Hydrogen–Halide Interactions in Aluminium Halide–4-Ethylpyridine Complexes

By T. N. HUCKERBY, J. W. WILSON, and I. J. WORRALL*

(*Chemistry Department, The University, Lancaster*)

${}^1H$ N.M.R. spectra of the three new 1 : 1 addition compounds 4-Et-C_5H_4N,AlX_3 (X = Cl, Br, or I) in the fused state have been measured at 60 Mc./sec. relative to internal tetramethylsilane. The results are given in the Table and the α-hydrogen spectra of the three compounds are shown in the Figure.

The spectra of the three compounds differ essentially only in the position and shape of the α-hydrogen peaks. There is an increasing shift to low field and increasing broadening of the peaks through the series Cl → Br → I. The iodide has the greatest shift of 35 c./sec. (relative to the ligand) and has completely lost its fine structure.

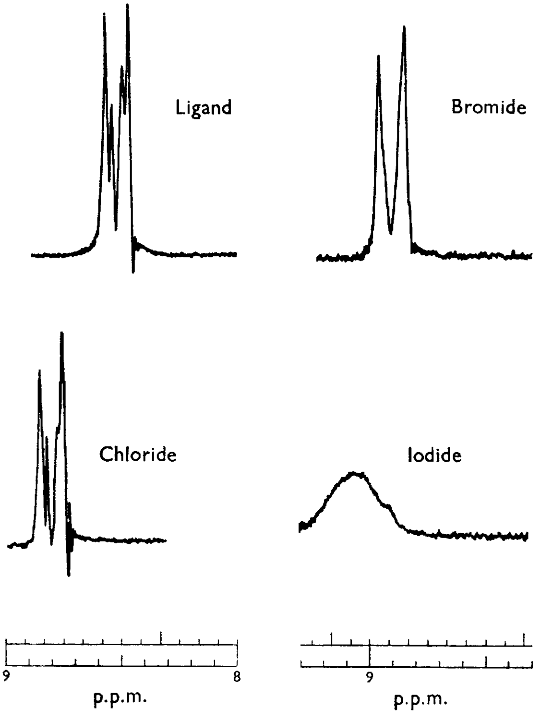

FIGURE. *α-Hydrogen resonances of fused* 1: 1 *aluminium halide–4-ethylpyridine complexes at* 87°

We attribute this effect to interactions between the halogens and α-hydrogens of the ligand. On the basis that the structures of the complexes have C_{3v} symmetry (with respect to the arrangement of the nitrogen and halogens about aluminium) then with increasing size of the halogen the α-hydrogen-halogen distance becomes smaller and the possibility of hydrogen bonding increases. The effect is thus stronger in the iodide complex, resulting in a greater downfield shift and very large quadrupole broadening. The broadening effect is less in the bromide and only very slight in the chloride complex from which it may be inferred that there is little interaction in the latter compound.

TABLE

^{1}H *N.m.r. chemical shifts (in c./sec.) from internal* Me_4Si *at* 87°

Group	Ligand 4-ethylpyridine	Complex Cl	Br	I
CH_3	66·5	83·0	83·5	84·0
CH_2	149·5	180·0	180·5	181·0
β-H	420·0	472·5	473·5	474·0
α-H	509·0	529·0	533·5	544·0

If this effect is due to genuine hydrogen bonding then this is yet another factor which must be considered in relation to the acceptor strengths of the Group III halides. We are examining other similar complexes to determine the extent to which the above effect persists.

We thank S.R.C. for an award (to J.W.W.).

(*Received, September 29th,* 1967; *Com.* 1041.)