Direct Observation of the Heptafluorodiborate(III) Ion, $B_2F_7^-$

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Summary ^{19}F n.m.r. spectra at -155 °C confirm that $B_2F_7^-$ exists as a fluorine-bridged species, the only known example of a halogen atom bridging two boron atoms.

While hydrogen bridging is a distinctive feature of the boron hydrides, halogen bridging has not been observed in the boron halides.[1] The only diboron species in which halogen bridging seemed probable is the $B_2F_7^-$ anion. This exists at low temperatures in solution[2] and in the solid state with large cations[3] but readily dissociates to give BF_3 and BF_4^-. The postulated fluorine bridge could not be detected by ^{19}F n.m.r. spectroscopy at -103 °C because of rapid chemical exchange.[2] Recently complexities caused by $B_2F_7^-$ formation in studies of ionic BF_3 adducts[4] have led us to reinvestigate the BF_3–BF_4^- system at lower temperatures, and we now report the ^{19}F spectrum of $B_2F_7^-$ at -155 °C.

A 1:1 solution of BF_3 and $Bu^n_4N^+BF_4^-$ (each 0·15 M) in $CHFCl_2$ gave a single exchange-averaged ^{19}F n.m.r. peak (146·0 ± 0·5 p.p.m. to high field of $CFCl_3$, 58·3 MHz) at -100 °C. This signal broadened and separated into two signals of relative intensities 1:6 between -110 and -140 °C. At -155 °C, the lowest temperature attainable before freezing of the solution, the smaller low-field signal (117 ± 1 p.p.m.) was still broad and unresolved while the high-field signal (151·4 ± 0·3 p.p.m.) had split into a doublet (J_{FBF} 95 ± 10 Hz). The spectrum is consistent with the presence of the fluorine-bridged anion $[F_3B\text{–}F\text{–}BF_3]^-$; it is difficult to rationalize any other structure. Exchange is still too fast at -155 °C for the bridging fluorine, with a lifetime one-sixth that of the terminal fluorines, to show the expected spin–spin splittings. The single fluorine bridge is apparently symmetrical although a rapid equilibration between two asymmetric structures cannot be excluded. The chemical shift of the -100 °C signal is a weighted average of the -155 °C signals, confirming that dissociation to give BF_4^- and BF_3 is slight at this temperature.[2]

When less BF_3 than BF_4^- was added to a sample, the -155 °C spectrum consisted of both BF_4^- (153·5 p.p.m.) and $B_2F_7^-$ resonances. The bridging (F_b) and terminal (F_t) resonances of $B_2F_7^-$ again coalesced at about -140 °C, as did the BF_4^- resonance. This is consistent with dissociation of $B_2F_7^-$ to BF_4^- and BF_3 followed by random recombination, as proposed previously.[5] When more BF_3 than BF_4^- was present the single averaged ^{19}F peak broadened at the lowest temperatures but did not separate even at -155 °C. Thus excess of BF_3 increases the rate of exchange.

The pronounced low-field shift of F_b (34 p.p.m. to low field of F_t) is in accord with bridging *vs.* terminal fluorine chemical shifts in a number of other fluorine-bridged systems.[6] The similarity of the -155 °C shifts of F_t and BF_4^- is a further strong indication that all fluorines are associated with tetrahedral boron. The coupling constant of 95 Hz is the first geminal FBF coupling to be reported and could perhaps be compared to geminal FCF couplings in saturated fluorocarbons (160—290 Hz).[7]

The weakness of the fluorine bridge in $B_2F_7^-$ contrasts with the strength of the single B–H–B bridge in $B_2H_7^-$.[8,9] The hydrogen bridge in $B_2H_7^-$ is more resistant to displacement than the hydrogen bridges of B_2H_6,[8] and similarly the fluorine bridge of $B_2F_7^-$ may be a particularly favourable case of fluorine bridging. This would explain the non-detection of B_2F_6 and related species proposed as intermediates in halogen redistribution.[1] This work suggests that such species may be directly observable by n.m.r. spectroscopy at extremely low temperatures.

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