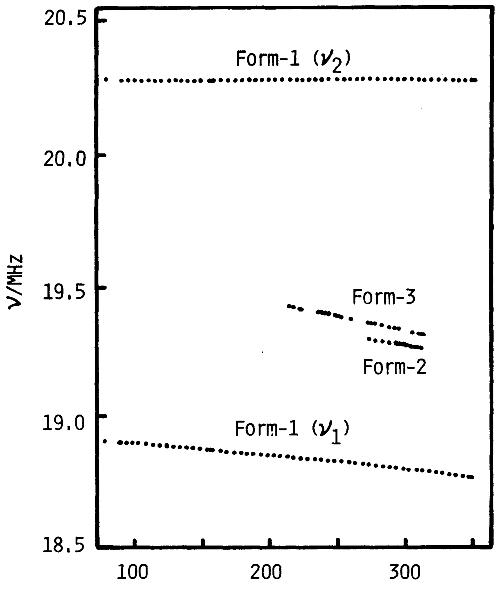

Fig. 1. Temperature dependence of ^{35}Cl resonance frequencies of $SnCl_4 \cdot 2Me_2O$.

frequency of the lower resonance line, ν_1, decreased monotonously with a rise in temperature, whereas the higher resonance line, ν_2, had a very small temperature coefficient and the minimum frequency was 20.278 MHz near 140 K and the maximum one 20.287 MHz near 285 K, suggesting the existence of intermolecular interaction.

Form-2 was unstable at room temperature and, in one night at the longest, changed to another modification (Form-3) which yielded also only one resonance line. When Form-2 was cooled to near 270 K, it changed immediately to Form-3. This transformation became rapid with lowering temperature. When Form-2 was cooled to 77 K, the absorption lines for Form-1 appeared immediately. Form-3 was also unstable and was transformed to Form-1 at room temperature in a day. This transformation also became rapid with lowering temperature, and this change took place immediately at temperature below less than ca. 210 K. The resonance frequencies for Form-2 and Form-3 decreased with a rise in temperature and faded out at 311 K and 314 K, respectively. Both the ν_1 and ν_2 lines in Form-1 disappeared at 350 K without broadening. When the sample was cooled rapidly to room temperature, it gave the same NQR line as did Form-2. Accordingly, this suggests a transition from the cis isomer to the trans one. Although the transition point was reproducible within ±1.5 K, the sample maintained at ca. 340 K for a day gave the same spectrum as did Form-2 at room temperature. Accordingly, the observed transition point seems not to be intrinsic.

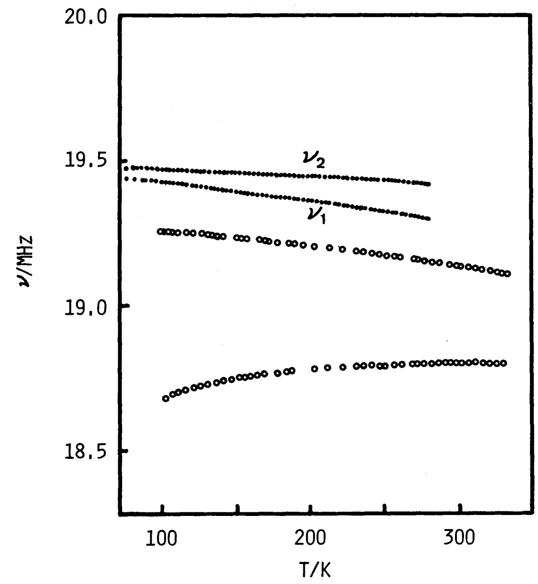

Fig. 2. Temperature dependence of ^{35}Cl resonance frequencies of $SnCl_4 \cdot 2Et_2O$ (●) and $SnCl_4 \cdot 2THF$ (○).

The temperature dependence of the NQR frequencies of $SnCl_4 \cdot 2Et_2O$ is shown in Fig. 2. The resonance lines decreased in frequency with a rise in temperature and disappeared near 280 K. For this complex, a trans geometry was proposed on the basis of the NQR[7] and the vibrational spectra.[11,14] In the trans complex with tetrahydrothiophen $SnCl_4 \cdot 2THT$, the geometry of which was determined by X-ray analysis,[15] no resonance lines were detected at room temperature, although two resonance lines were observed below ca. 210 K.[8,9] The resonance lines of $SnCl_4 \cdot 2THF$, which has a trans geometry in solid,[11] disappeared at 330 K as shown in Fig. 2. The temperature variations of the NQR frequencies of $SnCl_4 \cdot 2THF$ in the range of 100 to 300 K were in good agreement with those of $SnCl_4 \cdot 2THF$ reported by Rupp-Bensadon and Lucken.[9] In some cis-complexes such as $SnCl_4 \cdot 2POCl_3$,[16] $SnCl_4 \cdot 2SeOCl_2$,[16] $SnCl_4 \cdot 2MeCN$, and $SnCl_4 \cdot 2Me_3CCN$ the NQR lines could be detected up to the melting point. It is of interest that in the octahedral complexes of $SnCl_4$ the fade-out phenomenon of the NQR lines is characteristic of the trans geometry.

The Zeeman effect on the ^{35}Cl lines in Form-1 of

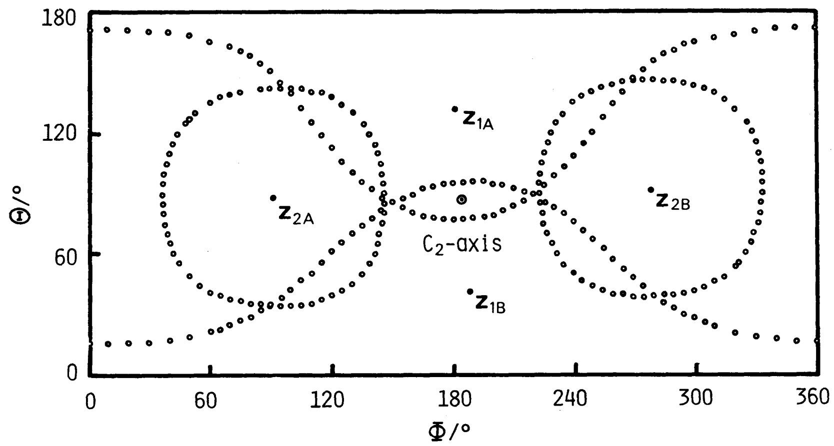

Fig. 3. Zero-splitting patterns of ^{35}Cl NQR lines in Form-1 of $SnCl_4 \cdot 2Me_2O$.

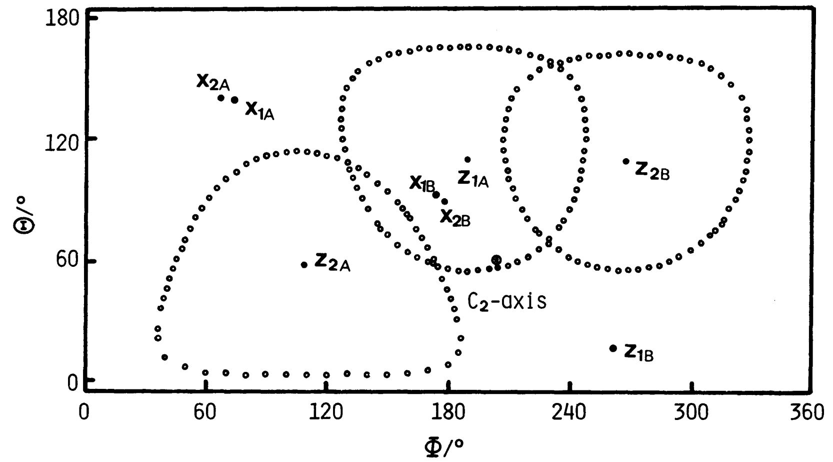

Fig. 4. Zero-splitting patterns of ^{35}Cl NQR lines in $SnCl_4 \cdot 2Et_2O$.

Table 1. ^{35}Cl NQR Parameters for $SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$

Compound		Frequency/MHz		η/%	e^2Qqh^{-1}/MHz
$SnCl_4 \cdot 2Me_2O$		77 K	293 K		
Form-1	ν_1	18.906	18.807	4.9	37.600
	ν_2	20.281	20.287	2.7	40.569
Form-2		—	19.279		
Form-3		—	19.340		
$SnCl_4 \cdot 2Et_2O$		77 K	235 K		
	ν_1	19.435	19.341	11.4	38.601
	ν_2	19.474	19.440	11.6	38.793

$SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Et_2O$ was observed at room temperature and at 235 K, respectively. The zero-splitting patterns are shown in Figs. 3 and 4, where z_i indicates the direction of the z axis of the efg tensor at the Cl atom which yields a ν_i resonance line. The observed loci were analyzed by the least squares method to obtain the direction of the efg tensor and the asymmetry parameter (η). The locus is expressed for ^{35}Cl nucleus as follows;

$$\sin^2 \theta_0 = 2/(3 - \eta \cos 2\phi_0), \tag{1}$$

where θ_0 and ϕ_0 are the polar and azimuthal angles, respectively. The NQR parameters are listed in Table 1. In $SnCl_4 \cdot 2Me_2O$ a pair of zero-splitting loci were obtained for each resonance line and a twofold axis was determined from the distribution of the Zeeman patterns. The resonance lines of $SnCl_4 \cdot 2Me_2O$ were comparatively weak and each NQR line gave partly overlapped Zeeman patterns. Consequently, the directions of the z axes of the efg tensors and the values of the asymmetry parameters were not so accurate. In $SnCl_4 \cdot 2Et_2O$ the lower resonance line, ν_1, gave only one locus although the two loci were obtained from the higher resonance line, ν_2, as shown in Fig. 4. The reason is because the efg axis of the partner locus is nearly parallel to the rf field. A twofold axis can be determined from the loci for the ν_2 line and the predicted direction of the missing z axis (z_{1B}) is shown in Fig. 4. Therefore, the crystals of these complexes belong to the monoclinic system.

Table 2. Angles between the efg z Axes in $SnCl_4 \cdot 2Me_2O$[a)]

	z_{1A}	z_{1B}	z_{2A}
z_{1B}	92.2°		
z_{2A}	93.5°	91.1°	
z_{2B}	91.1°	93.5°	173.4°

a) Estimated error ±0.3°.

The angles between the Sn–Cl bonds have been deduced, assuming that the principal z axis of the efg tensor is parallel to the Sn–Cl bond. The results for $SnCl_4 \cdot 2Me_2O$ are listed in Table 2. These angles reveal that Form-1 of $SnCl_4 \cdot 2Me_2O$ has a cis geometry. The ν_1 and ν_2 lines can be assigned to the equatorial and the axial chlorine atoms, respectively. The molecular geometry of Form-1 is shown in Fig. 5(a). The molecule possesses a twofold axis, parallel to that of the crystal. The bond angles in this complex are very similar to those of the other cis isomers of the octahedral $SnCl_4$ complexes found by X-ray studies.[17–19] In the monomeric cis-complexes, the angles of $\angle Cl_1SnCl_1$ are greater than 100° and those of $\angle Cl_2SnCl_2$ range from 161.9° to 166.6°. Therefore the molecule in Form-1 of $SnCl_4 \cdot 2Me_2O$ is less distorted.

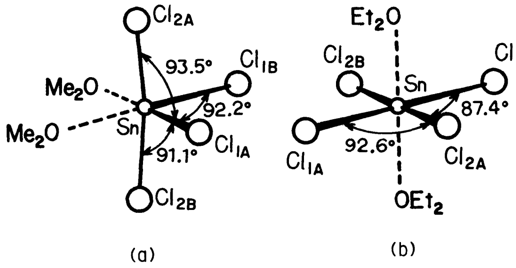

Fig. 5. Molecular shapes of Form-1 of $SnCl_4\cdot 2Me_2O$ (a) and $SnCl_4\cdot 2Et_2O$ (b).

Table 3. Angles between the efg Axes and the Crystal Axis in $SnCl_4\cdot 2Et_2O$[a)]

	z_1	x_1	x_2	C_2-axis
z_1				52.34°
z_2	92.58°			78.64°
Plane z_1z_2		86.59°	86.52°	40.59°

a) Estimated error ±0.05°.

It is concluded from the Zeeman analysis that the complex of Et_2O has a trans configuration. This is in agreement with the geometry proposed on the basis of the infrared and Raman spectra.[10,13] As shown in Fig. 4, two of the zero-splitting cones, one from each of the resonance lines, were assigned to each crystal site on the basis of the orientations of the efg axes. The z axes of these cones are nearly at right angles to each other, as can be seen from Table 3. This requires that there are two pairs of chemically equivalent chlorine atoms in a molecule and that the z axes at the chlorine atoms in each pair are collinear. Accordingly, the molecule of $SnCl_4\cdot 2Et_2O$ has an inversion center at the tin atom and the four Sn–Cl bonds are coplanar. The bond angle $\angle Cl_1SnCl_2$ is close to those in $SnCl_4\cdot 2Et_3P$ (89.9° and 90.1°).[20] The Sn–Cl_1 and Sn–Cl_2 bonds make angles of 52.3° and 78.6°, respectively, to the twofold axis of the crystal, as is shown in Table 3. The molecule has neither symmetrical plane nor symmetrical axis. The atomic arrangement around the tin atom is very similar to that in $SnCl_4\cdot 2Et_3P$.[20]

In the Et_2O complex, the Cl_1 atom has almost the same η-value as the Cl_2 atom. These values are somewhat greater than those found in the cis complexes.[16] The x axes of these chlorine atoms are nearly at right angles to the equatorial plane, as can be seen from Table 3. This suggests π interaction between the tin and chlorine atoms. The energy level of the oxygen $2p\pi$ orbital is about 3 eV lower than that of the chlorine $3p\pi$ orbital.[21,22] It is therefore predicted that the chlorine atom donates more charges to the vacant $d\pi$ orbital on the tin atom than the oxygen atom. On the other hand, the oxygen p orbitals do not take part in the π-bonding lying in the equatorial plane. If this is the case, the populations of the p_x orbital on the chlorine atom are more decreased. The difference in population between the p_x and p_y orbitals is estimated to be 0.027 by using the Bersohn's relation.[23] The ionic character of the Sn–Cl bond is calculated to be 57 per cent, assuming that the s character of the bonding orbital of the Cl atom is 0.15.[24]

In the cis isomer of the Me_2O complexes, the η-values are very small. Therefore, the Sn–Cl bonds are almost cylindrically symmetrical. The equatorial Cl atoms are 3 per cent more ionic than the axial ones. This trend is consistent with that in other cis complexes.[16] Since the trans isomers of the Me_2O complex have only one absorption line and the symmetry of the Me_2O moelcule is C_{2v}, the complexes are required to possess at least a twofold axis and a mirror plane. It is therefore considered that the trans complexes have C_{2h}, C_{2v}, or D_{2h} symmetry.

References

1) S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta,* **20**, 221 (1976).

2) D. Tudela and V. Fernadez, *J. Chem. Soc., Dalton Trans.,* **1985**, 1281.

3) S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta,* **22**, 191 (1977).

4) C. T. G. Knight and A. E. Merbach, *Inorg. Chem.,* **24**, 576 (1985).

5) C. T. G. Knight and A. E. Merbach, *J. Am. Chem. Soc.,* **106**, 804 (1984).

6) C. U. Davanzo and Y. Gushikem, *J. Chem. Soc., Dalton Trans.,* **1981**, 843.

7) Yu. K. Maksyutin, E. N. Gruyanova, E. A. Kravchenko, and G. K. Semin, *J. Chem. Soc., Chem. Commun.,* **1973**, 429.

8) P. J. Huggett, R. J. Lynch, T. C. Waddington, and K. Wade, *J. Chem. Soc., Dalton Trans.,* **1980**, 1164.

9) J. Rupp-Bensadon and E. A. C. Lucken, *J. Chem. Soc., Dalton Trans.,* **1983**, 495.

10) E. T. Hitchcock and P. J. Edving, *Anal. Chim. Acta,* **28**, 417 (1963).

11) I. R. Beattie and L. Rule, *J. Chem. Soc.,* **1965**, 2995.

12) D. C. Bradley, E. V. Caldwell, and W. Wardlaw, *J. Chem. Soc.,* **1957**, 3039.

13) D. Biedenkapp and A. Weiss, *Z. Naturforsch.,* **19a**, 1518 (1964).

14) I. R. Beattie and L. Rule, *J. Chem. Soc.,* **1964**, 3267.

15) I. R. Beattie, R. Hulme, and L. Rule, *J. Chem. Soc.,* **1965**, 1581.

16) M. Mishima, *J. Sci. Hiroshima Univ.,* **A46**, 41 (1982).

17) Y. Hermodsson, *Acta Crystallogr.,* **13**, 656 (1960).

18) C.-I. Bränden, *Acta Chem. Scand.,* **17**, 759 (1963).

19) M. Webster and E. A. Bränden, *J. Chem. Soc. A,* **1969**, 2443.

20) G. G. Mather, G. M. McLaughlin, and A. Pidcock, *J. Chem. Soc., Dalton Trans.,* **1973**, 1823.

21) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.,* **49**, 1254 (1953).

22) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.,* **84**, 540 (1962).

23) R. Bersohn, *J. Chem. Phys.,* **22**, 2078 (1954).

24) C. H. Townes and B. P. Dailey, *J. Chem. Phys.,* **17**, 782 (1949).