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Chlorine-35 NQR of Hexachlorodisilazane and the Si-Cl Bond of $SiCl_3$-Groups

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Chlorine-35 NQR of hexachlorodisiloxane (Cl_3SiO-$SiCl_3$), hexachlorodisilazane ($Cl_3SiN(H)SiCl_3$), and hexachlorodisilane ($Cl_3SiSiCl_3$) are measured with a superregenerative spectrometer. All samples exhibit complex chlorine NQR spectra: the average frequencies for $Cl_3SiOSiCl_3$, $Cl_3SiN(H)SiCl_3$, and $Cl_3SiSiCl_3$ are 19.89, 19.66, and 19.29 MHz respectively. The very small difference among the averages of the NQR frequency values of the three compounds may be due to the difference in the ionic character of the Si-Cl bond, and it may be due to an increase in the double-bond character of the $F^{\ominus}\overset{|}{\underset{|}{Si}}{=}Cl^{\oplus}$ type that the NQR frequency of $FSiCl_3$ is less than that of $SiCl_4$.

Experimental

The hexachlorodisilane and hexachlorodisiloxane were obtained from commercial sources. The hexachlorodisilazane was synthesized as follows: an ammonia gas diluted with a nitrogen gas was passed through ether containing silicon tetrachloride at $-75°C$.[1,2] The product was purified by distillation. All the compounds were measured at $-196°C$ with a superregenerative spectrometer, the details of which have been given elsewhere.[3]

Results and Discussion

The present authors asked Professor Whitehead[4] to measure the NQR of $Cl_3SiN(H)SiCl_3$. The frequencies he obtained were 19.723, 19.704, 19.699, 19.663, 19.635, and 19.551 ± 0.001 MHz, the mean value being 19.66 MHz. The NQR frequencies of $Cl_3SiSiCl_3$ and $Cl_3SiOSiCl_3$ we measured were in good accordance with those reported in the literature;[5] the mean values are 19.29 MHz for $Cl_3SiSiCl_3$ and 19.89 MHz for $Cl_3SiOSiCl_3$.

The increasing nuclear quadrupole resonance frequencies in the sequence from $Cl_3SiSiCl_3$, $Cl_3SiN(H)$-$SiCl_3$, $Cl_3SiOSiCl_3$ to $SiCl_4$[6] may reflect a decrease in the ionic character of the Si–Cl bond. This is consistent with the view that replacing a chlorine of $SiCl_4$ with the groups whose electronegativity decreases in the order $Cl > Cl_3SiO > Cl_3SiN(H) > Cl_3Si$ produces progressively less competition for silicon electrons and, hence, an increased ionic character in the Si–Cl bond.

When chlorine is replaced by fluorine, a still larger increase in the NQR frequency can be expected, since fluorine is much more electronegative than chlorine. However, the NQR frequency of $FSiCl_3$, 19.753 MHz[7]

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2) H. Bürger, M. Schultze, and U. Wannagat, *Inorg. Nucl. Chem. Lett.*, **3**, 43 (1967).
3) K. E. Weber and J. E. Todd, *Rev. Sci. Instr.*, **33**, 390 (1962).
4) M. A. Whitehead, Private Communication.
5) I. P. Biryukov, M. G. Voronkov, and I. A. Safin, "Tables of Nuclear Quadrupole Resonance Frequencies", Israel, IPST Press (1969).
6) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).
7) K. Hamada, G. A. Ozin, and E. A. Robinson, This Bulletin, **44**, 2555 (1971).

is less than the average frequency of $SiCl_4$, 20.390 MHz.[6] It has been proposed,[8] in order to explain such an unexpected consequence, that there is an increase in the double-bond character due to the contributions of resonant structures of the $F^{\ominus}\overset{|}{\underset{|}{Si}}{=}Cl^{\oplus}$ type. Since a double-bond character is in the direction of decreasing NQR frequencies, this effect could explain the decrease in the NQR frequency when chlorine is replaced by fluorine. The increase in the double-bond character due to a fluorine substitution may be clarified by the shortening of the Si–Cl distance. That is, the Si–Cl distance of $SiCl_4$ is 2.01 Å, but that of $SiClF_3$ is only 1.99Å.[8]

The increase in the NQR frequencies in the sequence from CF_3Cl, CF_2Cl_2, $CFCl_3$ to CCl_4 has been reported,[6] but the NQR frequencies of $SiCl_mF_{4-m}$ have not been previously reported, except for that of $SiFCl_3$.[7] Therefore, it would be of interest to obtain the NQR frequencies of SiF_2Cl_2 and SiF_3Cl; thus far, however, attempted NQR measurements of them have been unsuccessful.[7]

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8) L. Pauling, "The Nature of the Chemical Bond", 2nd Ed. Cornell University Press, Ithaca, N. Y. (1944).