

Unusual bridging fluorine discovered in one-of-a-kind interhalogen ion

BY ROSIE ROTHWELL 9 FEBRUARY 2024

For the first time, chemists have synthesised an interhalogen compound exhibiting a unique central fluorine atom coordinated by four BrF₅ groups.¹ The one-of-a-kind interhalogen ion in [NMe₄][Br₄F₂₁]·BrF₅ represents the first example of a central tetracoordinated fluorine bridging to neither metal nor hydrogen atoms.

Tetracoordinated fluorine atoms are known in ionic compounds, for example in CaF₂. And μ₄-fluorine atoms are present in the tetrahydrogen pentafluoride ion and a handful of metal compounds.

Last year, a team led by Florian Kraus from the Philipps University of Marburg in Germany, synthesised [Br₃F₁₆][−], ² which has a triple-coordinated central fluoride ion. Now, building on their previous work, Kraus and co-workers have used a sterically demanding [NMe₄]⁺ counter ion to form the bulkier μ₄-fluorine containing interhalogen ion, [Br₄F₂₁][−].

3D rendering of molecule [Br₄F₂₁]

Source: Royal Society of Chemistry / CCDC 2311055

The μ₄-F atom is surrounded by four BrF₅ molecules in a tetrahedron-like shape

Halogen fluorides are known for their extreme reactivity and the synthesis did not come without its challenges. The team first tried reacting pure BrF₅ with [NMe₄]F but a violent reaction between the two compounds caused a small explosion and a day's work was lost in an instant. On searching for an alternative method they came across research by Karl Christe from 1989³ that helped them to reliably access [NMe₄][BrF₆] and they went on to attempt a controlled reaction of [NMe₄][BrF₆] with excess BrF₅ at low temperatures. It worked. Graham Saunders, a synthetic fluorine chemist from the University of Waikato in New Zealand, comments 'technically it's very difficult work and it's very elegant'.

Picture 2

Source: (C) Florian Kraus/Philipps-Universität Marburg

It is the first example of a fluorine atom μ_4 -bridging to neither metal nor hydrogen atoms.

Deciphering the compound's structure also presented a challenge as it initially appeared very complex. However, by focusing on the centres of the ions and BrF₅ molecules, the team discovered its crystal structure was similar to the MgAgAs-type structure. 'Although the two compounds could not be more chemically different, they are structurally closely related,' says Marburg team member Martin Möbs. Additional quantum calculations reveal that the μ_4 -fluorine–bromine bonds are best described as ionic.

Related stories

Structure

An unprecedented supramolecular structure brings new complexities to life

A layer of three molecular chains organised into repeating near-ball shapes

Unique relaxation mechanism behind case of negative thermal expansion

3D image showing a 3D view of an abiotic, tetrameric, eight-helix bundle

Extraordinary crystal structure displays abiotic foldamer with unprecedented complexity

'To encapsulate a fluoride ion in a non-metallic inorganic framework such that it's bound to four different moieties is really quite extraordinary, because normally you would not anticipate that kind of bonding arrangement,' comments Thomas Lectka, an organofluorine chemist from Johns Hopkins University, US. 'It's an interesting result and I think it will spur more work into the halogens with fluorine,' adds Saunders.

But while the μ_3 -fluorine and μ_4 -fluorine polynuclear anions of BrF₅ have now been isolated, Möbs concludes that 'the anion in which the fluoride ion is surrounded by two BrF₅ molecules, [Br₂F₁₁][−], is still missing.'

Correction: The images were updated on 12 February 2024

References

1 M Möbs et al, Chem. Sci., 2024, DOI: 10.1039/d3sc06688f

2 M Möbs et al, Chem.–Euro. J., 2023, 29, e202301876 (DOI: 10.1002/chem.202301876)

3 W W Wilson and K O Christe, Inorg. Chem., 1989, 28, 4172 (DOI: 10.1021/ic00321a027)