Inorganic Chemistry

“Synthesis and Characterization of Novel Fluorinated Polyoxomolybdates”

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Supporting Information

Table of Contents

Table S1 Survey of the most important fluoromolybdate types	S1
Literature: Table S1	S2
Table S2 Elementary analyses	S3
Table S3 Fractional atomic coordinates for $\text{Na}_2\text{K}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 2\text{H}_2\text{O}$	S4
Figure S1. Coordination environments Cs1 and Cs2 in $\text{Li}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$	S5
Figure S2. Coordination environments Cs1 and Cs2 in $\text{Na}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$	S6
Figure S3. Rietveld refinement plot of the laboratory X-ray powder diffraction data of $\text{Na}_2\text{K}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 2\text{H}_2\text{O}$	S7
Figure S4. Electron density plot	S8
Figure S5. Unit cell diagrams of t- and m- $\text{Na}_2(\text{NMe}_4)_3\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 6\text{H}_2\text{O}$	S9

Table S1 Survey of the most important fluoromolybdate types

Molybdate	Ox. (Mo)	Structural Motif	Lit.
Isolated octahedra:			
M_2MoOF_5	V	$MoOF_5^{2-}$ octahedra	(1)
$MMoOF_5$	VI	$MoOF_5^-$ octahedra	(2)
$M_2MoO_2F_4$	VI	$MoO_2F_4^{2-}$ -octahedra	(3)
$M_3MoO_3F_3$	VI	$MoO_3F_3^{3-}$ octahedra	(4)
Dimers:			
$M[Mo_2O_2F_9]$	VI	pairs of corner-sharing octahedra	(5)
$M_3[Mo_2O_2F_9]$	V	pairs of corner-sharing octahedra	(6)
$M_4Mo_2O_5F_7(HF_2)_3 \cdot H_2O$	VI	corner-sharing $[Mo_2O_5F_6]^{4-}$ -anions	(7)
$M_4[Mo_2O_4F_6]$	V	edge-sharing octahedral pairs	(8)
$M_2[Mo_2O_4F_4(H_2O)_2]$	V	edge-sharing octahedral pairs	(8)
$M_3Mo_2O_6F_3$	VI	face-sharing octahedral pairs	(6)
Trimers:			
$M_5[Mo_3O_4F_9]$	IV	edge-sharing octahedra	(9)
$M_2MoO_3F_4$	VI	corner-sharing <i>trans</i> chains	(10)
$MMoO_2F_3$	V	corner-sharing <i>cis</i> chains	(11)
$M_2MoO_3F_2$	VI	corner-sharing <i>trans</i> chains	(12)
$MMoO_3F$	VI	double chains	(13)
Fluoromolybdate clusters:			
$[Mo_4O_{12}F_2]^{2-}$	VI	$[Mo_4O_{12}F_2] \cdot [Mo_6O_{19}]$ cluster pairs	(14)
$M_6[Mo_6O_{18}F_6]$	VI	$[Mo_6O_{18}F_6]^{6-}$ cluster	this work
$M_5[Mo_7O_{22}F_3]$	VI	$[Mo_7O_{22}F_3]^{5-}$ cluster	this work
$M_6[Mo_8O_{26}F_2]$	VI	$[Mo_8O_{26}F_2]^{6-}$ cluster	(15)

Literature: Table S1

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Table S2 Elementary analyses for hexafluorohexa- and trifluoroheptamolybdates (calculated values in *italics*; Type 2a compounds: calculation for $n = 6$)

Compound	F / %	H / %	N / %	C / %
$\text{Li}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$ (1)	7.69 / 6.99	0.63 / 0.74	---	---
$\text{Na}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$ (2)	6.58 / 6.85	0.69 / 0.72	---	---
$\text{Na}_2\text{K}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 2\text{H}_2\text{O}$ (2a)	8.70 / 8.85	0.84 / 0.93	---	---
$\text{Na}_2\text{Rb}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot n\text{H}_2\text{O}$ (2a)	7.54 / 7.74	0.79 / 0.81	---	---
$\text{Na}_2(\text{NH}_4)_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot n\text{H}_2\text{O}$ (2a)	9.13 / 9.47	2.14 / 2.33	2.14 / 2.33	---
0.9 $\text{Na}_4(\text{NMe}_4)_2\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 10\text{H}_2\text{O} \cdot$ 0.1 $\text{Na}_3(\text{NMe}_4)_2\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 9\text{H}_2\text{O}$ (3)	7.90 / 7.71	2.93 / 3.12	1.98 / 1.99	6.82 / 6.84
m- $\text{Na}_2(\text{NMe}_4)_3\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 6\text{H}_2\text{O}$	3.92 / 3.91	3.07 / 3.30	2.88 / 2.88	10.06 / 9.89
t- $\text{Na}_2(\text{NMe}_4)_3\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 6\text{H}_2\text{O}$	4.32 / 4.77	3.06 / 3.06	2.82 / 2.74	9.79 / 9.41

Table S3 Fractional atomic coordinates for Na₂K₄Mo₆O₁₈F₆·2H₂O

Atom	x	y	z
Mo1	0.6693(5)	0.4977(8)	0.8466(7)
Mo2	0.5075(4)	0.7588(8)	0.7742(5)
Mo3	0.3424(4)	0.7500(8)	0.9301(5)
Na1	0.405(2)	0.377(2)	0.801(2)
K1	0.9340(9)	0.639(1)	0.853(1)
K2	0.2503(8)	0.159(1)	0.981(1)
F1	0.543(2)	0.362(3)	0.892(3)
F2	0.605(2)	0.694(3)	0.957(3)
F3	0.431(2)	0.609(3)	0.849(4)
O1	0.752(2)	0.427(3)	0.063(3)
O2	0.553(3)	0.578(3)	0.745(3)
O3	0.460(2)	0.832(3)	0.976(3)
O4	0.726(2)	0.403(4)	0.757(4)
O5	0.713(2)	0.627(4)	0.708(3)
O6	0.427(2)	0.752(4)	0.626(3)
O7	0.575(3)	0.878(4)	0.736(3)
O8	0.259(2)	0.815(3)	0.773(3)
O9	0.311(2)	0.844(4)	0.012(4)
Water-O1	0.098(2)	0.878(3)	0.876(3)
Water-H1	0.149(2)	0.831(3)	0.943(3)
Water-H2	0.066(2)	0.924(3)	0.935(3)

Figure S1. Coordination environments of (a) Cs1 and (b) Cs2 in $\text{Li}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$ (ORTEP plots, 70 % probability).

Figure S2. Coordination environment of (a) Cs1 and (b) Cs2 in $\text{Na}_2\text{Cs}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 6\text{H}_2\text{O}$ (ORTEP plots, 70 % probability).

Figure S3. Rietveld refinement plot of the laboratory X-ray powder diffraction data of $\text{Na}_2\text{K}_4\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 2\text{H}_2\text{O}$. The experimental points, calculated profile and difference curves are shown. The ticks below the graph indicate the calculated peak positions. Some of the minor diffraction lines from the unidentified impurity can be seen in the Figure.

Figure S4. Electron density plot for the Mo4 and Na1-positions in $0.9 \text{ Na}_4(\text{NMe}_4)_2\text{Mo}_6\text{O}_{18}\text{F}_6 \cdot 10\text{H}_2\text{O} \cdot 0.1 \text{ Na}_3(\text{NMe}_4)_2\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 9\text{H}_2\text{O}$.

Figure S5. Unit cell diagram of t - (a) and m - $\text{Na}_2(\text{NMe}_4)_3\text{Mo}_7\text{O}_{22}\text{F}_3 \cdot 6\text{H}_2\text{O}$ (b) along the x-axis (a: ORTEP plot, 70 % probability).