

Hexafluoridomolybdates

Synthesis and Characterization of the Hexafluoridomolybdates(V) $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$)Riane E. Stene,^[a,b] Benjamin Scheibe,^[a] Winfried Petry,^[b] and Florian Kraus^{*[a]}

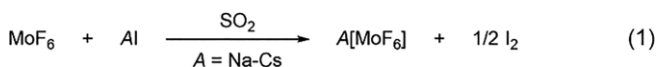
Abstract: The hexafluoridomolybdates(V), $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$), were synthesized by reacting molybdenum pentafluoride (MoF_5) with the alkali metal fluorides in anhydrous hydrogen fluoride (aHF) solution. Single crystals of $A[\text{MoF}_6]$ ($A = \text{Li}, \text{Na}, \text{Rb}, \text{Cs}$) were grown from solution and analyzed by single-crystal X-ray diffraction. The vibrational spectrum of each salt is reported in detail and compared to previously reported spectra. During analysis of the cubic modification of $\text{Na}[\text{MoF}_6]$ it was noticed that a phase transition occurs around 228 K. Some de-

tails regarding this phase transition are discussed. Attempts to determine the structure of the low-temperature phase of $\text{Na}[\text{MoF}_6]$ lead to the observation of the $\text{Na}[\text{MoF}_6] \cdot 2\text{HF}$ solvate. Additionally, in an attempt to synthesize $\text{Na}[\text{MoF}_7]$ by the oxidation of $\text{Na}[\text{MoF}_6]$ in chlorine trifluoride (ClF_3), a tetragonal modification of $\text{Na}[\text{MoF}_6]$ was observed. The crystal structures of the $\text{Na}[\text{MoF}_6] \cdot 2\text{HF}$ solvate and tetragonal modification of $\text{Na}[\text{MoF}_6]$ are also discussed in detail.

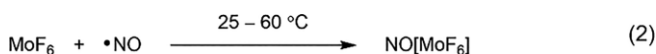
Introduction

Compounds having the formula $A[\text{MF}_6]$ ($A = \text{Li} - \text{Cs}$, $M = \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{Re}, \text{Ru}, \text{Os}, \text{Rh}, \text{Ir}, \text{Pt}, \text{Au}, \text{P} - \text{Bi}, \text{Br}, \text{U}, \text{Np}$) were first synthesized during the first half of the twentieth century. Studies on their crystal structure determinations can be found in the literature as early as 1938.^[1] Over the years, this class of compounds has given rise to seven different structure types, namely, $\text{Ba}[\text{SiF}_6]$,^[2] $\text{K}[\text{AsF}_6]$,^[3] $\text{K}[\text{NbF}_6]$,^[4] $\text{K}[\text{SbF}_6]$,^[5] $\text{Li}[\text{SbF}_6]$,^[6] $\text{Na}[\text{CrF}_6]$,^[7] and $\text{Na}[\text{SbF}_6]$.^[8] Some compounds of the type $A[\text{MF}_6]$ have been more intensively studied than others. It came to our attention during our studies of molybdenum fluorides that the hexafluoridomolybdates(V), $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) have received comparatively little attention over the past 60 years.

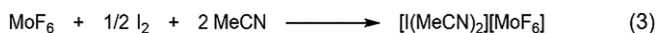
The hexafluoridomolybdates(V), $A[\text{MoF}_6]$ ($A = \text{Na} - \text{Cs}$), were first reported in 1957 by Hargreaves and Peacock.^[9] Traditionally, the synthesis of these compounds revolved around the oxidation of iodide (I^-) by molybdenum hexafluoride (MoF_6) in liquid sulfur dioxide solutions, see Equation (1).^[9–12]



Later, $\text{NO}[\text{MoF}_6]$ was synthesized through the reaction of MoF_6 with nitric oxide, see Equation (2).^[13]



Finally, Winfield and co-workers demonstrated that I_2 could be oxidized to “ I^{+} ” in acetonitrile solutions by MoF_6 to give $[(\text{NCMe})_2][\text{MoF}_6]$, see Equation (3).^[14,15]



The vibrational spectra of $A[\text{MoF}_6]$ ($A = \text{K}, \text{Cs}, \text{NO}, [(\text{NCMe})_2]$) have previously been described in the literature.^[11–15] In addition, powder X-ray diffraction was utilized to determine the lattice parameters of $A[\text{MoF}_6]$ ($A = \text{Na} - \text{Cs}, \text{NO}$).^[9,10,13] The hexafluoridomolybdates(V) of $\text{Na}, \text{Rb}, \text{Cs}$, and NO are reported to have cubic unit cells, whereas the unit cell of $\text{K}[\text{MoF}_6]$ is reported to be tetragonal.^[9,10,13] Only the $\text{Na}[\text{MoF}_6]$ salt, which crystallizes in the cubic space group $Fm\bar{3}m$, has been described in detail.^[10]

Herein we report a new synthetic method for the syntheses of the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) compounds. The vibrational spectrum of each salt is reported in detail. Additionally, the first single-crystal X-ray diffraction study of the hexafluoridomolybdates(V) $A[\text{MoF}_6]$ ($A = \text{Li}, \text{Na}, \text{Rb}, \text{Cs}$) was performed. It was observed that single crystals of $\text{Na}[\text{MoF}_6]$ grown in aHF crystallize in the cubic space group $Fm\bar{3}m$ at room temperature and appear to undergo a reversible phase transition at about 228 K. However, single crystals of $\text{Na}[\text{MoF}_6]$ grown in ClF_3 were observed to crystallize in the tetragonal space group $P4_21m$. Both modifications of $\text{Na}[\text{MoF}_6]$ are discussed in detail. Also reported is the crystal structure of the $\text{Na}[\text{MoF}_6] \cdot 2\text{HF}$ solvate.

Results and Discussion

Synthetic Techniques

First, MoF_5 was synthesized by reducing MoF_6 with carbon monoxide under UV irradiation, see Equation (4). After pumping

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

[b] *Neutron Research Source Heinz Maier-Leibnitz (FRM II), Technische Universität München, Lichtenbergstraße 1, 85748 Garching, Germany*

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.202000141>.

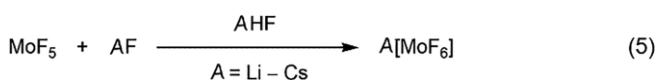
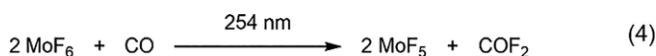
© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Table 1. Selected crystallographic data and details of the single-crystal structure determinations for the $A[\text{MoF}_6]$ ($A = \text{Li, Na, Rb, Cs}$) salts and the $\text{Na}[\text{MoF}_6]\cdot 2\text{HF}$ solvate.

	$\text{Li}[\text{MoF}_6]$	$\text{Na}[\text{MoF}_6]^{\text{[a]}}$	$\text{Na}[\text{MoF}_6]^{\text{[b]}}$	$\text{Na}[\text{MoF}_6]\cdot 2\text{HF}$	$\text{Rb}[\text{MoF}_6]$	$\text{Cs}[\text{MoF}_6]$
Empirical formula	F_6LiMo	F_6MoNa	F_6MoNa	$\text{F}_8\text{H}_2\text{MoNa}$	F_6MoRb	CsF_6Mo
Color and appearance	colorless block	colorless block	colorless block	colorless block	colorless block	colorless block
Molar mass/g mol ⁻¹	216.88	232.93	232.93	272.95	295.41	342.85
Crystal system	Trigonal	Cubic	Tetragonal	Orthorhombic	Trigonal	Trigonal
Space group (No.)	$R\bar{3}$ (148)	$Fm\bar{3}m$ (225)	$P4_2/m$ (113)	$Cccm$ (66)	$R\bar{3}$ (148)	$R\bar{3}$ (148)
Pearson symbol	$hR24$	$cF32$	$tP16$	$oC48$	$hR24$	$hR24$
$a/\text{\AA}$	5.1026(3)	8.1888(5)	5.0187(2)	6.3053(4)	7.5502(6)	7.7693(10)
$b/\text{\AA}$	12.5744(10)
$c/\text{\AA}$	13.5575(18)	..	9.0807(8)	7.9037(7)	7.6478(8)	8.0092(16)
$V/\text{\AA}^3$	305.70(5)	549.11(10)	228.72(3)	626.65(8)	377.56(7)	418.68(14)
Z	3	4	2	4	3	3
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	3.534	2.818	3.382	2.893	3.898	4.079
$\lambda/\text{\AA}$	0.71073 (Mo- K_{α})					
T/K	100	283	100	100	100	100
μ/mm^{-1}	3.25	2.50	3.00	2.25	12.25	8.81
$\theta_{\text{min}}/^\circ$	4.5	4.3	4.5	3.2	4.1	4.0
$\theta_{\text{max}}/^\circ$	33.3	32.7	30.5	33.3	33.2	31.5
hkl_{range}	$-7 \leq h \leq 7$ $-7 \leq k \leq 7$ $-20 \leq l \leq 20$	$-12 \leq h \leq 12$ $-12 \leq k \leq 12$ $-12 \leq l \leq 10$	$-7 \leq h \leq 6$ $-7 \leq k \leq 7$ $-10 \leq l \leq 12$	$-8 \leq h \leq 9$ $-19 \leq k \leq 18$ $-12 \leq l \leq 12$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$	$-11 \leq h \leq 10$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$
$R_{\text{int}}, R_{\sigma}$	0.028, 0.015	0.023, 0.005	0.055, 0.026	0.040, 0.022	0.055, 0.027	0.041, 0.025
$R(F)$ ($I \geq 2\sigma(I)$, all data)	0.011, 0.011	0.017, 0.017	0.039, 0.039	0.017, 0.019	0.020, 0.021	0.020, 0.022
$wR(F^2)$ ($I \geq 2\sigma(I)$, all data)	0.018, 0.018	0.046, 0.046	0.099, 0.010	0.042, 0.043	0.047, 0.047	0.040, 0.041
S (all data)	1.26	1.27	1.16	1.11	1.22	1.18
Data, parameter, restraints	269, 14, 0	76, 6, 0	397, 28, 0	646, 32, 0	325, 15, 0	305, 15, 0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}/e \text{\AA}^{-3}$	0.37, -0.60	0.47, -0.57	1.11, -1.41	0.95, -0.80	0.59, -0.62	0.85, -0.65

[a] Cubic modification of $\text{Na}[\text{MoF}_6]$. [b] Tetragonal modification of $\text{Na}[\text{MoF}_6]$.

off any remaining MoF_6 and the COF_2 formed during the reaction, phase-pure, crystalline MoF_5 was obtained and stored in an inert atmosphere glovebox until further use. To synthesize the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts, a 1:1 molar ratio of MoF_5 and AF ($A = \text{Li} - \text{Cs}$) was reacted in aHF solutions, see Equation (5). Single crystals of the $A[\text{MoF}_6]$ ($A = \text{Li, Na, Rb, Cs}$) salts were grown directly from aHF solution; single crystals of KMoF_6 suitable for single-crystal X-ray diffraction were not obtained. A new tetragonal modification of the $\text{Na}[\text{MoF}_6]$ salt was obtained after the cubic modification (synthesized in aHF) was dissolved in chlorine trifluoride (ClF_3). Additionally, a $\text{Na}[\text{MoF}_6]\cdot 2\text{HF}$ solvate was obtained after reacting MoF_5 and NaF in aHF solution at -78°C and pumping off the solvent at the same temperature.



Single-Crystal X-ray Analysis

All AMoF_6 ($A = \text{Li, Na, Rb, Cs}$) salts and the $\text{Na}[\text{MoF}_6]\cdot 2\text{HF}$ solvate reported here contain isolated $[\text{MoF}_6]^-$ anions surrounded by several of the respective alkali metal cations (and in the case of the solvate, HF molecules). Selected crystallographic data and details of the single-crystal structure determination are given in Table 1. The crystal structure of each salt/solvate will be discussed individually. Comparisons, when appropriate, will be

made to salts reported in this work or to previously reported compounds.

1. Single-Crystal Structure of $\text{Li}[\text{MoF}_6]$

$\text{Li}[\text{MoF}_6]$ crystallizes in the trigonal space group $R\bar{3}$ with the lattice parameters $a = 5.1026(3) \text{ \AA}$, $c = 13.5575(18) \text{ \AA}$, $V = 305.70(5) \text{ \AA}^3$, Z (formula units) = 3, $T = 100 \text{ K}$. Atomic coordinates and equivalent isotropic displacement parameters for $\text{Li}[\text{MoF}_6]$ are reported in Table 2. $\text{Li}[\text{MoF}_6]$ is isotopic to the previously reported $\text{Li}[\text{SbF}_6]$ salt.^[6]

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{iso} for $\text{Li}[\text{MoF}_6]$ at 100 K.

Atom	Position	x	y	z	$U_{\text{iso}}/\text{\AA}^2$
Mo(1)	$3a$	0	0	0	0.00758(5)
F(1)	$18f$	0.05021(10)	0.31974(10)	0.08034(3)	0.01180(9)
Li(1)	$3b$	0	0	1/2	0.0106(5)

The lithium cation is coordinated by six fluorine atoms (belonging to six different $[\text{MoF}_6]^-$ anions) to form an octahedron-like coordination polyhedron. The $\text{F}(1)-\text{Li}(1)-\text{F}(1)$ angles between adjacent fluorine atoms in this polyhedron range from $89.46(2)^\circ$ to $90.52(2)^\circ$. The Mo atom is also coordinated by six fluorine atoms to form an octahedron-like coordination polyhedron having adjacent $\text{F}(1)-\text{Mo}(1)-\text{F}(1)$ angles ranging from $89.48(2)^\circ$ to $90.52(2)^\circ$. The coordination of the Li^+ cations by the $[\text{MoF}_6]^-$ anions leads to the formation of a three-dimensional, infinite-network crystal structure, see Figure S1.

The Li^+ cations and Mo atoms build a face-centered cubic lattice similar to that observed in the NaCl structure type. In

other words, the Mo atoms, and Li⁺ cations are packed in cubic close packed arrays. Each Mo atom is surrounded by its nearest-neighbor Mo atoms to form a cuboctahedron (C.N. = 12); the Li⁺ cations are surrounded by neighboring Li⁺ cations in a similar manner, while the Li atoms reside in the octahedral holes of the Mo close packing, and vice versa. Figure S2 depicts the packing of Mo and Li⁺ along with the overall crystal packing observed in Li[MoF₆]. The atomic distances observed in Li[MoF₆] are reported in Table 3. A section of the crystal structure is shown in Figure 1.

Table 3. Select interatomic distances *d* for Li[MoF₆]. The multiplicity of all reported interatomic distances is 6.

Atom1	Atom2	<i>d</i> /Å
Mo(1)	F(1)	1.8697(4)
Li(1)	F(1)	2.0082(5)

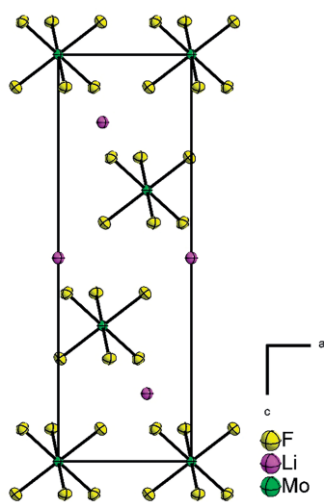


Figure 1. Section of the crystal structure of Li[MoF₆]. Displacement ellipsoids are shown at a 70 % probability level at 100 K.

2. Single-Crystal Structure of the Cubic Modification of Na[MoF₆]

The cubic modification of Na[MoF₆] crystallizes in the space group *Fm* $\bar{3}$ *m* with the lattice parameters *a* = 8.1888(5) Å, *V* = 549.11(10) Å³, *Z* = 4, *T* = 283 K. These lattice parameters agree nicely with those previously reported by Edwards and Peacock.^[10] Atomic coordinates and equivalent isotropic displacement parameters for the cubic modification of Na[MoF₆] are reported in Table 4. The cubic modification of Na[MoF₆] is isotopic to the cubic modification of the previously reported Na[SbF₆] salt.^[8,16]

Table 4. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} for the cubic modification of Na[MoF₆] at 100 K.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
Mo(1)	4 <i>a</i>	1	1/2	1/2	0.0232(3)
F(1)	24 <i>e</i>	0.7752(4)	1/2	1/2	0.0776(11)
Na(1)	4 <i>b</i>	1/2	1/2	1/2	0.0295(8)

The sodium cation is octahedrally coordinated by six fluorine atoms (belonging to six different [MoF₆][−] anions). The Mo atom

is also octahedrally coordinated by six fluorine atoms. The coordination of the Na⁺ cations by the [MoF₆][−] anions leads to the formation of a three-dimensional, infinite-network crystal structure, see Figure S3.

The Na⁺ cations and Mo atoms build a face-centered lattice similar to that observed in the NaCl structure type; the Mo(1) atoms, and Na(1) cations are packed in cubic close packed arrays. Each Mo atom is surrounded by its nearest-neighbor Mo atoms to form a cuboctahedron (C.N. = 12); Na⁺ is surrounded by its nearest neighbor Na⁺ cations in a similar manner. Figure S4 depicts the packing of Mo and Na⁺ cations along with the overall crystal packing observed in the cubic modification of Na[MoF₆]. A section of the crystal structure is shown in Figure 2.

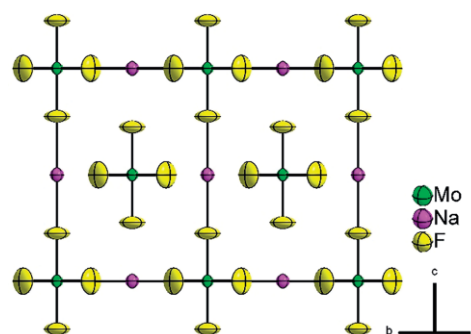


Figure 2. Section of the crystal structure of the cubic modification of Na[MoF₆]. Displacement ellipsoids are shown at a 50 % probability level at 283 K.

The atomic distances observed in the cubic modification of Na[MoF₆] are reported in Table 5. The Mo(1)–F(1) distance was observed to be 1.841(3) Å and the Na–F(1) distance to be 2.254(3) Å, whereas the corresponding distances were observed to be 1.74(3) Å and 2.36(3) Å, respectively, in the Na[MoF₆] structure determination performed by Edwards and Peacock.^[10] The differences in atomic distances stem from the fact that Edwards and Peacock based their structural determination of Na[MoF₆] on powder X-ray diffraction data, most likely (although not stated) obtained at room temperature, whereas the data reported here come from a single-crystal X-ray diffraction experiment performed at 10 °C.

Table 5. Select interatomic distances *d* for the cubic modification of Na[MoF₆]. The multiplicity of all reported interatomic distances is 6.

Atom1	Atom2	<i>d</i> /Å
Mo(1)	F(1)	1.841(3)
Na(1)	F(1)	2.254(3)

Moreover, it was noticed during the single-crystal X-ray analysis of the cubic modification of Na[MoF₆] that a low-temperature modification existed. When cubic single crystals of Na[MoF₆] were subjected to a 100 K nitrogen gas flow, the crystals would shatter and become unmeasurable. For this reason, the single-crystal data for the cubic modification of Na[MoF₆] was collected at 283 K. Using powder X-ray diffraction, it was determined that the cubic modification of Na[MoF₆] reported here begins to undergo a reversible phase transition at about

228 K. The structure of this low-temperature modification has yet to be determined. Even at temperatures as low as 213 K, the phase transition appears incomplete, likely due to kinetic reasons, see Figure 3. Attempts to obtain single crystals of Na[MoF₆] at low temperatures lead only to the observation of a Na[MoF₆]·2HF solvate (discussed later). Synthesis utilizing the Na[MoF₆] reported here in ClF₃ solutions lead to the discovery of yet another modification of Na[MoF₆], see below.

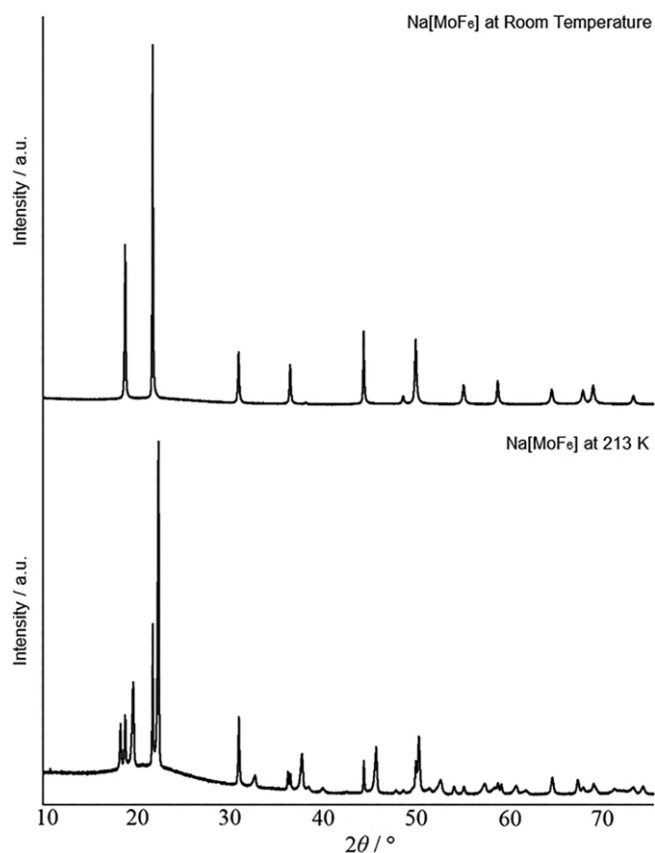


Figure 3. Top: powder diffraction pattern of the cubic modification of Na[MoF₆] at 293 K. Bottom: powder diffraction pattern of Na[MoF₆] at 213 K (about 15 K below the phase transition).

3. Single-Crystal Structure of the Tetragonal Modification of Na[MoF₆]

The tetragonal modification of Na[MoF₆] was obtained when the cubic modification of Na[MoF₆] (synthesized in aHF) was placed in ClF₃ and left at room temperature for about a week. After pumping off the remaining ClF₃, a small number of single crystals, amidst a powder-like sample, were suitable for single-crystal X-ray diffraction. The resulting tetragonal modification of Na[MoF₆] crystallizes in the space group *P*4₂*m* with the lattice parameters *a* = 5.0187 Å, *c* = 9.0807(8) Å, *V* = 228.72(3) Å³, *Z* = 2, *T* = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for the tetragonal modification of Na[MoF₆] are reported in Table 6. The tetragonal modification of Na[MoF₆] is isotypic to the previously reported Li[ReO₂F₄] salt.^[17] It is also thought, due to the distorted nature of the [MoF₆]⁻ anion in this crystal structure, that O/F disorder may be present for the F(1) atom. This would suggest an un-tight reac-

tion vessel that allowed moisture into the reaction mixture. Since the amount of crystalline sample was so small, IR and Raman spectra could not be obtained to prove or disprove O/F disorder and, therefore, the crystal structure will be further discussed as Na[MoF₆].

Table 6. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} for the tetragonal modification of Na[MoF₆] at 100 K.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
Mo(1)	2c	1/2	1	0.28429(9)	0.0182(4)
F(1)	4e	0.6880(11)	0.8120(11)	0.4065(7)	0.0315(17)
F(2)	4e	0.2388(10)	0.7388(10)	0.2600(8)	0.0298(14)
F(3)	4e	0.3211(10)	0.1789(10)	0.1163(7)	0.0255(15)
Na(1)	2c	0	1/2	0.0979(5)	0.0214(10)

In the tetragonal modification of Na[MoF₆], there is one symmetry independent Mo atom, one independent Na atom, and three independent F atoms, namely F(1), F(2), and F(3). The sodium cation is coordinated by two F(2) atoms and four F(3) atoms to produce a highly-distorted octahedron-like coordination polyhedron; it was observed that F(1) does not partake in Na⁺ coordination. Similarly, the Mo(1) atom is coordinated by six fluorine atoms to produce a highly-distorted octahedron-like coordination polyhedron. The coordination polyhedra of Na⁺ and Mo in the tetragonal modification of Na[MoF₆] are depicted in Figure 4. A list of selected angles observed in these coordination polyhedra is reported in Table 7. It was noted that similar distortion of coordination polyhedra, and similar angles within these polyhedra, were observed in Li[ReO₂F₄].^[17]

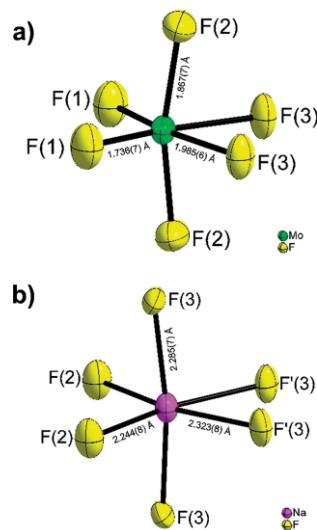


Figure 4. (a) Distorted, octahedron-like coordination polyhedron of the Mo atom in the tetragonal modification of Na[MoF₆]. (b) Distorted, octahedron-like coordination polyhedron of the Na⁺ cation in the tetragonal modification of Na[MoF₆]. Displacement ellipsoids are shown at a 70% probability level at 100 K.

Coordination of the Na⁺ cations by the [MoF₆]⁻ anions leads to the formation of two-dimensional, infinite sheets parallel to the *ab*-plane, see Figure S5. It was previously stated that the F(1) atoms did not participate in Na⁺ coordination; instead, the F(1) atoms are located on the outer edges of these infinite sheets. The F(1)⋯F(1) atomic distance between F(1) atoms on

Table 7. Select interatomic angles observed in the distorted coordination polyhedra in the tetragonal modification of Na[MoF₆]. In some cases, F(3) is referred to as F'(3) in order to highlight the fact that Na is coordinated by F(3) in two different manners. F'(3) refers to the F(3) atom having the longest Na–F atomic distance, refer to Figure 4.

	Interatomic angle/°
F(1)–Mo(1)–F(1)	100.5(5)
F(1)–Mo(1)–F(2)	94.34(14)
F(1)–Mo(1)–F(3)	90.0(3)
F(1)–Mo(1)–F(3) ^[a]	169.5(3)
F(2)–Mo(1)–F(2) ^[a]	166.4(5)
F(2)–Mo(1)–F(3)	84.78(18)
F(3)–Mo(1)–F(3)	79.6(4)
F(2)–Na(1)–F(2)	98.1(4)
F(2)–Na(1)–F(3)	87.25(13)
F(2)–Na(1)–F'(3)	97.8(2)
F(2)–Na(1)–F'(3) ^[a]	164.1(3)
F(3)–Na(1)–F(3) ^[a]	171.6(4)
F'(3)–Na(1)–F'(3)	66.3(3)
F(3)–Na(1)–F'(3)	93.51(17)

[a] These fluorine atoms are trans to one another in the octahedron-like coordination polyhedron.

adjacent sheets is 3.0932(82) Å (cf. the sum of the van der Waals radii for two fluorine atoms are reported by Pauling to be 2.7 Å and by Bondi to be 2.94 Å).^[18,19] In the solid-state structure of Li[ReO₂F₄], similar sheet formation is observed, albeit oxygen atoms occupy the outward edges of the infinite sheets, rather than fluorine atoms.

Upon comparison of the atomic distances in the tetragonal modification of Na[MoF₆], it was observed that the F(1) atoms, which are located on the edge of the infinite sheets and which do not participate in Na⁺ coordination, have the smallest Mo–F distance of 1.736(7) Å (cf. the Re–O distance in Li[ReO₂F₄] is 1.6782 Å). The Mo–F atomic distances involving F atoms which coordinate to the Na⁺ cations are notably larger, with values of 1.867(7) Å and 1.985(6) Å. A list of select interatomic distances for the tetragonal modification of Na[MoF₆] are reported in Table 8. A section of the crystal structure is shown in Figure 5.

Table 8. Select interatomic distances *d* for the tetragonal modification of Na[MoF₆]. The multiplicity of all reported interatomic distances is 2.

Atom1	Atom2	<i>d</i> /Å
Mo(1)	F(1)	1.736(7)
Mo(1)	F(2)	1.867(7)
Mo(1)	F(3)	1.985(6)
Na(1)	F(2)	2.244(8)
Na(1)	F(3)	2.285(7)
Na(1)	F(3)	2.323(8)

4. Single-Crystal Structure of the Na[MoF₆]-2HF Solvate

The Na[MoF₆]-2HF solvate crystallizes in the orthorhombic space group *Cccm* with the lattice parameters *a* = 6.3053(4) Å, *b* = 12.5744(10) Å, *c* = 7.9037(7) Å, *V* = 626.65(8) Å³, *Z* = 4, *T* = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for the Na[MoF₆]-2HF solvate are reported in Table 9, the packing diagram of Na[MoF₆]-2HF is depicted in Figure S6. To the best of our knowledge, the compound represents a new structure type.

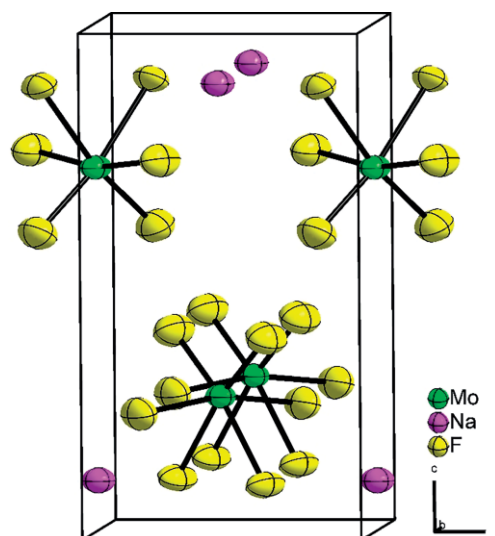


Figure 5. Section of the crystal structure of the tetragonal modification of Na[MoF₆]. Displacement ellipsoids are shown at a 70 % probability level at 100 K.

Table 9. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} for the Na[MoF₆]-2HF solvate at 100 K.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
Mo(1)	4 <i>f</i>	1/4	3/4	0	0.00945(7)
F(1)	16 <i>m</i>	0.20363(13)	0.14876(7)	0.33315(10)	0.01641(15)
F(2)	8 <i>l</i>	0.04076(15)	0.28736(9)	0	0.0181(2)
F(3)	8 <i>l</i>	0.1928(2)	0.05945(10)	0	0.0168(2)
H(1)	8 <i>l</i>	0.274(4)	0.102(3)	0	0.025(9)
Na(1)	4 <i>a</i>	0	0	1/4	0.01388(18)

In the Na[MoF₆]-2HF solvate, the sodium cation is coordinated by eight fluorine atoms (four fluorine atoms belonging to four different [MoF₆][−] anions and four fluorine atoms belonging to four different HF molecules) to form a dodecahedron-like coordination polyhedron. The molybdenum atom is coordinated by four F(1) atoms and two F(2) atoms to form an octahedron-like coordination polyhedron. The coordination of the Na⁺ cations by the [MoF₆][−] anions leads to the formation of a three-dimensional crystal structure, see Figure S7.

The molybdenum atoms are surrounded by eight neighboring Na⁺ cations to form rhombohedron-like coordination polyhedra. The Na⁺ cations are surrounded by eight nearest-neighboring Mo atoms to form square antiprismatic coordination polyhedra. These coordination polyhedra, along with the directional behavior of the Mo rhombohedron-like coordination polyhedra, are depicted in Figure S8.

Selected atomic distances observed in Na[MoF₆]-2HF are reported in Table 10. As mentioned previously, two distinct fluorine atoms coordinate to Mo(1). The Mo(1)–F(1) atomic distance is 1.8561(8) Å, whereas the Mo(1)–F(2) distance is slightly longer with a value of 1.8925(10) Å. This slightly longer distance can be explained by F(2)'s participation in hydrogen bonding to a molecule of HF. The F(3)–H(1)⋯F(2) distance of 2.5559(16) Å suggests a moderate degree of hydrogen bonding (cf. the F–H–F distance between neighboring HF molecules in crystalline HF is reported to be 2.49(1) Å, whereas the F–H⋯F

distance in the bifluoride anion in Na[HF₂] is reported to be 2.277(1) Å.^[20,21] The angle of this hydrogen bond is nearly linear with a value of 176.276(33)°. The F–H...F hydrogen-bond interaction between the F(2) atom of the [MoF₆][−] anion and the F(3) atom of the HF molecule is depicted in Figure S9.

Table 10. Select interatomic distances *d* for the tetragonal modification of Na[MoF₆].

Atom1	Atom2	<i>m</i>	<i>d</i> /Å
Mo(1)	F(1)	4	1.8561(8)
Mo(1)	F(2)	2	1.8925(10)
Na(1)	F(1)	4	2.3621(8)
Na(1)	F(3)	4	2.4375(7)
H(1)	F(3)	1	0.74(3)
H(1)	F(2)	1	1.8165(33)
F(2)	F(3)	1	2.5559(16)
F(3)	F(3)	1	2.8542(18)

Considering only HF coordination to the Na⁺ cations, the HF molecules coordinate to the Na⁺ cations to form Na⁺-bridging parallelograms which form infinite chains along the *c*-axis. These parallelograms are angled from one another at an angle of about 60°. The F(3)–F(3) distance between adjacent fluorine atoms belonging to the same parallelogram is 2.8542(18) Å. The parallelogram formed due to Na⁺ coordination by HF is shown in Figure 6. A section of the crystal structure of Na[MoF₆]·2HF is shown in Figure 7.

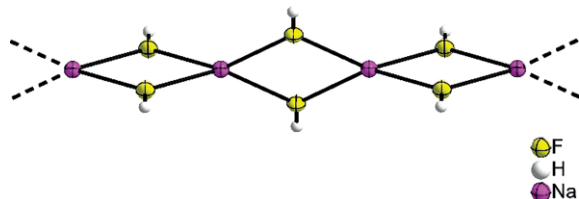


Figure 6. Coordination of Na⁺ by HF to form infinite chains of parallelograms along the *c*-axis. Displacement ellipsoids are shown at a 70% probability level at 100 K.

5. Single-Crystal Structure of Rb[MoF₆]

Rb[MoF₆] crystallizes in the trigonal space group *R* $\bar{3}$ with the lattice parameters *a* = 7.5502(6) Å, *c* = 7.6478(8) Å, *V* = 377.56(7) Å³, *Z* = 3, *T* = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for Rb[MoF₆] are reported in Table 11. Rb[MoF₆] is isotypic to the previously reported K[AsF₆] salt and to the Cs[MoF₆] salt reported here.^[3,22,23] Since the Rb[MoF₆] and Cs[MoF₆] salts are isotypic to each other, only the structure of the rubidium salt will be discussed in detail.

The rubidium cation is coordinated by twelve fluorine atoms (belonging to eight different [MoF₆][−] anions) to form a cuboctahedron-like coordination polyhedron. The Mo atom is coordinated by six fluorine atoms to form an octahedron-like coordination polyhedron. The F(1)–Mo(1)–F(1) angles in this coordination polyhedron range from 88.58(7)° to 91.42(7)°. The coordination of the Rb⁺ cations by the [MoF₆][−] anions leads to the formation of a three-dimensional network, see Figure S10.

When only the Mo atoms and Rb⁺ cations are considered, a lattice resembling that of CsCl was observed. In other words, a single [MoF₆][−] anion occupies the center of a cube generated

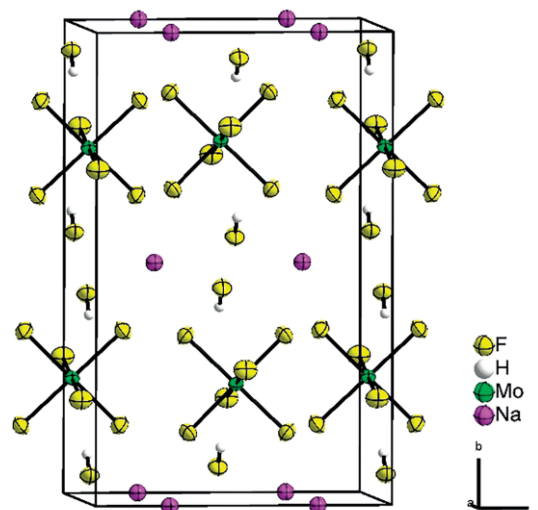


Figure 7. Section of the crystal structure of the Na[MoF₆]·2HF solvate. Displacement ellipsoids are shown at a 70% probability level at 100 K.

Table 11. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} for Rb[MoF₆] at 100 K.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
Mo(1)	3 <i>a</i>	0	0	0	0.00937(16)
F(1)	18 <i>f</i>	0.1615(2)	0.22344(19)	0.14468(19)	0.0173(3)
Rb(1)	3 <i>b</i>	0	0	1/2	0.01325(17)

by surrounding Rb⁺ cations and vice versa. A section of the crystal structure depicting this primitive cubic packing is shown in Figure S11. A section of the crystal structure is shown in Figure 8.

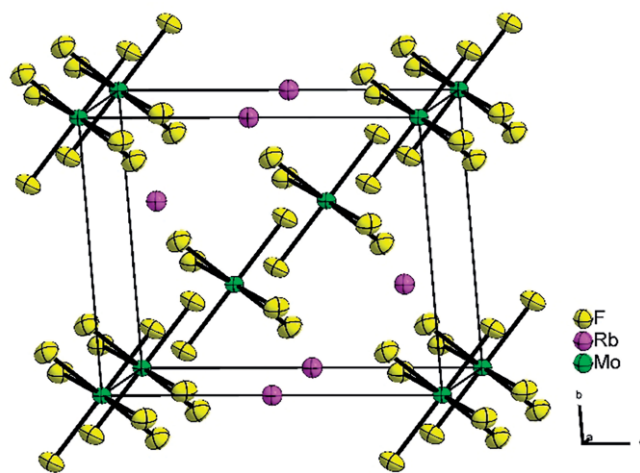


Figure 8. Section of the crystal structure of Rb[MoF₆]. Displacement ellipsoids are shown at a 70% probability level at 100 K.

A list of selected atomic distances in the Rb[MoF₆] and Cs[MoF₆] salts is reported in Table 12. The Mo(1)–F(1) atomic distances in both salts are comparable, having a value of 1.8708(12) Å for the rubidium salt and 1.8692(15) Å for the cesium salt. The A(1)–F(1) (*A* = Rb, Cs) distances are, understandably, significantly larger in the cesium salt than in the rubidium

salt due to the larger ionic radius of Cs⁺. The Rb(1)–F(1) distances in Rb[MoF₆] are 2.9272(12) Å and 3.1080(15) Å, whereas the cesium salts have corresponding atomic distances of 3.0725(16) Å and 3.2768(16) Å.

Table 12. Select interatomic distances *d* for Rb[MoF₆] and Cs[MoF₆]. The multiplicity of all reported interatomic distances is 6.

Atom1	Atom2	<i>d</i> /Å, Rb[MoF ₆]	<i>d</i> /Å, Cs[MoF ₆]
Mo(1)	F(1)	1.8708(12)	1.8692(15)
A(1) ^[a]	F(1)	2.9272(12)	3.0725(16)
A(1) ^[a]	F(1)	3.1080(15)	3.2768(16)

[a] A = Rb in the case of the Rb[MoF₆] salt; A = Cs in the case of the Cs[MoF₆] salt.

6. Single-Crystal Structure of Cs[MoF₆]

Cs[MoF₆] crystallizes in the trigonal space group *R* $\bar{3}$ with the lattice parameters *a* = 7.7693(10) Å, *c* = 8.0092(16) Å, *V* = 418.68(14) Å³, *Z* = 3, *T* = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for Cs[MoF₆] are reported in Table 13. It was observed that Cs[MoF₆] is isotopic to the previously reported K[AsF₆] salt and the Rb[MoF₆] salt reported here.^[3,22,23] A discussion of the Rb[MoF₆] salt, along with its comparison to the Cs[MoF₆] salt is found in the previous section.

Table 13. Atomic coordinates and equivalent isotropic displacement parameters *U*_{iso} for Cs[MoF₆] at 100 K.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} /Å ²
Mo(1)	3 <i>a</i>	0	0	0	0.01345(18)
F(1)	18 <i>f</i>	0.0532(2)	0.2158(2)	0.1371(2)	0.0225(4)
Cs(1)	3 <i>b</i>	0	0	1/2	0.0165(2)

Vibrational Spectroscopy

An ATR-IR spectrum for each A[MoF₆] (A = Li – Cs) salt was collected at 25 °C in the region of 4000 to 400 cm⁻¹. The IR band locations and their assignments are reported in Table 14;

Table 14. IR bands observed in the A[MoF₆] (A = Li – Cs) salts. All band locations are given in cm⁻¹.

Li[MoF ₆]	Na[MoF ₆] ^[a]	K[MoF ₆]	K[MoF ₆] ^[b]	Rb[MoF ₆]	Cs[MoF ₆]	Cs[MoF ₆] ^[b]	Assignment
			249			250	ν_4 , $\delta(\text{MoF}_6^-)$
				470 495	484		
544					506		
610	605	544	639	552 588	552 594	635	ν_3 , $\nu(\text{Mo-F})$
860						910	Hydrolysis product
953		980	935 970			940 980	Hydrolysis product Hydrolysis product
1034	1024	1007	1020	1019	1012	1028	Hydrolysis product
1053							$\nu(\text{Mo-O})$
1164	1143	1152		1143 1193	1147		$\nu(\text{Mo-O})$ $\nu_2 + \nu_3$
	1243	1236		1243	1246		$\nu_1 + \nu_3$
	1309	1309		1306			
		1441					
1770							

[a] Cubic modification of Na[MoF₆]. [b] Data obtained from the previous work of Beuter and Sawodny.^[4]

no bands were observed above 1800 cm⁻¹. As an example of an IR spectrum typical of this series, the IR spectrum of K[MoF₆] is depicted in Figure 9; the remaining IR spectra are depicted in Figures S12 – S15. Additionally, Raman spectra were obtained for each A[MoF₆] (A = Li – Cs) salt at 25 °C from about 0 to 1800 cm⁻¹. The Raman band locations and their assignments are listed in Table 15. As an example of a Raman spectrum typical of this series, the Raman spectrum of K[MoF₆] is depicted in Figure 10; the remaining Raman spectra are depicted in Figures S16 – S19. IR and Raman spectra were not collected for the tetragonal modification of Na[MoF₆] or the Na[MoF₆] \cdot 2HF solvate. In order to aid in vibrational band assignments, powder X-ray diffraction patterns of all salts were obtained. These diffraction patterns showed the Na[MoF₆] and Rb[MoF₆] salts to be phase-pure, while the Li[MoF₆], K[MoF₆] and Cs[MoF₆] salts had some impurities. Unfortunately, the identities of these impurities could not be determined. It is unclear whether these impurities have active IR or Raman vibrations. Nevertheless, the powder X-ray diffraction patterns are reported in Figures S20 – S24.

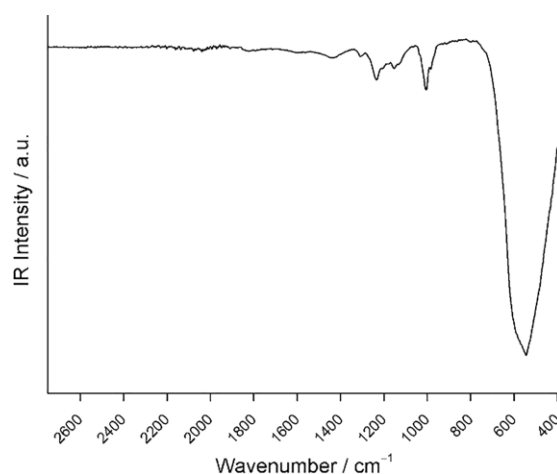


Figure 9. IR spectrum of K[MoF₆] in the region of 2750 to 400 cm⁻¹.

Table 15. Raman bands observed in the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts. All band locations are given in cm^{-1} .

$\text{Li}[\text{MoF}_6]$	$\text{Na}[\text{MoF}_6]$ ^[a]	$\text{K}[\text{MoF}_6]$	$\text{K}[\text{MoF}_6]$ ^[b]	$\text{Rb}[\text{MoF}_6]$	$\text{Cs}[\text{MoF}_6]$	$\text{Cs}[\text{MoF}_6]$ ^[b]	Assignment
257	236	241 296		236 312	233 292 307	274	$\nu_5, \delta(\text{MoF}_6^-)$
487		579 625		638	589	598	$\nu_2, \nu(\text{Mo-F})$
711	693	686	687	678 788	676 797	685	$\nu_1, \nu(\text{Mo-F})$
1047	902 1029 1057	970 1011		1016 1031 1090	1014		$\nu(\text{Mo-O})$ $\nu(\text{Mo-O})$
1108							
1588	1580	1573		1580	1585		

[a] Cubic modification of $\text{Na}[\text{MoF}_6]$. [b] Data obtained from the previous work of Beuter and Sawodny.^[4]

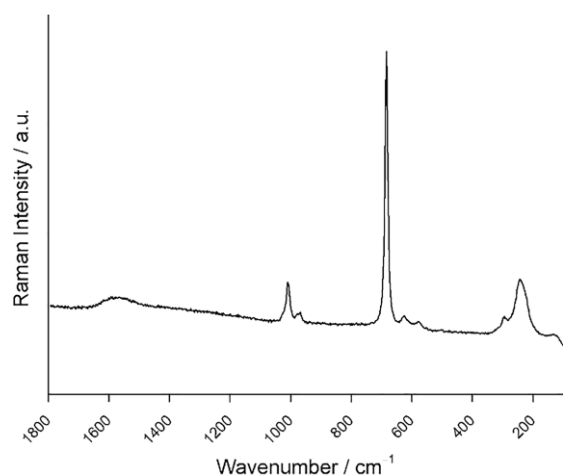


Figure 10. Raman spectrum of $\text{K}[\text{MoF}_6]$ in the region of 100 to 1800 cm^{-1} .

The IR and Raman spectra of $\text{K}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$ were previously investigated by Beuter and Sawodny.^[12] The IR and Raman band locations and assignments determined in this previous work are also reported in Table 14 and Table 15, respectively. The authors of this study argued that although the $[\text{MoF}_6]^-$ anions found in the solid-state structures of these salts may not be perfectly octahedral (with the exception of the cubic modification of $\text{Na}[\text{MoF}_6]$), they were able to analyze the vibrational spectra based on O_h symmetry.^[12] Similarly, the spectra obtained here could be analyzed on the basis of O_h symmetry – three Raman active bands: $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $F_{2g}(\nu_5)$, and two IR active bands: $F_{1u}(\nu_3)$ and $F_{1u}(\nu_4)$.^[24]

However, the ν_4 IR band could not be observed because it lies outside the range investigated here.

In the work of Beuter and Sawodny, the ν_1 , ν_2 , and ν_3 bands are assigned to Mo–F stretching, whereas the ν_4 and ν_5 bands are assigned to $[\text{MoF}_6]^-$ deformation.^[12] A similar band assignment is made in this work. Additionally, some infrared-active binary combination bands were observed in the IR spectra reported here, refer to Table 14 and Table 15. On the strong ν_3 bands observed in the spectra of $\text{Li}[\text{MoF}_6]$, $\text{Rb}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$ salts, several smaller shoulder bands can be seen. These bands are also thought to arise from combination bands,

although no specific assignment was given to these bands. Furthermore, a series of bands located between 900 and 1053 cm^{-1} in all IR spectra reported here could not be explained by combination bands. Beuter and Sawodny also observed this series of bands in the IR spectra of $\text{K}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$. They attributed these bands to hydrolysis species and suspected the bands occurring between 1000 and 1050 cm^{-1} to arise from the presence of the $[\text{Mo}_2\text{O}_2\text{F}_9]^-$ anion. We have recently reported a series of $A[\text{Mo}_2\text{O}_2\text{F}_9]$ ($A = \text{Li} - \text{Cs}$) salts having similar Mo–O stretching bands,^[25] however, we have not assigned the bands arising between 1000 and 1053 cm^{-1} to any particular anion. It is clear from the presence of these bands, however, that some hydrolysis has occurred.

Near the ν_1 band in the Raman spectra of $\text{K}[\text{MoF}_6]$ and $\text{Rb}[\text{MoF}_6]$, there is one observed band (one in each spectrum) that is thought to be a combination band. However, in the spectrum of $\text{Rb}[\text{MoF}_6]$, this band, located at 638 cm^{-1} may actually be the ν_2 vibration. Additionally, in the Raman spectra of all $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts reported here, there is a band located between 1573 and 1588 cm^{-1} . Because this band is observed in all spectra, it is also thought to be a combination band, although a direct assignment is not given. Additionally, several shoulder bands are observed near the ν_5 band in the Raman spectra of $\text{K}[\text{MoF}_6]$, $\text{Rb}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$. These bands are also likely combination bands. In the Raman spectra of all salts, evidence for hydrolysis is given by Mo–O stretching band(s) arising between 1011 and 1057 cm^{-1} . In the lithium salt, two bands arising at 487 and 1107 cm^{-1} could not be identified. The presence is either due to impurities, combination bands, or overtone bands.

Conclusions

A new synthetic route for the synthesis of the hexafluoridomolybdates(V), $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$), was presented, whereby MoF_5 was treated with the respective alkali metal fluoride in aHF solution. IR and Raman spectra were reported for each $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salt and were analyzed on the basis of O_h symmetry. The IR and Raman spectra reported here compliment the previously reported spectra of $\text{K}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$ and provide the first

comprehensive study of the vibrational spectra of the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts.

The crystal structures of $A[\text{MoF}_6]$ ($A = \text{Li}, \text{Na}, \text{Rb}, \text{Cs}$) were determined using single-crystal X-ray diffraction and were discussed in detail. The lattice parameters of the cubic modification of $\text{Na}[\text{MoF}_6]$ reported here show good agreement with previously reported lattice parameters.^[9,10] A new, tetragonal modification of $\text{Na}[\text{MoF}_6]$ was obtained when the cubic modification of $\text{Na}[\text{MoF}_6]$ was dissolved in ClF_3 and its crystal structure was discussed in detail. Additionally, the synthesis of the $\text{Na}[\text{MoF}_6] \cdot 2\text{HF}$ solvate was also presented and its crystal structure was discussed in detail. The lattice parameters of $\text{Rb}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$ were previously reported as belonging to the cubic crystal system,^[9] whereas the respective lattice parameters reported here are described by the trigonal crystal system. These differences are suspected to arise based on the quality of the data, where the previously reported lattice parameters relied on the indexing of powder X-ray diffraction data. Lastly, single crystals of $\text{K}[\text{MoF}_6]$ suitable for single-crystal X-ray diffraction were not obtained and the powder X-ray diffraction pattern of the salt could not be indexed, possibly due to the presence of impurities. As such, a discussion regarding the crystal structure of $\text{K}[\text{MoF}_6]$ was not given.

To conclude, the work reported here provides a straight-forward synthetic route for the synthesis of the hexafluoridomolybdates(V), $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$). A thorough study on their vibrational spectra was performed, providing the first complete vibrational analysis of this series of salts. Additionally, a higher-level analysis was performed to determine the crystal structures of these salts. From this analysis, the previously reported lattice parameters for $\text{Na}[\text{MoF}_6]$ could be verified, whereas the previously reported ones for $\text{Rb}[\text{MoF}_6]$ and $\text{Cs}[\text{MoF}_6]$ were found to be incorrectly determined and are re-reported here.^[9,10] This report provides a deeper understanding of the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts and can be used as a basis for their further investigation.

Experimental Section

General Procedures and Materials: All operations were performed in either stainless steel (316 L) or Monel metal Schlenk lines, which were passivated with 100 % fluorine (99 %, Solvay) at various pressures before use. Preparations were carried out in an atmosphere of dry and purified argon (5.0, Praxair). Molybdenum hexafluoride (99 %, ABCR) was distilled once prior to usage. Anhydrous HF (Fluka Analytical, > 99.9 %), which was stored over $\text{K}_2[\text{NiF}_6]$ (analytically pure, homemade), was distilled twice before use. Perfluoroethylene/perfluoropropylene copolymer, FEP, was used to produce reaction vessels. All alkali metal fluorides ($\text{Li} - \text{Cs}$, >99 %, Merck) used were heated at 150 °C under vacuum to drive out any HF and then stored under argon in an inert atmosphere glovebox.

Synthesis of $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$)

First, MoF_5 was synthesized by the reduction of MoF_6 by UV light under a carbon monoxide (CO) atmosphere. For this reaction, 3.74 grams MoF_6 (17.80 mmol) were distilled to a 300 mL quartz vessel that was previously evacuated and flame dried. After the MoF_6 was frozen at the bottom of the vessel with liquid nitrogen, 800 mbar CO (approximately 9.79 mmol) was added. The reaction vessel was

transferred to a homemade UV reactor to allow irradiation by UV light (254 nm). After about 12 hours, any COF_2 formed was evacuated and 800 mbar of fresh CO was added to the reaction vessel. The vessel was irradiated for an additional 12 hours before completion. Any remaining CO and COF_2 formed during the reaction were removed in vacuo and the MoF_5 product was transferred to an inert atmosphere glovebox for storage. A quantitative amount of MoF_5 was obtained. IR and Raman spectroscopy, and powder X-ray diffraction showed no evidence of impurities.

To synthesize the $A[\text{MoF}_6]$ ($A = \text{Li} - \text{Cs}$) salts, an approximately 1:1 molar ratio of MoF_5 and AF ($A = \text{Li} - \text{Cs}$) was added to an FEP reaction vessel under an inert atmosphere in a glovebox. The reaction vessel was attached to a metal vacuum line and evacuated and flushed with argon 3 times. Approximately 2 to 4 mL of aHF was condensed onto the reactants at -196 °C. The reaction vessels were warmed to room temperature, producing blue solutions in all cases. Once all reactants had dissolved, the aHF was slowly pumped off to produce crystalline samples of which the bulk phase appeared blue, while single crystals under the microscope appeared colorless. The products were transferred to an inert atmosphere glovebox for storage.

Synthesis of $\text{Li}[\text{MoF}_6]$

Under inert atmosphere, 100.80 mg of MoF_5 (0.53 mmol) and 16.60 mg of LiF (0.63 mmol) were placed in an FEP reaction vessel. Approximately 2 mL aHF were condensed on top of the reaction mixture. After warming to room temperature, and after all reactants had dissolved, the aHF was slowly pumped off over a period of about 5 hours. The blue crystalline product obtained was stored in a PTFE container under argon in a glovebox.

Synthesis of the cubic modification of $\text{Na}[\text{MoF}_6]$

Under inert atmosphere, 100.10 mg of MoF_5 (0.52 mmol) and 22.46 mg of NaF (0.53 mmol) were placed in an FEP reaction vessel. Approximately 4 mL aHF were condensed on top of the reaction mixture. After warming to room temperature, and after all reactants had dissolved, the aHF was slowly pumped off over a period of about 5 hours. The blue crystalline product obtained was stored in a PTFE container under argon in a glovebox.

Synthesis of the tetragonal modification of $\text{Na}[\text{MoF}_6]$

Under inert atmosphere, 25 mg of the cubic modification of $\text{Na}[\text{MoF}_6]$ (0.11 mmol) were placed in an FEP reaction vessel. Approximately 1 mL of ClF_3 (99 %, homemade) was condensed on top of the blue, crystalline sample. The reaction vessel was stored for a week. Afterwards, the remaining ClF_3 was pumped off from the sample. A white, primarily powdered sample was obtained. A small amount of colorless single crystals had formed. Measurement of these crystals using single-crystal X-ray diffraction showed them to belong to a tetragonal modification of $\text{Na}[\text{MoF}_6]$.

Synthesis of the $\text{Na}[\text{MoF}_6] \cdot 2\text{HF}$ solvate

Under inert atmosphere, 111.79 mg of MoF_5 (0.59 mmol) and 23.02 mg of NaF (0.89 mmol) were placed in an FEP reaction vessel. Approximately 3 mL aHF were condensed on top of the reaction mixture. The reaction vessel was placed in a dry ice-2-propanol bath (-78 °C). Once all reactants had dissolved, the aHF was slowly pumped off over a period of about 24 hours. A blue crystalline product was obtained and stored in the original FEP vessel at -80 °C. Single crystals of the product were selected at -78 °C.

Synthesis of $\text{K}[\text{MoF}_6]$

Under inert atmosphere, 100.79 mg of MoF_5 (0.53 mmol) and 33.47 mg of KF (0.58 mmol) were placed in an FEP reaction vessel.

Approximately 4 mL aHF were condensed on top of the reaction mixture. After warming to room temperature, and after all reactants had dissolved, the aHF was slowly pumped off over a period of about 5 hours. The blue crystalline product obtained was stored in a PTFE container under argon in a glovebox. Unfortunately, no suitable specimen for single-crystal diffraction was obtained.

Synthesis of Rb[MoF₆]

Under inert atmosphere, 100.71 mg of MoF₅ (0.53 mmol) and 54.55 mg of RbF (0.52 mmol) were placed in an FEP reaction vessel. Approximately 4 mL aHF were condensed on top of the reaction mixture. After warming to room temperature, and after all reactants had dissolved, the aHF was slowly pumped off over a period of about 5 hours. The blue crystalline product obtained was stored in a PTFE container under argon in a glovebox.

Synthesis of Cs[MoF₆]

Under inert atmosphere, 100.67 mg of MoF₅ (0.53 mmol) and 79.73 mg of CsF (0.52 mmol) were placed in an FEP reaction vessel. Approximately 4 mL aHF were condensed on top of the reaction mixture. After warming to room temperature, and after all reactants had dissolved, the aHF was slowly pumped off over a period of about 5 hours. The blue crystalline product obtained was stored in a PTFE container under argon in a glovebox.

Single-crystal X-ray Diffraction: X-ray structure analysis of the single crystals of A[MoF₆] (A = Li, Na, Rb, Cs) and the Na[MoF₆]·2HF were carried out with a STOE IPDS 2 or 2T diffractometer with plane graphite-monochromated molybdenum radiation (Mo-K_α, λ = 0.71073 Å) generated by a sealed X-ray tube (12 × 0.4 mm long fine focus), and a detector resolution of 6.67 pixels mm⁻¹. Evaluation and integration of the diffraction data was carried out using the X-Area software, and absorption corrections were made through integration using the X-Red32 and X-Shape program within the parent software.^[26] The structures were solved using Direct Methods (SHELXT 2014/5) and refined against F² (SHELXL-2018/3).^[27,28] Representations of the crystal structure were created using the Diamond software.^[29]

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition number CSD 1983383 (for Li[MoF₆]), 1983384 (for the cubic modification of Na[MoF₆]), 1983385 (for the tetragonal modification of Na[MoF₆]), 1983386 (for the Na[MoF₆]·2HF solvate), 1983387 (Rb[MoF₆]), and 1983388 (for Cs[MoF₆]).

Powder X-ray Diffraction: Powder X-ray diffraction patterns were obtained with a Stadi-MP-Diffractometer (STOE) using Cu-K_α radiation (λ = 1.54051 Å), a germanium monochromator, and a Mythen1K detector. The data were handled using the WINXPOW software.^[30] The compound was filled into borosilicate capillaries, which were previously flamed dried under vacuum, and sealed using a hot tungsten wire under inert atmosphere in a glovebox.

IR Spectroscopy: The IR spectra were measured on an alpha FTIR spectrometer (Bruker) using a diamond ATR unit under an Ar atmosphere. The spectrum was processed with the OPUS software package.^[31]

Raman Spectroscopy: The A[MoF₆] (A = Li – Cs) salts were loaded into 0.3 mm borosilicate capillaries and the Raman spectra were

measured in backscattering geometry by means of a Raman microscope inVia (Renishaw), using a frequency-doubled Nd:YAG laser (532 nm wavelength). The spectra were recorded in confocal mode between 2 cm⁻¹ and 1792 cm⁻¹. The laser power was reduced to 5 % to prevent degradation of the samples.

Acknowledgments

F. K. would like to thank the Deutsche Forschungsgemeinschaft (DFG) for funding and Solvay for their donations of fluorine. The authors would like to thank Prof. Dr. Bernhard Roling for Raman spectroscopy measurement time.

Keywords: Molybdenum · Fluorides · Alkali metals · Structure elucidation · Synthetic methods

- [1] N. Schrewelius, *Z. Anorg. Allg. Chem.* **1938**, 238, 241–254.
- [2] J. L. Hoard, W. B. Vincent, *J. Am. Chem. Soc.* **1940**, 62, 3126–3129.
- [3] R. B. Roof, *Acta Crystallogr.* **1955**, 8, 739–739.
- [4] H. Bode, H. v. Döhren, *Naturwissenschaften* **1957**, 44, 179–179.
- [5] H. Bode, E. Voss, *Z. Anorg. Allg. Chem.* **1951**, 264, 144–150.
- [6] J. H. Burns, *Acta Crystallogr.* **1962**, 15, 1098–1101.
- [7] Z. Mazej, E. Goresnik, *Eur. J. Inorg. Chem.* **2008**, 2008, 1795–1812.
- [8] G. Teufer, *Acta Crystallogr.* **1956**, 9, 539–540.
- [9] G. B. Hargreaves, R. D. Peacock, *J. Chem. Soc.* **1957**, 4212.
- [10] A. J. Edwards, R. D. Peacock, *J. Chem. Soc.* **1961**, 4247.
- [11] R. D. Peacock, D. W. A. Sharp, *J. Chem. Soc.* **1959**, 2762–2767.
- [12] A. Beuter, W. Sawodny, *Z. Anorg. Allg. Chem.* **1976**, 427, 37–44.
- [13] J. R. Geichman, E. A. Smith, S. S. Trond, P. R. Ogle, *Inorg. Chem.* **1962**, 1, 661–665.
- [14] G. M. Anderson, I. F. Fraser, J. M. Winfield, *J. Fluorine Chem.* **1983**, 23, 403–404.
- [15] G. M. Anderson, J. M. Winfield, *J. Chem. Soc., Dalton Trans.* **1986**, 337.
- [16] H. Sowa, *Acta Crystallogr., Sect. A* **1997**, 53, 25–31.
- [17] W. J. Casteel, D. A. Dixon, N. LeBlond, P. E. Lock, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* **1999**, 38, 2340–2358.
- [18] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, Cornell Univ. Press, Ithaca, New York, **1960**.
- [19] A. Bondi, *J. Phys. Chem.* **1964**, 68, 441–451.
- [20] M. Atoji, W. N. Lipscomb, *Acta Crystallogr.* **1954**, 7, 173–175.
- [21] S. I. Troyanov, *Crystallogr. Rep.* **2005**, 50, 773–778.
- [22] J. A. Ibers, *Acta Crystallogr.* **1956**, 9, 967–969.
- [23] G. Gafner, G. J. Kruger, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **1974**, 30, 250–251.
- [24] B. Weinstock, G. L. Goodman, in *Advances in Chemical Physics* (Ed.: I. Prigogine), John Wiley & Sons, Inc., Hoboken, NJ, USA, **1965**, pp. 169–319.
- [25] R. E. Stene, B. Scheibe, A. J. Karttunen, W. Petry, F. Kraus, *Eur. J. Inorg. Chem.* **2019**, 2019, 3672–3682.
- [26] X-Area, STOE & Cie GmbH, Darmstadt, Germany, **2011**.
- [27] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112–122.
- [28] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, 71, 3–8.
- [29] H. Putz, K. Brandenburg, *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact, Bonn, Germany, **2015**.
- [30] STOE WinXPOW, STOE & Cie GmbH, Darmstadt, Germany, **2015**.
- [31] OPUS, Bruker Optik GmbH, Ettlingen, Germany, **2009**.

Received: February 11, 2020