Nuclear Quadrupole Resonance and Structure of the Dichloride, HCl_2^-, Ion

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Summary ^{35}Cl quadrupole resonance signals have been observed in eight salts of the HCl_2^- or DCl_2^- ion, all of which fall into two classes according as to whether the ^{35}Cl frequencies lie near 12 or 20 MHz: the results for $CsCl,\frac{1}{3}(H_3O^+HCl_2^-)$ show that the low frequency signal is associated with a symmetric HCl_2^- ion, and the small shift observed on deuteration can be explained in terms of a flat or nearly flat symmetric potential well.

SINCE the dichloride ion, HCl_2^-, is one of the simplest hydrogen-bonded systems, a detailed knowledge of its structure in crystals is of considerable importance to current theories. Two groups of workers[1,2] have detected ^{35}Cl quadrupole resonance signals in $NMe_4^+HCl_2^-$ near 20 MHz and in $NEt_4^+HCl_2^-$ near 12 MHz and have claimed that these different frequencies correspond to different structures, the former to an unsymmetrial and the latter to a symmetrical ion. We present more convincing evidence in support of this claim from a study of ^{35}Cl quadrupole resonance in a series of salts containing the HCl_2^- and DCl_2^- ions, including the mixed salt $CsCl,\frac{1}{3}(H_3O^+HCl_2^-)$ in which a recent *X*-ray structure analysis[3] has shown the HCl_2^- ion to have a mirror plane perpendicular to the Cl · · · Cl axis, and therefore to be symmetrical in contrast to that in the NMe_4^+ salt, where the mirror plane is lacking.[4] A complete list of our present studies is given in the Table; the ^{35}Cl frequencies were recorded on the Decca Radar n.q.r. spectrometer, which automatically eliminates sidebands, and were read off the chart to ±0·005 MHz.

The $CsCl,\frac{1}{3}(H_3O^+HCl_2^-)$ salt shows one frequency, consistent with the space group of the crystal, and this lies near 12 MHz, supporting the argument that HCl_2^- frequencies in this region belong to symmetrical ions. This argument does not distinguish between ions with a true symmetric potential and those with a double potential well with rapid tunnelling.[5] An interesting difference is observed between the ^{35}Cl frequencies of the two types of HCl_2^- ion on deuteriation: the high frequency or asymmetric type, *viz.* the salts of NMe_4^+ and Cs^+, shift down frequency by nearly 0·8 MHz, whereas the low frequency or 'symmetric' type, *viz.* the salts of NEt_4^+ and $Cs^+,\frac{1}{3}H_3O^+$, remain practically constant. We relate this shift in the asymmetric salts to the large change in the bending frequency observed in the inelastic neutron-scattering spectra[6] from 657 cm^{-1} in $Cs^+HCl_2^-$ to 480 cm^{-1} in $Cs^+DCl_2^-$, a change that would be expected in strong but asymmetric hydrogen bonds. Deuteriation shifts have also been observed[7] in $NaAuCl_4,2H_2O$, where the hydrogen bond is certainly asymmetric. The deuteriation shifts in the dichloride salts may be compared with those in solid HCl itself. In solid HCl at 77°K the ^{35}Cl quadrupole resonance frequency is at 26·469 MHz;[8,9] this value is shifted to 27·310 MHz in solid DCl at the same temperature, a shift of 0·841 MHz compared to 0·78 MHz in the tetramethylammonium dichloride (unsymmetric) and about 0·12 MHz in the tetraethylammonium dichloride (symmetric). In the symmetric dichloride salts the bond presumably has a flat or nearly flat potential well, and the change in the mean ^{35}Cl frequency with displacement of the H (or D) co-ordinates is at or near a minimum so that the shift on deuteration is small.

^{35}Cl *Quadrupole resonance frequencies in eight salts of the dichloride ion*

		^{35}Cl Frequencies in MHz	
	At 77°K	At higher temperatures (°K)	
$Me_4N^+HCl_2^-$ ..	20·26	19·925 (195)	19·51 (294)
$Me_4N^+DCl_2^-$ ..	21·04	20·75 (195)	20·23$_5$ (294)
$Et_4N^+HCl_2^-$ ..	12·48	[a]	11·89 (294)
$Et_4N^+DCl_2^-$ ..	[a]	12·38 (195°)	12·01 (294)
$Cs^+HCl_2^-$	[a]	21·17 (166°)	20·47 (294)
$Cs^+DCl_2^-$	[a]	21·64 (239)	21·28 (294)
$CsCl,\frac{1}{3}(H_3O^+HCl_2^-)$	[a]	11·94 (203)	11·89$_5$ (294)
$CsCl,\frac{1}{3}(D_3O^+DCl_2^-)$	[a]	12·07 (237)	12·05 (294)

[a] Not observed.

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[1] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, 1966, **70**, 2702; 1967, **71**, 3697.
[2] T. E. Haas and S. M. Welsh, *J. Phys. Chem.*, 1967, **71**, 3363.
[3] L. W. Schroeder and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 594.
[4] J. S. Swanson and J. M. Williams, *Inorg. Nuclear Chem. Letters*, to be published.
[5] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," Benjamin, New York, 1968, ch. 3.
[6] G. C. Stirling, C. J. Ludman, and T. C. Waddington, *J. Chem. Phys.*, 1970, in the press.
[7] C. W. Fryer and J. A. S. Smith, *J. Chem. Soc.* (*A*), 1970, in the press.
[8] R. Livingston, *J. Phys. Chem.*, 1953, **57**, 496.
[9] H. C. Meal and H. C. Allen, *Phys. Rev.*, 1953, **90**, 348.