Salts of Hexafluorobenzene Cation, $C_6F_6^+$

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Summary Interaction of $O^+AsF_6^-$ with hexafluorobenzene in WF_6 solution yields a bright yellow paramagnetic solid $C_6F_6^+AsF_6^-$.

ALTHOUGH the unusually high electron affinities of the heavier transition metal hexafluorides (particularly those of PtF_6 and IrF_6) suggested[1] their utility in synthesising salts of the $C_6F_6^+$ ion ($I = 9{\cdot}97$ eV),[2] nevertheless attempts by Jha to prepare $C_6F_6^+PtF_6^-$ resulted in fluorination of the C_6F_6 by the PtF_6.[3] More recently we have obtained a bright-orange solid from interaction of IrF_6 with C_6F_6 in tungsten hexafluoride solution, which we believe to be $C_6F_6^+IrF_6^-$. Unfortunately this compound decomposes quickly on warming towards room temperature. Evidently the hexafluorometallate(v) anions of the noble metals are too labile and too strongly oxidizing for these approaches to $C_6F_6^+$ salt synthesis to be effective.

Since the AsF_6^- ion has considerable kinetic stability it appeared that the $O_2^+AsF_6^-$ salt, with its potent one-electron oxidizer O_2^+ ($E = 12{\cdot}2$ eV),[4] would be suitable for $C_6F_6^+$ generation. Tungsten hexafluoride was used as solvent for the hexafluorobenzene and as moderator for the vigorous reaction (fluorocarbon solvents were less satisfactory in the latter function). In a typical experiment C_6F_6 and WF_6 were co-condensed onto O_2AsF_6 powder at −196°, held in a Teflon FEP or quartz reaction vessel. Oxygen was evolved quantitatively on warming towards 0°, according to the equation:

$$O_2AsF_6 + C_6F_6 \xrightarrow{WF_6} C_6F_6AsF_6 + O_2$$

The yield of $C_6F_6^+AsF_6^-$ in preparations of this kind is *ca.* 40%. The solid product is a bright-yellow powder which decomposes fully in 5—6 h at *ca.* 20° but has been kept for several weeks at −15°.

I.r. spectra of the freshly-prepared powder have absorption maxima at 1490(br,s), 1240(w), 1190(m), 1030(s), and 700(vs), compared with 1531(vs), 1368(s), and 1020(vs) cm^{-1} for the gas-phase hexafluorobenzene molecule[5] and 700 cm^{-1} for hexafluoroarsenate ion.[6]

E.s.r. spectra of dilute solutions in HF, as well as of the pure solid, exhibit an unresolved broad symmetric signal at $g = 2{\cdot}0063$. Bazhin *et al.* report[7] that solutions of C_6F_6 in superacids give resolved spectra with $g = 2{\cdot}0038$ which they attribute to $C_6F_6^+$. Accurate bulk susceptibility measurements have been difficult to obtain because of decomposition in the course of the manipulation of the samples, but the data show that the Curie law is obeyed in the temperature range 3·8—71·5 K and that the magnetic moment is in excess of 1·3 B.M. (the thermal decomposition products are diamagnetic).

The salt $C_6F_6^+AsF_6^-$ dissolves appreciably in anhydrous HF at 25° and may be recrystallized from it by cooling. The resulting orange crystals, m.p. 69·1° (decomp.), shown to be identical with the original powder by *X*-ray photography, are hexagonal, $R\bar{3}$ (by Weissenberg photography) with $a_0 = 10{\cdot}55(1)$, $c_0 = 7{\cdot}66(1)$ Å, $U = 738{\cdot}3$ Å,[3] $Z = 3$, $D_c = 2{\cdot}53$ g cm^{-3}. A complete structure determination is in progress but it is already clear that the $C_6F_6^+$ entity (which is expected to exhibit a Jahn–Teller distortion) must either be disordered in its lattice placement or else possess three-fold axial symmetry.

In accord with its low ionization potential, nitric oxide ($I = 9{\cdot}25$ ev)[4] interacts quantitatively with $C_6F_6AsF_6$:

$$C_6F_6AsF_6 + NO \longrightarrow NOAsF_6 + C_6F_6$$

the C_6F_6 being identified by i.r. spectroscopy and the $NOAsF_6$ by its characteristic *X*-ray-powder and Raman spectra.

The dioxygenyl fluoroantimonates ($O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$)[8] also oxidize C_6F_6 (in WF_6) to yield $C_6F_6^+$ salts in almost quantitative yield. The former yields a friable solid and the latter a lower melting material. The fluoroantimonates are thermally more stable than the fluoroarsenate but crystalline samples are more difficult to obtain.

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