MAIN-GROUP CHEMISTRY

I will bond IF hard pressed

“there is a growing need to expand our chemical design intuition to encompass the high-pressure regime”

Being relatively small and electronegative, halogen atoms feature in a great number of high-valent species, such as NaCl_3 , HgF_4 and IF_7 . The latter features heptacoordinate I(VII) — the highest coordination number for a main-group atom in a neutral compound. The chemical space occupied by iodine fluorides is rich, especially when one considers what can form at high pressures. A team led by Guochun Yang, Yan-ming Ma and Martin Rahm have used computational methods to survey this vast space, and they describe in *Chemical Science* how they came across IF_8 as an energetically viable octacoordinate compound.

“Atomistic structure prediction of materials is extremely difficult because it involves classifying a huge number of energy minima

on a multidimensional lattice energy surface,” reflects Ma. A particularly efficient way to explore such a surface is particle swarm optimization, whereby several potential solutions are each guided towards energy minima according to both the viability of their present positions and the viability of other solution positions. Beginning with I:F ratios, temperature ($T \rightarrow 0$) and pressure as inputs, one can search a surface for minimum energy structures, which can subsequently be optimized using density functional theory.

At ambient pressure, IF_3 , IF_5 and IF_7 exist as distorted T-shaped, square-pyramidal and pentagonal-bipyramidal molecules, respectively. When the pressure is ramped up in silico, Yang, Ma, Rahm and colleagues predict, for example, that IF_3 polymerizes (23 GPa) before decomposing into IF_5 and I_2 (140 GPa). The team also discovered new species that are thermodynamically stable at 300 GPa. These include IF_8 as well as the higher fluorides IF_{10} , IF_{11} and IF_{12} that also feature octacoordinate I on account of having ‘free’ F_2 in their lattices.

In atomic I, the 5d orbitals lie so high in energy above the 5p set that hybridization is impossible. The situation is very different when the same I atom is at the centre of a distorted cube defined by eight F atoms that come close when the system is subjected to 300 GPa. Here, the 5d orbitals, split by the cubic ligand field into lower-lying e_g and higher-lying t_{2g} sets, can overlap with filled F-centred orbitals in an interaction familiar to inorganic chemists.

The team computed the relative occupancies of the I-centred valence orbitals to be $s^1p^{1.7}d^1$, confirming the relevance of the 5d set to the frontier molecular orbitals of IF_8 , a truly hypervalent molecule. At ambient pressure, the anion $[\text{IF}_8]^-$ has a square antiprismatic I(VII) centre and is also hypercoordinated. However, the I 5d orbitals are too high in energy to participate in covalent bonding and it would be contentious to call $[\text{IF}_8]^-$ hypervalent.

Yang and co-workers acquired independent evidence for the involvement of 5d orbitals in the bonding of IF_8 by calculating its projected density of (electronic) states, which indicates mixing of I 5d orbitals with other I and F valence orbitals. Moreover, the Fermi level intersects the F 2p band, suggesting that crystalline IF_8 is metallic and has F-centred vacancies. Thus, IF_8 is not an I(VIII) complex but is best considered an I(VII) centre surrounded by a set of eight F⁻ ligands in which there is one (delocalized) hole.

Although predicted to be stable at high pressures and ultralow temperatures, IF_8 is dynamically unstable towards dissociation under ambient pressure — a likely reason why this compound, which would be challenging to prepare, has escaped the attention of many. Rahm points out “there is a growing need to expand our chemical design intuition to encompass the high-pressure regime.” Only then will we see how far we can push hypercoordination and hypervalence in main-group compounds.

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ORIGINAL ARTICLE Luo, D. et al. A hypervalent and cubically coordinated molecular phase of IF_8 predicted at high pressure. *Chem. Sci.* <https://doi.org/10.1039/C8SC04635B> (2019)

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