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Molybdenum Fluorides

Lewis Acidic Behavior of MoOF₄ towards the Alkali Metal Fluorides in Anhydrous Hydrogen Fluoride Solutions

Riane E. Stene, Benjamin Scheibe, Antti J. Karttunen, Winfried Petry, and Florian Kraus

Abstract: Previous studies performed on samples of MoOF₄ dissolved in anhydrous hydrogen fluoride (aHF) solutions have indicated the presence of the [Mo₂O₂F₉]⁻ anion. Building upon this earlier work, MoOF₄, and MF (M = Li–Cs) were dissolved in aHF solutions to produce M[Mo₂O₂F₉] (M = Li–Cs) salts. Structural analysis of the obtained compounds was performed using single-crystal X-ray diffraction. This study provides the first single crystal structures for the [Mo₆V²O₄F₉]⁻ anion. Additionally, IR and Raman spectroscopy were used to characterize each salt. These spectra were compared to calculated ones for the solid-state structure of each salt using the DFT-PBE0 density functional method. The calculated spectra were used to give band assignments in the experimentally obtained spectra.

Introduction

Trifluorido trioxido molybdate(VI) anions, [MoO₃F₃]³⁻, such as those in K₃MoO₃F₃ and Cs₂RbMoO₃F₃, have been shown to display many applicable physical properties, most notably ferroelectricity. In addition, molybdenum oxide fluoride anions, in which the molybdenum atoms have d⁰ electronic configurations, may exhibit second-order Jahn–Teller distortion. This distortion, characterized by a displacement of the Mo atom from the center of its octahedral coordination environment, and alternating atomic distances between the Mo and neighboring bridging fluorine/oxygen atoms, can yield compounds displaying metallic, ferroelectric, and magnetic behaviors. In order to exploit potential promising physical and chemical properties, many molybdenum oxide fluorides have been synthesized to date. However, little remains known regarding the chemical properties of the simplest MoVI molybdenum oxide fluoride, MoOF₄.

MoOF₄ was first synthesized in 1907 by Ruff and Eisner, whereby aHF was condensed onto molybdenum oxide tetra-chloride (MoOCl₄). MoOF₄ is a white solid having a melting point of 97 °C and a boiling point of 186 °C (under ambient atmospheric pressure). The crystal structure of MoOF₄, which is related to that of VF₅, is characterized by essentially octahedrally-coordinated Mo atoms linked into infinite chains by cis-bridging fluorine atoms. The solid-state structure of MoOF₄ features Mo atoms in distorted octahedral surroundings and alternating Mo–(μ-F) atomic distances, see Figure 1.

MoOF₄ has been described in the literature as being a weak Lewis acid and fluoride ion acceptor, with WOF₄ being, comparatively, both a stronger Lewis acid and fluoride ion acceptor. A detailed understanding of the Lewis acid and fluoride ion acceptor behavior of MoOF₄ in aHF was given by Bougon and co-workers, who studied aHF solutions containing MoOF₄ and fluoride ion donors using Raman and ¹⁹F NMR spectroscopy. Their study determined that MoOF₄ forms a chemical equilibrium in aHF solutions between the [Mo₂O₂F₉]⁻, [MoOF₄]⁺, [MoOF₆]²⁻ anions, depending on the [HF₂]⁻ concentration available in solution, as shown in Equations 1–3. It was predicted that higher concentrations of [HF₂]⁻ drives the chemical equilibrium of each reaction to the right, and thus
pushes the chemical equilibrium from the left side of Equation 1 to the right side of Equation 3.[13–15]

$$2 \text{MoOF}_4 + [\text{HF}]^2 → \text{Mo}_2\text{O}_2\text{F}_9^- + 2 \text{HF} \quad (1)$$

$$[\text{Mo}_2\text{O}_2\text{F}_9^-] + [\text{HF}]^2 → 2 [\text{MoF}_5^-] + \text{HF} \quad (2)$$

$$[\text{MoF}_5^-] + [\text{HF}]^2 → [\text{MoF}_6]^{2-} + \text{HF} \quad (3)$$

Similarly, a study aimed at determining the interaction of MoOF₄ with acetylacetone in acetonitrile solution also reported evidence for the formation of the [Mo₂O₂F₉]⁻ anion.[14] Additionally, work performed by Holloway and Schrobilgen described the formation of KrF₂·nMoF₆ (n = 1–3) and XeF₂·nMoF₄ (n = 1–4) adducts, in which a structurally related anion, MoOF₄, to which an F atom from a XeF₂ ligand is bound, was observed.[13,15] These studies shed much light on the complex equilibria and solution chemistry MoOF₄ can exhibit.[12–15] How- er, despite the potential of MoOF₄ to give rise to new chemical species, very little literature exists in which MoOF₄ was used as a starting reagent in chemical reactions.[12–22] Therefore, the goal of this work was to expand the current knowledge of the chemical behavior of MoOF₄ in aHF solutions by reacting it with the alkali metal fluorides. As a result, the series of M[Mo₂O₂F₉] (M = Li–Cs) salts was obtained. Structural analysis of these salts, performed using single-crystal X-ray diffraction, provides the first crystal structures containing the [Mo₂O₂F₉]⁻ anion. The structures of these anions will be compared to the previously reported [Mo₂O₂F₉]³⁻ anions. Furthermore, vibrational spectroscopy was studied using IR and Raman techniques and the obtained spectra were compared to quantum chemically calculated solid-state spectra. A discussion on the synthesis of the M[Mo₂O₂F₉] (M = Li–Cs) salts is presented, along with suggestions as to the possible synthesis of M[MoOF₅] and M₂[MoOF₆] (M = Li–Cs) salts.

### Results and Discussion

**Synthesis of the M[Mo₂O₂F₉] (M = Li–Cs) Salts**

First, MoOF₄ was synthesized through the hydrolysis of MoF₆ by silicon dioxide in aHF, see Equations 4 and 5.[23] After pumping off the unreacted aHF and the SiF₄ formed during the reaction, the MoOF₄ product was stored in an inert atmosphere glovebox until further use. Next, a 1:1 molar ratio of MoOF₄ and the respective alkali metal fluoride was reacted in an aHF solution to obtain the M[Mo₂O₂F₉] (M = Li–Cs) salts, see Equation 6. Single crystals of the salts were grown directly from aHF solution. However, as evidenced by X-ray powder diffraction, as well as IR and Raman spectroscopy, the compounds could not be obtained phase-pure. Evidence suggests the impurities to be

$$\text{SiO}_2 + 4 \text{HF} \underset{aHF}{\rightarrow} \text{SiF}_4 + 2 \text{H}_2\text{O} \quad (4)$$

$$\text{MoF}_6 + \text{H}_2\text{O} \underset{aHF}{\rightarrow} \text{MoOF}_5 + 2 \text{HF} \quad (5)$$

$$2\text{MoOF}_4 + \text{MF} \underset{aHF}{\rightarrow} [\text{Mo}_2\text{O}_2\text{F}_9]\text{MF}_2 \quad (6)$$

### Table 1. Selected crystallographic data and details of the single crystal structure determination for the M[Mo₂O₂F₉] (M = Li–Cs) salts.

| M[Mo₂O₂F₉] | Li[Mo₂O₂F₉] | Na[Mo₂O₂F₉] | K[Mo₂O₂F₉] | Rb[Mo₂O₂F₉] | Cs[Mo₂O₂F₉] |
|------------|-------------|-------------|-------------|-------------|-------------|
| Empirical formula | F₉LiMo₉O₂ | F₉NaMo₉O₂ | F₉KMo₉O₂ | F₉RbMo₉O₂ | F₉CsMo₉O₂ |
| Color and appearance | colorless blocks | colorless blocks | colorless blocks | colorless blocks | colorless blocks |
| Molar mass /g mol⁻¹ | 401.82 | 417.87 | 433.98 | 480.35 | 527.79 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group type (No.) | P1(2) | P2/c(13) | P2/c(13) | P2/c(13) | P2/c(13) |
| Pearson symbol | aP28 | mP28 | mP28 | mP28 | mP28 |
| a/Å | 5.087(2) | 8.141(8) | 5.438(6) | 5.624(8) | 5.916(7) |
| b/Å | 8.445(6) | 6.5008(8) | 5.0712(3) | 5.1994(6) | 5.4203(7) |
| c/Å | 10.0254(4) | 8.6741(10) | 15.1497(10) | 14.9973(8) | 14.7154(7) |
| α° | 66.432(3) | 66.432(3) | 66.432(3) | 66.432(3) | 66.432(3) |
| β° | 77.268(4) | 113.025(7) | 105.842(6) | 106.748(5) | 108.544(4) |
| γ° | 89.436(4) | 113.025(7) | 105.842(6) | 106.748(5) | 108.544(4) |
| V/Å³ | 383.61(3) | 422.65(7) | 401.96(5) | 419.58(4) | 447.36(4) |
| Z | 2 | 2 | 2 | 2 | 2 |
| ρcalcd /g cm⁻³ | 3.479 | 3.284 | 3.586 | 3.802 | 3.918 |
| λ/Å | 0.71073 (Mo-Kα) | 0.71073 (Mo-Kα) | 0.71073 (Mo-Kα) | 0.71073 (Mo-Kα) | 0.71073 (Mo-Kα) |
| T/K | 100 | 100 | 100 | 100 | 100 |
| µ /mm⁻¹ | 3.41 | 3.14 | 3.77 | 8.88 | 6.93 |
| βmax /° | 89.436(4) | 113.025(7) | 105.842(6) | 106.748(5) | 108.544(4) |
| Δhkl /mm⁻¹ | 33.4 | 33.3 | 28.7 | 33.3 | 32.0 |
| hkl range | –7 ≤ h ≤ 7 | –12 ≤ h ≤ 12 | –7 ≤ h ≤ 7 | –8 ≤ h ≤ 8 | –8 ≤ h ≤ 8 |
| –13 ≤ k ≤ 13 | –10 ≤ k ≤ 10 | –6 ≤ k ≤ 6 | –8 ≤ k ≤ 8 | –8 ≤ k ≤ 8 |
| –15 ≤ l ≤ 15 | –11 ≤ l ≤ 13 | –20 ≤ l ≤ 19 | –23 ≤ l ≤ 23 | –20 ≤ l ≤ 23 |
| Rint, Rwp | 0.075, 0.043 | 0.093, 0.042 | 0.043, 0.032 | 0.110, 0.053 | 0.030, 0.015 |
| R(F) (I > 2σ(I), all data) | 0.036, 0.051 | 0.057, 0.074 | 0.019, 0.037 | 0.030, 0.032 | 0.026, 0.030 |
| wR(F)² (I > 2σ(I), all data) | 0.066, 0.072 | 0.112, 0.120 | 0.033, 0.036 | 0.063, 0.064 | 0.063, 0.064 |
| S (all data) | 1.10 | 1.14 | 1.01 | 1.10 | 1.26 |
| Data, parameter, restraints | 2949, 134, 0 | 1640, 65, 0 | 1039, 66, 0 | 1625, 66, 0 | 1556, 65, 0 |
| Δρmax, Δρmin /e Å⁻³ | 1.25, –1.36 | 1.40, –2.15 | 0.54, –0.68 | 1.07, –1.93 | 1.43, –2.17 |

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the respective adducts of \( [\text{HF}]_n \) \((n = 1, 2)\), and other, yet unidentified, compounds.

**Single Crystal X-ray Analysis**

All \( \text{M}[\text{Mo}_2\text{O}_2\text{F}_9] \) \((\text{M} = \text{Li}–\text{Cs})\) salts contain \( [\text{Mo}_2\text{O}_2\text{F}_9]^– \) anions surrounded by several of the respective alkali metal cations. The \( [\text{Mo}_2\text{O}_2\text{F}_9]^– \) anion can be thought of as two \( \text{MoOF}_4 \) units bridged by a fluoride anion, as shown in Figure 2. The anion may be described by the Niggli formula \( _0[^2\text{MoO}_{1/1}\text{F}_{4/1}\text{F}_{1/2}]^2 \). Selected crystallographic data and details of the single crystal structure determination are given in Table 1. The single crystal structures of each salt will be discussed individually; comparisons, when appropriate, will be noted. A comparison of the salts reported here to the previously reported \( (\text{NH}_4)_3[\text{MoV}\text{O}_2\text{F}_9] \) and \( \text{K}[\text{NMe}_4][\text{MoV}\text{O}_2\text{F}_9] \) \( \cdot \text{H}_2\text{O} \) salts will be presented at the end of this section.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters \( U_{\text{eq}} \) for \( \text{Li}[\text{Mo}_2\text{O}_2\text{F}_9] \).

| Atom   | Position | x    | y    | z    | \( U_{\text{eq}} / \AA^2 \) |
|--------|----------|------|------|------|-----------------------------|
| Mo(1)  | 2i       | 0.1303(6) | 0.0260(4) | 0.21547(3) | 0.01007(8) |
| Mo(2)  | 2i       | 0.1678(6) | 0.54561(4) | 0.71704(3) | 0.01090(3) |
| F(000) | 2i       | 0.0199(5) | 0.2704(3) | 0.2089(3) | 0.0173(4) |
| F(2)   | 2i       | 0.3716(4) | 0.0654(3) | 0.3193(2) | 0.0149(4) |
| F(3)   | 2i       | 0.3681(5) | 0.1676(3) | 0.0370(2) | 0.0176(4) |
| F(4)   | 2i       | 0.8591(5) | 0.0382(3) | 0.1194(3) | 0.0202(5) |
| F(5)   | 2i       | 0.1320(4) | 0.0507(3) | 0.6034(2) | 0.0150(4) |
| F(6)   | 2i       | 0.0744(5) | 0.6040(3) | 0.1106(3) | 0.0174(4) |
| F(7)   | 2i       | 0.0966(5) | 0.4190(3) | 0.3876(3) | 0.0179(4) |
| F(8)   | 2i       | 0.6307(4) | 0.2556(3) | 0.4345(2) | 0.0145(4) |
| F(9)   | 2i       | 0.6051(5) | 0.4503(3) | 0.1575(3) | 0.0194(5) |
| O(1)   | 2i       | 0.2293(6) | 0.8352(4) | 0.2272(3) | 0.0181(5) |
| O(2)   | 2i       | 0.3227(6) | 0.3989(4) | 0.6656(3) | 0.0207(6) |
| Li(1)  | 1c       | 0.440(3) | 0.607(2) | 0.0221(18) | 0.023(3) |
| Li(2)  | 2i       | 0.6051(5) | 0.2556(3) | 0.4345(2) | 0.0145(4) |

When the \( [\text{Mo}_2\text{O}_2\text{F}_9]^– \) anion is viewed from the side, so that the respective Mo atoms are eclipsing, it can be seen that the adjacent F atoms are nearly eclipsing. The smallest of these

Figure 2. The \( [\text{Mo}_2\text{O}_2\text{F}_9]^– \) anion observed in \( \text{Rb}[\text{Mo}_2\text{O}_2\text{F}_9] \). Displacement ellipsoids are shown at a 70 % probability level at 100 K.
torsion angles range between 2.393(11)° and 6.781(12)°. Upon comparison of the torsion angles between Ft atoms in the $M[\text{Mo}_2\text{O}_2\text{F}_9]$ ($M = \text{Na}-\text{Cs}$) salts, a trend became apparent: the larger the respective cation, the larger the respective torsion angles. That is, nearly eclipsing Ft atoms were observed in Li$[\text{Mo}_2\text{O}_2\text{F}_9]$ while a more staggered conformation of Ft atoms was observed in Cs$[\text{Mo}_2\text{O}_2\text{F}_9]$. A schematic showing the differences in torsion angle can be seen in Figure S4. A complete list of torsion angles observed in Li$[\text{Mo}_2\text{O}_2\text{F}_9]$ is reported in Table S1. A list of selected atomic distances and angles observed in the $M[\text{Mo}_2\text{O}_2\text{F}_9]$ ($M = \text{Li}-\text{Cs}$) salts is reported in Table 3.

In comparison to the other salts reported here, Li$[\text{Mo}_2\text{O}_2\text{F}_9]$ has the largest range for its Mo–Ft atomic distances, ranging from 1.829(2) to 1.895(2) Å. Additionally, the shortest Mo–μ–F atomic distances were observed in Li$[\text{Mo}_2\text{O}_2\text{F}_9]$, ranging from 2.110(2) to 2.114(2) Å. The Mo–O atomic distances in Li$[\text{Mo}_2\text{O}_2\text{F}_9]$ have values of 1.650(3) and 1.653(3) Å and the Mo–Ft atomic distance is 2.1489(15) Å. The Mo–μ–F atomic distance range between 9.087(21)° and 15.491(22)°. These angles are larger than those observed in Li$[\text{Mo}_2\text{O}_2\text{F}_9]$ but smaller than those observed in K$[\text{Mo}_2\text{O}_2\text{F}_9]$. A list of all torsion angles observed in Na$[\text{Mo}_2\text{O}_2\text{F}_9]$ is reported in Table S2. Na$[\text{Mo}_2\text{O}_2\text{F}_9]$ has the longest Mo–O atomic distance in the series, having a value of 1.660(5) Å. Mo–Ft atomic distances range between 1.828(4) and 1.871(4) Å. The Mo–μ–F atomic distance is 2.1489(15) Å and the Mo–μ–F–Mo angle is 150.7(3)°. A section of the crystal structure of Na$[\text{Mo}_2\text{O}_2\text{F}_9]$ is shown in Figure 3. To the best of our knowledge, the compound represents a new structure type.

The coordination of the [Mo$_2$O$_2$F$_9$]$^-$ anions to the sodium cations again leads to the formations of two-dimensional infinite sheets which are parallel to the b–c plane, see Figure S6.

Table 4. Atomic coordinates and equivalent isotropic displacement parameters $U_{iso}$ for Na[Mo$_2$O$_2$F$_9$].

| Atom | Position | $x$ | $y$ | $z$ | $U_{iso}$/Å$^2$ |
|------|----------|----|----|----|---------------|
| Mo(1)| 4g       | 0.25927(6) | 0.76012(7) | 0.43034(6) | 0.01342(13)  |
| F(1) | 2e       | 0   | 0.6764(8) | 1/4 | 0.0208(11)   |
| F(2) | 4g       | 0.2791(6) | 0.4755(6) | 0.4260(6) | 0.0266(9)    |
| F(3) | 4g       | 0.1433(6) | 0.2804(7) | 0.0763(5) | 0.0267(9)    |
| F(4) | 4g       | 0.1647(6) | 0.0246(6) | 0.3934(6) | 0.0276(10)   |
| F(5) | 4g       | 0.3084(7) | 0.2154(10)| 0.7429(6) | 0.0394(13)   |
| O(1) | 4g       | 0.4602(7) | 0.1857(7) | 0.0735(6) | 0.0218(9)    |
| Na(1)| 2e       | 0   | 0.3027(5) | 1/4 | 0.0176(7)    |

The smallest torsion angles between adjacent Ft atoms (seen when the [Mo$_2$O$_2$F$_9$]$^-$ anion is viewed along the Mo–Mo axis) range between 9.087(21)° and 15.491(22)°. These angles are larger than those observed in Li[Mo$_2$O$_2$F$_9$] but smaller than those observed in K[Mo$_2$O$_2$F$_9$]. A list of all torsion angles observed in Na[Mo$_2$O$_2$F$_9$] is reported in Table S2. Na[Mo$_2$O$_2$F$_9$] has the longest Mo–O atomic distance in the series, having a value of 1.660(5) Å. Mo–Ft atomic distances range between 1.828(4) and 1.871(4) Å. The Mo–μ–F atomic distance is 2.1489(15) Å and the Mo–μ–F–Mo angle is 150.7(3)°. A section of the crystal structure of Na[Mo$_2$O$_2$F$_9$] is shown in Figure 4. To the best of our knowledge, the compound represents a new structure type.

Figure 3. Section of the crystal structure of Li[Mo$_2$O$_2$F$_9$]. Displacement ellipsoids are shown at a 70% probability level at 100 K, grey atoms indicate Li atoms with site disorder.

Figure 4. Section of the crystal structure of Na[Mo$_2$O$_2$F$_9$]. Displacement ellipsoids are shown at a 70% probability level at 100 K.

3. Single Crystal Structure of K[Mo$_2$O$_2$F$_9$]

K[Mo$_2$O$_2$F$_9$] crystallizes in the monoclinic space group P2/c with the lattice parameters $a = 5.4386(4)$, $b = 5.0712(3)$, $c = 15.1497(10)$ Å, $\beta = 105.842(6)$°, $V = 401.96(5)$ Å$^3$, $Z = 2$, $T = 100$ K. Atomic coordinates and equivalent isotropic displacement parameters for K[Mo$_2$O$_2$F$_9$] are reported in Table 5. It was observed that the K[Mo$_2$O$_2$F$_9$], Rb[Mo$_2$O$_2$F$_9$], and Cs[Mo$_2$O$_2$F$_9$] salts are isotypic to each other, so only the potassium salt will be discussed in detail. Additionally, these salts are also isotypic to the previously reported [H$_3$O]W$_2$O$_2$F$_9$ salt. [23]

In the K[Mo$_2$O$_2$F$_9$] salt, the K$^+$ cation is coordinated by twelve F atoms, ten Ft atoms and two μ-F atoms (belonging to four different [Mo$_2$O$_2$F$_9$]$^-$ anions), creating a distorted anti-
cuboctahedral coordination polyhedron around the cation. A depiction of the coordination environment surrounding the K⁺, Rb⁺, and Cs⁺ cations is shown in Figure S7. The coordination of the [Mo₂O₂F₉]⁻ anions to the K, Rb, and Cs cations, respectively, leads to the formation of two-dimensional infinite sheets parallel to the a–b plane, see Figure S8.

The smallest torsion angles between adjacent Ft atoms (seen when the [Mo₂O₂F₉]⁻ anion is viewed along the Mo–Mo bond) range between 31.596(73)° and 36.571(76)°. Similar torsion angles are observed in the rubidium salt. A complete list of torsion angles observed in the potassium, rubidium, and cesium salts are compared, it is seen that a slight increase in the angle is observed with increase in cation size. Other than this trend, no obvious trend in Mo–μ-F–Mo angles could be determined for the [Mo₂O₂F₉]⁻ (M = Li–Cs) series. A section of the crystal structure of K[Mo₂O₂F₉] is shown in Figure 5.

Furthermore, a trend among the isotypic crystal structures was observed: as the cation increases from K to Cs, the length of the a- and b-axes increase while the length of the c-axis decreases. The increase in cation size pushes the [Mo₂O₂F₉]⁻ anions away from each other within the two-dimensional infinite layers. This outward displacement within the layers allows for a compression of the crystal structure along the c-axis as M--O (M = K–Cs) distances decrease with increases in cation size, refer to Figure S9.

4. Single Crystal Structure of Rb[Mo₂O₂F₉]

Rb[Mo₂O₂F₉] crystallizes with the lattice parameters a = 5.6244(3), b = 5.1946(2), c = 14.9973(8) Å, α = 106.748(5)°, β = 89.748(5)°, γ = 90.000(2)°, V = 419.58(4) Å³, Z = 2, T = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for Rb[Mo₂O₂F₉] are reported in Table 6.

The torsion angles between adjacent Ft atoms (Figure S4) are similar to those in K[Mo₂O₂F₉], and range between 35.034(62)° and 39.652(66)°. The Mo–O–Mo–μ-F–Mo angle observed in Rb[Mo₂O₂F₉] has a value of 138.89(10)°, a value larger than that observed in the potassium salt, but smaller than that observed in the cesium salt.

5. Single Crystal Structure of Cs[Mo₂O₂F₉]

Cs[Mo₂O₂F₉] crystallizes with the lattice parameters a = 5.9162(3), b = 5.4203(3), c = 14.7154(7) Å, α = 107.888(3)°, β = 108.554(4)°, γ = 90.000(2)°, V = 5.9162(3) Å³, Z = 4, T = 100 K. Atomic coordinates and equivalent isotropic displacement parameters for Cs[Mo₂O₂F₉] are reported in Table 7.

The torsion angles between adjacent Ft atoms (Figure S4) range between 40.607(13)° to 44.819(14)°. The Mo–O atomic distances range between 1.8439(14) and 1.8547(14) Å, while the Mo–Ft distances range between 1.646(2) and 1.8598(17) Å. The smallest Mo–μ-F–Mo distance in Rb[Mo₂O₂F₉] is 4.0098(2) Å, while the Mo–O distance has a value of 2.1624(7) Å. Cs[Mo₂O₂F₉] has a Mo–μ-F–Mo angle of 138.89(10)°, a value larger than that observed in the potassium salt, but smaller than that observed in the cesium salt.
distance in Cs[Mo₂O₂F₉] is 1.651(3) Å. The Mo–F₄ atomic distances range between 1.847(3) and 1.860(3) Å, and the Mo–μ–F atomic distance is 2.1509(14) Å. The Mo–F₄–Mo angle has a value of 140.7(2)°, giving rise to an angle larger than those observed in the potassium and rubidium salts, but smaller than those found in the sodium and lithium salts.

Upon comparison of the salts reported here, it is seen that Li[Mo₂O₂F₉] crystallizes in the triclinic space group P2₁/a. The potassium, rubidium, and cesium salts were observed to be isotypic to one another, as well as the previously reported H₂O[W₂O₇F₉] salt. In the crystal structures of the M[Mo₂O₂F₉] (M = Li–Cs) salts, the [Mo₂O₂F₉]⁻ anion coordinates to the respective cation to form infinite sheets. These sheets are parallel to the (011) plane in Li[Mo₂O₂F₉], the b–c plane in Na[Mo₂O₂F₉], and the a–b plane in the potassium, rubidium and cesium salts.

The Mo–μ–F, Mo–F₄ and Mo–O atomic distances found in the M[Mo₂O₂F₉] (M = Li–Cs) salts are comparable to those found in other molybdenum fluorides and oxyfluorides.[11,27] No obvious explanation could be found to explain the trend in Mo–μ–F–Mo angles observed in the salts reported here. It was observed that torsion angles between adjacent F₄ atoms, however, steadily increased with increasing cation size.

Lastly, to conclude this section, a comparison of the MoVI salts reported in this work will be made to the previously reported K₂(NMe₄)[MoV–F₄][30] and the previously reported K₂(NMe₄)[MoV–F₄]·3H₂O and (NH₄)₃[MoV–F₄][31] salts. In the crystal structures of the MoVI salts reported here, it was shown that the Mo–O distances are comparable, whereas the Mo–F atomic distances are, on average, larger in the [MoV–F₄][30] salts than in the [MoV–F₄]·3H₂O and (NH₄)₃[MoV–F₄][31]. This observation is expected since the repulsion arising from the additional negative charge found in the [Mo(V)–F₄][30] salts can be mitigated by larger Mo–F–Mo angles. Furthermore, upon comparison of atomic distances in the [Mo(V)₂–F₄][30] anions to the [Mo(VI)₂–F₄][30] anions reported here, it was shown that the Mo–O distances are comparable, whereas the Mo–F atomic distances are, on average, larger in the [Mo(VI)₂–F₄][30] anions. Again, such an observation is expected because the presence of additional negative charge on the [Mo(VI)₂–F₄][30] anion leads to increased electronic repulsion between the F and Mo atoms, which subsequently increases Mo–F atomic distances.

**Infrared Spectroscopy**

An IR spectrum for each M[Mo₂O₂F₉] (M = Li–Cs) salt was collected at 25 °C in the region of 4000 to 400 cm⁻¹. Band positions are listed in Table 8. Calculated IR spectra were obtained for the solid-state structure of each salt using the DFT-PBE0 density functional method; combination bands and overtones

| Li[Mo₂O₂F₉] | Na[Mo₂O₂F₉] | K[Mo₂O₂F₉] | Rb[Mo₂O₂F₉] | Cs[Mo₂O₂F₉] |
|-------------|-------------|-------------|-------------|-------------|
| 403 ν(Mo–F₄) | 434 ν(Mo–F₄) | 412 ν(Mo–F₄) | 407 ν(Mo–F₄) | 408 ν(Mo–F₄) |
| 470 ν(Mo–F₄) | 593 ν(Mo–F₄) | 451 | 468 | 492 |
| 552 νₓ(Mo–F₄) | 564 νₓ(Mo–F₄) | 569 νₓ(Mo–F₄) | 553 ν(Mo–F₄) | 593 ν(Mo–F₄) |
| 614 νₙ(Mo–F₄) | 630 ν(Mo–F₄) | 525 ν(Mo–F₄) | 627 ν(Mo–F₄) | 646 ν(Mo–F₄) |
| 663 ν(Mo–F₄) | 697 ν(Mo–F₄) | 697 ν(Mo–F₄) | 649 ν(Mo–F₄) | 646 ν(Mo–F₄) |
| 847 | 846 | 863 | 857 | 850 |
| 958 | 941 | 911 | 907 | 968 |
| 988 | 976 | 976 | 956 | 977 |
| 1017 ν(Mo–O) | 1019 ν(Mo–O) | 1015 ν(Mo–O) | 1037 ν(Mo–O) | 1018 ν(Mo–O) |
| 1101 (ν₂ HF₂⁻)[30] | 1157 (ν₂ HF₂⁻) [31] | 1211 (ν₂ HF₂⁻) [29,30] | 1300 | 1366 |
| 1580 (ν₃ HF₂⁻) [29,30] | 1743 (ν₃ HF₂⁻) [30,31] | 2359 (combination H₂F₄⁻) [31] |
bands were not accounted for. Experimental spectra correlated well with the calculated spectra (Figure 6; Figures S10–S13, Tables S4–S8), however, the experimentally obtained spectra show additional bands belonging to by-products. Powder diffraction patterns of each sample were recorded to aid in the identification of the by-products. However, due to the quality of the diffraction patterns, unambiguous identification of the by-products was not possible. Therefore, a discussion of potential by-products will be provided based on the reported IR spectra. Powder diffraction patterns are shown in Figures S15–S19.

The remaining experimentally obtained and calculated IR spectra of salts containing the \([\text{MoO}_2\text{F}_9]^-\) anion. \([\text{MoOF}_5]\) was reported, they observed a series of bands in the IR region of 930 to 975 cm\(^{-1}\).\(^{[16]}\) They attributed the observation of these bands to hydrolysis products of the \([\text{MoO}_2\text{F}_9]\) salt.\(^{[16]}\) However, since the samples presented in this work were handled under strictly-dried atmospheres, and because there is no evidence of water or hydroxides in the spectra presented here, it seems highly unlikely that the bands observed in this work arise because of hydrolysis products. Moreover, in the work of Bougon and co-workers, \([\text{NO}[\text{MoF}_5]\) bands in the IR region of 930 to 975 cm\(^{-1}\).\(^{[16]}\) They attributed the observation of these bands to hydrolysis products of the \([\text{NO}[\text{MoF}_5]\) and \([\text{ClOF}_2][\text{MoF}_5]\) salts correlate well to those observed in this work. However, the authors observed bands at 910, 935, 967, 973, and 983 cm\(^{-1}\) in the spectrum of \([\text{NO}[\text{MoF}_5]\) which do not belong to the \([\text{MO}[\text{F}_5]\) anion. They assigned the band at 983 cm–1 to NO\([\text{MOF}_5]\ but because there is no evidence of water or hydroxides in the spectra presented here, it seems highly unlikely that the bands observed in this work arise because of hydrolysis products. Moreover, in the work of Bougon and co-workers, NO\([\text{MOF}_5]\) bands in the IR region of 930 to 975 cm\(^{-1}\).\(^{[16]}\) They attributed the observation of these bands to hydrolysis products of the NO\([\text{MOF}_5]\) and ClOF\(_2\)[MoF\(_5\)] salts correlate well to those observed in this work. However, the authors observed bands at 910, 935, 967, 973, and 983 cm\(^{-1}\) in the spectrum of NO\([\text{MOF}_5]\) which do not belong to the \([\text{MO}[\text{F}_5]\) anion. They assigned the band at 983 cm–1 to NO\([\text{MOF}_5]\) but gave no further discussion on the occurrence of the remaining bands.\(^{[12]}\)

To determine if the \([\text{MOF}_5]^+\) anion is responsible for the observation of bands arising between 850 and 990 cm\(^{-1}\) which do not belong to the \([\text{MO}[\text{F}_5]\) anion. The work of Beuter and Sawodny, in which \([\text{Rb}[\text{MO}[\text{F}_5]\) was reported, they observed a series of bands in the IR region of 850 to 990 cm\(^{-1}\).\(^{[13]}\) They attributed the observation of these bands to hydrolysis products of the \([\text{Rb}[\text{MO}[\text{F}_5]\) salt.\(^{[13]}\) However, since the samples presented in this work were handled under strictly-dried atmospheres, and because there is no evidence of water or hydroxides in the spectra presented here, it seems highly unlikely that the bands observed in this work arise because of hydrolysis products. Moreover, in the work of Bougon and co-workers, \([\text{NO}[\text{MO}[\text{F}_5]\) bands in the IR region of 930 to 975 cm\(^{-1}\).\(^{[16]}\) They attributed the observation of these bands to hydrolysis products of the \([\text{NO}[\text{MO}[\text{F}_5]\) and \([\text{ClOF}_2][\text{MO}[\text{F}_5]\) salts correlate well to those observed in this work. However, the authors observed bands at 910, 935, 967, 973, and 983 cm\(^{-1}\) in the spectrum of NO\([\text{MO}[\text{F}_5]\) which do not belong to the \([\text{MO}[\text{F}_5]\) anion. They assigned the band at 983 cm–1 to NO\([\text{MO}[\text{F}_5]\) but gave no further discussion on the occurrence of the remaining bands.\(^{[12]}\)

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lated IR spectrum, though, it can be said that the bands arising between 850 to 970 cm⁻¹ in the spectra reported in this work are not observed because of a possible presence of the [MoOF₅]⁻ anion. The fact that similar bands are seen in the IR spectra of previously reported [Mo₂O₂F₉]⁻ anions, though, may provide insight into the complex equilibria that seemingly exists during the formation of the [Mo₂O₂F₉]⁻ anion.

Raman Spectroscopy

Raman spectra were obtained for each M[Mo₂O₂F₉] (M = Li–Cs) salt at 25 °C from about 0 to 1200 cm⁻¹. Except for K[Mo₂O₂F₉], all spectra were recorded at an excitation wavelength of 532 nm. The K[Mo₂O₂F₉] salt showed strong fluorescence at this wavelength and so Raman data for this salt was collected at an excitation wavelength of 785 nm. Band locations for these experimental spectra are listed in Table 9. Calculated Raman spectra from 0 to 1200 cm⁻¹ were obtained for the solid-state structures of each salt using the DFT-PBE0 density functional method. Experimentally obtained spectra correlated well with the calculated spectra, however, the experimentally obtained spectra show additional bands belonging to by-products (Figure 7; Figures S20–S23, Tables S10–S14). Powder diffraction patterns of each sample were recorded to aid in the identification of the by-products. However, due to the quality of the diffraction patterns, unambiguous identification of the by-products was not possible. Therefore, a discussion of potential by-products will be provided based on the reported Raman spectra.

Band assignments in Table 9, when given, were made by the visual inspection of the calculated normal modes using the Jmol software[28] and through direct comparison to the experimentally obtained bands. As an example of a typical spectrum obtained from these salts, the Raman spectrum of Na[Mo₂O₂F₉] is given in Figure 7. The remaining experimentally obtained and calculated Raman spectra are shown in Figures S20–S24.

Table 9. Experimental Raman bands observed in the M[Mo₂O₂F₉] (M = Li–Cs) salts. When given, a description of vibrational modes is as follows: ν = stretching, δ = deformation, ρw = wagging, ρr = rocking, ρt = twisting, s = symmetric, as = asymmetric. Fμ refers to the bridging fluorine atoms and Ft refers to terminal fluorine atoms.

| Li[Mo₂O₂F₉] | Na[Mo₂O₂F₉] | K[Mo₂O₂F₉][a] | Rb[Mo₂O₂F₉] | Cs[Mo₂O₂F₉] |
|-------------|-------------|-------------|-------------|-------------|
| 194 ν(F⁻–Mo–F⁻) | 211 δ(F⁻–Mo–F⁻) | 202 ρ(F⁻–Mo–F⁻) | 221 δ(F⁻–Mo–F⁻); ρ(F⁻–Mo–F⁻) | 220 δ(F⁻–Mo–F⁻); ρ(F⁻–Mo–F⁻) |
| 222 δ(F⁻–Mo–F⁻) | 220 δ(F⁻–Mo–F⁻); ρ(F⁻–Mo–F⁻) | 268 δ(F⁻–Mo–O⁻) | 268 δ(F⁻–Mo–O⁻) | |
| 299 δ(F⁻–Mo–O⁻) | 305 δ(F⁻–Mo–F⁻); ρ(F⁻–Mo–F⁻) | 313 δ(F⁻–Mo–F⁻); F⁻–Mo–O⁻) | 319 ρ(F⁻–Mo–O⁻) | 396 |
| 319 δ(F⁻–Mo–O⁻) | 303 δ(F⁻–Mo–F⁻); ρ(F⁻–Mo–F⁻) | 312 δ(F⁻–Mo–F⁻); F⁻–Mo–O⁻) | 317 δ(F⁻–Mo–O⁻) | |
| 416 | 566 νₚ(Mo–F⁻) | 571 νₚ(Mo–F⁻) | 572 νₚ(Mo–F⁻) | 558 |
| | 576 νₚ(Mo–F⁻) | | | |
| 669 νₖ(Mo–F⁻) | 668 νₚ(Mo–F⁻) | 646 νₚ(Mo–F⁻) | 656 νₚ(Mo–F⁻); νₚ(Mo–F⁻) | 676 νₚ(Mo–F⁻) |
| 694 νₖ(Mo–F⁻) | 691 νₚ(Mo–F⁻) | 681 νₚ(Mo–F⁻) | 678 νₚ(Mo–F⁻) | |
| 941 938 971 983 | 922 962 977 976 |
| 1027 ν(Mo–O⁻) | 1029 ν(Mo–O⁻) | 1028 ν(Mo–O⁻) | 1025 ν(Mo–O⁻) | 1020 ν(Mo–O⁻) |

[a] Data collected at a wavelength of 785 nm.
The bands arising from the [Mo$_2$O$_2$F$_9$]$^-$ anion in the M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts correlate well with the Raman bands reported for the ClOF$_2$[Mo$_2$O$_2$F$_9$] and NO[Mo$_2$O$_2$F$_9$] salts.[12] The Raman spectra of each salt, in the region of about 0 to 400 cm$^{-1}$, is dominated by various Mo–O and Mo–F deformation, wagging, rocking, and twisting modes. Similar to 145 cm$^{-1}$, additional bands arising from the Mo–F stretching (and other vibrational modes). This calculated stretching mode $\nu$ (A$_{1g}$) and the librational lattice mode (E$_g$), which occur at about 630 and 145 cm$^{-1}$, respectively.[33] Since the backgrounds in the early region of the Raman spectra are large, it is hard to determine if any bands are present around 100 cm$^{-1}$. Additionally, bands arising from the Mo–F stretching modes of the [Mo$_2$O$_2$F$_9$]$^-$ anion occur in the region where the symmetric stretching mode of the HF$_2^-$ anion is expected to occur. It is, therefore, difficult to identify the presence of the bifluoride anion in these Raman spectra. Moreover, the presence of the HF$_2^-$ anion was evidenced in the IR spectrum of K[Mo$_2$O$_2$F$_9$]. However, the Raman spectrum of K[Mo$_2$O$_2$F$_9$] shows no foreign bands (i.e. all bands could be assigned to the [Mo$_2$O$_2$F$_9$]$^-$ anion). Reasons for this observation may stem from the fact that this Raman spectrum was collected at 785 nm and it was noticed that the background in this spectrum was much higher than those seen in the other spectra. It could be that the noise in this spectrum masks any bands arising from the HF$_2^-$ anion.

Just as in the IR spectra, the Raman spectra of all salts, with the exception of K[Mo$_2$O$_2$F$_9$], show a series of bands around 900 to 1000 cm$^{-1}$ which are not explained by the presence of the [Mo$_2$O$_2$F$_9$]$^-$ anion. In the spectra of Li[Mo$_2$O$_2$F$_9$], Rb[Mo$_2$O$_2$F$_9$], and Cs[Mo$_2$O$_2$F$_9$], these bands have considerable intensities when compared to the bands arising from the [Mo$_2$O$_2$F$_9$]$^-$ anion. In the spectrum of Na[Mo$_2$O$_2$F$_9$], however, these bands are quite weak in comparison to the [Mo$_2$O$_2$F$_9$]$^-$ anion bands, and in the spectrum of K[Mo$_2$O$_2$F$_9$] these bands are missing entirely. In the work of Bougon and co-workers, in which NO[Mo$_2$O$_2$F$_9$] was synthesized, they described an IR band at 983 cm$^{-1}$, which was sometimes present in the Raman spectrum as a weak band.[12] They attribute this band to the presence of NO[MoOF$_4$].

Again, to determine if the [MoOF$_3$]$^-$ anion was present in our samples, a Raman spectrum of a Cs$_6$[MoOF$_3$]$^-$ anion was calculated using the DFT-PBEO density functional method and the def2-TZVP basis set and is shown in Figure S24 (band locations and intensities reported in Table S15). This spectrum showed a band at 1038 cm$^{-1}$ corresponding to Mo–O stretching and several other bands below 700 cm$^{-1}$ corresponding to Mo–F stretching (and other vibrational modes). This calculated Raman spectrum correlates well to previously reported Raman spectra of salts containing the [MoOF$_3$]$^-$ anion.[12,32] Moreover, the calculated Raman spectrum of the [MoOF$_3$]$^-$ anion is somewhat similar to the calculated Raman spectra of the [Mo$_2$O$_2$F$_9$]$^-$ anions calculated here. Therefore, as was the conclusion in the IR spectroscopy analysis, it would be hard to determine the presence of the [MoOF$_3$]$^-$ anion in the sample mixtures with Raman spectroscopy alone. Based on the calculated Raman spectrum, though, it can be said that the bands arising between 900 to 970 cm$^{-1}$ in the Raman spectra reported in this work are not observed because of a possible presence of the [MoOF$_3$]$^-$ anion.

Conclusions

A series of M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts was synthesized through the reaction of MoOF$_4$ with the respective alkali metal fluoride in an aHF solution. The crystal structures of these salts were studied using single-crystal X-ray diffraction. All crystal structures show a layered structure motif. The potassium, rubidium and cesium salts are isotypic. In the case of the lithium salt, disorder was shown by one of the lithium atoms. In all compounds, the [Mo$_2$O$_2$F$_9$]$^-$ anion is observed, which can be thought of as two MoOF$_4$ units bridged by a fluorine anion. IR and Raman spectroscopy were employed to obtain the vibrational spectra of the M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts. Calculated IR and Raman spectra were obtained for the solid state of each salt using the DFT-PBE0 density functional method in order to aid in the assignment of bands in the experimentally obtained spectra. The calculated IR and Raman spectra agree nicely with the experimentally obtained spectra. Evidence for hydrogen fluoride adducts, such as [HF($Farcld)_n]$ (n = 1,2) were observed in some cases. The synthesis of phase-pure M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts was not realized, although their phase-pure synthesis may be possible in solvents which would not directly interact with the starting materials.

It is clear that the reaction conditions leading to the production of the M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts is quite complex, as indicated by the variety of by-products observed within the samples (as evidenced by the IR and Raman spectra and powder X-ray diffraction patterns). Studies in the past which have tried to produce the [MoOF$_3$]$^-$ anion have observed that, in systems with relatively low free F$^-$ concentration, the [Mo$_2$O$_2$F$_9$]$^-$ anion is preferably produced. If the concentration of free F$^-$ is increased, by increasing the concentration of the fluoride salt(s) used, then the [MoOF$_3$]$^-$ anion and, subsequently, the [MoOF$_3$]$^{2-}$ anion may be successfully produced. Since the M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts produced in this work were synthesized using a 1:1 molar ratio of MoOF$_4$ to MF $(M = Li$–Cs), which gave moderate concentrations of free F$^-$ in aHF solution, it is understandable that the M[Mo$_2$O$_2$F$_9$] $(M = Li$–Cs) salts were preferably obtained over species such as M[MoOF$_3$] or M$_2$[MoOF$_4$] $(M = Li$–Cs). The M[MoOF$_3$] and M$_2$[MoOF$_4$] $(M = Li$–Cs) salts may be obtainable if the starting concentration of the respective alkali metal fluoride is increased substantially in comparison to MoOF$_4$.

Experimental Section

General Procedures and Materials: All operations were performed in either stainless steel (316 L) or Monel metal vacuum lines, which
were passivated with 100 % fluorine 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 K2[SiF6], was distilled twice before use. Fluorinated ethylene propylene, FEP (15.90x19.05 mm – 3/4”), was used to produce reaction vessels.

**Synthesis of Li[Mo2O2F9]:** First, MoOF4 was synthesized through the hydrolysis of Mo6F8 in aHF using quartz wool. For this reaction, 0.56 grams of quartz wool, SiO2 (9.32 mmol) was added to an FEP vessel and attached to a metal vacuum line and evacuated and flushed with argon three times. 3 mL of aHF and 5 grams of MoO3 (23.82 mmol) were condensed onto the quartz wool at −196 °C. The reaction vessel was warmed to room temperature and stored for 1 week. After the reaction was completed, as indicated by complete solvation of the SiO2 wool, all volatile products were removed and the MoO2F4 was stored under argon in a glovebox. IR and powder X-ray diffraction showed no evidence of impurities in the MoO2F4 sample.

To produce the M[Mo2O2F9] (M = Li–Cs) salts, an approximately 1:1 molar ratio of MoO2F4 and MF (M = Li–Cs) was mixed using an agate mortar and pestle in an inert atmosphere glovebox and transferred to an FEP reaction vessel. The reaction vessel was attached to a metal vacuum line and evacuated and flushed with argon 3 times. 4 to 6 mL of aHF was condensed onto the reactants and at −196 ºC. The reaction vessels were warmed to room temperature, producing colorless solutions in all cases. Once all reactants had dissolved, the aHF was slowly pumped off to produce colorless, crystalline samples. The products were transferred into an inert atmosphere glovebox for storage. It was noticed after months of storage the samples began to turn gray-blue.

**Synthesis of Li[Mo2O2F9]:** Under inert atmosphere, 123.91 mg of MoOF4 (0.66 mmol) and 17.90 mg of LiF (0.69 mmol) were placed in an FEP reaction vessel. 4 mL of aHF were condensed on top of the reaction mixture. After warming to room-temperature the aHF was slowly pumped off over a period of 5 hours. Product was stored in a PTFE container under argon in a glovebox.

**Synthesis of Na[Mo2O2F9]:** Under inert atmosphere, 125.07 mg of MoOF4 (0.67 mmol) and 27.90 mg of NaF (0.66 mmol) were placed in an FEP reaction vessel. 4 mL of aHF were condensed on top of the reaction mixture. After warming to room-temperature the aHF was slowly pumped off over a period of 5 hours. Product was stored in a PTFE container under argon in a glovebox.

**Synthesis of K[Mo2O2F9]:** Under inert atmosphere, 126.15 mg of MoOF4 (0.67 mmol) and 39.08 mg ofKF (0.67 mmol) were placed in an FEP reaction vessel. 4 mL of aHF were condensed on top of the reaction mixture. After warming to room-temperature the aHF was slowly pumped off over a period of 5 hours. Product was stored in a PTFE container under argon in a glovebox.

**Synthesis of Rb[Mo2O2F9]:** Under inert atmosphere, 127.82 mg of MoOF4 (0.68 mmol) and 69.91 mg of RbF (0.67 mmol) were placed in an FEP reaction vessel. 6 mL of aHF were condensed on top of the reaction mixture. After warming to room-temperature the aHF was slowly pumped off over a period of 5 hours. Product was stored in a PTFE container under argon in a glovebox.

**Synthesis of Cs[Mo2O2F9]:** Under inert atmosphere, 128.78 mg of MoOF4 (0.69 mmol) and 102.82 mg of CsF (0.68 mmol) were placed in an FEP reaction vessel. 6 mL of aHF were condensed on top of the reaction mixture. After warming to room-temperature the aHF was slowly pumped off over a period of 5 hours. Product 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 M[Mo2O2F9] (M = Li–Cs) were carried out with a STOE IPDS 2T diffractometer with plane graphite-monochromated molybdenum radiation (Mo-Kα, λ = 0.71073 Å) generated by a sealed X-ray tube (12 x 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. [34] The structures were solved using Direct Methods (SHELXT 2014/5) and refined against F² (SHELXL-2018/3). [35,36] Representations of the crystal structure were created using the Diamond software. [17]

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: crys-data@fiz-karlsruhe.de), on quoting the depository numbers CSD-1903263 (Li[Mo2O2F9]), CSD-1903264 (Na[Mo2O2F9]), CSD-1903262 (K[Mo2O2F9]), CSD-1903266 (Rb[Mo2O2F9]), and CSD-1903265 (Cs[Mo2O2F9]).

**Powder X-ray Diffraction:** Powder X-ray diffraction patterns were obtained with a StadiMP diffractometer (Stoe) using Cu-Kα radiation (λ = 1.54059 Å), a germanium monochromator and a Mythen1K detector. The samples were placed in 0.3 mm glass capillaries and sealed using a hot tungsten wire and Pizein. The data were processed in and graphical representations were created using the WinXPOW software. [38]

**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. [39]

**Raman Spectroscopy:** The M[Mo2O2F9] (M = 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.

**Computational Details:** Periodic quantum chemical calculations were carried out for the M[Mo2O2F9] (M = Li–Cs) salts using the DFT-PBE density functional method (DFT). [40,41] A triple-zeta-valence + polarization (TZVP) level basis set was applied for Mo and split-valence + polarization (SVP) level basis sets were applied for the other atoms. The basis set for Mo was taken from previous study on MoF6. [27] The basis sets for Li, Na, K, Rb, Cs, O, and F were also taken from previous studies (see Supporting Information for full basis set details). [42–45] All calculations were carried out using the CRYSTAL17 program package. [46] The reciprocal space for the salts was sampled using the respective Monkhorst-Pack-type k-point grid: Li[Mo2O2F9]: 4x3x2, Na[Mo2O2F9]: 3x4x3, K[Mo2O2F9]: 4x4x2, Rb[Mo2O2F9]: 4x4x2, Cs[Mo2O2F9]: 2x4x2. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used for all calculations. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. Default optimization convergence thresholds were applied in all calculations. The XYZ coordinates used in the computational calculations of each salt in the solid-state, and the [MoOF4]²⁻ anion, are reported in Tables S16–S21.

The harmonic vibrational frequencies, IR intensities, and Raman intensities were obtained by using the computational scheme implemented in CRYSTAL17 [5–8]. [47–50] The Raman intensities were calcu-
lated 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.[28]

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Keywords: Molybdenum · Fluorides · Oxides · Crystal structures · IR spectroscopy · Raman spectroscopy

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