

GAS PHASE INORGANIC IONS APPROACHING THE COMPLEXITY OF SOLID STATE SPECIES

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Are Supramolecular or Self-Assembly terms that can be applied to gas phase ions? Can gas phase ions assemble into highly complex supramolecular species of defined structure held together by significant intermolecular forces?

Intermolecular interactions are influenced by substantial electrostatic energies whether in solution, the solid state or the gas phase. If large gas phase ions are made up of associated species such as positive or negative ions is this supramolecular chemistry?

In this work we focus on cyanoferrate anions, specifically $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$, with spikey surfaces expected to affect patterns of association. These anions are associated here with phenylphosphonium cations, Ph_4P^+ , MePh_3P^+ , the sodium ion, Na^+ and the potassium ion K^+ .

A variety of cluster anions and cations have been observed, but in general the anions are more abundant. The figure shows the high mass negative ion spectrum of $(\text{Ph}_4\text{P})_3[\text{Fe}(\text{CN})_6]$ and the inset is the overlap of two ions, $[(\text{Ph}_4\text{P})_5\{\text{Fe}(\text{CN})_6\}_2]^-$ and $[(\text{Ph}_4\text{P})_{10}\{\text{Fe}(\text{CN})_6\}_4]^{2-}$. These ions are clearly large species approaching the complexity of solid state species.

