A ^{35}Cl Nuclear Quadrupole Resonance Study of the *cis-trans* Isomerism of Tin Tetrachloride Complexes

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Summary On the basis of MO calculations and n.q.r. spectra of $SnCl_4 \cdot 2D$ a dependence of frequency splittings and shifts on *cis-trans* isomerism has been found.

In recent years n.q.r. techniques have been used to determine the electronic structure of the octahedral complexes $SnCl_4 \cdot 2D$.[1–5]

We have studied the relationship between the spectral multiplicities and *cis-trans* isomerism of octahedral complexes, $MX_4 \cdot 2D$, and tried to estimate the limitations of the n.q.r. method when applied to such problems.

An approximate calculation of electron density distribution in octahedral systems $MX_4 \cdot 2D$ has been made assuming that there is no bonding other than σ-bonding and that no distortions are caused by the difference between X and D. We used the MO system for an octahedral complex with O_h symmetry.

Symmetry considerations indicate that in a *trans*-isomer all four halogen atoms are chemically equivalent while in a *cis*-isomer there are two pairs of chemically non-equivalent atoms.

The approach used here suggests that: (i) the average frequencies of ^{35}Cl for *trans*- and *cis*-isomers must be different; (ii) in the *cis*-isomer spectrum the frequencies of the equatorial atoms must be higher than those of axial atoms.

TABLE ^{35}Cl *n.q.r. spectra of* $\mathrm{SnCl_4\cdot 2D}$ *complexes*

No.	Complex	MHz	*S/N*
(1)	$\mathrm{SnCl_4}$[9]	23·719	1
		24·140	1
		24·226	1
		24·294	1
(2)	$\mathrm{SnCl_4\cdot 2Et_2O}$[8]	19·438	1
		19·473	1
(3)	$\mathrm{SnCl_4\cdot MeO(CH_2)_2OMe}$	19·620	
(4)	$\mathrm{SnCl_4\cdot MeO(CH_2)_4OMe}$	19·428	1
		20·160	1
(5)	$\mathrm{SnCl_4\cdot 2POCl_3}$[8]	19·035	1
		19·807	1
		21·146	2
(6)	$\mathrm{SnCl_4\cdot 2EtOH}$	17·498	1
		17·750	1
		20·120	1
		20·568	1
(7)	$\mathrm{SnCl_4\cdot 2MeOCH_2Cl}$	20·058	2
		21·648	1
		21·912	1
(8)	$\mathrm{SnCl_4\cdot 2PhCH_2Cl}$	19·014	1
		19·146	1
		23·644	1
		24·090	1
(9)	$\mathrm{SnCl_4\cdot PhNO_2}$	20·832	2
		20·952	2
		23·152	1
		23·208	1
		23·336	2

The spectral splittings are maximum at lowest charge-transfer and decrease with increasing charge-transfer finally giving a single intense line. This indicates equal dative properties for D and X.

To verify these points we have studied the ^{35}Cl n.q.r. spectra of several six-co-ordinated tin chloride complexes at 77 K on a pulse n.q.r. spectrometer IS-2.

The splitting patterns of the spectra show that complexes (2), (3), and (4) have a *trans*-configuration while complexes (6—9) have a *cis*-configuration (see Table). This assignment for complexes (2), (3), and (5) agrees with *X*-ray[6] and i.r. data.[7]

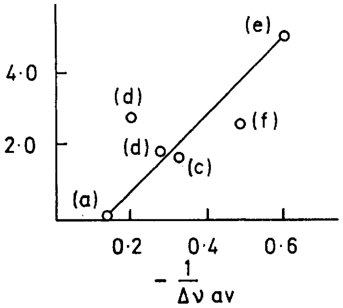

FIGURE. *Spectral splitting values* $\delta\nu$/MHz vs. *average shift* ($-1/\Delta\nu_{\mathrm{av}}$) *to lower frequencies in* ^{35}Cl *n.q.r. spectra of* $\mathrm{SnCl_4\cdot 2D}$ *complexes; reference point* $\mathrm{SnCl_4}$: (a) $\mathrm{SnCl_6}$;[2] (b) $\mathrm{SnCl_4\cdot 2POCl_3}$; (c) $\mathrm{SnCl_4\cdot 2MeOCH_2Cl}$; (d) $\mathrm{SnCl_4\cdot 2EtOH}$; (e) $\mathrm{SnCl_4\cdot 2PhCH_2Cl}$; (f) $\mathrm{SnCl_4\cdot PhNO_2}$.

The *X*-ray data for the complex $\mathrm{SnCl_4\cdot 2POCl_3}$ show that the axial Sn–Cl distances are equal while equatorial ones differ from each other by 0·05 Å. This confirms the assignment of the higher frequency line to the equatorial chlorine atoms and the lower frequency doublet to the axial atoms.

Shifts to a lower frequency on complex formation are caused by charge-transfer. We attempted to correlate the splitting values ($\delta\nu$) with average shifts to a lower frequency ($\Delta\nu_{\mathrm{av}}$) with respect to the spectrum of pure $\mathrm{SnCl_4}$. The Figure shows that the splitting between the lines of axial and equatorial chlorines decreases with increasing average shift of ^{35}Cl resonances caused by acceptor molecules.

A significant deviation from this relationship in the spectrum of $\mathrm{SnCl_4\cdot 2EtOH}$ may be due to the formation of the hydrogen bond OH · · · Cl.

Thus both calculations and experimental studies indicate that the splitting pattern in n.q.r. spectra of the octahedral complexes $\mathrm{MX_4\cdot 2D}$ is closely related to the electron structure and geometry. This makes it possible to predict n.q.r. splittings on the basis of structural data for octahedral complexes as well as to determine the positions of donor molecules in the octahedron by a simple analysis of the spectra.

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