Chlorine-35 Nuclear Quadrupole Resonance Studies on Some Tin(IV) Chloride Adducts

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The ^{35}Cl n.q.r. spectra of a series of tin(IV) chloride adducts $SnCl_4{\cdot}2L$ [L = MeCN, $CH_2{=}CHCN$, Bu^{t}CN, PhCN' $CH_2(CN)_2$, 1,2-$C_6H_4(CN)_2$, SMe_2O, or tht (tetrahydrothiophen)] have been recorded at various temperatures and used to deduce whether these complexes are *cis* or *trans*. A *trans* structure is indicated for $SnCl_4{\cdot}2$tht, *cis* structures for the remainder. When compared with other published n.q.r. and structural data, our results indicate that the ^{35}Cl n.q.r. frequencies are related to the Sn–Cl bond lengths in such systems. The higher ^{35}Cl n.q.r. frequencies tend to be associated with the shorter bonds, though the frequencies also vary markedly with temperature.

OF the large number of known tin(IV) chloride adducts $SnCl_4{\cdot}2L$ or $SnCl_4{\cdot}L{-}L$ [1,2] (L = a unidentate Lewis base; L–L = a bidentate Lewis base), the compounds *cis*-$SnCl_4{\cdot}2L$ (L = SMe_2O,[3] MeCN,[4] PCl_3O,[5] or $SeCl_2O$ [6]), *cis*-$SnCl_4{\cdot}NC(CH_2)_3CN$,[7] and *trans*-$SnCl_4{\cdot}2$py [8] (py = pyridine) have been the subjects of *X*-ray crystallographic studies. The vibrational spectra of many other adducts [9–15] have been used to deduce whether they were *cis* or *trans*, though not always unambiguously [11,12] unless isotopic enrichment [16,17] was used to aid assignment. Since ^{35}Cl nuclear quadrupole resonance studies are in principle capable of distinguishing between *cis* and *trans* isomers $SnCl_4{\cdot}2L$ or $SnCl_4{\cdot}L{-}L$,[18,19] we have recorded the ^{35}Cl n.q.r. spectra of the series of adducts $SnCl_4{\cdot}2L$ [L = MeCN, $CH_2{=}CHCN$, Bu^{t}CN, PhCN, $CH_2(CN)_2$, 1,2-$C_6H_4(CN)_2$, SMe_2O, or tht (tetrahydrothiophen, C_4H_8S)]. We report and discuss the structural implications in this paper.

EXPERIMENTAL

Tin(IV) chloride was purified by vacuum distillation; the Lewis bases were purified and dried by recommended procedures.[20] The nitrile adducts $SnCl_4{\cdot}2RCN$ (R = Me, $CH_2{=}CH$, Bu^t, or Ph) were prepared from solutions of the Lewis acid (20 mmol) and base (45 mmol) in toluene (50 cm^3), separating as crystals when the solutions were chilled or concentrated by evaporation. After being washed with cold toluene they gave satisfactory analyses [see Table deposited in Supplementary Publication No. SUP 22739 (2 pp.)].† The dinitrile adducts $SnCl_4{\cdot}2CH_2(CN)_2$ [21] and $SnCl_4{\cdot}2C_6H_4(CN)_2$ [*not* the 1 : 1 adducts $SnCl_4{\cdot}CH_2(CN)_2$ and $SnCl_4{\cdot}C_6H_4(CN)_2$] precipitated when solutions of equimolar proportions (or proportions rich in dinitrile) were mixed, and were purified by washing with dry toluene. They were insoluble in aprotic solvents and apparently solvolysed by protic solvents.

The dimethyl sulphoxide adduct $SnCl_4{\cdot}2SMe_2O$ was prepared by the method of Cotton and Francis,[22] recrystallised from hot water, and dried *in vacuo* at 70 °C. The tetrahydrothiophen adduct $SnCl_4{\cdot}2$tht precipitated when tht was added to a solution of $SnCl_4$ in pentane, and was also prepared in dichloromethane (in which it is very soluble) from appropriate proportions of the reagents. The hexachlorostannate(IV) salt, $[Ph_2CNH_2]_2[SnCl_6]$, was prepared from $SnCl_4$ and $2Ph_2CNH_2Cl$ in CH_2Cl_2. Chlorine-35 nuclear quadrupole resonance spectra were recorded on a Decca commercial, mid-range spectrometer using Zeeman modulation. The positions of the line centres were determined after side-band suppression. Low-temperature spectra were recorded using samples cooled by nitrogen gas evaporating from liquid nitrogen. Temperatures were recorded using a Comark electronic thermometer and a copper–constantan thermocouple.

RESULTS AND DISCUSSION

Stereochemistry of Adducts $SnCl_4{\cdot}2L$.—In principle, the number and spacing of the absorptions in the n.q.r. spectra of adducts $SnCl_4{\cdot}2L$ can be used to deduce whether they are *cis* or *trans*.[18,19] Figure 1 shows the possible forms the spectra may take. At least two resonances [Figure 1(*a*)(*i*)] are expected for *cis* adducts, arising from the two distinct types of chlorine atom (axial and equatorial) they contain, though either of these resonances [Figure 1(*a*)(*ii*)] or both of them [Figure 1(*a*)(*iii*)] may be further split if the chemically equivalent

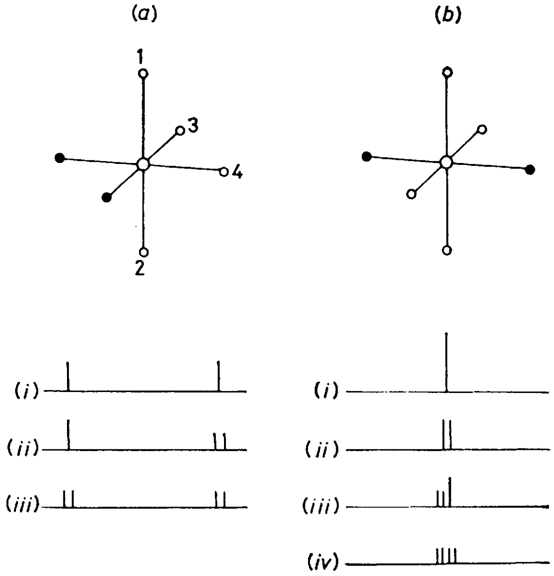

FIGURE 1 Possible forms of the ^{35}Cl n.q.r. spectra of $SnCl_4{\cdot}2L$, (*a*) *cis* form, (*b*) *trans* form

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

nuclei occupy different lattice sites. By contrast, the spectrum of a ***trans*** adduct may consist of a single resonance [Figure 1(*b*)(*i*)], since all four chlorine atoms occupy chemically equivalent positions, though again secondary splitting may occur, through asymmetry in the ligands L or lattice effects, to generate a total of two, three, or four resonances [Figure 1(*b*)(*ii*)—(*iv*)]. These secondary splittings are considered unlikely to exceed 2%[23]—5%[24] of the observed absorption frequency.

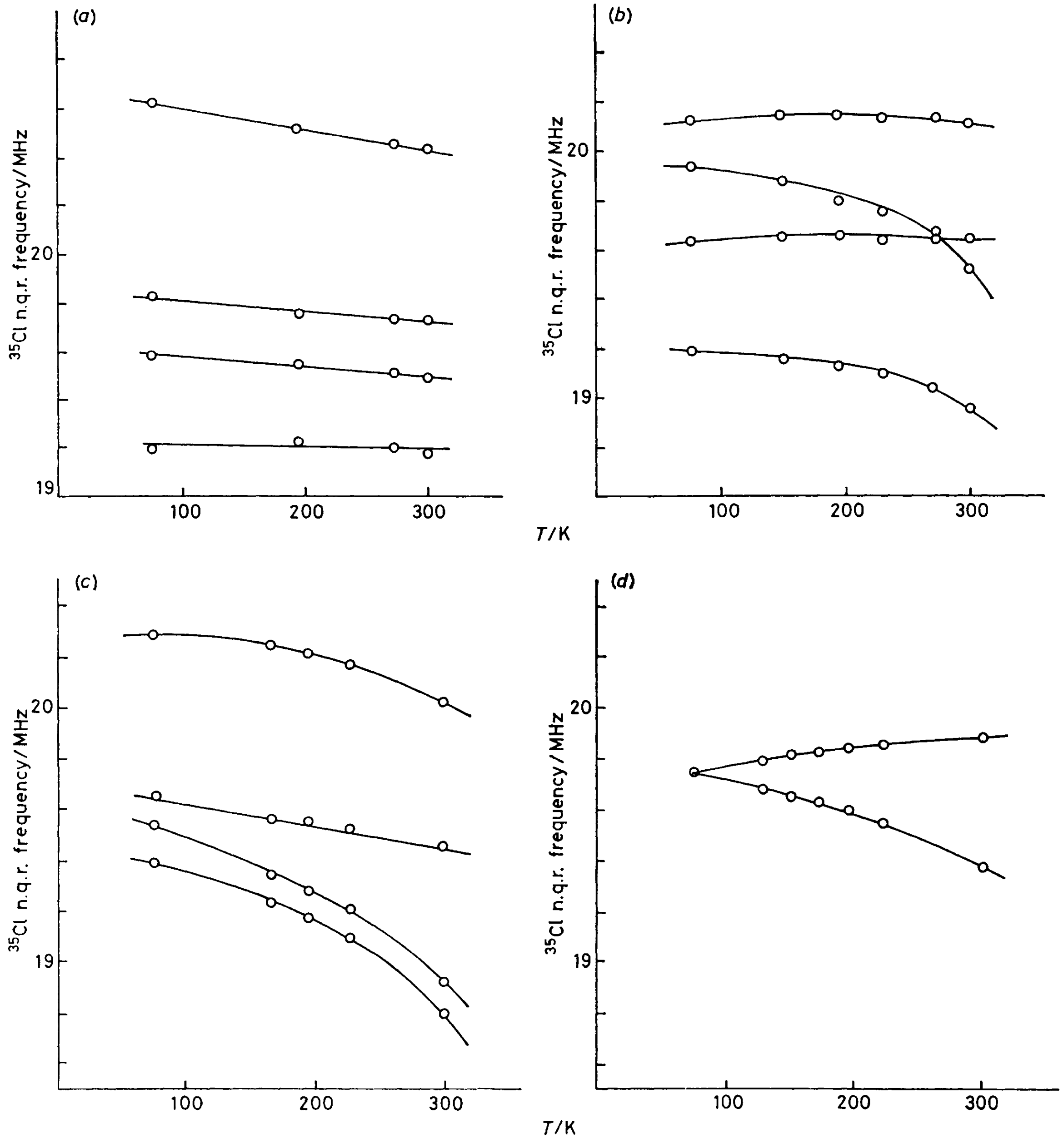

FIGURE 2 Temperature dependence of the ^{35}Cl n.q.r. spectra of the nitrile adducts of $SnCl_4$: (*a*) $SnCl_4 \cdot 2MeCN$; (*b*) $SnCl_4 \cdot 2CH_2$=CHCN; (*c*) $SnCl_4 \cdot 2Bu^tCN$; (*d*) $SnCl_4 \cdot 2PhCN$

Details of the n.q.r. spectra recorded are given in Table 1. Spectra recorded at a single temperature rarely fell obviously into one particular category of those shown in Figure 1, so the temperature dependence of the spectra was determined by recording them at 77, 195, and 300 K. Figure 2 illustrates the temperature dependence of the spectra of the nitrile adducts $SnCl_4 \cdot 2RCN$ (R = Me, CH_2=CH, Bu^t, or Ph).

Chemically equivalent nuclei are expected to show the same type of temperature dependence of their absorption frequencies. In each of Figures 2(*b*)—(*d*) two distinct types of temperature dependence are apparent, with pairs of lines having closely related temperature coefficients $(d\nu/dT)_{av.}$, corresponding to the axial and equatorial chlorine sites in a *cis* adduct. Values of $(d\nu/dT)_{av.}$ are listed in Table 1. The situation is less clear for the acetonitrile adduct $SnCl_4{\cdot}2MeCN$ [Figure 2(*a*)], though similar temperature dependence is shown by at least one pair of the lines, and the overall spread of frequencies, 1.43 MHz, is too great to be attributable to solid-state splitting of chemically equivalent nuclei, so a *cis* configuration is indicated here too.

The succinonitrile ($NCCH_2CN$) and phthalonitrile (*o*-NCC_6H_4CN) adducts did not give satisfactory spectra throughout the temperature range. However, the appearance of three widely spaced lines of relative intensity 2 : 1 : 1 (Table 1) suggests that these adducts also have *cis* structures. Indeed, a *cis* structure appears to be the norm for nitrile adducts $SnCl_4{\cdot}2RCN$. Nitriles are effectively ' pointed ' ligands, their donor atoms project out from the rest of the molecule, so crowding of one ligand by another in a *cis* adduct is not important even in the case of pivalonitrile, Bu^tCN. The same is probably true of the sulphoxide ligand. The adduct $SnCl_4{\cdot}2SMe_2O$ is known to have a *cis* structure.[3]

TABLE 1

^{35}Cl N.q.r. frequencies at various temperatures of tin(IV) chloride adducts and the salt $[Ph_2CNH_2]_2[SnCl_6]$

	ν/MHz[a]			$\left(\frac{d\nu}{dT}\right)_{av.}$/
Compound	77 K	195 K	300 K	Hz K^{-1}
$SnCl_4{\cdot}2MeCN$	19.192	19.225	19.175	−76
	19.580	19.545	19.485	−426
	19.825	19.750	19.725	−448
	20.625	20.514	20.433	−861
$SnCl_4{\cdot}2CH_2{=}CHCN$	19.19	19.13	18.96	−1 013
	19.64	19.66	19.56	−359
	19.94	19.80	20.65	−1 300
	20.13	20.15	20.11	−90
$SnCl_4{\cdot}2Bu^tCN$	19.390	19.180	18.800	−2 650
	19.535	19.278	18.925	−2 740
	19.650	19.550	19.406	−1 090
	20.285	20.217	20.025	−1 170
$SnCl_4{\cdot}2PhCN$	19.753	19.61	19.33	−1 897
		19.85	19.85	435
$SnCl_4{\cdot}2CH_2(CN)_2$	19.40(2)	19.35(2)	19.35(2)	−224
	20.10(1)	20.13(1)	20.19(1)	403
	21.57(1)	21.57(1)	21.58(1)	44
$SnCl_4{\cdot}2C_6H_4(CN)_2$	19.08(2)			
	22.09(1)			
	22.22			
$SnCl_4{\cdot}2SMe_2O$	16.92	16.86	16.7[b]	−942
	17.17	16.96	16.8[b]	−1 704
	17.98	17.86	17.7[b]	−1 166
	18.74	18.52	18.4[b]	−1 570
$SnCl_4{\cdot}2tht$	17.42	17.33		−763
	17.88	17.75		−1 102
$[Ph_2CNH_2]_2[SnCl_6]$	16.19(1)		16.11(1)	−381
	17.70(2)		16.35(1)	−6 053
			18.14(1)	−1 973

[a] Peaks are of equal intensity unless relative intensities are given in parentheses. [b] No resonances were observed for $SnCl_4{\cdot}2SMe_2O$ at 300 K; the frequencies listed are estimated values, obtained by extrapolation from the spectra at 77 K and 195 K, assuming a linear variation of ν with temperature.

The tetrahydrothiophen adduct $SnCl_4{\cdot}2tht$ gives a ^{35}Cl n.q.r. spectrum containing two closely spaced absorptions with similar temperature dependence (Table 1), thus resembling ether adducts $SnCl_4{\cdot}2R_2O$,[18] and indicating the *trans* structure, Figure 1(*b*), that had been inferred from a thorough vibrational spectroscopic study [12] supported by *X*-ray powder photographs and dielectric-constant data. Other workers [14] have reported that adding tht to a pentane solution of $SnCl_4$ affords the *cis* adduct $SnCl_4{\cdot}2tht$. However, we found no evidence of this. The n.q.r. spectra of $SnCl_4{\cdot}2tht$ samples, and the temperature dependence of these spectra, are identical, and consistent with a *trans* structure, whether the samples are prepared by mixing the components in dichloromethane or by precipitation from pentane.

Although the ^{35}Cl n.q.r. spectroscopic data listed in Table 1 and illustrated in Figure 2 provide a useful guide to the stereochemistry of these adducts, and so indicate the value of n.q.r. spectroscopy for structure elucidation, the limitations of the method were evident when we attempted to record the spectra of four further tin(IV) chloride adducts, *viz.* $SnCl_4[NC(CH_2)_xCN]$ ($x = 2, 3,$ or 4) [7] and $SnCl_4{\cdot}2py$.[8] No resonance could be detected for any of these, even at 77 K.

Lewis-base Strengths.—For tin(IV) chloride adducts $SnCl_4{\cdot}2L$ in general, the drop in ^{35}Cl frequency (relative to unco-ordinated $SnCl_4$) on complex formation is expected to reflect the donor properties of the ligand L.[25-27] A strong Lewis base L would be expected to transfer considerable electron density to the chlorine atoms of $SnCl_4$, so reducing their n.q.r. frequencies. On this basis, the averages of the n.q.r. frequencies in Table 1 lead to the following sequence of Lewis-base strengths: $1,2\text{-}C_6H_4(CN)_2 < CH_2(CN)_2 < PCl_3O < MeCN < PhCN \leqslant CH_2{=}CHCN \sim Bu^tCN < SMe_2O$.

TABLE 2

Sn–Cl Bond length–^{35}Cl n.q.r. frequency correlations

Compound	d(Sn–Cl)/ pm	Ref.	^{35}Cl n.q.r. frequency/ MHz
$SnCl_4{\cdot}2MeCN$	235.6	4	19.175
	235.5		19.485
	234.1		19.725
	233.9		20.433
$SnCl_4{\cdot}2SMe_2O$	247	3	16.7
	244		16.8
	242		17.7
	236		18.4
$SnCl_4{\cdot}2PCl_3O$	236	6, 33	18.873
	233		19.110
	231		20.945
$[4\text{-}ClC_5H_4NH]_2[SnCl_6]$	246.3	24, 34	14.97
	241.9		17.32
	241.4		17.52
$[Ph_2CNH_2]_2[SnCl_6]$	245.6		16.10
	242.6		16.35
	241.3		18.14
$[NMe_4]_2[SnCl_6]$	240.2	35	16.663
$K_2[SnCl_6]$	241.1		15.064
$Rb_2[SnCl_6]$	242.3		15.60
$Cs_2[SnCl_6]$	242.3		16.05
$[NH_4]_2[SnCl_6]$	242.1		15.475

Bond Length–^{35}Cl N.Q.R. Frequency Correlations.—Correlations between ^{35}Cl n.q.r. frequencies and M–Cl bond lengths have been noticed for various systems.[28-30] For example, linear relationships have been reported for chlorocyclophosphazenes,[28,29] platinum(II) chloride adducts,[30] and tetrachloroiodates [31] and a non-linear but nevertheless well defined relationship has been noted for a series of mercury(II) chloride systems.[32] Our own data, together with data from the literature (Table 2), show that, despite the sometimes marked *temperature* dependence of n.q.r. frequencies illustrated in Table 1 and Figure 2, a similar correlation between ^{35}Cl n.q.r. frequencies and Sn–Cl bond lengths exists in the case of tin(IV) chloride adducts.

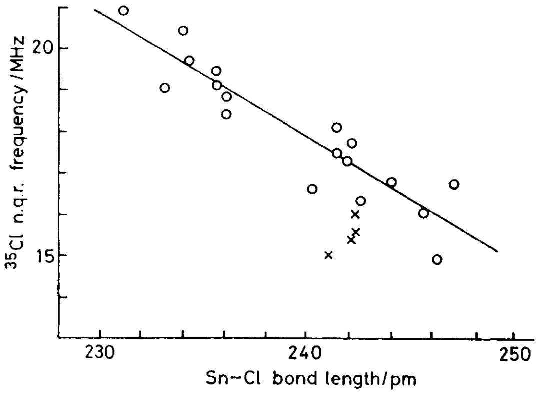

FIGURE 3 Sn–Cl bond length correlation with ^{35}Cl n.q.r. frequency, $SnCl_4$·2L (○) and $M_2[SnCl_6]$ (×)

In order to explore the relationship between the ^{35}Cl n.q.r. frequencies and Sn–Cl bond lengths quoted in Table 2, it is necessary to assign particular resonances to specific chlorine nuclei. One method of assignment commonly adopted is to assume that the longest bonds in a particular compound have the greatest ionic character and hence the lowest n.q.r. frequency, an assumption that appears reasonable if there is little or no π bonding in the Sn–Cl bond. Figure 3 shows the data from Table 2 plotted on this basis.

The considerable deviation of certain points from the line in Figure 3 may well arise from perturbation of the electric-field gradient at certain nuclei by neighbouring nuclei. For example, studies on the hexachlorostannates of K$^+$, Rb$^+$, Cs$^+$, NH_4^+, and NMe_4^+ led Brill *et al.*[35] to conclude that there was no bond length–frequency correlation for these salts because of perturbations of the $SnCl_6^{2-}$ anions by the cations. For this reason, the data for the potassium, rubidium, caesium, and ammonium salts have been omitted from the regression procedure. (Table 3 shows the effect on r^2 of their inclusion.) However, since the correlation with the other data improves as the cation in $M_2[SnCl_6]$ becomes softer (*i.e.* in the sequence K$^+$ < Rb$^+$ < Cs$^+$ < NH_4^+ < NMe_4^+), the data for $[NMe_4]_2[SnCl_6]$ were included in the regression.

TABLE 3

Linear relationships ($y = mx + c$) between ^{35}Cl n.q.r. frequencies (y/MHz) and Sn–Cl bond lengths (x/pm)

	A	B
m	−30.73	−33.20
c	91.58	97.34
$r^{2\,a}$	0.87	0.90
m^{b}	−33.88	−40.26
c^{b}	98.86	113.72
$r^{2\,b}$	0.78	0.73

A relates individual frequencies to individual bond lengths
B relates average frequency to average bond length for each compound

[a] r^2 = Correlation coefficient. [b] Assignments made including data for salts $M_2[SnCl_6]$.

In view of the broad correlation between $\nu(^{35}Cl)$ and d(Sn–Cl) that is illustrated in Figure 3, we consider that Sn(5d)–Cl(3p) π bonding is not significant in these systems, because if it were the shorter bonds would be expected to give rise to the lower ^{35}Cl n.q.r. frequencies, the opposite of the trend observed.

It is worth pointing out that the applicability of the empirical relations developed above probably implies that the asymmetry parameter, η, of the electric-field gradient round the ^{35}Cl nucleus is either small or does not vary from one complex to the next, so that the observed n.q.r. frequency is directly related to the nuclear quadrupole coupling constant. Evidence[36] from the study of ^{127}I n.q.r. in SnI_4 and $SnI_4 \cdot 2S_8$, where the asymmetry parameter can be determined directly, indicates that it has a value <0.04.

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