Nuclear Quadrupole Resonance and Stereochemistry. Part 8.[†] *cis–trans* Isomerism in Octahedral $SnCl_4L_2$ Complexes

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The ^{35}Cl n.q.r. spectra of several octahedral complexes of tin tetrachloride, $SnCl_4L_2$ (L = donor ligand), have been measured as a function of temperature between 77 K and room temperature. The significance of the n.q.r. data to the question of the *cis* or *trans* relationship of the two ligands is discussed and it is shown that the n.q.r. results must be interpreted with considerable caution.

Tin tetrachloride forms a wide variety of complexes of general formula $SnCl_4L_2$ where L is a donor molecule. In these compounds the tin atom is in an octahedral environment, and thus potentially two isomers, with L in *cis* or *trans* mutual orientations, can be prepared. For a few complexes the crystal structures have been determined [1,2] but in most cases more indirect methods of structure assignment using i.r.,[3,4] n.m.r.,[5] Mössbauer,[6–8] and n.q.r. spectra have been employed. As briefly described below, n.q.r. applied to the ^{35}Cl nuclei has been proposed as a simple and unambiguous method of determining the *cis* or *trans* nature of the complex [9] but a warning against a too facile interpretation of the n.q.r. data has recently been published.[12] We have independently reached the same conclusion, although for a largely different series of ligands, and we report our results here. Like Waddington and co-workers [12] we believe that useful structural information can be obtained from ^{35}Cl n.q.r. data but that measurements at several different temperatures are necessary before a structure assignment can be attempted.

Experimental

Complexes were prepared by dropwise addition of a slight excess of a 10% solution of redistilled tin tetrachloride in methylene chloride to a 10% solution of the donor in the same solvent at 0 °C. The precipitated complex was washed with a little dry carbon tetrachloride and sealed in a glass ampoule for n.q.r. measurements. All operations were carried out under an atmosphere of dry nitrogen or argon. The n.q.r. spectra were measured on a Decca super-regenerative spectrometer, frequencies were measured against harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802A digital thermometer and variable temperatures between 77 K and room temperature obtained using a cryostat controlled with an Artronix 5301-E temperature controller. The Table shows the resonance frequencies and temperature coefficients for a variety of complexes.

Results and Discussion

The possibility of using the ^{35}Cl n.q.r. frequencies of $SnCl_4L_2$ complexes to determine the *cis* or *trans* relationship of the L depends essentially on the behaviour of just one parameter. With a cylindrically symmetric ligand in the isolated molecule for the *trans* complex all four chlorine atoms are equivalent and there would be just one n.q.r. frequency, whereas for the *cis* complex the chlorine atoms fall into two distinct classes and two n.q.r. frequencies would be observed. For non-cylindrically symmetric ligands and for molecules in the solid state this ideal situation would be disturbed and in both cases up to four resonances, or even more if there are several inequivalent molecules in the unit cell, could be observed. However, if the frequency splittings induced by the non-cylindrical nature of the ligand or intermolecular interactions in the solid state are smaller than the frequency difference between the two groups of chlorine atoms in the *cis* complex, the pattern of frequencies, grouped close to a single value for the *trans* complex or forming two distinct groups for the *cis* complex, will suffice to determine the molecular geometry. The relative magnitude of the above effects on the ^{35}Cl n.q.r. frequencies is thus crucial to the utility of the n.q.r. method in this context.

Table. ^{35}Cl resonance frequencies and temperature coefficients at 150 K for various octahedral complexes $SnCl_4L_2$

L	Temp. (K)	ν/MHz	$\frac{1}{\nu}\left(\frac{\delta\nu}{\delta T}\right)_{150} \times 10^5$
Tetrahydrofuran	110	18.697	4.452
	110	19.256	−3.287
Tetrahydrothiophen	77	17.432	−3.791
	77	17.897	−5.356
1,2-Dimethoxyethane [a]	102	19.608	−10.226 [b]
	102	19.652	−5.848 [b]
Hexamethylphosphoramide	77	17.775	−0.447
	77	18.039	−3.325
Trimethyl phosphate	77	18.240	−1.195
	89	18.452	−3.475
	89	18.946	−1.709
	89	19.036	−10.091

[a] 1 : 1 complex. [b] Temperature coefficient calculated at 250 K.

In a recent study of related antimony pentachloride complexes, $SbCl_5L$, we have shown that the difference between the ^{35}Cl n.q.r. frequency of the unique chlorine atom *trans* to the ligand and those of the four remaining chlorine atoms is small and comparable to the intermolecular effects.[13] For the alkly nitrile complexes $SnCl_4(RCN)_2$, Waddington and co-workers [12] have likewise shown that the n.q.r. method cannot be relied upon to distinguish the position of the ligand, at least if the measurements are carried out at only one temperature.

The problems involved in using the n.q.r. method are illustrated by Figure 1 where the ^{35}Cl frequencies of the tetrahydrofuran (thf) complex, $SnCl_4(thf)_2$, are shown as a function of temperature. From 77 to 106 K there are at least four very weak signals. At 106 K a phase change occurs and just two intense signals, at 18.697 and 19.256 MHz, are observed. The temperature dependences of these two resonances are however quite different, one being positive and the other negative. The magnitudes of the temperature dependences

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[†] Part 7 is ref. 13.

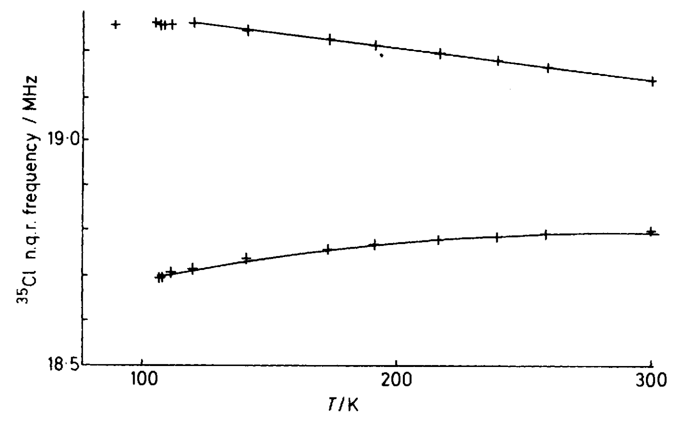


Figure 1. Temperature dependence of the ^{35}Cl n.q.r. frequencies of $SnCl_4(thf)_2$

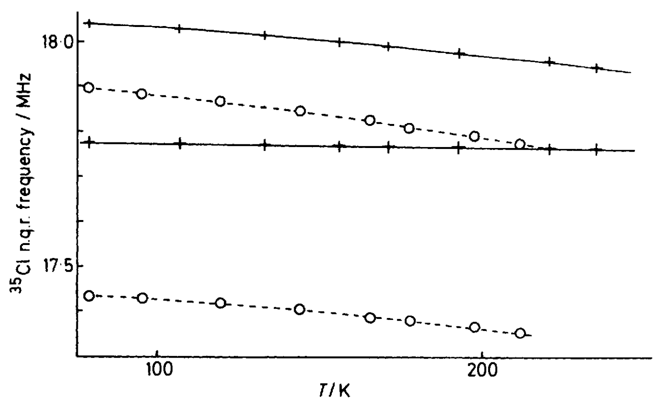


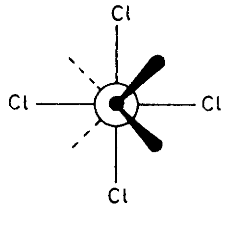
Figure 2. Temperature dependence of the ^{35}Cl n.q.r. frequencies of $SnCl_4(hmpa)_2$ (+) and $SnCl_4(tht)_2$ (○)

are nevertheless quite small so that at 300 K the two frequencies are still separated by 0.315 MHz.

For a *trans* complex, where, for the ideal molecule, all four chlorine atoms lie in the same plane, the temperature dependences of the ^{35}Cl n.q.r. frequencies (which depend on the amplitudes of the various molecular motions) might be expected to be rather similar even if the actual resonance frequencies themselves are different owing to small departures of the molecular structure from the ideal D_{4h} symmetry. This criterion of similar temperature dependence for the *trans* complexes was indeed proposed by Waddington and co-workers[12] as a result of their studies on nitrile complexes. For the present complex this criterion thus indicates a *cis* structure. Vibrational spectra have however been taken to indicate a *trans* structure.[3]

Although the over-simple correlation between the number of resonance frequencies and the molecular geometry is certainly incorrect this is not to say that this parameter yields no structural information. When complexed, the local symmetry of a symmetric ether such as thf is at most C_s. If this is attached to a $SnCl_4$ group in the *trans* position and if the two ether fragments are staggered so that their symmetry planes coincide, the molecule overall can retain a two-fold improper axis for almost any disposition of the $SnCl_4$ group, even one in which all four chlorine atoms are not in the same plane, see structure I. Such a complex would exhibit just two ^{35}Cl resonance frequencies. For the *cis* configuration the situation is very different since the *cis*-$SnCl_4$ fragment has only C_{2v} symmetry. Two pairs of equivalent chlorine atoms will only persist in the complex for orientations of the two C_s ligands such that either the overall C_{2v} symmetry is maintained, see structure II (both ligand symmetry planes lying in the same symmetry plane of the C_{2v} $SnCl_4$ fragment), or the symmetry drops to C_2, see structure III (the ligand symmetry planes symmetrically disposed about a symmetry plane of the $SnCl_4$ fragment).

On these grounds a *trans* configuration for an ether complex showing two resonance frequencies appears more likely although the *cis* configuration is not ruled out. Thus in this case n.q.r. furnishes two pieces of indirect evidence, the temperature coefficients and the number of resonances, which are contradictory.



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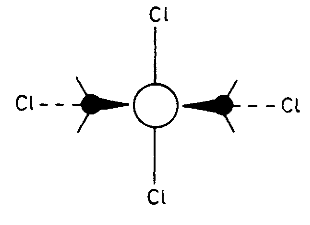

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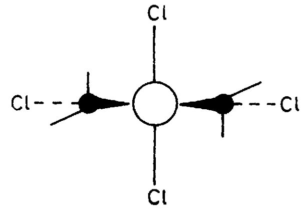

III

The situation for the complexes with tetrahydrothiophen (tht) and hexamethylphosphoramide (hmpa), for which the results are shown in Figure 2, is more straightforward. Both complexes show two resonances over the whole temperature range and for these two resonances the temperature coefficients are fairly similar. The above remarks concerning the number of resonances are true for both ligands and we have no hesitation, in agreement with the i.r. studies,[3] in assigning *trans* configurations to both of these compounds.

It has been claimed[14] that the thf complex can be prepared in the *cis* form if n-pentane is used as the solvent in the preparation. Waddington and co-workers[12] were unable to find any n.q.r. evidence of this *cis* form, all samples showing the same n.q.r. spectrum. We confirm this observation and numerous attempts both by Dr. E. Turin at the University of Lausanne and ourselves have failed to produce a sample with an n.q.r. spectrum different from that shown in Figure 2.

For the trimethyl phosphate (tmp) complex four resonances were observed covering a range of frequencies of 800 kHz at low temperature (Figure 3). Three of the temperature dependences are rather similar while that of the highest frequency is much more negative with the result that at 310 K the frequency spread is only 400 kHz. Infrared studies have indicated the *cis* configuration;[15] the n.q.r. results are not in disagreement with this but do not really provide any information one way or the other.

The last system studied here is that of the 1 : 1 complex with 1,2-dimethoxyethane (dme). If this complex is monomeric it can only have the *cis* configuration and the isolated molecule would have only two ^{35}Cl n.q.r. frequencies. A

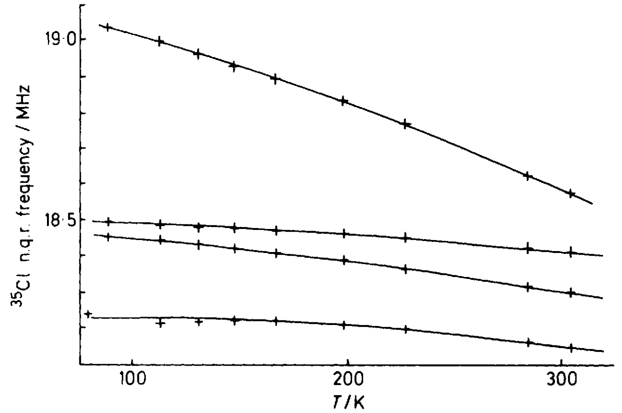

Figure 3. Temperature dependence of the ^{35}Cl n.q.r. frequencies of $SnCl_4(tmp)_2$

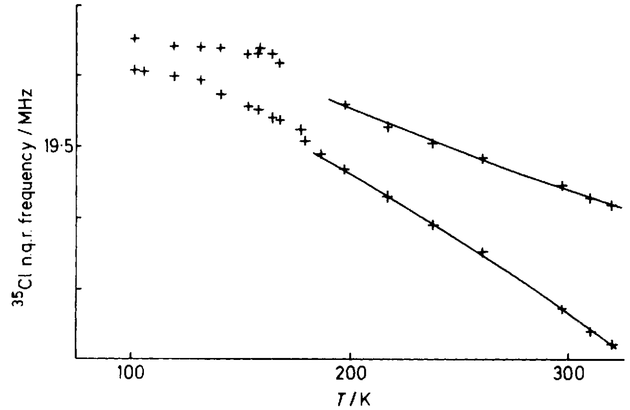

Figure 4. Temperature dependence of the ^{35}Cl n.q.r. frequencies of $SnCl_4(dme)_2$

polymeric complex could however have either the *cis* or *trans* configuration. The n.q.r. results are shown in Figure 4. At low temperatures, in agreement with previous observations,[9] only a single broad resonance centred at 19.6 MHz can be seen. On raising the temperature two fairly strong signals, accompanied by several weaker ones, appeared. At around 185 K almost all the signals disappeared but on increasing the temperature two signals of equal intensity appeared. The temperature dependences of these two signals are rather different, one being the usual negative slope, negative second derivative variety whereas the second has a negative slope but a positive second derivative. On these grounds it is tempting to assign the *cis* structure to this complex in the high-temperature phase but it must be admitted that the only certain point demonstrated by the n.q.r. data is the phase change which may or may not be accompanied by a change in molecular structure. In view of the weakness and multiplicity of the lines in the low-temperature region it is possible that the complex is a disordered polymer.

In conclusion therefore, and in agreement with the results of Waddington and co-workers, the ^{35}Cl n.q.r. spectra of the $SnCl_4L_2$ complexes do not provide an easy means of distinguishing between *cis* and *trans* isomers and at best can only provide supporting evidence for a structure assignment.

Acknowledgements

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