The $As_2F_{11}^-$ Ion

By P. A. W. DEAN, R. J. GILLESPIE,* and R. HULME
(*Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*)

Summary N.m.r. evidence is presented for the presence of the $As_2F_{11}^-$ ion in the products of reaction of AsF_5 with $(R_4N)AsF_6$.

IT has been shown[1] that a mixture of AsF_5 and AsF_6^- (as the tetrabutylammonium salt) in methylene chloride undergoes fast fluorine exchange on an n.m.r. time-scale at all temperatures studied, and it has been suggested that the fluorine-bridged $As_2F_{11}^-$ ion may be an intermediate in the exchange process. Ions of the type $(As_nF_{5n+1})^-$ have also been postulated[2] to account for the differences between the low-temperature i.r. spectrum of $NOF_3,xAsF_5$ and the i.r. spectrum of $NOF_2^+AsF_6^-$. There has, however, been no definitive evidence for the existence of the $As_2F_{11}^-$ ion, and preparative fluorine chemists have often used AsF_5 as a fluoride acceptor, in preference to SbF_5, to ensure formation of a simple hexafluoro-anion.

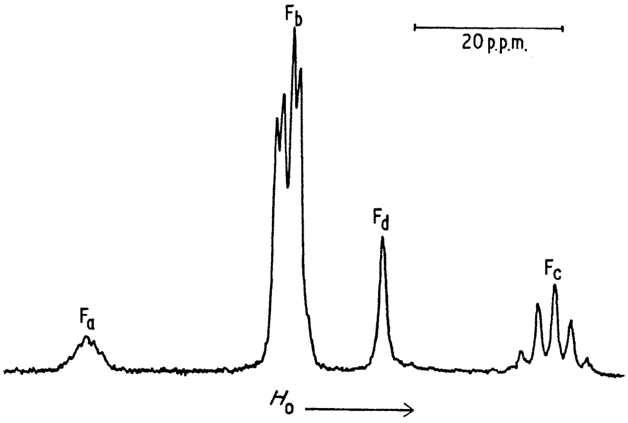
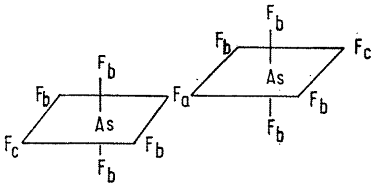


FIGURE. *The* ^{19}F *n.m.r. spectrum of* $Bu_4N^+[AsF_6(AsF_5)_{0\cdot94}]^-$ *in sulphuryl chlorofluoride solution at* −140°.

We have found that when the solvent is removed at −78° from sulphur dioxide or anhydrous hydrogen fluoride solutions of equimolar amounts of AsF_5 and $(Et_4N)AsF_6$ or $(Bu_4N)AsF_6$, quantitative addition of AsF_5 to the salts has occurred giving products (I) and (II), respectively. There is also some evidence that larger amounts of AsF_5 can be complexed at low temperatures. At room temperature (I) and (II) are initially colourless, but with time some charring of (II) occurs. Both products have low vapour pressures [*ca.* 0·5 mm. and 2·1 mm. at 0° for (I) and (II), respectively]; the i.r spectrum of the vapour confirms it to be AsF_5.

The ^{19}F n.m.r. spectrum of (II) in sulphuryl chlorofluoride was obtained; we were unable to find a suitable low-temperature solvent for (I). At −140° the spectrum of a product of composition $Bu_4N^+[AsF_6(AsF_5)_{0\cdot94}]^-$ in SO_2ClF showed, in addition to a single line from the solvent, the more complex spectrum in the fluorine-on-arsenic region that is shown in the Figure. The single line F_d, at +61·6 p.p.m. from external $CFCl_3$† is attributed to AsF_6^-. The resonances F_a, F_b, and F_c, at +21·1, +48·6, and +85·0 p.p.m. from external $CFCl_3$,† have intensities 1 : 8 : 2 and are assigned to the $As_2F_{11}^-$ anion:



The fine structure in the spectrum compares well with that

---

† Chemical shifts were measured relative to the solvent line and converted to external $CFCl_3$ using

$$\delta\ (CFCl_3) = \delta\ (SO_3ClF) - 99{\cdot}1\ \text{p.p.m.}$$

observed for the $Sb_2F_{11}^-$ ion.[3] The resonance F_b is a double doublet by coupling to both F_a and F_c, whilst the resonance F_c is a quintet by coupling to the four closest fluorines only, coupling to F_a being near-zero. The signal due to F_a is then expected to show nine lines from coupling with the eight fluorines F_b; the centre five of these can be seen in the fine structure of F_a. The coupling constants J_{ab}, J_{bc}, and J_{ac} are 51, 127, and *ca.* 0 Hz., respectively. These values are close to those observed[1] between fluorines bonded to arsenic in the $AsSbF_{11}^-$ ion (J_{ab}, J_{bc}, and J_{ac} = 47, 126, and *ca.* 0 Hz., respectively).

The i.r. spectra of both products were obtained on the powders between silver chloride plates. Both show complex absorptions between 650 and 770 cm.$^{-1}$ which are assigned to stretching modes of the terminal fluorines. In addition, (I) gives a weak single band at 481 cm.$^{-1}$ and (II) a similar band at *ca.* 500 cm.$^{-1}$, in the region expected for vibrations involving stretching of the As–F–As bridge. Christe and Maya[2] observed a band at 491 cm.$^{-1}$ for $NOF_3,xAsF_5$ which they attributed to a polymeric anion. The corresponding vibration ν(Sb–F–Sb) for the $Sb_2F_{11}^-$ anion has been observed at 523 cm.$^{-1}$ in $VO_2^+Sb_2F_{11}^-$,[4] 485 cm.$^{-1}$ in $Se_4^{2+}(Sb_2F_{11}^-)_2$,[5] and *ca.* 479 cm.$^{-1}$ in $CsSb_2F_{11}$.[6]

Our observations are in accord with the formulation of the products (I) and (II) as salts containing the $As_2F_{11}^-$ ion. The i.r. spectra of both products, and the low-temperature ^{19}F n.m.r. spectrum of (II) in SO_2ClF are consistent with the anion having the expected fluorine-bridged structure.

We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research for financial assistance.

(*Received, July 7th*, 1969; *Com.* 983.)

---

[1] S. Brownstein, *Canad. J. Chem.*, 1969, **47**, 605.

[2] K. O. Christe and W. Maya, *Inorg. Chem.*, 1969, **8**, 1253.

[3] R. J. Gillespie and K. C. Moss, *J. Chem. Soc.* (*A*), 1966, 1180; J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Canad. J. Chem.*, 1969, **47**, 1655.

[4] J. Weidlein and K. Dehnicke, *Z. anorg. Chem.*, 1966, **348**, 278.

[5] R. J. Gillespie and G. Pez, *Inorg. Chem.*, 1969, **8**, 1229.

[6] P. A. W. Dean and R. J. Gillespie, unpublished observations.