

Angewandte

Check for updates

Chlorine Fluorides

How to cite: Angew. Chem. Int. Ed. 2020, 59, 16002-16006 International Edition: doi.org/10.1002/anie.202006268 German Edition: doi.org/10.1002/ange.202006268

Improved Access to Organo-Soluble Di- and Tetrafluoridochlorate-(I)/(III) Salts

P. Pröhm, J. R. Schmid, K. Sonnenberg, P. Voßnacker, S. Steinhauer, C. J. Schattenberg, R. Müller, M. Kaupp, and S. Riedel*

Abstract: A facile one-pot gram-scale synthesis of tetraalky $lammonium tetrafluoridochlorate(III) [cat][ClF_4] ([cat] =$ $[NEt_3Me]^+$, $[NEt_4]^+$) is described. An acetonitrile solution of the corresponding alkylammonium chloride salt is fluorinated with diluted fluorine at low temperatures. The reaction proceeds via the $[ClF_2]^-$ anion which is structurally characterized for the first time. The potential application of $[ClF_4]^$ salts as fluorinating agents is evaluated by the reaction with diphenyl disulfide, Ph_2S_2 , to pentafluorosulfanyl benzene, *PhSF*₅. *The CN moieties in acetonitrile and* $[B(CN)_4]^-$ are transferred in CF₃ groups. Exposure of carbon monoxide, CO, leads to the formation of carbonyl fluoride, COF₂, and elemental gold is dissolved under the formation of tetrafluoridoaurate $[AuF_4]^-$.

Chlorine fluorides (CIF, CIF₃, CIF₅) are amongst the most reactive compounds known.^[1] These very strongly oxidizing gases should only be handled in special equipment made from metal, including stainless steel, copper, nickel, Monel and other Cu/Ni alloys or from perfluorinated polymers such as PTFE, KEL-F or PFA. Especially ClF₃ and ClF₅ can under certain conditions exceed the reactivity of elemental fluorine. Exposure to organic material leads to violent reactions in many cases and only carefully chosen reaction conditions (especially dilution of the chlorine fluoride) can avoid dangerous explosions; however, acetonitrile is known to be resistant against bromo and chloro fluorine compounds.^[2] ClF₃ reacts with nitrosyl fluoride or alkali metal fluorides under formation of the corresponding tetrafluoridochlorate-(III) salts.^[3,4] Alkali metal tetrafluoridochlorates can also be formed via exposure of the corresponding alkali metal

M. Sc. C. J. Schattenberg, Dr. R. Müller, Prof. Dr. M. Kaupp Technische Universität Berlin, Department of Chemistry: Theoretical Chemistry

Sekr. C7, Strasse des 17. Juni 135, 10623 Berlin (Germany) E-mail: martin.kaupp@tu-berlin.de



Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202006268.

chlorides (CsCl, RbCl, KCl) towards elemental fluorine at elevated temperatures.^[5] More soluble tetrafluoridochlorate-(III) salts, for example, alkylammonium salts, can be obtained by salt metathesis with the corresponding alkylammonium fluorides in propionitrile at low temperatures.^[3] However, only few examples of stable anhydrous alkylammonium fluorides are known.^[6] Nevertheless, cation metathesis was used to synthesize the tetramethylammonium and 1,1,3,3,5,5hexamethylpiperidinium (pip) tetrafluoridochlorate(III) salts.^[3,7] Additionally, [NMe₄][CIF₄] was observed as a decomposition product of [NMe₄][ClF₆].^[8] The difluoridochlorate(I) anion, [ClF₂]⁻, is so-far only reported with a limited amount of counter ions (K⁺, Rb⁺, Cs⁺, NO⁺) and only characterized by vibrational spectroscopy.^[9,10] To the best of our knowledge the chemistry of di- and tetrafluoridochlorates was only studied rudimentarily. Hence, we present a CIF₃-free, gram scale synthesis of organo-soluble tetraalkylammonium tetrafluoridochlorate and explore its chemical properties. We exposed triethylmethylammonium chloride [NEt₃Me]Cl to dilute fluorine (10% in argon) in acetonitrile or propionitrile at low temperatures [Equation (1)]. In the beginning of the fluorination a slight yellow color of the solution was observed. We hypothesize that small amounts of chlorine are formed. However, it was not possible to detect any vibrational band of Cl₂ via Raman spectroscopy. In the process of further fluorination the solution decolorized again. For the synthesis of highly concentrated solutions we used $[NEt_3Me][Cl_3]^{[11]}$ as a starting material due to its enhanced solubility in acetonitrile in comparison to tertraalkylammonium chlorides like [NEt₄]Cl or [NMe₄]Cl. It is worth mentioning that all starting materials are commercially available and the reaction proceeds in standard laboratory glassware in contrast to the reported synthesis with ClF₃.

 $[NEt_{3}Me]Cl + 2\,F_{2} \xrightarrow[-35^{\circ}C, R=Me,Et]{} [NEt_{3}Me][ClF_{4}]$ (1)

We characterized the obtained solution by Raman and $^{19}\mathrm{F}$ NMR spectroscopy. The $^{19}\mathrm{F}$ NMR spectrum (Figure S2 in the Supporting Information) shows one main resonance at 67 ppm for $[ClF_4]^-$ which is in good agreement with previously reported values (66.8 ppm).^[7] The Raman spectrum (Figure 1) measured at -196°C shows, besides the bands of the cation and solvent, three bands at 500 cm^{-1} , 408 cm^{-1} and 278 cm⁻¹, which are attributed to the a_{1g} , the b_{1g} , and the b_{2g} vibration in the D_{4h} symmetric molecule in agreement with literature values $(508 \text{ cm}^{-1}, 415 \text{ cm}^{-1}, 278 \text{ cm}^{-1})$.^[7,12]

By exchange of the cation to tetraethylammonium $[NEt_4]^+$ we were able to grow single crystals suitable for single crystal X-Ray diffraction. [NEt₄][ClF₄] crystallizes in

^[*] M. Sc. P. Pröhm, J. R. Schmid, Dr. K. Sonnenberg, M. Sc. P. Voßnacker, Dr. S. Steinhauer, Prof. Dr. S. Riedel Freie Universität Berlin, Institut of Chemistry and Biochemistry Fabeckstr. 34/36, 14195 Berlin (Germany) E-mail: s.riedel@fu-berlin.de

^{© 2020} The Authors. Published by Wiley-VCH Verlag GmbH & Co. O KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

¹⁶⁰⁰² Wiley Online Library



Figure 1. Raman spectrum of [NEt₃Me][ClF₄] in acetonitrile at -196 °C.

the space group C2/c. The chlorine atom occupies the Wyckhoff position 4c (site symmetry $P\bar{1}$). The $[ClF_4]^-$ is only slightly distorted from D_{4h} symmetry with two crystallographically inequivalent Cl-F bonds, d(Cl-F1) = 180.6(2) pm and d(Cl-F2) = 179.3(2) pm and rectangular bond angles \measuredangle (F1-Cl-F2) = 90.01(5)° and \measuredangle (F2-Cl-F1') = 89.99(5)°, see Figure 2. Overall, the anion is in good agreement with the structures reported in the literature ([cat][ClF₄], [cat] = K^+ , Rb^+ , Cs^+ , NO^+ [pip]⁺) and is only slightly less distorted than in the reported structures of [pip][ClF₄] and [NO][ClF₄] (see Table S2).^[3] The shortest cation anion contact is an F-H hydrogen bridge and was determined to 242.3(1) pm, the corresponding F...(H)-C distance was determined to 336.5(3) pm. Additionally, we calculated the Hirshfeld surface which is also showing a short cation anion contact (Figure S16).

The addition of 1.2 equiv. fluorine to a solution of $[NEt_3Me]Cl$ in acetonitrile yields a mixture of $[ClF_2]^-$ and $[ClF_4]^-$ anions. Again, we were able to characterize this mixture by vibrational and ¹⁹F NMR spectroscopy. The Raman spectrum (Figure 3) of this mixture at -196 °C shows the characteristic bands of $[ClF_4]^-$ and additionally



Figure 2. Crystal structure [NEt₄][ClF₄]. Displacement ellipsoids are shown at 50% probability at 100 K. Selected bond lengths [pm] and bond angles [°]: F1–Cl1 179.2(2), F2–Cl1 180.6(2) F1-Cl1-F2 89.99(5), F2-Cl1-F1' 90.01(5). Hydrogen atoms omitted for clarity.^[29]



Figure 3. Raman spectrum of $[NEt_3Me]_3[CIF_4][CIF_2]_2$ in acetonitrile at -196 °C.

one band at 455 cm⁻¹ which can be assigned to the symmetric stretch vibration of $[ClF_2]^-$, similar to those reported for solid KClF₂ (475 cm⁻¹) and RbClF₂ (476 cm⁻¹).^[10] The harmonic frequency of the symmetric stretching mode for free $[ClF_2]^-$ is calculated to 453 cm⁻¹ (CCSD(T)/def2-TZVPP) which is in good agreement with our assignment.^[13] The differences between the value reported by us and the literature values can be explained by the stronger coordination of the alkali metal cation in the solid-state in comparison with the tetraalkylammonium cation.

The ¹⁹F NMR spectrum (Figure S3) shows two signals. The one at 67 ppm can be assigned to the $[ClF_4]^-$ anion (see above). We assigned the second signal at -125 ppm to the $[ClF_2]^-$ anion since the Raman spectrum showed the corresponding band at 455 cm⁻¹ before and after the measurement of the NMR spectrum.

Table 1 provides our computed ¹⁹F shifts for the full series of anions $[XF_n]^-$ (X = Cl, Br, I; n = 2, 4, 6), using two functionals (the BHLYP global hybrid and the LH12ct-SsifPW92 local hybrid) that have been shown to provide superior ¹⁹F shieldings compared to B3LYP.^[14,15] The computations BP86-D3(BJ)(COSMO,CH₃CN))/def2used TZVPPD structures and DFT(COSMO,CH₃CN)-GIAO// pcSseg-4/ANO-RCC-unc shielding computations (with pcSseg-4 basis sets for F, Cl, Br and the uncontracted ANO-RCC basis for I; see Supporting Information for further computational details and additional data). The available experimental data for n = 4, 6 are reproduced rather well at the two levels used. As shown by separate four-component relativistic computations (Table S5 in Supporting Information), both spin-orbit and scalar relativistic effects are small, in most cases a few ppm, at most about 13 ppm for $[IF_2]^-$. The small spin-orbit effects can be understood from an inefficient transfer mechanism to the fluoride nuclei.^[16] However, the computed ¹⁹F shifts for the difluoridohalide anions are too shielded by 60-100 ppm (more so for BHLYP than for LH12ct-SsifPW92). This is clearly outside the error margins of these two density functionals or of relativistic contribu-

Angew. Chem. Int. Ed. 2020, 59, 16002–16006 © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim www.angewandte.org 16003

Table 1: Calculated ¹⁹ F NMR	chemical shifts relative to CFCl ₃ (in ppm) of
$[XF_n]^-$ (X = Cl, Br, I; n = 2, 4,	6) in comparison with experimental values.

Molecule	δ_{exp}	$\delta_{ ext{BHLYP}}{}^{[a]}$	$\delta_{ t LH12ct-sifPW92}{}^{[a]}$
[CIF ₂] ⁻	-125 ^[b]	-202	-174
$[C F_4]^-$	67 ^[7]	68	61
$[C F_6]^-$	-	278	249
$[BrF_2]^-$	-210 ^[3a]	-296	-273
$[BrF_4]^-$	-37 ^[8]	-42	-45
$[BrF_6]^-$	94 ^[8]	129	112
$[IF_2]^-$	$-286, -282^{[3a, 17]}$	-360	-348
$[IF_4]^-$	-106 ^[3a, 18]	-111	-117
[IF ₆] ⁻	13 ^[19]	30	14

[a] DFT(COSMO,CH₃CN)-GIAO/pcSseg-4/ANO-RCC-unc//BP86-D3 (BJ)(COSMO,CH₃CN))/def2-TZVPPD data. [b] This work.

tions. Closer inspection reveals that the highly negative fluorine charges in the difluorido anions give rise to specific $F \cdots H - C$ interactions with the acetonitrile solvent, which is not the case for the four- and six-coordinate cases. These strong interactions are not covered by the implicit COSMO solvent model but become apparent when using more explicit treatments of solvation. Detailed studies of these interesting fluoro-specific interactions are underway and will be reported elsewhere.

By slowly cooling a reaction mixture of [NEt₃Me]Cl with 1.2 equiv. fluorine in acetonitrile, single crystals of [NEt₃Me]₃[ClF₄][ClF₂]₂ were obtained (for further details see Supporting Information, Figure S17). Replacing F₂ by ClF as a fluorination agent we were able to synthesize neat [NEt₃Me][ClF₂]. The Raman spectrum (Figure S6) shows one main band at 457 cm⁻¹ which is in good agreement with data from [NEt₃Me]₃[ClF₄][ClF₂]₂ (455 cm⁻¹). The compound crystallizes in the space group *P*12₁/*c*1 (Figure 4). The two anionic moieties F1Cl1F1' and F2ACl2F2A' are both half occupied with Cl1 on Wyckhoff position 2b (site symmetry *P*1) and Cl2 on Wyckhoff position 2c (site symmetry *P*1). The Cl–F bond lengths are 185.24(6) pm (Cl1–F1) and 184.6(2) (Cl2–F2A). The calculated bond length of the free [ClF₂]⁻ is 186.8 pm (CCSD(T)/def2-TZVPP).^[13] The bonding situation



Figure 4. Crystal structure of $[NEt_3Me][ClF_2]$. Displacement ellipsoids are shown at 50% probability at 100 K. Selected bond lengths [pm]: F1-Cl1 185.24(6), F2A-Cl2 184.6(2). Hydrogen atoms omitted for clarity.^[29]

is best described by a 3-center-4-electron bond. The Cl–F bond lengths in $[ClF_2]^-$ are significantly elongated in comparison with solid ClF (162.8(1) pm).^[20] It is well-known from polyhalide chemistry that the bond length of a dihalogen is elongated upon coordination by a Lewis base due to the donation of electron density into the $\sigma^*(Cl-F)$ orbital.^[12,21] As anticipated, the $[ClF_2]^-$ anion is computed to be more thermochemically stable towards halogen loss than $[Cl_3]^-$ and $[F(Cl)_2]^-$ which is due to more ionic interactions of the ClF moiety in comparison to Cl_2 .^[12,22]

We examined the stability of $[NEt_3Me][ClF_4]$ in acetonitrile solution via ¹⁹F NMR spectroscopy. Surprisingly, it showed only slow decomposition at room temperature over a month via fluorination of the organic solvent and the cation. However, the isolated solid is significantly more reactive. We observed explosions in several cases at temperatures above -40 °C. Consequently, we avoided the isolation of larger quantities of $[NEt_3Me][ClF_4]$ and instead worked with solutions in propionitrile or acetonitrile with concentrations in the range of $0.66 \text{ mol}1^{-1}$ to $8.8 \text{ mol}1^{-1}$.

We envisioned [NEt₃Me][ClF₄] as a fluorinating and oxidation reagent for the synthesis of highly fluorinated moieties such as trifluoromethyl (-CF₃), pentafluorosulfanyl $(-SF_5)$ or fluoridometallates $([MF_x]^-)$. Trifluoromethyl and pentafluorosulfanyl derivatives have a growing importance in pharmaceutical- and agrochemistry.^[23,24,25] Recently, Togni and co-workers reported on a non-gaseous reagent to access aryl tetrafluorido- λ^6 -sulfanyl chlorides (Ar-SF₄Cl), a key intermediate for the synthesis of pentafluorosulfanyl aryls (Ar-SF₅).^[24] Beier and co-workers recently studied the direct fluorination with dilute elemental fluorine and disulfides to directly obtain pentafluorosulfanyl aryls, a process with industrial application.^[25] As a proof of concept we exposed diphenyl disulfide, Ph₂S₂, to a solution of [NEt₃Me][ClF₄] in propionitrile at -50 °C to directly obtain phenylsulfur pentafluoride, PhSF₅. As by-products the cis- and trans-PhSF₄Cl were observed (Table 2 Entry 1, for further details see Supporting Information). PhSF₅ can be prepared in pure form by removal of both PhSF₄Cl isomers by hydrolysis. Simultaneously, residual fluorochlorates are hydrolysed.^[26]

Addition of the Lewis acid boron trifluoride, BF_3 , to a solution of $[NEt_3Me][ClF_4]$ in acetonitrile led to the formation of CH_3CF_3 , the CN activation product of the solvent acetonitrile, amongst other components. To increase the selectivity of this reaction, we synthesized the acetonitrile- BF_3 complex and substituted the solvent, from nitrile-based solvents to chlorofluorocarbons. Dichlorofluoromethane (CHFCl₂, R-21) turns out to be sufficiently stable towards

Table 2: Reactivity Studies with [NEt₃Me][ClF₄].

Entry	Substrate	Lewis acid	Product
1	Ph_2S_2	_	PhSF₅, PhSF₄Cl
2	MeCN	BF ₃	MeCF ₃
3	[B(CN)₄] [−]	BF ₃	$[B(CF_3)_x(CN)_{4-x}]^-$
4	[Au(CN) ₂] ⁻	BF ₃	cis-[AuF ₂ (CF ₃)(CN)] ^{-[a]}
5	Au	_	[AuF ₄] ⁻
6	со	_	COF ₂

[a] Minor product.

 F_2 and $[ClF_4]^-$ and also dissolves the starting material [NEt₃Me]Cl. Combination of two dichlorofluoromethane solutions containing [NEt₃Me][ClF₄] and MeCN·BF₃ leads to the formation of CH₃CF₃ (Table 2 Entry 2, for further details see Supporting Information). This is reminiscent of the reaction between succinonitrile and BrF₃.^[27] We also examined the reactivity towards the tetracyanidoborate anion $[B(CN)_4]^-$. With addition of the Lewis acid BF₃ we observed the conversion of the cyanido ligands to trifluoromethyl ligands. This result is analogous to the synthesis of $[B(CF_3)_4]^$ from [B(CN)₄]⁻ and ClF₃ in anhydrous HF.^[28] However, we did not achieve full conversion but a distribution of different borate anions with trifluormethyl and cyanido ligands $[B(CF_3)_x(CN)_{4-x}]^-$ (Table 2 Entry 3, for further details see Supporting Information). Additionally, we exposed the [BF₃(CN)]⁻ anion to [NEt₃Me][ClF₄] but only fluorination to $[BF_4]^-$ was observed. The reaction of $[NEt_3Me][ClF_4]$ with dicyanidoaurate(I) $[Au(CN)_2]^-$ is not selective, however, we were able to identify one Au-CF₃ containing product in the reaction mixture via NMR spectroscopy, that is, cis- $[AuF_2(CF_3)(CN)]^-$ (Table 2 Entry 4, for further details see Supporting Information). Another promising application for [NEt₃Me][ClF₄] is the dissolution of noble metals such as gold. After the addition of a piece of elemental gold, the solution containing $[ClF_4]^-$ turns yellow. The ¹⁹F NMR spectroscopic analysis reveals the formation of mainly $[AuF_4]^-$ (Table 2 Entry 5, for further details see Supporting Information) and traces of other chloridofluoridoaurates $([AuF_3Cl]^- \text{ and } cis-[AuF_2Cl_2]^- \text{ see Figure S12})$. Exposure of [NEt₃Me][ClF₄] in propionitrile to an atmosphere of CO results in the formation of carbonyl fluoride (COF₂) within 30 min (Table 2 Entry 6, for further details see Supporting Information).

In conclusion, we developed a facile and fast synthetic procedure to obtain a soluble source of highly reactive $[ClF_4]^$ in the form of [NEt₃Me][ClF₄] avoiding gaseous ClF₃ which tends to react explosively when exposed to organic matter. We characterized this compound by NMR and Raman spectroscopy and, additionally, single crystal X-Ray diffraction for the analogous [NEt₄][ClF₄]. Furthermore, we presented the first structural and 19F NMR spectroscopic proof of the [CIF₂]⁻ anion. All experimental results are supported by quantum-chemical calculations. Additionally, we showed several applications of $[NEt_3Me][ClF_4]$ as a highly reactive fluorinating agent for the transformation of aryl disulfides into the corresponding pentafluorosulfanyl aryls, nitriles and cyanido complexes into the corresponding trifluoromethyl compounds, carbon monoxide into carbonyl fluoride and the dissolution of elemental gold. In further studies we will explore a broader substrate scope to develop a widely applicable fluorinating reagent for organic and inorganic chemists.

Caution! Fluorine, even under dilute conditions, is extraordinarily reactive and can react violently with organic materials under the formation of HF. Similarly, tetrafluoridochlorate(III) and difluoridochlorate(I) are strongly oxidizing compounds, which can decompose violently under certain conditions when exposed to organic materials. Exposure to acidic compounds (e.g. water or boron trifluoride) greatly enhances the reactivity due to the in situ formation of ClF₃. Additionally, precipitation also greatly enhances the reactivity of tetrafluoridochlorate(III) and difluoridochlorate(I) compounds, leading to explosions at temperatures above -40 °C. Usage of PFA, FEP or PTFE may lower the risk of injury.

Acknowledgements

We gratefully acknowledge the ZEDAT at Freie Universität Berlin for providing computing resources. Additionally, we are grateful for donations of chemicals from the Solvay company. SPP 1708 is acknowledged for funding. Furthermore, PP acknowledges VCI for providing PhD funding (Kekulé Fellowship). Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 387284271—SFB 1349. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: chlorine fluorides · fluorination reagents · strong oxidizers

- D. Naumann, *Fluor und Fluorverbindungen*, Steinkopff, Heidelberg, **1980**.
- [2] a) K. R. Brower, J. Fluorine Chem. 1986, 31, 333; b) F. Kraus, Nachr. Chem. 2019, 67, 17; c) G. Schiemann, K. Bromme, B. Cornils, Chem. Ber. 1965, 98, 3410; d) G. Schiemann, M. Kühnhold, B. Cornils, Liebigs Ann. Chem. 1968, 714, 62; e) H. Meinert, U. Groβ, Z. Chem. 1969, 9, 190.
- [3] a) X. Zhang, K. Seppelt, Z. Anorg. Allg. Chem. 1997, 623, 491;
 b) B. Scheibe, S. I. Ivlev, A. J. Karttunen, F. Kraus, Eur. J. Inorg. Chem. 2020, 1319.
- [4] a) E. D. Whitney, R. O. MacLaren, T. J. Hurley, C. E. Fogle, J. Am. Chem. Soc. 1964, 86, 4340; b) E. D. Whitney, R. O. MacLaren, C. E. Fogle, T. J. Hurley, J. Am. Chem. Soc. 1964, 86, 2583; c) K. O. Christe, J. P. Guertin, Inorg. Chem. 1966, 5, 473; d) K. O. Christe in IUPAC, XXIVth Int. Cong. Pure Appl. Chem. 1974, 115.
- [5] a) L. B. Asprey, J. L. Margrave, M. E. Silverthorn, J. Am. Chem. Soc. 1961, 83, 2955; b) D. H. Kelly, B. Post, R. W. Mason, J. Am. Chem. Soc. 1963, 85, 307.
- [6] a) K. O. Christe, W. W. Wilson, R. D. Wilson, R. Bau, J. A. Feng, J. Am. Chem. Soc. 1990, 112, 7619; b) A. R. Mahjoub, X. Zhang, K. Seppelt, Chem. Eur. J. 1995, 1, 261; c) H. Sun, S. G. DiMagno, J. Am. Chem. Soc. 2005, 127, 2050; d) S. Elias, N. Karton-Lifshin, L. Yehezkel, N. Ashkenazi, I. Columbus, Y. Zafrani, Org. Lett. 2017, 19, 3039.
- [7] W. W. Wilson, K. O. Christe, Inorg. Chem. 1989, 28, 4172.
- [8] K. O. Christe, W. W. Wilson, R. V. Chirakal, J. C. P. Sanders, G. J. Schrobilgen, *Inorg. Chem.* 1990, 29, 3506.
- [9] a) K. O. Christe, J. P. Guertin, *Inorg. Chem.* 1965, *4*, 905; b) K. O. Christe, J. P. Guertin, *Inorg. Chem.* 1965, *4*, 1785.
- [10] K. O. Christe, W. Sawodny, J. P. Guertin, *Inorg. Chem.* 1967, 6, 1159.
- [11] R. Brückner, Dissertation, Freie Universität Berlin, Berlin, 2016.
- [12] K. O. Christe, W. Sawodny, Z. Anorg. Allg. Chem. 1968, 357, 125.
- [13] F. A. Redeker, A. Kropman, C. Müller, S. E. Zewge, H. Beckers, B. Paulus, S. Riedel, *J. Fluorine Chem.* 2018, 216, 81.

Angew. Chem. Int. Ed. 2020, 59, 16002–16006 © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim www.angewandte.org 16005



- [14] C. J. Schattenberg, K. Reiter, F. Weigend, M. Kaupp, J. Chem. Theory Comput. 2020, 16, 931.
- [15] T. Kupka, Magn. Reson. Chem. 2009, 47, 959.
- [16] M. Kaupp, O. L. Malkina, V. G. Malkin, P. Pyykkö, *Chem. Eur. J.* 1998, 4, 118.
- [17] K. O. Christe, W. W. Wilson, G. W. Drake, M. A. Petrie, J. A. Boatz, J. Fluorine Chem. 1998, 88, 185.
- [18] K. O. Christe, W. W. Wilson, G. W. Drake, D. A. Dixon, J. A. Boatz, R. Z. Gnann, J. Am. Chem. Soc. 1998, 120, 4711.
- [19] K. O. Christe, W. W. Wilson, Inorg. Chem. 1989, 28, 3275.
- [20] R. Boese, A. D. Boese, D. Bláser, M. Y. Antipin, A. Ellern, K. Seppelt, Angew. Chem. Int. Ed. Engl. 1997, 36, 1489; Angew. Chem. 1997, 109, 1538.
- [21] a) B. Schmidt, K. Sonnenberg, H. Beckers, S. Steinhauer, S. Riedel, Angew. Chem. Int. Ed. 2018, 57, 9141; Angew. Chem. 2018, 130, 9279; b) K. Sonnenberg, P. Pröhm, N. Schwarze, C. Müller, H. Beckers, S. Riedel, Angew. Chem. Int. Ed. 2018, 57, 9136; Angew. Chem. 2018, 130, 9274; c) S. I. Ivlev, A. J. Karttunen, R. Ostvald, F. Kraus, Z. Anorg. Allg. Chem. 2015, 641, 2593; d) S. I. Ivlev, A. J. Karttunen, R. V. Ostvald, F. Kraus, Chem. Commun. 2016, 52, 12040; e) K. Sonnenberg, L. Mann, F. A. Redeker, B. Schmidt, S. Riedel, Angew. Chem. Int. Ed. 2020, 59, 5464; Angew. Chem. 2020, 132, 5506.
- [22] a) T. J. Van Huis, J. M. Galbraith, H. F. Schaeffer, *Mol. Phys.* 1996, *89*, 607; b) A. B. Sannigrahi, S. D. Peyerimhoff, *Chem. Phys. Lett.* 1985, *119*, 119; c) L. Chen, D. E. Woon, T. H. Dunning, *Comput. Theor. Chem.* 2017, *1116*, 73; d) K. S. Thanthiriwatte, J. M. Spruell, D. A. Dixon, K. O. Christe, H. D. B. Jenkins, *Inorg. Chem.* 2014, *53*, 8136.

- [23] a) D. Lentz, K. Seppelt in Chemistry of hypervalent compounds (Ed.: K.'y. Akiba), Wiley-VCH, Weinheim, **1999**; b) H. L. Yale, J. Med. Chem. **1959**, 1, 121; c) T. Umemoto, L. M. Garrick, N. Saito, Beilstein J. Org. Chem. **2012**, 8, 461; d) P. R. Savoie, J. T. Welch, Chem. Rev. **2015**, 115, 1130.
- [24] C. R. Pitts, D. Bornemann, P. Liebing, N. Santschi, A. Togni, Angew. Chem. Int. Ed. 2019, 58, 1950; Angew. Chem. 2019, 131, 1970.
- [25] J. Ajenjo, B. Klepetářová, M. Greenhall, D. Bím, M. Culka, L. Rulíšek, P. Beier, *Chem. Eur. J.* **2019**, *25*, 11375.
- [26] W.-T. Tsai, J. Hazard. Mater. 2011, 190, 1.
- [27] M. T. Baker, J. A. Ruzicka, J. H. Tinker, J. Fluorine Chem. 1999, 94, 123.
- [28] E. Bernhardt, G. Henkel, H. Willner, G. Pawelke, H. Bürger, *Chem. Eur. J.* 2001, 7, 4696.
- [29] Deposition Number(s) 1948998 (for [NEt₄][ClF₄]) and 2004243 (for [NEt₃Me][ClF₂]) 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.

Manuscript received: April 30, 2020 Revised manuscript received: May 18, 2020 Accepted manuscript online: May 27, 2020 Version of record online: July 15, 2020