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Interhalogen Chemistry

Synthesis and Characterization of the Tetrafluoridochlorates(III)
 $A[\text{ClF}_4]$ ($A = \text{K}, \text{Rb}, \text{Cs}$)Benjamin Scheibe,^[a] Sergei I. Ivlev,^[a] Antti J. Karttunen,^[b] and Florian Kraus^{*[a]}

Abstract: Single-crystalline tetrafluoridochlorates(III) $A[\text{ClF}_4]$ ($A = \text{K}, \text{Rb}, \text{Cs}$) were synthesized from solvolysis reactions of alkali metal fluorides in liquid chlorine trifluoride. The structures were examined by means of single-crystal X-ray diffraction. $\text{K}[\text{ClF}_4]$ crystallizes in the $\text{K}[\text{BrF}_4]$ structure type, whereas the Rb and Cs compounds crystallize in the $\text{Li}[\text{AuF}_4]$ structure type.

The compounds were further characterized by Raman and IR spectroscopy. Solid-state quantum-chemical calculations with hybrid density functional methods reproduced the experimental structures and enabled the interpretation of the experimental Raman and IR spectra.

Introduction

The first preparation of tetrafluoridochlorates(III) of the alkali metals, $A[\text{ClF}_4]$ ($A = \text{K}, \text{Rb}, \text{Cs}$), was probably accomplished by direct fluorination of the respective chlorides.^[1–3] The authors first discussed a possible formation of polyfluorides of the type “ AF_2 ” ($A = \text{K}, \text{Rb}$) and “ AF_3 ” ($A = \text{Rb}, \text{Cs}$).^[1–3] These results were disputed at a meeting of the Gesellschaft Deutscher Chemiker in 1950 and later revised by the same authors, who showed that the products contained alkali metal fluoridochlorates(III) as well as the alkali metal fluorides.^[2,4] Polyfluorides have so far only been obtained under cryogenic conditions with the matrix isolation technique.^[5–7]

Others have also prepared tetrafluoridochlorate(III)-containing products by fluorination of alkali metal chlorides at high pressures and/or temperatures.^[8–10] The syntheses of tetrafluoridochlorates(III) are also possible by solvolysis reactions of alkali metal fluorides, AF ($A = \text{K}, \text{Rb}, \text{Cs}$) in ClF_3 .^[11–13] This approach is also commonly used for the syntheses of tetrafluoridobromates(III), see Equation (1).^[14,15] The $[\text{MF}_4]^-$ -compounds of iodine, gold and silver are also known.^[15–17]

More complex anions with higher MF_3 content, such as $[\text{M}_2\text{F}_7]^-$ and $[\text{M}_3\text{F}_{10}]^-$, have been reported and are so far limited to the BrF_3 and AuF_3 systems.^[18–22] The $[\text{M}_2\text{F}_7]^-$ anions show a μ_2 -bridging fluorine atom and have been obtained in the compounds $\text{A}[\text{Br}_2\text{F}_7]$ ($A = \text{Rb}, \text{Cs}, \text{PbF}$) and $\text{Cs}[\text{Au}_2\text{F}_7]$.^[18–22] Thus far, the $[\text{Br}_3\text{F}_{10}]^-$ anion has the highest MF_3 content, exhibiting a

 $A = \text{e.g. K, Rb, Cs}$ $M = \text{Cl, Br}$

central μ_3 -bridging F atom, and was obtained as the Rb and Cs salts.^[20] The possibility of anions of the composition $[\text{M}_4\text{F}_{13}]^-$ for Au and Br has been the subject of a theoretical study.^[23]

Here, we report on the syntheses, structure determinations, vibrational spectroscopic characterizations and hybrid density functional theory calculations of the tetrafluoridochlorates(III), $\text{A}[\text{ClF}_4]$ ($A = \text{K}, \text{Rb}, \text{Cs}$).

Results and Discussion

The tetrafluoridochlorates(III) of K, Rb and Cs were synthesized by a solvolysis reaction of the respective alkali metal fluoride in liquid ClF_3 , see Equation (2).

 $A = \text{K, Rb, Cs}$

Single crystals of $\text{K}[\text{ClF}_4]$ and $\text{Rb}[\text{ClF}_4]$ were obtained by carefully heating suspensions of the alkali metal fluorides in ClF_3 up to 50 °C in an air bath. In the case of $\text{Cs}[\text{ClF}_4]$, single crystals were obtained by slowly removing excess ClF_3 from solutions in vacuo.

Single Crystal X-ray Diffraction

Potassium tetrafluoridochlorate(III) crystallizes in the tetragonal space group $I4/mcm$ (No. 140) with four formula units per unit cell, Pearson symbol $tI24$ and Wyckoff sequence 140, $I4a$. The compound is isotypic to $\text{K}[\text{BrF}_4]$.^[24,25] See Table 1 for selected

[a] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany
E-mail: f.kraus@uni-marburg.de

[b] Department of Chemistry and Materials Science, Aalto University, 00076 Aalto, Finland

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.202000106>.

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Table 1. Selected crystallographic data and details of the structure determinations of the compounds A[ClF₄] (A = K, Rb, Cs).

	[K][ClF ₄]	Rb[ClF ₄]	Cs[ClF ₄]
Formula	KClF ₄	RbClF ₄	CsClF ₄
Molar mass / g mol ⁻¹	150.55	196.92	244.35
Space group (No.)	<i>I4/mcm</i> (140)	<i>C2/c</i> (15)	<i>C2/c</i> (15)
<i>a</i> /Å	6.0372(3)	10.4131(8)	10.908(2)
<i>b</i> /Å	<i>a</i>	4.8957(4)	5.4275(11)
<i>c</i> /Å	10.7566(6)	8.4012(7)	8.4068(17)
β /°	90	103.843(3)	108.98(3)
<i>V</i> /Å ³	392.05(4)	415.85(6)	470.67(18)
<i>Z</i>	4	4	4
Pearson symbol	<i>tI24</i>	<i>mS24</i>	<i>mS24</i>
$\rho_{\text{calc.}}$ /g cm ⁻³	2.55	4.55	3.45
μ /mm ⁻¹	1.97	3.15	8.38
Color	colorless	colorless	colorless
Crystal morphology	block	block	block
Crystal size/mm ³	0.104 × 0.152 × 0.168	0.050 × 0.051 × 0.074	0.007 × 0.037 × 0.075
<i>T</i> /K	100	100	100
λ /Å	0.71073 (Mo-K α)	0.71073 (Mo-K α)	0.71073 (Mo-K α)
No. of reflections	4904	9473	1449
θ range/°	3.79–39.35	4.03–37.82	3.95–26.71
Range of Miller indices	–10 ≤ <i>h</i> ≤ 10 –10 ≤ <i>k</i> ≤ 10 –18 ≤ <i>l</i> ≤ 19	–17 ≤ <i>h</i> ≤ 17 –8 ≤ <i>k</i> ≤ 8 –14 ≤ <i>l</i> ≤ 14	–13 ≤ <i>h</i> ≤ 11 –6 ≤ <i>k</i> ≤ 6 –10 ≤ <i>l</i> ≤ 10
Absorption correction	multi-scan	multi-scan	integration
<i>T</i> _{max} , <i>T</i> _{min}	0.77, 0.67	0.54, 0.45	0.37, 0.31
<i>R</i> _{int} , <i>R</i> _{σ}	0.030, 0.012	0.034, 0.020	0.071, 0.055
Completeness of the data set	1.000	1.000	0.998
No. of unique reflections	339	1122	502
No. of parameters	13	31	30
No. of restraints	0	0	0
No. of constraints	0	0	0
<i>S</i> (all data)	1.15	1.07	1.06
<i>R</i> (<i>F</i>) (<i>I</i> ≥ 2 σ (<i>I</i>), all data)	0.017, 0.023	0.022, 0.029	0.035, 0.049
<i>wR</i> (<i>F</i> ²) (<i>I</i> ≥ 2 σ (<i>I</i>), all data)	0.035, 0.036	0.037, 0.038	0.061, 0.065
Extinction coefficient	0.0113(16)	0.0033(4)	–
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ /e Å ⁻³	0.39, –0.27	0.58, –0.61	0.88, –0.80

crystallographic data and details of the structure determinations. Atom coordinates and isotropic displacement parameters are given in Table 2. Anisotropic displacement parameters are reported in the Supporting Information.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} of K[ClF₄].

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
[K](1)	4 <i>a</i>	1/2	1/2	1/4	0.00868(9)
Cl(1)	4 <i>d</i>	1/2	0	1/2	0.00649(9)
F(1)	16 <i>l</i>	0.64919(7)	0.14919(7)	0.38201(5)	0.01265(12)

The chlorine atom occupies the Wyckoff position 4*d* (site symmetry *m.mm*) and is surrounded by the fluorine atom F(1) and its three symmetry-equivalent F atoms, F(1)#1–F(1)#3, forming the almost square but planar [ClF₄][–] anion, see Figure 1. The Cl–F distance is 1.7982(6) Å and the F–Cl–F angles are 89.79(4) and 90.21(4)°. These values nicely agree with structure determinations on other [ClF₄][–] salts, which were measured at 130 K: NO[ClF₄] (1.727(1) and 1.874(1) Å; 89.36(5)–91.32(9)° and 179.33(7)°) and 1,1,3,3,5,5-hexamethylpiperidinium[ClF₄] (1.759(2)–1.814(1) Å, 88.90(7)–91.16(7)°, 178.42(7)° and 178.68(8)°).^[17]

The potassium atom occupies the Wyckoff position 4*a* (site symmetry 422) and is surrounded by eight fluorine atoms in

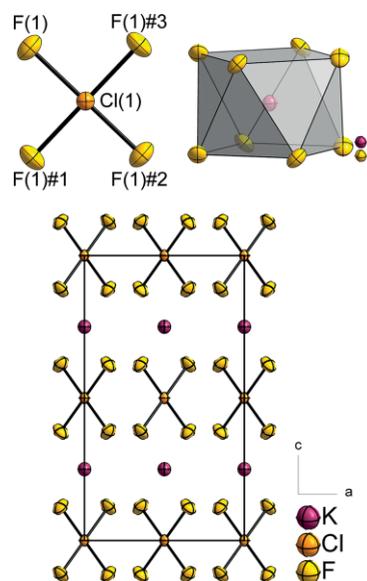


Figure 1. Top: Left: Tetrafluoridochlorate(III) anion observed in K[ClF₄]. Symmetry transformations for the generation of equivalent atoms: #1 1 – *x*, –*y*, *z*; #2 1/2 – *y*, 1/2 – *x*, 1 – *z*; #3 1/2 + *y*, –1/2 + *x*, 1 – *z*. Right: Coordination polyhedron of K(1) in K[ClF₄]. Bottom: Crystal structure of K[ClF₄] projected along the *b* axis. The displacement ellipsoids are shown at the 90 % probability level at 100 K.

the shape of a distorted square-antiprism. A projection of the crystal structure of $\text{K}[\text{ClF}_4]$ is shown in Figure 1.

The $[\text{ClF}_4]^-$ anions are isolated and are superimposed when viewed along the a axis. Along the c axis, the anions are oriented at 90° towards one another. The fluorine atoms of the $[\text{ClF}_4]^-$ anion each coordinate to two potassium atoms. The Cl atoms are each surrounded by eight K atoms in the shape of a cube and vice versa, being similarly arranged like the Cs and Cl atoms in CsCl .^[26]

The salts $\text{Rb}[\text{ClF}_4]$ and $\text{Cs}[\text{ClF}_4]$ are isotypic and crystallize in the monoclinic space group $C2/c$ (No. 15) with four formula units per unit cell, Pearson code $mS24$ and Wyckoff sequence 15, Ped . Therefore, the compounds are isotypic to $\text{Li}[\text{AuF}_4]$.^[16] See Table 1 for selected crystallographic data and details of the structure determinations. Atom coordinates and isotropic displacement parameters are given in Table 3 and Table 4. Anisotropic displacement parameters are reported in the Supporting Information. The chlorine atom occupies the Wyckoff position 4d (site symmetry $\bar{1}$) and is surrounded by the fluorine atoms F(1) and F(2) and its symmetry-equivalent atoms F(1)#1 and F(2)#1, see Figure 2. The Cl(1)–F(1) distance is 1.8034(9) Å in the Rb and 1.794(4) Å in the Cs compound, respectively. The Cl(1)–F(2) distance is 1.7930(9) Å in the Rb and 1.792(4) Å in the Cs salt, respectively. The Cl–F distances of the latter salt are equal within the tripled standard uncertainties. The F(1)–Cl(1)–F(2) angles are 89.33(4) and 90.67(4)° in $\text{Rb}[\text{ClF}_4]$ and 89.14(19) and 90.9(2)° in $\text{Cs}[\text{ClF}_4]$. The F–Cl–F angles of the two salts are equal within the tripled standard uncertainties and nicely agree with the above-mentioned data of other $[\text{ClF}_4]^-$ salts.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters U_{iso} of $\text{Rb}[\text{ClF}_4]$.

Atom	Position	x	y	z	$U_{\text{iso}}/\text{\AA}^2$
Rb(1)	4e	1/2	0.22368(4)	1/4	0.01348(6)
Cl(1)	4d	3/4	3/4	1/2	0.01066(8)
F(1)	8f	0.57241(8)	0.72418(18)	0.43421(11)	0.01627(16)
F(2)	8f	0.76854(9)	0.47384(19)	0.36710(11)	0.02005(18)

Table 4. Atomic coordinates and equivalent isotropic displacement parameters U_{iso} of $\text{Cs}[\text{ClF}_4]$.

Atom	Position	$\text{Cs}[\text{ClF}_4]$			$U_{\text{iso}}/\text{\AA}^2$
		x	y	z	
Cs(1)	4e	1/2	0.20405(12)	1/4	0.0177(2)
Cl(1)	4d	3/4	3/4	1/2	0.0153(5)
F(1)	8f	0.5787(4)	0.6935(8)	0.4368(5)	0.0242(9)
F(2)	8f	0.7725(4)	0.4850(7)	0.3844(5)	0.0268(10)

The Rb/Cs atom occupies the Wyckoff position 4e (site symmetry 2) and is coordinated by twelve fluorine atoms in the shape of a distorted anti-cuboctahedron. The crystal structure of $\text{Rb}[\text{ClF}_4]$ is shown in Figure 2. The fluorine atoms of the $[\text{ClF}_4]^-$ anion each coordinate to three different alkali metal cations. The Cl atoms are surrounded by six alkali metal cations in the shape of a distorted octahedron and vice versa. The Rb/Cs and Cl atoms thus have a similar arrangement to the Na and Cl atoms in NaCl .^[27]

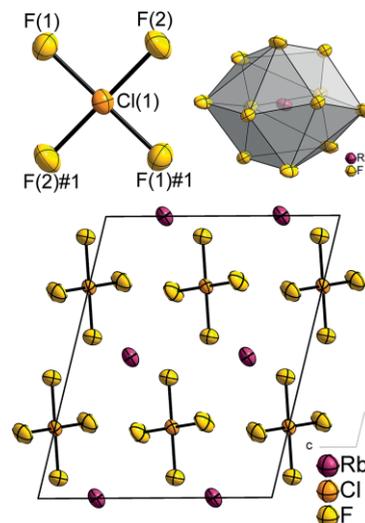


Figure 2. Top: Left: Tetrafluoridochlorate(III) anion observed in $\text{Rb}[\text{ClF}_4]$ and in the isotypic $\text{Cs}[\text{ClF}_4]$. Symmetry transformation for the generation of equivalent atoms: #1 $3/2 - x$, $3/2 - y$, $1 - z$. Right: Coordination polyhedron of Rb(1) in $\text{Rb}[\text{ClF}_4]$. Bottom: Crystal structure of $\text{Rb}[\text{ClF}_4]$ projected along the b axis. The displacement ellipsoids are shown at the 90% probability level at 100 K. $\text{Cs}[\text{ClF}_4]$ is isotypic to $\text{Rb}[\text{ClF}_4]$.

The lattice parameters and atomic positions of the three compounds reported here were fully optimized with the DFT-PBE0 method using the CRYSTAL17 program package.^[28,29] The lattice parameters and the xyz coordinates of the optimized structures are given in the Supporting Information. The cell volumes of the optimized structures are bigger than the experimentally obtained ones: 4% for $\text{K}[\text{ClF}_4]$, and 6.5% for both $\text{Rb}[\text{ClF}_4]$ and $\text{Cs}[\text{ClF}_4]$. Thus, the interaction between the alkali metal cations and the $[\text{ClF}_4]^-$ anions is probably somewhat underestimated by the DFT-PBE0 method that was employed. The calculated Cl–F distances are only slightly longer than the experimental ones: 1.82 Å in $\text{K}[\text{ClF}_4]$; 1.81 and 1.83 Å in $\text{Rb}[\text{ClF}_4]$; 1.82 Å in $\text{Cs}[\text{ClF}_4]$.

Vibrational Spectroscopy

The experimental Raman and IR spectra of the tetrafluoridochlorates(III) are shown in Figure 3. Values and band assignments are given in Table 5 and Table 6. The Raman and IR spectra of the compounds were also calculated with the DFT-PBE0 method and the calculated band positions, assignments and figures are given in the Supporting Information. The $[\text{ClF}_4]^-$ ion has D_{2h} (mmm) symmetry in $\text{K}[\text{ClF}_4]$ and C_i ($\bar{1}$) symmetry in $\text{Rb}[\text{ClF}_4]$ and $\text{Cs}[\text{ClF}_4]$, deviating from the ideal D_{4h} ($4/mmm$) symmetry.

In the Raman spectra, the symmetric in-phase Cl–F stretching modes, $\nu_s(\text{ClF}_4)$, are observed at slightly above 500 cm^{-1} and the symmetric out-of-phase Cl–F stretching modes, $\nu_s(\text{ClF}_4)$, at approximately 415 cm^{-1} . The values shift towards lower energy with increasing cation size. The scissoring vibration of the $[\text{ClF}_4]^-$ ion is observed in the range of $290\text{--}260\text{ cm}^{-1}$, showing no dependency on the cation size. Below 150 cm^{-1} , further deformation vibrational modes – twisting, umbrella bending and rocking – of the $[\text{ClF}_4]^-$ ion are observed,

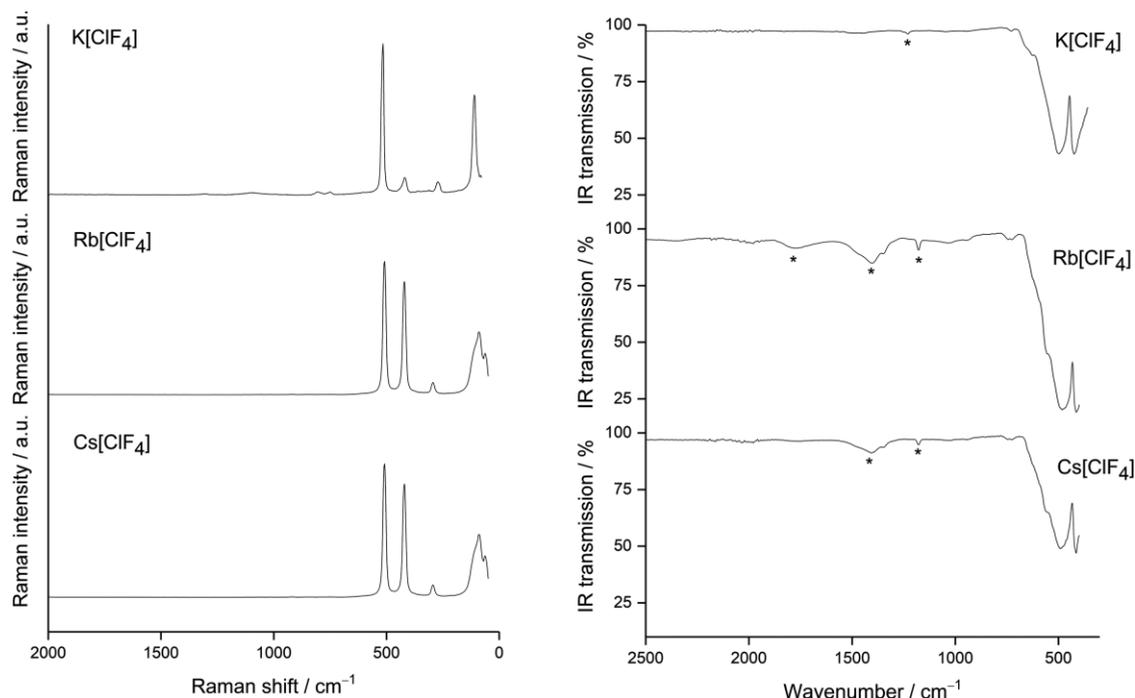


Figure 3. Left: Low-resolution (300/mm grating) Raman spectra of $A[\text{ClF}_4]$ ($A = \text{K, Rb, Cs}$) measured at room temperature under perfluorinated oil (K) or in glass vials (Rb, Cs). Single crystal of $\text{K}[\text{ClF}_4]$ and powder samples of $\text{Rb}[\text{ClF}_4]$ and $\text{Cs}[\text{ClF}_4]$. Right: ATR-IR spectra of $A[\text{ClF}_4]$ ($A = \text{K, Rb, Cs}$) measured at room temperature. Asterisks denote bands that stem from hydrogen fluoride adduct impurities of the alkali metal fluorides, $[\text{AF}(\text{HF})_n]$.

Table 5. Comparison and assignment of Raman-active bands of tetrafluoridochlorates(III), $A[\text{ClF}_4]$ ($A = \text{K, Rb, Cs}$). All values in cm^{-1} .

Compound	$\nu_s(\text{ClF}_4)$ in-phase	$\nu_s(\text{ClF}_4)$ out-of-phase	$\delta(\text{ClF}_4)$ scissoring	Reference
$[\text{ClF}_4]$	515	416	272, 265	this work
	530, 529	424	275, 263	DFT-PBE0
$\text{Rb}[\text{ClF}_4]$	503	415	288	this work
	505	417	288	[30]
	502	414	287	[10]
	518, 517	422	281, 280	DFT-PBE0
$\text{Cs}[\text{ClF}_4]$	501	411	284	this work
	507	418	290	[31]
	518, 517	422, 417	279, 278	DFT-PBE0

Table 6. Comparison and assignment of IR-active bands of tetrafluoridochlorates(III), $A[\text{ClF}_4]$ ($A = \text{K, Rb, Cs}$). All values in cm^{-1} .

Compound	$\nu_{as}(\text{ClF}_4)$	$\delta(\text{ClF}_4)$ umbrella bending	Reference
$\text{K}[\text{ClF}_4]$	498	424	this work
	563, 540	429	DFT-PBE0
$\text{Rb}[\text{ClF}_4]$	559 (shoulder), 482	413	this work
	486	430	[32]
	627, 534, 522	422, 421	DFT-PBE0
$\text{Cs}[\text{ClF}_4]$	552 (shoulder), 491	414	this work
	590	425	[13]
	541	436	[30]
	478	425	[32]
	595, 556, 538, 523	424, 420	DFT-PBE0

which are coupled with the respective cation. These values nicely agree with our calculated values and Raman spectra that have been reported thus far.^[10,30,31]

As was previously mentioned, the reported IR data of the tetrafluoridochlorates(III) are not as consistent as the Raman data.^[15] In most studies Pyrex glass Schlenk lines were used for the handling of ClF_3 or the products were not handled under inert conditions, leading to impure compounds.^[8,13,30,32] We also observed impurity bands in the IR spectra, especially when the ClF_3 used was not free from traces of HF. These bands are observed above 1000 cm^{-1} and are caused by HF-adducts of the alkali metal fluorides, $[\text{AF}(\text{HF})_n]$, ($A = \text{K, Rb, Cs}$; n being usually 1–3).^[33,34] This highlights the fact that HF is a stronger Lewis-base than ClF_3 and thus displaces it from the tetrafluoridochlorates(III).^[35]

Nevertheless, in the IR spectra two broad bands are seen in the region of 600 to 400 cm^{-1} which can be attributed to the $[\text{ClF}_4]^-$ ion. The first one, with a maximum at approximately 500 cm^{-1} , can be assigned to the asymmetric Cl–F stretching mode, $\nu_{as}(\text{ClF}_4)$, and the latter one at circa 420 cm^{-1} to the umbrella bending vibration of the $[\text{ClF}_4]^-$ ion. The calculated frequencies for the stretching modes are somewhat overestimated by the DFT-PBE0 method that was employed. The calculated Raman and IR spectra otherwise nicely agree with our experimental results.

Conclusions

The tetrafluoridochlorates(III), $A[\text{ClF}_4]$ ($A = \text{K, Rb, Cs}$), were synthesized from solvolysis reactions of the alkali metal fluorides in liquid ClF_3 in single-crystalline form. Structure determination by single-crystal X-ray diffraction showed that $\text{K}[\text{ClF}_4]$ is isotypic to $\text{K}[\text{BrF}_4]$, whereas $\text{Rb}[\text{ClF}_4]$ and $\text{Cs}[\text{ClF}_4]$ are isotypic to $\text{Li}[\text{AuF}_4]$.

The Raman and IR spectra could be interpreted on the basis of quantum-chemical solid-state calculations.

Experimental Section

General: All operations were performed on a Monel metal Schlenk line, which was passivated with 100 % fluorine and chlorine trifluoride at various pressures before use. Moisture-sensitive compounds were stored and handled in an Ar-filled glove box (MBraun). Reaction vessels were made out of fluoropolymer (perfluoroalkoxy alkanes, PFA) and passivated with fluorine before use. Preparations were carried out in an atmosphere of dry and purified argon (5.0, Praxair). Chlorine trifluoride was stored over NaF to remove traces of HF. Caution! Fluorine, chlorine trifluoride, and tetrafluoridochlorates(III) must be handled using appropriate protective gear with ready access to proper emergency treatment procedures in the event of contact. The aforementioned are potent oxidative fluorinators that are only stable under the rigorously anhydrous conditions employed in the experimental procedures outlined in the Experimental Section. They react vigorously to explosively upon hydrolysis or contact with organic materials. The utmost precautions must be taken when disposing of these materials and their derivatives.

Synthesis: K[ClF₄]: A PFA reaction vessel was loaded with 12.3 mg KF (0.218 mmol) inside a glove box and attached to a stainless-steel valve. An excess of ClF₃ (approximately 0.35 g, 3.8 mmol) was then condensed onto the solid at 77 K. The resulting suspension was gently heated in an air bath to approximately 50 °C for two hours. The remaining ClF₃ was then slowly pumped off and the colorless product (21.2 mg isolated, calculated: 31.87 mg) was transferred into the glove box. Rb[ClF₄]: A PFA reaction vessel was loaded with 28.1 mg RbF (0.269 mmol) inside a glove box and attached to a stainless-steel valve. An excess of ClF₃ (approximately 0.40 g, 4.3 mmol) was then condensed onto the solid at 77 K. The resulting suspension was gently heated in an air bath to approximately 50 °C for one hour. The remaining ClF₃ was then slowly pumped off and the colorless product (43.2 mg isolated, calculated: 52.97 mg) was transferred into the glove box. Cs[ClF₄]: A PFA reaction vessel was loaded with 20.9 mg CsF (0.138 mmol) inside a glove box and attached to a stainless-steel valve. An excess of ClF₃ (approximately 0.25 g, 2.7 mmol) was then condensed onto the solid at 77 K. The resulting solution was kept at room temperature for several hours. The remaining ClF₃ was then slowly pumped off and the colorless product (28.3 mg isolated, calculated: 33.61 mg) was transferred into the glove box. The mass balances of the three reactions indicate that a full conversion of the alkali metal fluorides to the respective tetrafluoridochlorates(III) was not achieved under the chosen conditions. Also, not all of the solid product could be isolated from the reaction vessels.

Single-Crystal X-ray Diffraction: Crystals of the moisture-sensitive compounds were selected under dried perfluorinated oil (Fomblin YR1800, Solvay, stored over molecular sieves 3 Å) and mounted on a MiTeGen loop. Intensity data of suitable crystals were recorded with a D8 Quest diffractometer (Bruker) or an IPDS2T diffractometer (STOE). The diffractometers were operated with monochromatized Mo-K_α radiation (0.71073 Å, multi layered optics (D8 Quest) or graphite monochromator (IPDS2T)) and equipped with a PHOTON 100 CMOS detector (D8 Quest) or an image plate detector (IPDS2T). Evaluation, integration and reduction of the diffraction data was carried out with the APEX3 software suite (D8 Quest) or the X-Area software suite (IPDS2T).^[36,37] The diffraction data was corrected for absorption utilizing the multi-scan method of SADABS within the APEX3 software suite (D8 Quest) or the integration method with

the modules X-Shape and X-Red32 of the X-Area software suite (IPDS2T). The structures were solved with dual-space methods (SHELXT) and refined against F^2 (SHELXL).^[38,39] For Rb[ClF₄] one systematic absence violation ($|l| > 3\sigma(|l|)$) is observed for space group C2/c (No. 15). Solution and refinement in the subgroups Cc (No. 9) and C2 (No. 5) showed correlation for some atoms. Subsequently, space group C2/c was chosen, which was also indicated by the Addsym function in PLATON.^[40,41] The highest residual electron densities after the final refinements were the following: K[ClF₄]: 0.68 Å distant from atom Cl(1); Rb[ClF₄]: 1.58 Å distant from atom F(2); Cs[ClF₄]: 1.05 Å distant from atom Cs(1). Representations of the crystal structures were created with the Diamond software.^[42]

CCDC 1980748 (for Cs[ClF₄]), 1980749 (for Rb[ClF₄]), and 1980750 (for K[ClF₄]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

IR and Raman spectroscopy: The IR spectra were recorded on a Bruker alpha FT-IR spectrometer using an ATR Diamond module with a resolution of 4 cm⁻¹. The spectrometer was located inside a glovebox (MBraun) under argon atmosphere. The spectra were processed with the OPUS software package.^[43] The Raman spectra were measured at room temperature with a Monovista CRS+ confocal Raman microscope (Spectroscopy & Imaging GmbH) using a 532 nm solid-state laser and either a 300 grooves/mm (low-resolution mode, FWHM: <4.62 cm⁻¹) or a 1800 grooves/mm (high-resolution mode, FWHM: <0.368 cm⁻¹) grating.

Density Functional Calculations: Periodic quantum-chemical calculations were carried out for the A[ClF₄] (A = K, Rb, Cs) salts using the PBE0 density functional method (DFT-PBE0).^[28,29] A triple-zeta-valuation + polarization (TZVP) level basis set was applied for F and Cl and split-valuation + polarization (SVP) level basis sets were applied for K, Rb and Cs. The basis sets were derived from the Karlsruhe def2 basis sets and taken from previous studies (F, Cl, K, Cs) or listed in the Supporting Information (Rb).^[44–47] All calculations were carried out with the CRYSTAL17 program package.^[48] The reciprocal space for the salts was sampled using the following Monkhorst-Pack-type *k*-point grids: K[ClF₄]: 4×4×4, Rb[ClF₄]: 5×5×3, Cs[ClF₄]: 5×5×3. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, 16 were used for all calculations. Both the atomic positions and lattice parameters were fully optimized within the constraints imposed by the space group symmetry. Default DFT integration grids and optimization convergence thresholds were applied in all calculations. The xyz coordinates used in the calculations of each salt are given in the Supporting information. The harmonic vibrational frequencies, IR intensities and Raman intensities were obtained through usage of the computational scheme implemented in CRYSTAL17.^[49–52] The Raman intensities were calculated for a polycrystalline powder sample (total isotropic intensity in arbitrary units). The Raman spectra were obtained by using a pseudo-Voigt band profile (50:50 Lorentzian:Gaussian) and an FWHM of 8 cm⁻¹. The Raman spectra were simulated taking into account the experimental setup ($T = 298.15$ K, $\lambda = 532$ nm). For the IR spectra, a Lorentzian lineshape and an FWHM of 8 cm⁻¹ was used. The band assignments were carried out by visual inspection of the normal modes using the J mol program package.^[53]

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