Literature discussion of “Fluoride-Ion Donor Properties of AsF5”

M. Gerken and co-workers, *Inorg. Chem.* **2024**, *63*, 7619-7630.

**Instructions:**

*Answer the following questions after reading the Introduction:*

1. Write out a general, non-ligand induced autoionization reaction for AsF5. Identify and label the resultant acid and base in the products.
2. Is this system best described as a Bronsted acid-base system or a Lewis acid-base system?

*Read the Results and Discussion section, and answer the following questions:*

**Synthesis and Properties**

1. The authors report isolating the autoionization product, [AsF4(phen)]+ and the adduct, (AsF5)2•bipy, with the bidentate ligands as seen in eqns 1 and 3, respectively. Following this, they attempt a similar synthesis using monodentate pyridine and DMAP. What occurs when they employ the monodentate analogs, pyridine and DMAP? What is this ascribed to?

**Crystal and Molecular Structure**

1. Figure 1 shows the crystal structure of [AsF4(phen)][AsF6]. What unit cell does it adopt and what, in general, are the parameters for this cell? How does the unit cell for [AsF4(phen)][Sb2F11] compare?
2. Looking at Figure 2, what is the point group for the [AsF4(phen)]+ cation?
3. In the crystal structure of [AsF4(phen)]+ the angle between the equatorial F atoms (F3–As–F4) is slightly larger than 90°. What is the cause of this deformation?

**19F NMR Spectroscopy**

1. Figure 4 contains the 19F NMR spectrum of [AsF4(phen)][AsF6] and the axial and equatorial F atoms on the cation are visible at -36.6 and -79.7 ppm, respectively. How was this assignment made?
2. Why do the Fax and Feq signals appear as broad singlets in the spectrum even at low temperature?

**Molecular Orbitals**

1. Referring to the HOMO and LUMO for both [AsF4(phen)]+ and the adduct, (AsF5)2•bipy in Fig. 8, do these orbitals appear to be more s or p in nature? Are they more metal or ligand-centered? How can you tell?
2. How well does the analysis of the HOMO and LUMO match with phen and bipy’s position on the spectrochemical series?

**Autoionization vs Adduct Formation**

1. Both phen and bipy are similar bidentate, N-based ligands, but reaction of phen results in autoionization of AsF5 while bipy forms a 2:1 As:bipy adduct. What structurally can account for this difference in reactivity?