Nuclear Quadrupole Resonance of Gallium and Chlorine in some Donor–Acceptor Complexes of Gallium Trichloride

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Summary The gallium n.q.r. frequencies in donor–acceptor complexes of gallium trichloride are an order of magnitude more sensitive to changes in the ligand than are the chlorine frequencies, but both reflect trends in the available gas-phase heats of formation of the compounds.

SINCE nuclear quadrupole resonance (n.q.r.) frequencies are related to bond polarities, the observation of n.q.r. in suitable donor–acceptor complexes provides a means of investigating the relative donor powers of different ligands. When halogen resonances are used for this purpose, however, the chemical shifts in the n.q.r. frequency caused by changes in the ligand are small because the halogen is not directly involved in the co-ordinate bond, and they are often comparable to splittings caused by intermolecular effects in the solid. In this context, complexes of gallium trichloride are of particular interest since it is possible to detect the n.q.r. of the gallium acceptor atom as well as that of chlorine, and some preliminary measurements are reported here for sixteen complexes of the type ligand,$GaCl_3$. It is found that the two sets of frequencies are approximately linearly related but that the gallium frequency is an order of magnitude more sensitive to change of ligand than is the chlorine frequency. In all but three cases the gallium resonance frequencies are also unusual in that their temperature coefficients are positive.

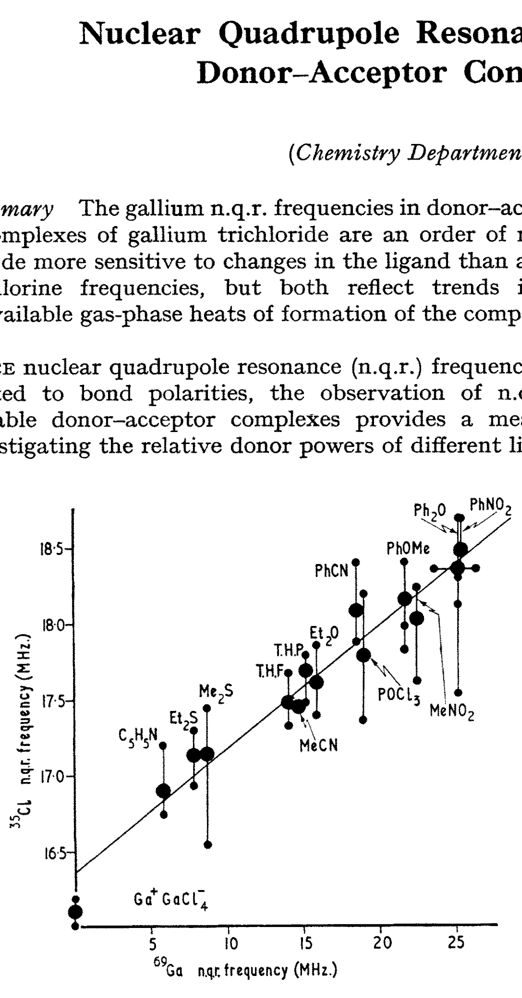

FIGURE 1. *Plot of* ^{35}Cl *against* ^{69}Ga *n.q.r. frequencies both measured at 77° K, in adducts of the type* ligand,$GaCl_3$. *The large circles represent the weighted mean* ^{35}Cl *frequency for each complex and the straight line is the least-squares line through these points. In the adducts of tetrahydropyran and diethyl sulphide the* ^{69}Ga *resonances were not detectable at temperatures as low as 77°K and therefore their frequencies at 77°K were estimated from plots of frequency against temperature.*

The resonance frequencies, measured at 77°K using a Decca n.q.r. spectrometer, are given in Figure 1 in which the ^{35}Cl frequencies (and also the weighted mean ^{35}Cl frequency, ν_{Cl}) are plotted against the ^{69}Ga frequency (ν_{Ga}) for each complex. The equation of the least-squares straight line through the data is $\nu_{Cl} = 16{\cdot}326 + 0{\cdot}826\ \nu_{Ga}$. No gallium resonances have yet been detected in either $NH_3,GaCl_3$ or piperidine,$GaCl_3$ and it is presumed that they lie below the lower frequency limit (4·5 MHz.) of the present investigation. Similarly, the gallium n.q.r. frequency in gallium dichloride is assumed to be zero because of the tetrahedral symmetry of the $GaCl_4^-$ ion.[1] In the case of $POCl_3,GaCl_3$ a second triplet of ^{35}Cl lines was detected with mean frequency 30·428 MHz. These are attributed to the $POCl_3$ group and their frequencies are comparable to those observed in complexes where oxygen is known to be the donor.[2]

All the complexes in which gallium resonances were detected have spectra which are consistent with the monomeric structure recently inferred for several similar complexes from far-i.r. data.[3] Only the methyl cyanide adduct, however, has the *single line* ^{35}Cl n.q.r. spectrum which suggests full C_{3v} symmetry in the solid. Structures involving chlorine bridges are rendered improbable by the absence of a ^{35}Cl resonance near 14·7 MHz., as already noted by Srivastava in the case of the diethyl ether complex,[4] and the measurement of the ^{35}Cl n.q.r. frequencies in gallium dichloride now enables ionic structures involving the ion $GaCl_4^-$ to be eliminated.

The high sensitivity to changes in the ligand and the relative insignificance of crystal splittings in the gallium n.q.r. suggest that, provided there are no large variations in the asymmetry parameter, the gallium n.q.r. frequency may prove to be a useful guide to the relative strength of the co-ordinate bond in the different complexes; the weaker the donor, the higher the frequency. This is substantiated by the good correlation of both the ^{69}Ga and mean ^{35}Cl n.q.r. frequencies with available gas-phase heats of formation[5] (Figure 2). Although the ^{35}Cl mean frequencies are more subject to uncertainty from crystal effects, they also reflect trends in the thermochemical data quite well. This provides some justification for their use in series of compounds where n.q.r. of the acceptor atom is not feasible. The large deviation in the case of $NH_3,GaCl_3$ suggests that the structure of this complex may differ from that of the others.

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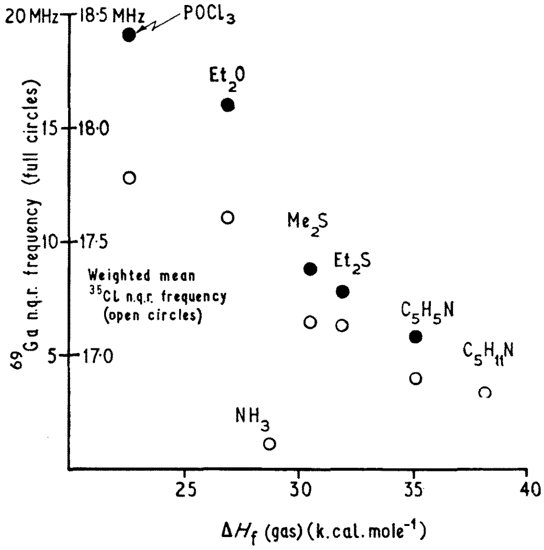

FIGURE 2. *Correlation of the weighted mean* ^{35}Cl *n.q.r. frequencies (open circles) and* ^{69}Ga *frequencies (full circles) in the adducts with available gas-phase heats of formation of the donor–acceptor bond.*

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