^{35}Cl Nuclear Quadrupole Resonance of Donor–Acceptor Complexes. Part II.[1]

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^{35}Cl N.q.r. frequencies of chlorine atoms in various donor molecules forming complexes with Lewis acids are reported and compared with those of the free donor molecule. An extensive study of complexes of 2-, 3-, and 4-chloropyridine with a variety of acceptors shows that the nature of the acceptor has little effect on the resonance frequency and that the further the chlorine atom is removed from the donor center the smaller is the effect on the resonance frequency. Both σ and π bonding of the chlorine atom to the donor group are affected to about the same extent.

In previous papers we and others have reported and discussed the effect of complex formation on the ^{35}Cl resonance frequencies of boron trichloride,[1-3] and it was shown that although the resonance frequencies reflect the strength of the donor–acceptor bond as determined by a variety of techniques, the spread in resonance frequencies is small.

In the present paper we report two further aspects of the same problem: for a given donor type, how the perturbation produced by complexation is distributed among the different atoms of a donor molecule and how perturbation varies with the acceptor molecule.

EXPERIMENTAL

Preparations.—All the donor and acceptor compounds were commercially available products. The boron trichloride adducts were prepared as in ref. 1 with the exception of the adduct with 2,6-dichloropyridine which only crystallised from methylene chloride containing an excess of boron trichloride after several weeks at −20°. The antimony pentachloride adducts were prepared by dropwise addition of a solution of the donor in carbon tetrachloride to a well stirred solution of the base in the same solvent at 0°. The complex thus precipitated was filtered and dried, the whole operation being carried out with the exclusion of atmospheric moisture. The hydrochlorides were prepared by passing dry gaseous hydrogen chloride through a carbon tetrachloride solution of the base. The sulphates, perchlorates, and sulphonates, and the complexes with bismuth trichloride, stannous chloride, and mercuric chloride were prepared according to the methods in ref. 4, as was the methiodide of 3-chloropyridine. The physical characteristics of those compounds previously reported in the literature corresponded with the published parameters: satisfactory analyses were obtained for new compounds.

^{35}Cl *N.q.r. Spectra.*—Samples (1 g) sealed in glass vials immersed in a bath of liquid nitrogen were measured on a Decca super-regenerative n.q.r. spectrometer, the frequencies being measured both by the crystal-controlled internal marker and a Hewlett–Packard 5300 A digital frequency meter.

RESULTS AND DISCUSSION

N.q.r. frequencies, ν_Q, of ^{35}Cl (I 3/2) are related to the coupling constant, e^2Qq, and the asymmetry parameter, η, by equation (1). The determination of η is not straightforward and has not been attempted here; in

$$\nu_Q = \left[\frac{e^2Qq}{2}\right]\left[1 + \frac{\eta^2}{3}\right]^{\frac{1}{2}} \qquad (1)$$

most of the molecules reported here it is unlikely to be much greater than 0·1 and hence the above expression is well approximated by (2). In many of the molecules

$$\nu_Q = e^2Qq/2 \qquad (2)$$

we have studied the chlorine atom is attached to a conjugated system and the bond can have a partial double character, π. The approximate relationship (3) then holds between the coupling constant, the ionic character

$$e^2Qq = -\left[1 - i - \frac{\pi}{2}\right]e^2Qq_0 \qquad (3)$$

of the bond, i, and π, where $-e^2Qq_0$ is the coupling constant of the free chlorine atom (*ca.* 110 MHz). The signs of the coupling constants have not been determined experimentally: they are however certainly negative.[5,6]

Table 1 shows the ^{35}Cl resonance frequencies for a series of chloropyridine and chlorobenzonitrile complexes. The former range from straightforward donor–acceptor complexes with metal halides through more or less hydrogen bonded pyridinium salts to the extreme case of an *N*-methylpyridinium iodide. In every case, ν_Q for the chlorine atom in the donor portion is greater in the complexed than in the uncomplexed form although in some cases the difference (Δ) is hardly significant in view of the uncertainties introduced by the fact that these measurements all refer to the solid state.

As expected Δ decreases as the distance between the chlorine atom and the donor atom increases but the corresponding changes in i and π are not however necessarily parallel or even in the same direction. In the pyridine series the value of π in the 3-position is least likely to be affected by complexation[7,8] and we will

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assume that Δ is due entirely to a change in *i*. The change in *i* in the 2-, 3-, and 4-positions is mainly due to inductive effects; these are known to be attenuated with distance by roughly 1/3 for every additional bond.[9] Hence the change in *i* alone would bring about values of Δ of *ca.* 6·2 and 0·7 MHz respectively for the 2- and 4-positions. These estimates imply that both *i* and π have increased by similar amounts in 2-chloropyridine to produce the observed value of Δ of 4·4 MHz.

TABLE 1

^{35}Cl N.q.r. frequencies (MHz) of 77 K for boron trichloride complexes. The figures in parentheses indicate the approximate relative intensities

	^{35}Cl Resonance frequencies (MHz)			
Donor	BCl_3 group	Complexed donor	Free donor	Δ (MHz)
2-Chloropyridine	22·275 (1) 22·462 (2)	38·572	34·194	4·378
3-Chloropyridine	21·311 (1) 22·080 (2)	37·305	35·238	2·067
4-Chloropyridine	21·561 (2) 21·643 (1)	36·585	34·739 34·748 35·031 35·042	1·695
2,6-Dichloropyridine	20·216 (1) 20·983 (1) 21·080 (2) 22·045 (2)	38·500 38·516	34·666	3·842
3,5-Dichloropyridine	21·881 21·963 22·272	37·474 37·920	35·601	2·096
2-Chlorobenzonitrile	22·467 (2) 23·169 (1)	36·452	35·410 35·453 35·500 35·541	0·976
3-Chlorobenzonitrile	22·256 22·331 22·429	35·777	35·248	0·529
4-Chlorobenzonitrile	22·149 22·261 22·383	35·852	35·171	0·681
2,6-Dichlorobenzonitrile	22·124 22·228 22·243	36·86 37·03 37·12 37·19	36·197 36·328	0·83
CH_3OCH_2Cl *	21·873 22·138 22·184	35·772	30·180	5·592
CH_3SCH_2Cl	21·817 (2) 21·933 (1) 22·083 (2) 22·154 (1)	37·963 38·031	33·104	4·893
PhCOCl		34·164 †	29·918	4·246
p-$ClC_6H_4COCH_3$ ‡		35·877 †	34·605	1·259

* The frequency of the free donor is in agreement with that previously determined by one of us (E. A. C. Lucken, *J. Chem. Soc.*, 1959, 2954) but not with those reported (29·917, 30·306, MHz) by H. Hooper and P. J. Bray, (*J. Chem. Phys.*, 1960, **33**, 334). † Complexes with antimony pentachloride. ‡ The frequency of the free donor agrees with that reported by P. J. Bray and R. G. Barnes (*J. Chem. Phys.*, 1957, **27**, 551) but not with that (35·111 MHz) reported by M. J. Dewar and M. L. Herr (*Tetrahedron*, 1971, **27**, 2377).

This hypothesis is supported by the values for cyanogen chloride. The complex with BCl_3 is not suitable in this context since here BCl_3 adds across the double bond[10] (frequencies at 77 K: 22·013, 22·357, 38·268, 38·559 MHz), but in three complexes, $ClCN \longrightarrow MCl_5$ where M = Sb, Nb, or Ta the resonance frequency is not significantly different from that of the free ligand.[11,12] Since in this case *both* π orbitals of the chlorine atoms can participate in the multiple bond the coupling constant is given by equation (4) and the unchanged frequency implies equal and opposite changes in *i* and π.

$$e^2Qq = -(1 - i - \pi)e^2Qq_0 \qquad (4)$$

A further demonstration that both *i* and π change on complexation is afforded by the results for chloromethyl methyl ether and chloromethyl methyl sulphide where Δ is 5·59 and 4·89 MHz respectively. Although the electronic structure of α-chloro-ethers is more complex than the chemical formula suggests[13] there is unlikely to be any significant double bond character to the bond either before or after complexation. The value of Δ due only to a change in *i* when a first-row element is complexed is thus 5·6 MHz, in fair agreement with the value 6·2 MHz deduced above. The situation in the chloro-ethers must be contrasted with that in benzoyl chloride whose structure is analogous to that of 2-chloropyridine and where Δ, admittedly with antimony pentachloride as acceptor,[14] is 4·25 MHz. Here there is no doubt that in the free ligand there is considerable carbon–chlorine double bonding since the asymmetry parameters[15] in acid chlorides is of the order of 0·2.

The situation thus far is clear: where double-bond character already exists complexation increases it so that the resonance frequency increase is less than expected. The transfer of electrons from chlorine atom to the donor centre is of the order of 0·1 and the effect is progressively attenuated as the distance between the two centres is increased. This attenuation is also illustrated for the benzonitriles where only the *o*-chloro-derivatives show a significant increase. In this context the relatively large change in *p*-chloroacetophenone of 1·26 MHz is surprising.

The value of Δ in 4-chloropyridine is higher than expected, but this could be due to intermolecular rather than intramolecular effects. For this reason and to see if there is any appreciable difference between acceptors, a range of complexes of the chloropyridines were studied and the results are summarized in Table 2. With the notable exception of 2-chloropyridine–boron trichloride the value of Δ is almost independent of the nature of the donor even in the extreme case when, in 3-chloropyridine, the nitrogen atom has been quaternized. This justifies the inclusion of the antimony pentachloride complexes of

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cyanogen chloride and benzoyl chloride in the above discussion.

The ^{35}Cl resonance frequencies of the BCl_3 group in these complexes follow the same trends as those reported previously,[1-3] although as before the total spread in frequency is not very great and not too different from the spread in frequency within any particular compound. However the relative order of donating power set out in the previous studies is maintained.

TABLE 2

^{35}Cl Frequencies (MHz at 77 K) of chloropyridines complexed with various acceptors

Acceptor	2-Chloropyridine ν_Q(MHz)	Δ	3-Chloropyridine ν_Q(MHz)	Δ	4-Chloropyridine ν_Q(MHz)	Δ
HCl	37·55	3·36	37·05	1·81	35·94	1·05
$HClO_4$	37·815	3·83	37·042	1·80	35·98	1·09
H_2SO_4	37·593	3·40	37·10	1·87	36·193	1·30
p-$MeC_6H_4SO_3H$	38·064 38·112	3·89	37·08	1·84		
	37·596	3·45	37·34	2·10	36·26	1·37
$(NO_2)_3C_6H_2OH$	37·698					
BCl_3	38·572	4·38	37·305	2·07	36·585	1·69
$SbCl_5$	37·872	3·68	37·076	1·84		
$HgCl_2$	38·190	4·0			36·122 36·162 36·382 36·609	1·43
$BiCl_3$	37·413	3·22			36·399	1·51
$SnCl_2$	37·894	3·70	37·174	1·94		
CH_3I			37·331	2·09		

In the complex of 2,6-dichloropyridine the spread is exceptionally great (1·8 MHz) and the average frequency is 1 MHz less than that of the 2-chloro-derivative. These facts may be indicative of weakening of the B–N bond due to the steric effect of the two adjacent chlorine atoms together with an appreciable distortion of the BCl_3 group from C_{3v} symmetry.

To sum up, the formation of donor–acceptor complexes results in considerable changes in the resonance frequency of a chlorine atom adjacent to the donor centre provided that both σ and π bonding are not both considerably modified. As expected the magnitude of such changes falls off rapidly as the distance between the chlorine atom and the donor centre increases.

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