

New structural units in molybdenum oxyfluoride chemistry

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Abstract

The solvothermal syntheses and crystal structures of five new molybdenum oxyfluorides are presented. These exhibit three novel structural units, each containing Mo in a reduced oxidation state: a dimeric $[\text{Mo}_2\text{O}_4\text{F}_2(\text{C}_2\text{H}_8\text{N}_2)_2]$ unit (Mo^{4+}), a tetrameric $[\text{Mo}_4\text{O}_8\text{F}_{10}]^{6-}$ unit (Mo^{5+}) and an infinite chain $[\text{MoOF}_3]_n^-$ unit (Mo^{4+}). Mo-Mo bonding is observed in each of the new building units.

Keywords

Molybdenum oxyfluoride; solvothermal synthesis; metal-metal bonding; crystal structure

Highlights

- A facile route to novel reduced molybdenum oxyfluorides
- New dimer and tetramer units containing Mo-Mo bonds
- First example of a reduced, infinitely extended molybdenum oxyfluoride

1. Introduction

The synthetic and structural chemistry of metal oxyfluorides (more precisely ‘oxide fluorides’) is relatively under-developed compared to the corresponding oxide chemistry¹. Recently we have greatly expanded the chemistry of vanadium oxyfluorides, in particular using solvothermal methods, and this has led to a reasonably well-developed understanding of the factors that dictate their compositional and structural features²⁻⁷. In the case of molybdenum oxyfluorides (MoOFs) both solid-state and solution-based methods have been used in the past to prepare a select number of examples of MoOFs containing a variety of structural building units. A summary of the major structural elements that are known for relatively fluorine-rich compositions (ie. O/F \leq 3/1) is presented in Table 1. We note that the majority of these examples are purely inorganic, though there are a couple of ‘hybrid’ cases. In addition, there are further examples of ‘fluorinated polyoxomolybdates’, which have typically higher O/F ratios^{21,22}. We have now begun to explore the solvothermal chemistry of molybdenum in fluorine-rich environments, and here we report some of our preliminary results, in which we isolate three novel structural/compositional building units, each containing Mo in a partially reduced oxidation state.

2. Experimental

2.1 Materials and Methods: All chemicals were purchased from commercial sources and used without further purification. Phase purity of the reaction products was established by comparison of powder X-ray diffraction patterns simulated on the basis of the observed

crystal structures to those measured experimentally on a Stoe STADI/P powder diffractometer, using $\text{CuK}\alpha_1$ radiation. In addition, CHN analysis was carried out (Table 2)

2.2 General Synthesis: Our syntheses are typically carried out in a systematic manner, starting from a simple reaction composition comprising a molybdenum source (MoO_3), hydrofluoric acid (HF, 48% aq.), a mixed water/ethylene glycol (EG) solvent, and an added ‘template’, which may be either an inorganic salt or an organic amine. These are mixed and heated together in a sealed Teflon-lined autoclave for 24 hours. Within each compositional system, variations are made to (i) the water / ethylene glycol ratio (ii) the MoO_3 / template ratio and (iii) the temperature.

For the five reaction products described herein, the specific details of the reactions used to prepare single crystals are given in Table 2.

2.3 X-ray Crystallography: Single crystals were analysed using a Rigaku Mercury CCD equipped with graphite monochromated $\text{MoK}\alpha$ radiation. Intensity data were collected by the narrow frame method at 93 K and corrected for Lorentz and polarisation effects as well as absorption by Multi-Scan techniques. All structures were solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97²³. All non-H atoms were refined with anisotropic thermal parameters; H atoms in **1**, **2** and **5** were treated as ‘riding’. Hydrogen atoms on the NH_4^+ ions in **3** were not located. Correct assignments of O/F atoms were confirmed by bond-valence sum (BVS) analysis^{24,25}. Crystallographic details are provided in Table 3, with selected bond distances in Table 4. Full crystallographic details (cif format) have been deposited*.

3. Results

3.1 Description of the crystal structures

3.1.1 $[\text{C}_2\text{H}_{10}\text{N}_2]_2[\text{Mo}_2\text{O}_5\text{F}_6]$ (1**)** exhibits the corner-shared octahedral dimer unit $[\text{Mo}_2\text{O}_5\text{F}_6]^{4-}$ previously observed in $\text{Ba}_4[\text{Mo}_2\text{O}_5\text{F}_6]\text{F}(\text{HF}_2)_3 \cdot x\text{H}_2\text{O}$ (ref. 15). The structure has one crystallographically-distinct Mo site, which is confirmed as Mo^{6+} by BVS calculations. The dimer may be regarded as composed from two *fac*- MoO_3F_3 octahedra fused through a common O atom (Figure 1). These dimers are interconnected through a hydrogen-bond network *via* the ethylenediammonium cations. The geometry within the dimer is very similar to that observed in the previously reported example¹⁵, and the details of this structure are reported here mainly as a comparison to compound **2**.

3.1.2 $[\text{Mo}_2\text{O}_4\text{F}_2(\text{C}_2\text{H}_8\text{N}_2)_2] \cdot \text{C}_2\text{H}_6\text{O}_2$ (2**)** is an unusual compound incorporating a neutral octahedral dimer (Figure 2) in which two symmetry-equivalent octahedral Mo centres are coordinated by bridging oxide ligands, terminal O/F ligands (disordered) and bidentate ethylenediammine ligands. A molecule of solvent is also incorporated. Elemental analysis supports the assignment of this guest as a neutral ethylene glycol molecule, rather than an ethylenediammine molecule or its protonated cation. The resultant assignment of the 50:50 O/F occupancy of the terminal sites is required by the BVS analysis, which confirms the Mo oxidation state to be +5 (also in agreement with the short Mo-Mo distance suggesting Mo-Mo bonding).

3.1.3 $(\text{NH}_4)_6[\text{Mo}_4\text{O}_8\text{F}_{10}]$ (3**) and $\text{K}_6[\text{Mo}_4\text{O}_8\text{F}_{10}]$ (**4**)** are isostructural compounds based on a novel tetrameric unit (Figure 3(a)). Bonds to the bridging versus terminal O and F atoms

follow the expected trends in bond-length/strength and confirm the oxidation states of the two independent Mo sites as +5. This is again in agreement with the observation of a short inter-octahedral Mo-Mo contact through the shared O(3)/O(3)' edge. The tetrameric anionic units pack in a 'herring-bone' fashion (Figure 3(b)) into layers in the *bc* plane which then stack along *a*, interspersed by the counter-cations (Figure 3(c)).

3.1.4 [C₄H₁₂N₂]_{0.5}[MoOF₃] (5) adopts a novel infinite zig-zag chain structure (Figure 4(a)). The building unit (Figure 4(b)) consists of a single octahedral Mo⁴⁺ centre coordinated by four bridging F atoms and single, terminal F and O atoms. The resulting chains are aligned along the *c*-direction and are separated from neighbouring chains along *a* by the protonated piperazinium template (Figure 4(c)). Within each chain there is a distinct alternation of 'long-short' Mo-F bond lengths and corresponding Mo-Mo interoctahedral contacts, once again indicative of Mo-Mo bonding.

4. Discussion and Conclusions

The dimeric unit in compound **1** has been previously observed, but the other compounds exhibit novel structural units. Compound **2** exhibits only the second example of the coordination of an N-donor ligand in a MoOF. Compounds **3** and **4** introduce the first example of a highly fluorinated tetrameric unit in MoOF chemistry. The [Mo₄O₈F₁₀]⁴⁻ unit is topologically analogous to the [V₄O₄F₁₄]⁶⁻ unit we have previously observed²; the higher O/F ratio in the present case is accommodated by each Mo atom having three oxide ligands, in both terminal and bridging modes, rather than just the terminal V=O group and bridging F ligands in the VOF analogue. We are aware of two previously known examples of tetrameric MoOF units (not listed in Table 1); these both contain Mo(VI) and have much lower F/O ratios. The [Mo₄O₁₂F₂]²⁻ unit has two octahedral Mo centres bridged through a fluoride 'edge' and capped by two tetrahedral MoO₄ groups²⁶. The [Mo₄O₁₂F₃]³⁻ unit has two edge-sharing octahedral dimers further fused *via* a four-coordinate F⁻ ligand²⁷. The previously known MoOF chain structures each incorporate Mo in the +VI oxidation state. Compound **5** represents the first example of an infinite connectivity MoOF with Mo in a reduced state. The edge-sharing chain seen in NaMoO₃F¹⁸ is the most closely related to that observed in **5**, however it differs in the relative orientation of the shared edges along the chain, in addition to the oxidation state of the Mo and the O/F ratio. In NaMoO₃F *cis*-edges are shared, through a common three-coordinated O atom, resulting in a planar zig-zag conformation (Figure 4a). In **5** the edges shared are neither directly *cis* or *trans* to each other, and this results in a 'stepped' rather than 'planar' zig-zag chain (Figure 4a).

Our previous systematic studies on the solvothermal chemistry of vanadium oxyfluorides have highlighted several general features in the structural and compositional features of the reaction products versus key synthetic variables. In particular, for the same reaction mixture an increase in reaction temperature typically results in both a reduction in the average vanadium oxidation state and an increase in the dimensionality of the vanadium oxyfluoride sublattice⁴. Both of these features can be seen in our preliminary exploration of the molybdenum oxyfluoride systems presented here. For example, the reactions used to prepare **1** and **2** differ significantly in the reaction temperature. Raising the temperature from 100 °C to 140 °C results in reduction of Mo from the +VI to the +IV state and also an increased degree of condensation, from corner-shared to edge-shared octahedra. Each of the three reactions carried out at higher temperatures leads to further condensation of the MoOF sublattice; to tetrameric units in **3** and **4**, and to the chain moiety in **5**. Reactions analogous to those used to prepare **3** and **4**, if carried out at 100 °C, produce the known

monomeric compounds $(\text{NH}_4)_2\text{MoOF}_5^{10}$ and $\text{K}_2\text{MoO}_2\text{F}_4 \cdot \text{H}_2\text{O}^8$, respectively. Of course, further systematic work is required to expand on this understanding and, ultimately, be able to control both structural features and oxidation state to a finer degree. Our recent observation^{6,7} of the ability of ionic liquid solvents to control both oxidation state and dimensionality in VOF systems may be of benefit in this regard.

The observation of reduced Mo in compounds **2** – **5** is of interest, first as it gives rise to the opportunity for Mo-Mo bonding but also as it may lead to further opportunities in the preparation of a variety of electronically-active materials in these systems. Considering the metal-metal bonding first, the Mo-Mo inter-octahedral contacts shown in Table 4 are all in the range 2.52 – 2.55 Å. This compares to the Mo-Mo contact distances observed in many reduced molybdenum oxides and phosphates based on edge-sharing octahedral units²⁸⁻³⁰. When these Mo-Mo bonded arrays occur in extended chain or layer arrangements metallic behaviour often occurs, as in $\text{La}_2\text{Mo}_2\text{O}_7^{29}$. However, in the case of **5** this is unlikely as the Mo-Mo distances alternate, long-short, along the chain.

Mo-Mo bonding generally results in a spin-paired $S = 0$ ground state, with consequent diamagnetic behaviour. However, if some of the spins remain unpaired, then exotic magnetic behaviour may result. An exciting recent example³¹ occurs in the compound $\text{LiZn}_2\text{Mo}_3\text{O}_8$, a mixed valence system with an average Mo oxidation state of +3.67. Here, only six of the seven available d electrons are held in Mo-Mo bonds, and the seventh remains unpaired and delocalised over a triangular Mo_3O_{13} cluster. Geometric magnetic frustration results in a possible ‘resonating valence-bond’ ground state.

Being able to control and exploit the variable red-ox behaviour within these MoOFs, in parallel with the occurrence or absence of Mo-Mo bonding, is therefore of potential interest to the development of new candidate low dimensional quantum magnetic systems. Another highly topical area where they may be potential for development of new MoOF-based materials is lithium battery technology. The easily accessible reduced oxidation states together with the propensity for fluorides to increase the maximum electrical redox potential³² means that there is great scope for producing candidate cathode materials in these systems. For both these applications, the observation of simultaneous extended connectivity and reduced Mo oxidation state, observed in **5**, is particularly significant.

In summary, we have shown that solvothermal synthesis, in mixed water-ethylene glycol solvents, provides a facile route to the preparation of highly fluorinated, reduced molybdenum oxyfluorides. The compounds prepared so far exhibit some novel features and provide food-for-thought in the design of more specifically targeted compositions and structure types with potentially interesting electronic properties, for example. Further work to understand and control Mo oxidation state, structural connectivity and dimensionality may pave the way for preparing novel materials with scientifically and technologically interesting electronic/electrical properties in MoOF-based systems.

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***Crystal Data**

Crystallographic data for structures **1**, **2** and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 885588-90. Copies of the

data can be obtained, free of charge, on application to CCDC (e-mail: deposit@ccdc.cam.ac.uk). Corresponding cif files for structures **3** and **4** have been deposited with the Inorganic Crystal Structure Database; deposition numbers 424782 and 424783 (e-mail: crysdata@fiz-karlsruhe.de).

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Table 1. Some previous examples of ‘fluorine-rich’ MoOF bulding units

Compound Formula	Structural Unit	Mo Ox. State	Ref
$K_2[MoOF_5].H_2O$	Monomer	V	8
$K_2[MoO_2F_4].H_2O$	<i>cis</i> -monomer	VI	8
$Ag_3[MoO_3F_3](Ag_3MoO_4)$	<i>fac</i> -monomer	VI	9
$Cs_3[Mo_2O_6F_3]$	Face-sharing dimer (F-bridge)	VI	10
$[MoO(S_2CNEt_2)_3]_2[Mo_2O_4F_6]$	Edge-sharing dimer (F-bridge)	VI	11
$(NH_4)_2[Mo_2O_4F_4(H_2O)_2]$	Edge-sharing dimer (O-bridge)	V	12
$(NH_4)_3[Mo_2O_2F_9]$	Corner-sharing dimer (F-bridge)	V	10
$K_2(NMe_4)[Mo_2O_2F_8(H_2O)]$	Corner-sharing dimer (F-bridge)	V	13
$(C_4H_4N_2)_3Ag_3[Mo_2O_4F_7]$	Corner-sharing dimer (F-bridge)	VI	14
$Ba_4[Mo_2O_5F_6]F(HF_2)_3$	Corner-sharing dimer (O-bridge)	VI	15
$K(NMe_4)_2[Mo_3O_6F_9]$	Corner-sharing trimer (X-bridge)	VI	13
$(NH_4)_5[Mo_3O_4F_9]$	Edge-sharing trimer (O-bridge)	IV	16
$(C_8H_{16}N)_2Na_4[Mo_6O_{18}F_6].6H_2O$	Planar edge-sharing hexamer	VI	17
$NaMoO_3F$	<i>cis</i> -Edge-sharing chain (O-bridge)	VI	18
$CsMoO_2F_3$	<i>cis</i> -Corner-sharing chain (F-bridge)	VI	19
$(NH_4)_2MoO_3F_2$	<i>trans</i> -Corner-sharing chain (O-bridge)	VI	20

Table 2. Synthetic conditions and analytical data. Each reaction composed 0.144 g (1 mmol) MoO_3 and 0.5 ml HF (48%, aq) together with the components below. Reaction duration was 24 hours in each case.

Compound	H ₂ O (ml)	EG (ml)	‘template’		T(°C)	CHN (%) (expected)	CHN (%) (found)
1	1	5	en	0.5 ml	100	9.42, 3.95, 10.98	9.58, 3.13, 11.05
2	5	5	en	0.5 ml	140	15.14, 4.66, 11.77	13.62, 4.45, 11.76
3	1	5	NH ₄ OH (30%)	1 ml	160	0, 2.99, 10.38	0, 2.80, 10.02
4	2	5	KNO ₃	0.30 g	160	-	-
5	1	5	pip	0.258 g	190	11.28, 2.84, 6.58	11.93, 2.79, 6.43

Abbreviations: EG = ethylene glycol; en = ethylene diammine; pip = piperazine.

Table 3. Crystallographic parameters for compounds **1-5**

Compound	1	2	3	4	5
Formula	Mo ₂ O ₅ F ₆ C ₄ H ₂₀ N ₄	Mo ₂ O ₆ F ₂ C ₆ H ₂₂ N ₄	Mo ₄ O ₈ F ₁₀ H ₂₄ N ₆	Mo ₄ O ₈ F ₁₀ K	MoOF ₃ C ₂ H ₆ N
Space Group	C2/c	C2/c	Pmnn	Pmnn	C2/c
a [Å]	17.686(3)	21.006(3)	6.309(1)	6.0483(7)	15.616(9)
b [Å]	6.3262(9)	6.0562(7)	9.457(2)	9.351(1)	8.355(5)
c [Å]	13.510(2)	11.272(1)	14.957(3)	14.487(2)	9.517(6)
β [°]	108.485(4)	97.324(4)			
V [Å ³]	1433.6(4)	1422.3(3)	892.4(3)	819.4(2)	118.467(7)
Z	4	4	2	2	8
ρ _{calc} [g cm ⁻³]	2.364	2.252	2.924	3.795	2.592
μ [mm ⁻¹]	1.844	1.827	2.889	4.656	2.370
Crystal Size [mm]	0.2 x 0.2 x 0.2	0.22 x 0.15 x 0.08	0.10 x 0.03 x 0.03	0.10 x 0.10 x 0.03	0.19 x 0.17 x 0.15
F(000)	1000	952	728	872	816
Reflns Collected	4566	7260	5428	4889	6598
Independent Reflns	1775	1693	898	1030	1925
R _{int}	0.023	0.113	0.022	0.027	0.023
Obsd Data [I>2σ(I)]	1304	1248	868	896	1656
Data/ Parameters	1775/96	1693/95	898/76	1030/76	1925/73
GOF on F ²	1.13	1.23	1.25	1.26	1.11
R1, wR2 [I>2σ(I)]	0.0247, 0.0608	0.0985, 0.1436	0.0320, 0.0810	0.0419, 0.0840	0.0285, 0.0663
R1, wR2 (all data)	0.0281, 0.0635	0.1393, 0.1517	0.0333, 0.0819	0.0456, 0.0852	0.0321, 0.0682

Table 4. Selected bond lengths (Å) and bond valences, s_{ij} (valence units) for **1-5**

1: [C₂H₁₀N₂]₂[Mo₂O₅F₆]		
Bond	Bond Length (Å)	s _{ij}
Mo1-O1	1.707(2)	1.720
Mo1-O2	1.702(2)	1.743
Mo1-O3	1.901(1)	1.009
Mo1-F1	2.084(2)	0.474
Mo1-F1	2.007(2)	0.584
Mo1-F2	2.151(2)	0.396
		ΣMo1 = 5.94

2: [Mo₂O₄F₂(C₂H₈N₂)₂].C₂H₆O₂		
Bond	Bond Length (Å)	<i>S_{ij}</i>
Mo1-O1	1.877(6)	1.086
Mo1-O1'	1.934(6)	0.931
Mo1-F1/O2*	1.842(5)	0.46/0.60
Mo1-F2/O3*	1.885(5)	0.41/0.53
Mo1-N1	2.227(7)	0.555
Mo1-N2	2.149(6)	0.685
		ΣMo1 = 5.25
Mo1-Mo1	2.522(2)	

*= Disordered atoms

3: (NH₄)₆[Mo₄O₈F₁₀]		
Bond	Bond Length (Å)	<i>S_{ij}</i>
Mo1-O1	1.690(5)	1.801
Mo1-O3	1.948(4)	0.897
Mo1-O3'	1.948(4)	0.897
Mo1-F1	2.040(3)	0.534
Mo1-F1'	2.040(3)	0.534
Mo1-F3	2.152(4)	0.395
		ΣMo1 = 5.06
Mo2-O2	1.674(5)	1.881
Mo2-O3	1.950(4)	0.892
Mo2-O3'	1.950(4)	0.892
Mo2-F2	2.049(3)	0.521
Mo2-F2'	2.049(3)	0.521
Mo2-F3	2.173(4)	0.373
		ΣMo2 = 5.08
Mo1-Mo2	2.552(1)	

4: K₆[Mo₄O₈F₁₀]		
Bond	Bond Length (Å)	<i>S_{ij}</i>
Mo1-O1	1.689(6)	1.806
Mo1-O3	1.938(4)	0.921
Mo1-O3'	1.938(4)	0.921
Mo1-F1	2.016(3)	0.570
Mo1-F1'	2.016(3)	0.570

Mo1-F3	2.153(5)	0.394
		$\Sigma\text{Mo1} = 5.18$
Mo2-O2	1.679(6)	1.855
Mo2-O3	1.948(4)	0.897
Mo2-O3'	1.948(4)	0.897
Mo2-F2	2.041(3)	0.533
Mo2-F2'	2.041(3)	0.533
Mo2-F3	2.156(4)	0.390
		$\Sigma\text{Mo2} = 5.11$
Mo1-Mo2	2.542(1)	

5: [C₄H₁₂N₂]_{0.5}[MoOF₃]		
Bond	Bond Length (Å)	<i>s_{ij}</i>
Mo1-O1	1.685(2)	1.825
Mo1-F1	2.118(2)	0.433
Mo1-F2	2.174(2)	0.372
Mo1-F2'	2.214(2)	0.334
Mo1-F3	1.973(2)	0.640
Mo1-F3'	2.043(2)	0.530
		$\Sigma\text{Mo1} = 4.13$
Mo1-Mo1	2.544(2)	

Figures

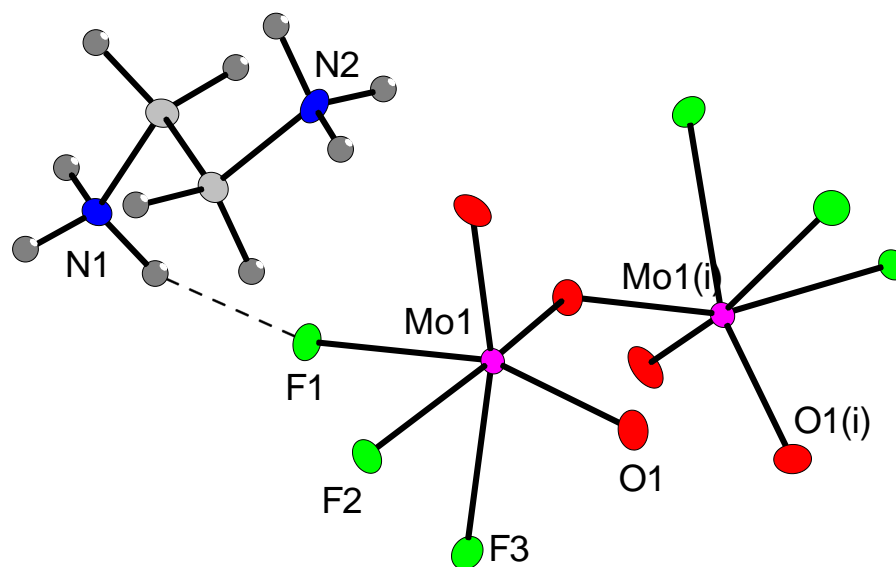


Figure 1 Building unit in **1**. Atoms drawn as 50% probability ellipsoids. Symmetry operator: (i) $1-x, y, \frac{1}{2}-z$.

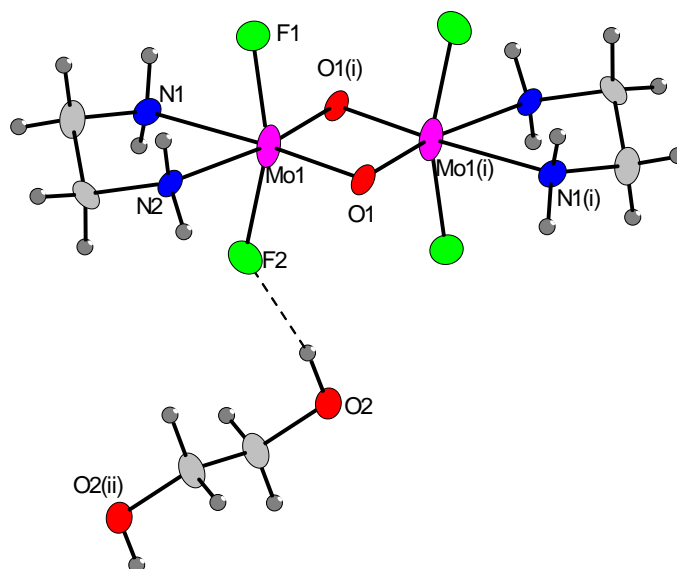


Figure 2 Building unit in **2**. Symmetry operator: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

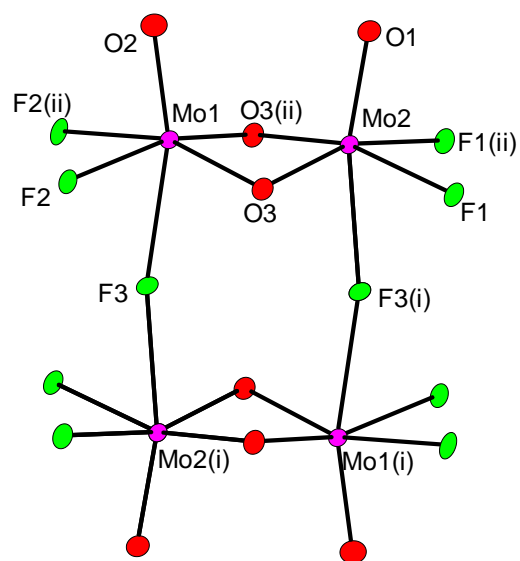


Figure 3a Tetramer unit in **3** and **4**. Symmetry operators: (i) $x, -y, -z$ (ii) $-x, y, z$.

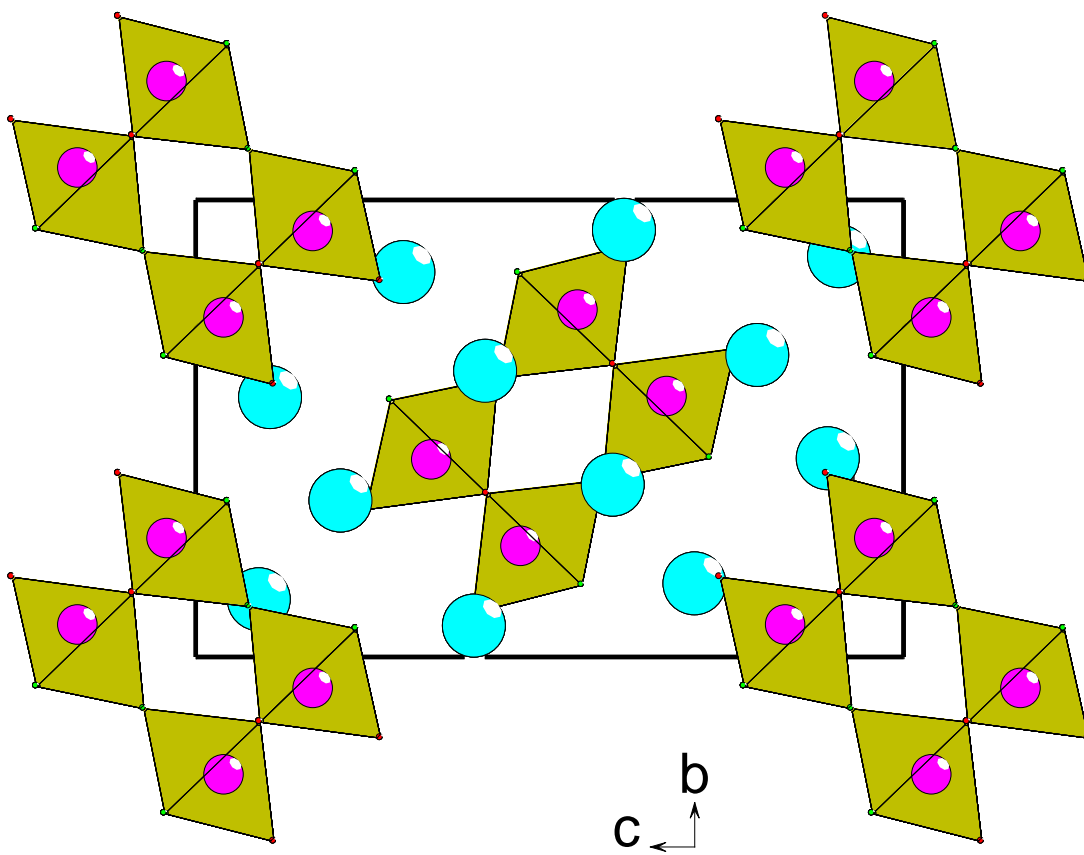


Figure 3b Packing of tetrameric units in **3** and **4**, along the a -axis.

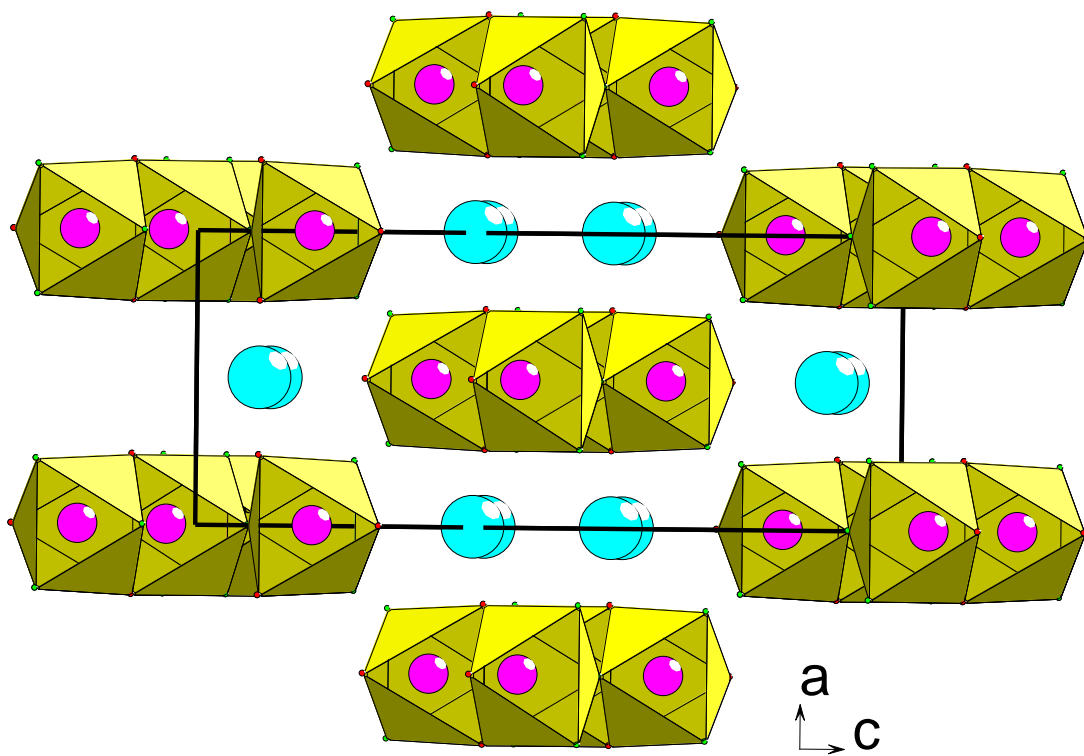
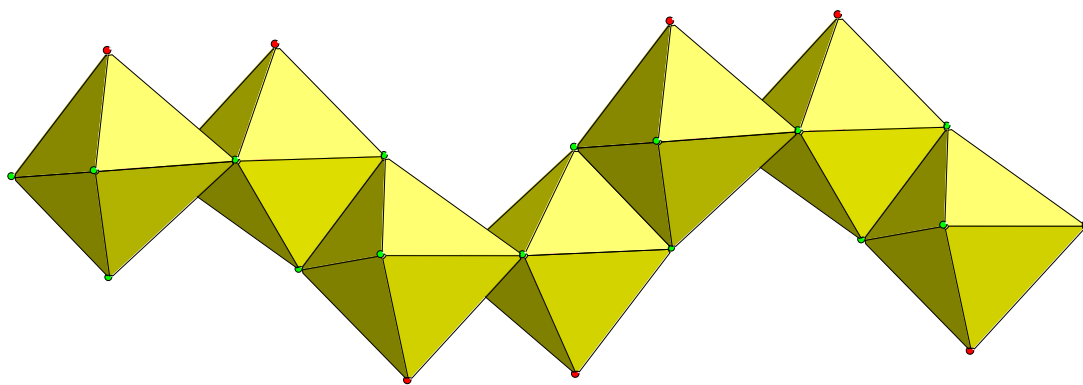


Figure 3c Packing of tetrameric units in **3** and **4**, along the b -axis.



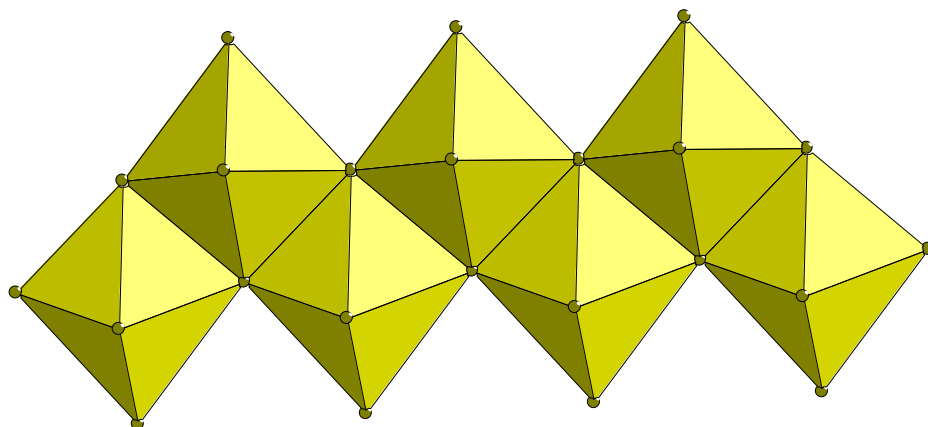


Figure 4a ‘Stepped zig-zag’ $[\text{MoOF}_3]_n$ edge-sharing octahedral chain motif in **5** (above) compared to the ‘planar zig-zag’ $[\text{MoO}_3\text{F}]_n$ chain in NaMoO_3F .

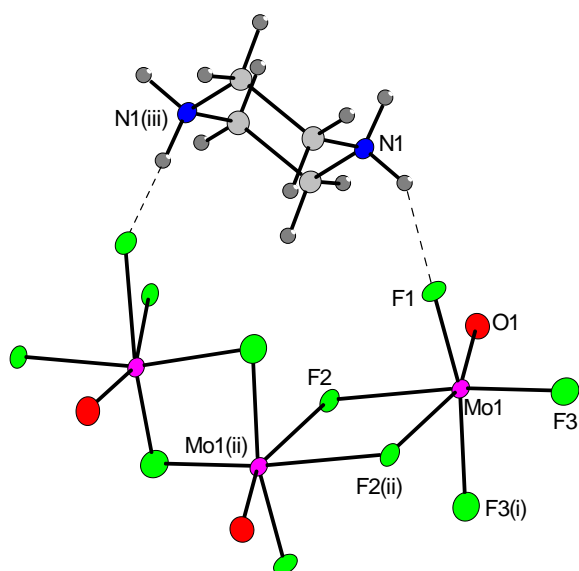


Figure 4b Building unit in **5**. Symmetry operators: (i) $1 - x, y, \frac{1}{2} - z$ (ii) $1 - x, 1 - y, -z$ (iii) $\frac{1}{2} - x, \frac{3}{2} - y, -1 - z$.

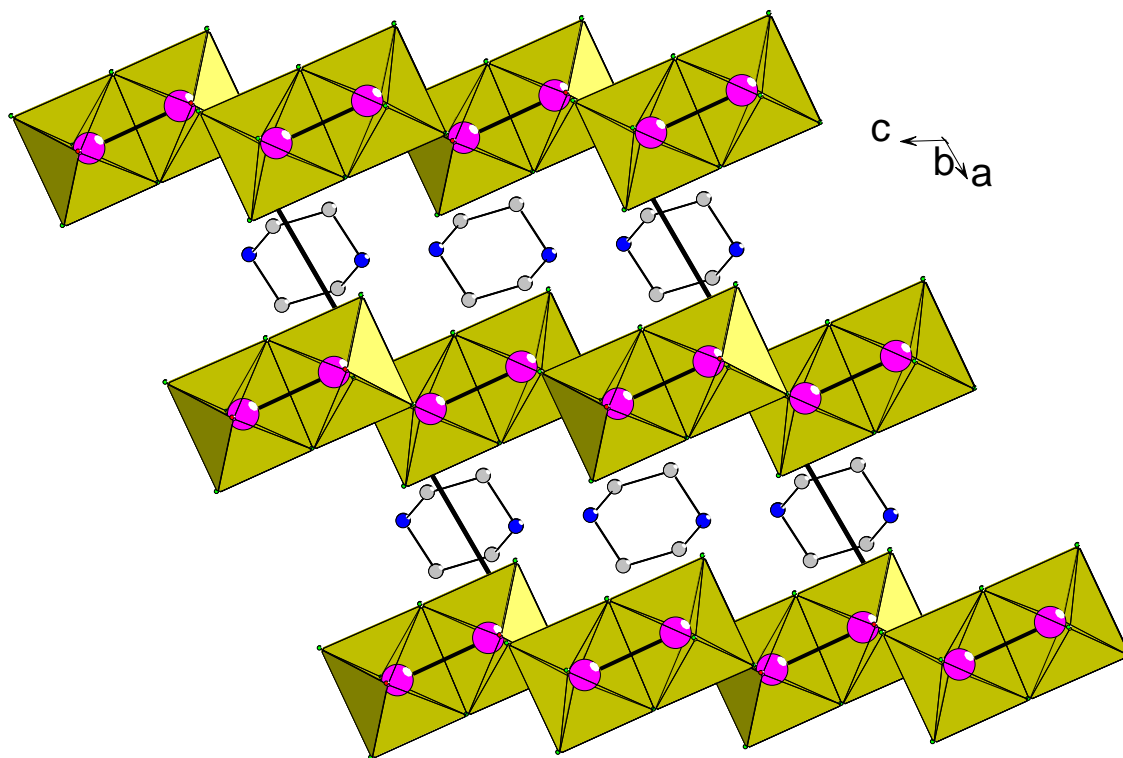


Figure 4c Unit cell packing in **5**, with Mo-Mo bonds highlighted. H atoms are not shown.

Graphical Abstract:

Solvothermal synthesis provides a facile route to reduced molybdenum oxyfluorides containing novel metal-metal bonded units.

