Abstract: Reaction of CsF with ClF₃ leads to Cs[Cl₃F₁₀]. It contains a molecular, propeller-shaped [Cl₃F₁₀]⁻ anion with a central μ⁻F atom and three T-shaped CIF₃ molecules coordinated to it. This anion represents the first example of a heteropolynhalide anion of higher ClF₃ content than [ClF₄]⁻ and is the first Cl-containing interhalogen species with a μ⁻bridging F atom. The chemical bonds to the central μ⁻F atom are highly ionic and quite weak as the bond lengths within the coordinating XF₃ units (X = Cl, and also calculated for Br, I) are almost unchanged in comparison to free XF₃ molecules. Cs[Cl₃F₁₀] crystallizes in a very rarely observed A₁[5B₁⁵] structure type, where cations and anions are each pseudohexagonally close packed, and reside, each with coordination number five, in the trigonal bipyramidal voids of the other.

Fluorine containing interhalogen cations and anions derive from the neutral halogen fluorides. Those containing bridging μ-F atoms are very scarce. Overviews of (homo and hetero) polyhalogen cations and anions have been given in recent review articles.[1–5] So far, the only known species with polyhalogen cations and anions have been given in recent reviews.[1–5] From the neutral halogen fluorides. Those containing bridging μ-F atom. The chemical bonds to the central μ⁻F atom are highly ionic and quite weak as the bond lengths within the coordinating XF₃ units (X = Cl, and also calculated for Br, I) are almost unchanged in comparison to free XF₃ molecules. Cs[Cl₃F₁₀] crystallizes in a very rarely observed A₁[5B₁⁵] structure type, where cations and anions are each pseudohexagonally close packed, and reside, each with coordination number five, in the trigonal bipyramidal voids of the other.

The compound contains the propeller-shaped [Cl₃F₁₀]⁻ anion in Cs⁺ symmetry (Figure 1). However, the deviation of the molecule from Cs⁺ symmetry is small. The anion can be thought of as a central fluoride ion which is coordinated by the Cl atoms of three surrounding ClF₃ molecules. The central μ⁻bridging F atom (F(1) in Figure 1) lies 0.522(2) Å above a virtual plane formed by the Cl atoms with Cl-μ⁻F-Cl angles of 113.53(9) to 116.12(8). Its structure is correctly predicted by VSEPR theory and there seems to be an additional interaction to the Cs⁺ counterion residing above the apex of the trigonal-pyramidal anion (Figure 1).

In contrast, the quantum-chemically calculated gas-phase minimum structure is D₃-symmetric (TURBOMOLE, DFT-PBE0/TZVP, see Supporting Information), that is the μ⁻F atom and the Cl atoms reside within a plane and the Cl-μ⁻F-Cl angles are 120°.[19–22] Even when the geometry optimization is started from C₃ symmetry, where the μ⁻F atom is displaced from the virtual plane formed by the Cl atoms, the D₃-symmetric structure is reobtained.

![Figure 1. The Lewis structure of the [ClF₁₀]⁻ anion and its structure in the salt Cs[Cl₃F₁₀]. The displacement ellipsoids are shown at the 70% probability level at 100 K. Fluorine atoms drawn in yellow, chlorine atoms in green, and caesium atoms in sky blue.](image-url)
In the crystal structure, the ClF₃ units are essentially planar and are rotated around the μ₋-F–Cl bond in the same direction, which leads to the propeller shape of the anion. That is, the ClF₃ units are tilted in comparison to the virtual plane formed by the Cl atoms by 33.47° (3), 36.41° (6), and 44.77° (4). The anion is thus similarly shaped as the [BrF₄]⁻ anion, see below.[19] The Cl atoms are surrounded by four F atoms each in a quadrilateral, almost planar manner. The μ₋–F–Cl distances are in the range of 2.243(2) to 2.265(2) Å. The F atoms cis-bound relative to μ₋-F show F₋–Cl distances from 1.730(2) to 1.747(2) Å, while the trans-bound F atoms show F₋–Cl distances of 1.600(2) to 1.615(2) Å. These are comparable with the Cl–F–Cl distances reported for the orthorhombic modification of ClF₃ (1.716 and 1.621 Å) and thus support the description of the anion having a central fluoride anion coordinated by three ClF₃ molecules.[23] We will see below that the chemical bond between the μ₋-F atom and the three chlorine atoms is almost ionic. Also, a comparison with 2.248(2)/C₁₃⁸, the Fcis below that the chemical bond between the rhombic modification of ClF₃ (1.716 and 1.621 Å) and thus similar to those in the solid-state structures of the halogen calculated coordination number of that plane formed by the Cl atoms by 33.34(7), 36.41(6), and is true for with the atomic distances and angles reported here. The same optimization is started from the pyramidal X–F distance, which leads to the propeller shape of the anion. [10] The Cl atoms are surrounded by four F atoms: yellow, Cl atoms: green.

Figure 2. The two intrinsic bond orbitals (IBOs) showing the Cl–μ₋-F–Cl bonds in the [ClF₂₃]⁻ anion.[20] The percentages indicate the contribution of the Cl atoms and of the μ₋-F atom to the IBO. The larger the percentage, the more polarized the bond. For comparison: For a gas-phase NaF molecule, in which the bond should be highly ionic, the contribution of the F atom is 96%. In the Hz molecule, which has a purely covalent bond, the contribution of each atom is 50%. If the summation of the percentages does not add up to 100%, then other atoms contribute—less than 1%—to the IBO. For further details, see the Supporting Information. F atoms: yellow, Cl atoms: green.

Surprisingly, Cs[Cl₃F₁₀] can be regarded as a simple AB structure type. The Cs+ cations ("A") are coordinated by five [ClF₂₃]⁻ anions ("B"), that is C. N. (Cs⁺) = 5, and that exclusively via the F₋ and μ₋-F atoms. The arrangement of the Cs cations corresponds to the hexagonal-close packed with the layers arranged perpendicular to the c axis (Figure 3). Into the empty channels (parallel to the c axis), the terminally bound F₋ atoms protrude (see center of Figure 3). The μ₋-F atoms, which may be seen as the centers of gravity of the [ClF₂₃]⁻ anions ("B"), are also arranged in a hexagonal-close packed manner with the layers also perpendicular to the c axis. Their coordination number is also five. Thus, the two pseudohexagonal-close packed lattices of A and B interpenetrate in such a way that each ion is surrounded by five of its counterions in a trigonal bipyramidal manner. That is, the partial charge in all three anions, followed by the F₋ atom of the XF₃ units. The F₋ atoms are the least negatively partially charged F atoms. The partial charges of the atoms follow the expected trend in line with decreasing electronegativities XAR(Cl) > XAR(Br) > XAR(I), that is, the iodine atoms are more positively partially charged than the Cl atoms and the F atoms are most negatively partially charged in [IF₆]⁻.[21] The two IBOs representing the Cl–μ₋-F–Cl bond in the [ClF₂₃]⁻ anion are shown in Figure 2. Further IBOs showing the other F–Cl bonds, as well as the respective IBOs for [BrF₄]⁻ and [IF₆]⁻ are reported in the Supporting Information. The percentages next to the atoms show the contribution of each atom to the IBO. The higher the contribution of an atom to the IBO in %, the more ionic is the bond. The contribution of the μ₋-F atom to the respective IBO is above 90% in all three anions, showing a highly polarized covalent, that is essentially ionic, bond (Figure 2 and Figures S2–S4). The heavier halogen atoms only have minor contributions to the IBO. Within the series, the contributions of the atoms follow the expected trend, which is due to the decrease of the electronegativities from Cl to I.

After the description of the molecular structure of the anion we come to the description of the crystal structure of Cs[Cl₃F₁₀].
packing of Cs[Cl\textsubscript{3}F\textsubscript{10}] can be described as a simple A\textsuperscript{5}B\textsuperscript{5} structure type. Of course, the situation is somewhat more complicated because the [Cl\textsubscript{3}F\textsubscript{10}]\textsuperscript{−} ion is not spherical. But if we take idealized planar [Cl\textsubscript{3}F\textsubscript{10}]\textsuperscript{−} ions, the resulting space group is that of the hexagonal-close packing, P\textsubscript{6}_3/mmc (aristotype). Distortion of the planar [Cl\textsubscript{3}F\textsubscript{10}]\textsuperscript{−} ions to their real structure entails a symmetry reduction to the actual space group P\textsubscript{12}1\textsubscript{1}/n\textsubscript{1}; that can be represented by the B\textsuperscript{n}mighausen tree\textsuperscript{29–33} shown in Figure S1. The crystal structure of the compound and its relation to the hexagonal aristotype is shown in Figure 3 and explained in detail in the Supporting Information.

A related structural motif of an A\textsuperscript{5}B\textsuperscript{5} structure type is known to occur as a substructure in the Ni\textsubscript{2}In structure type, where one kind of Ni atoms reside in the octahedral voids and the other kind of Ni atoms in the trigonal bipyramidal voids of hexagonal-close packed layers. The coordination number of each cation and anion is five. The [Cl\textsubscript{3}F\textsubscript{10}]\textsuperscript{−} anion is propeller-shaped with a symmetry close to C\textsubscript{3}; as the central μ\textsubscript{3}-F atom is surrounded in trigonal-pyramidal manner by the three Cl atoms, while quantum-chemical gas-phase calculations predict the anion to be D\textsubscript{3h}-symmetric with the μ\textsubscript{5}-F atom in plane with the Cl atoms. The recorded Raman spectrum of Cs[Cl\textsubscript{3}F\textsubscript{10}] is in excellent agreement with the quantum-chemically calculated one for the solid-state. So far there is no experimental evidence for the existence of a [Cl\textsubscript{2}F\textsubscript{7}]\textsuperscript{−} anion.
that would be the analogue to the known \([\text{Br}_2\text{F}_7^-]\) anion, or for anions with an even higher ClF content than \([\text{Cl}_3\text{F}_{10}]^-\), such as a \([\text{Cl}_4\text{F}_{13}]^-\) anion. Investigations to obtain compounds containing such anions are ongoing, as well as analogous ones that derive from ClF.

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Conflict of interest

The authors declare no conflict of interest.

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[1] I. C. Tornieporth-Ötting, T. M. Klapotke, Heteroat. Chem. 1993, 4, 543 – 552.
[2] S. Brownridge, I. Krossing, J. Passmore, H. D. B. Jenkins, H. K. Roobottom, Coord. Chem. Rev. 2000, 197, 397 – 481.
[3] H. Haller, S. Riedel, Nachr. Chem. 2012, 60, 865 – 867.
[4] H. Haller, S. Riedel, Z. Anorg. Allg. Chem. 2014, 640, 1281 – 1291.
[5] K. Sonnenberg, L. Mann, F. A. Redeke, B. Schmidt, S. Riedel, Angew. Chem. Int. Ed. 2020, 59, 5464 – 5493; Angew. Chem. 2020, 132, 5506 – 5535.
[6] S. I. Ivlev, A. J. Karttunen, M. R. Buchner, M. Conrad, F. Kraus, Angew. Chem. Int. Ed. 2018, 57, 14640 – 14644; Angew. Chem. 2018, 130, 14850 – 14855.
[7] K. O. Christe, C. J. Schack, Inorg. Chem. 1970, 9, 1852 – 1858.
[8] L. Stein, J. Fluorine Chem. 1985, 27, 249 – 256.
[9] S. Ivlev, P. Woidy, V. Sobolev, I. Gerin, R. Ostvald, F. Kraus, Z. Anorg. Allg. Chem. 2013, 639, 2846 – 2850.
[10] S. I. Ivlev, A. J. Karttunen, R. V. Ostvald, F. Kraus, Chem. Commun. 2016, 52, 12040 – 12043.
[11] K. O. Christe, Inorg. Chem. 1972, 11, 1215 – 1219.
[12] A. R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt, Angew. Chem. Int. Ed. Engl. 1989, 28, 1526 – 1527; Angew. Chem. 1989, 101, 1528 – 1529.
[13] J. Bandemer, M. Sachs, S. I. Ivlev, A. J. Karttunen, F. Kraus, Eur. J. Inorg. Chem. 2020, 64 – 70.
[14] L. B. Asprey, J. L. Margrave, M. E. Silverthorn, J. Am. Chem. Soc. 1961, 83, 2955 – 2956.
[15] E. D. Whitney, R. O. MacLaren, C. E. Fogle, T. J. Hurley, J. Am. Chem. Soc. 1964, 86, 2583 – 2586.
[16] E. D. Whitney, R. O. MacLaren, T. J. Hurley, C. E. Fogle, J. Am. Chem. Soc. 1964, 86, 4340 – 4342.
[17] X. Zhang, K. Seppelt, Z. Anorg. Allg. Chem. 1997, 623, 491 – 500.
[18] B. Scheibe, S. I. Ivlev, A. J. Karttunen, F. Kraus, Eur. J. Inorg. Chem. 2020, 1319 – 1324.
[19] TURBOMOLE V7.3, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989 – 2007, TURBOMOLE GmbH, since 2007, 2018.
[20] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297 – 3305.
[21] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865 – 3868.
[22] C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158 – 6170.
[23] R. D. Burbank, F. N. Bensey, J. Chem. Phys. 1953, 21, 602 – 608.
[24] R. D. Burbank, F. N. Bensey, J. Chem. Phys. 1957, 27, 982 – 983.
[25] S. Hoyer, K. Seppelt, Angew. Chem. Int. Ed. 2000, 39, 1448 – 1449; Angew. Chem. 2000, 112, 1512 – 1514.
[26] G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834 – 4843.
[27] G. Knizia, J. E. M. N. Klein, Angew. Chem. Int. Ed. 2015, 54, 5518 – 5522; Angew. Chem. 2015, 127, 5609 – 5613.
[28] A. L. Allred, E. G. Rochow, J. Inorg. Nucl. Chem. 1958, 5, 264 – 268.
[29] H. Barnighausen, MATCH 1980, 9, 139 – 175.
[30] International Tables for Crystallography, Volume A1: Symmetry Relations Between Space Groups (Eds.: H. Wondratschek, U. Müller), Springer, Dordrecht, 2010.
[31] U. Müller, Symmetry Relationships between Crystal Structures: Applications of Crystallographic Group Theory in Crystal Chemistry, Oxford University Press, Oxford, 2013.
[32] U. Müller, Symmetriebedingungen zwischen verwandten Kristallstrukturen, Vieweg + Teubner, Wiesbaden, 2012.
[33] U. Müller, Relaciones de Simetría Entre Estructuras Cristalinas, Editorial Síntesis, Madrid, 2013.
[34] F. Laves, H. J. Wallbaum, Z. Angew. Mineral. 1942, 4, 17 – 46.
[35] H. Haas, M. Jansen, Angew. Chem. Int. Ed. 1999, 38, 1909 – 1911; Angew. Chem. 1999, 111, 2033 – 2035.
[36] H. Haas, M. Jansen, Z. Anorg. Allg. Chem. 2000, 626, 1174 – 1178.
[37] J. C. Schön, M. Jansen, Angew. Chem. Int. Ed. Engl. 1996, 35, 1286 – 1304; Angew. Chem. 1996, 108, 1358 – 1377.
[38] S. Limpijunnong, W. R. L. Lambrecht, Phys. Rev. B 2001, 63, 104103.
[39] R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rétat, S. Casassa, J. Baima, S. Salustro, et al., Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8, e1360.
[40] S. I. Ivlev, M. Conrad, F. Kraus, Z. Kristallogr. - Cryst. Mater. 2019, 234, 415 – 418.
[41] Deposition Number(s) 1992456 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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