

Molybdenum Difluoride Dioxide, MoO₂F₂

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 MoO_2F_2 is prepared by pyrolysis of $(Na^+H_2O)_2$ cis $-MoO_2F_4^{2-}$. A preliminary model of the structure is obtained from powder data: it has a triangular columnar structure with three fluorine bridges between the three molybdenum atoms and with oxygen bridges between the layers. (a = 1605, b = 384, c = 1395 pm, Pnma, Z = 12). The closest related structure is that of TiF₄, except that the orientation of the triangular columns is different.

Introduction

The theoretical interest on MoO_2F_2 is twofold. First, its molecular structure is expected to be different from main group compounds with similar composition, for example, SO_2F_2 . The structures of the latter ¹ can qualitatively be described by the valence shell electron pair repulsion model.² This simple model fails for MoO_2F_2 . Theoretical predictions based on calculations predict an O=Mo=O angle of about 106° and the F-Mo-F angle at 113°.³

Experimental values for the MoO₂F₂ molecular structure seem to be unknown, but the related MoO₂Cl₂ has indeed such a structure with O=Mo=O 104.0(20)° and Cl-Mo-Cl 112.0(10)°.⁴ Simplified, it can be said that two double bonded atoms to transition metal atoms will preferentially have angles close to 90° to avoid occupation of the same metal d-orbital by the π bonds of the ligands.

The solid state structure of MoO_2F_2 is also unknown. Certainly the molecule will undergo polymerization via ligand bridging, a coordination number of six with a close to octahedral structure is most likely, with two bridges between molybdenum atoms. Alternatively, a five coordinate polymer with one bridge could also occur. Among transition metal fluoride oxides bridging occurs usually through the F atoms; MoOF₄ is a prominent example out of very many known compounds.⁵ If this behavior is applied to MoO_2F_2 ,

However, there are exceptions from these simple rules: Isoelectronic NbOF₃ and also TaOF₃ obviously have six coordinated metal atoms in a SnF₄ type structure, but there seems to be an O, F disorder with some oxygen atoms also in

cis position to each other.

bridging positions.^{6,7} ReO₃F, where a six coordination would demand at least one bridging oxygen atom, has indeed a helical chain structure with one fluorine and one oxygen bridge in *cis* position, while the other two oxygen atoms are *cis* positioned in terminal positions.⁸ TcO₃F is isoelectronic to MoO_2F_2 . In the solid state it is a fluorine bridged dimer with additionally one weak O···Tc interaction, so the coordination could be described as 5 + 1.9

then a model would result in which all fluorine atoms are in bridging positions, and the oxygen atom are terminal and in

 MoO_2F_2 is reported to be obtained in the reactions 1^{10} , 2^{11} , 3^{12} , 4^{13} , $5^{14,15}$, 6^{14} , and 7^{16} as follows:

$$MoO_{3} + NF_{3} \xrightarrow{430^{\circ}C} MoO_{2}F_{2} \text{ (mass spectrum)} + NO^{+}MoO_{2}F_{3}^{-}$$
(1)

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Table 1. Crystallographic Data for Na₂MoO₂F₄·H₂O, MoO₂F₂·2DMF, and MoO₂F₂

	$Na_2MoO_2F \cdot H_2O$	$MoO_2F_2 \cdot 2DMF$	$MoO_2F_2^a$
chemical formula	F ₄ H ₂ MoNa ₂ O ₃	$C_6F_2H_{14}MoN_2O_4$	F ₂ MoO ₂
$M_{ m r}$	265.92	312.13	165.94
cryst. syst.	orthorhombic	monoclinic	orthorhombic
space group	$P2_{1}2_{1}2_{1}$ (No. 19)	C2/c	Pnma (No. 62)
temp (°C)	-140	-140	23
a/pm	543.6(1)	1253.8(2)	1605.9(8)
b/pm	575.5(1)	782.4(1)	386.46(1)
c/pm	1914.3(4)	1157.1(2)	1395.14(7)
<i>ss</i> /deg	90	98.982(3)	90
$V/10^{6} \mathrm{pm}^{3}$	598.86	1121.2	864.5(2)
Z	4	4	12
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	2.95	1.849	3.825
μ/mm^{-1}	2.36	1.195	4.4
measured and independent	7349, 1822	9379, 1711	232
$R(F^{1}), R_{w}(F^{2}), S$	0.0473, 0.1199, 1.262	0.0205, 0.0541, 1.120	$0.15(R_{I})$
parameters	93	75	35

^a Powder data, *Rietveld* refinement, see text and Figure 3.

$$MoO_3 + LiF \xrightarrow{500^\circ C} MoO_2F_2 \text{ (gas ir.)}$$
 (2)

$$MoO_3 + SeF_4 \rightarrow MoO_2F_2 \cdot SeF_4$$
 (3)

 $MoO_3 + IF_5 \rightarrow 2MoO_2F_2 \cdot 3IF_5$ (4)

 $MoO_2Cl_2 + HF \rightarrow MoO_2F_2$ (5)

$$MoO_2Cl_2 + XeF_2 \xrightarrow{HF} MoO_2F_2$$
 (i.r.) (6)

$$Na_2MoO_4 + IF_5 \xrightarrow{120^\circ C} MoO_2F_2(Raman)$$
 (7)

There is so far no reliable mode of preparation for MoO_2F_2 . The first two reactions show the presence of MoO_2F_2 molecules in the gaseous state at high temperature. Reactions 3 and 4 produce adducts, whose structural details are unknown. We will show below that MoO_2F_2 does not tolerate anhydrous HF, so that the products of reaction 5 and 6 cannot be MoO_2F_2 , as indicated also by the published vibrational spectra. Reaction 7 produces a product similar to that of reaction 6, and also adduct formation with IF₅ is expected.¹⁰

Experimental Section

General experimental procedures:

Moisture sensitive materials were handled in the dry argon atmosphere of a glovebox with a water content of less than 1 ppm. Volatile compounds were manipulated in a vacuum line.

Solvents were dried by standard methods. NMR spectra were recorded using a JEOL NMR-LA 400 spectrometer (¹H at 399.65 MHz, ¹³C at 100.4 MHz, and ¹⁹F at 376.00 MHz). Chemical shift values are reported with respect to tetramethylsilane (TMS) (¹H, ¹³C) and CCl₃F (¹⁹F). Raman spectra were recorded on a Bruker RFS 100 FT-Raman spectrometer. Mass spectra were recorded on a Varian MAT 711 instrument.

Single crystals were handled in a special device ¹⁷, cut to an appropriate size, and mounted on a Bruker SMART CCD

1000 TU diffractometer, using Mo K α irradiation, a graphite monochromator, a scan width of 0.3° in ω , and a measuring time of 20 s per frame. After semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement¹⁸. Results are summarized in Table 1, experimental details in Table 2.

Powder data were obtained first with a Stoe Stadi/P powder diffractometer with Cu K α radiation and a sample in a 0.3 mm silica capillary. In a second experiment the diffraction measurements were performed in Bragg–Brentano reflection geometry on a Bruker AXS D8 Advance diffractometer equipped with a secondary graphite monochromator (Cu K α radiation) and scintillation detector. This sample powder was handled in a glovebox and filled into the recess of a sealable airtight sample holder, yielding a flat surface of the sample bed. The data acquisition was performed in five consecutive scans with a counting time of 3 s/step and a step width of 0.02° 2 θ . After confirming that the diffraction patterns exhibited no significant change over the total acquisition time of 20 h, the five data sets were summed up to yield a total counting time of 15 s/step.

Na₂MoO₂F₄·2H₂O. Na₂MoO₂F₄ is obtained by dissolving 1 g of Na₂MoO₄ in 3 mL of hydrofluoric acid containing 13.3% HF by warming under stirring to approximately 50 °C. The colorless solvent is cooled to room temperature, and a colorless solid crystallizes out. The liquid is decanted, and the solid is dried in vacuum, see below. Single crystals of Na₂MoO₂F₄·2H₂O are grown by slow cooling from 50 °C to room temperature.

¹⁹F-NMR (D₂O, RT): δ = 84.21 ppm, $w_{1/2} \approx$ 1000 Hz. Raman (solid, RT): 971(100), 922(50), 571(10), 549(2), 427(2), 380(25), 311(25), 299(10,sh), 276(4), 229(1), 207(2), 179(2), 144(4), 144(10), 94(10) cm⁻¹. IR (NaCl, RT): 3436 (m, vbroad), 193(w), 1889(w), 1852(w), 1632(w), 1381(w), 974(vs), 930(vs), 582(vs), 550(vs), 442(s), 407(vs) cm⁻¹

 MoO_2F_2 . Na₂MoO₂F₄·2H₂O is dried overnight in vacuum and filled into a Monel cylinder, with a water cooled top. Slow heating to 400° in vacuum for 24 h results in the formation of a yellow-gray sublimate at the cooled top of the cylinder. Resublimation in a 30 mm long silica tube in vacuum results in a slightly yellow, plastic material. A 200 mg portion of this is filled into a silica tube, oxygen up to 1 bar is added, and the silica tube is sealed. Repeated slow heating to 280° and cooling to 240 °C produced a white, cottonlike material. Only material with direct

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Table 2. Mo-O and Mo-F Bond Lengths (pm) and Angles (deg)

	$Na_2MoO_2F_2 \cdot H_2O$	MoO ₂ F ₂ ·2DMF
Мо-О	168.5(5), 170.6(6)	169.5(1) 223.5(1) ^b
Mo-F	ax^{a} 192.8(5), 196.3(5) eq^{a} 206.4, 212.6(4)	189.9(1)
О-Мо-О	102.7(3)	103.3(1) 78.38(6) ^b
F-Mo-F	ax 158.2(2) eq 75.6(2)	155.19(8)
	Mo	$D_2F_2^c$

Mo-O _{br} ^d	194.2(5), 195.7(7), 194.4(4)
$Mo-F_{br}$	212(2), 215(3), 209(2), 203(2), 205(3), 203(2)
$Mo-O, F_t^e$	173(2)-177(3)
Mo-O-Mo	169(3), 162(2), 167(2)
Mo-F-Mo	167(2), 170(2), 152(2)

 a ax = axial, eq = equatorial relative to the MoO₂ plane. b Mo···O contacts to DMF. c powder data, *Rietveld* refinement, see text. d br = bridging atom. e Terminal, disordered O and F atoms.

contact to the silica wall turned slightly blue, indicating reduction to lower molybdenum compounds.

Raman spectrum (yellow plastic material). 1085 (w, MoOF₄),

1013 s, 852 s, br, 685 m, 450 w, br, 397 m, 280 m, 154 w, cm⁻¹. Raman spectrum (white cryst.): 1085 (w, MoOF₄), 1014 m, 830 vs, 581 w, 396 w, 374 w, 353 w, 344, 281 m, 271 w, sh, 281 m, 271 w, ch $_{202}^{-1}$ w, $_{202}^{$

271 w, sh, 202 w, 189 w, 117 w, cm⁻¹. Mass spectrum, (EI rel to ⁹⁸Mo), m/z = 168 (MoO₂F₂⁺, 100%), 149 (MoO₂F⁺, 45%), 133 (MoOF⁺, 10%), 130 (MoO₂⁺, 10%), 114(MoO⁺, 5%), 98 (Mo⁺, 5%).

 $MoO_2F_2 \cdot 2DMF$. A 300 mg portion of the yellow sublimate is loaded into a prepassivated 8 mm PFA ampule. *N*,*N*-dimethylformamide (DMF, 3 mL) is added to the ampule followed by 1 mL of propionitrile. The mixture is allowed to warm to room temperature, stirred for 15 min to homogenize, and cooled slowly to -78 °C to give colorless crystals of the air stable compound $MoO_2F_2 \cdot 2DMF$.

X-ray Powder Measurement and Structure Determination. Powder data could be indexed resulting in lattice constants as shown in Table 1. The orthorhombic cell with $V = 864.5 \times$ 10^6 pm^3 contains 12 molecular units, if a volume of $17-18 \times$ 10⁶ pm³ is assumed for O and F atoms and Mo atoms occupying octahedral holes. At this point it became evident that the structure may be related to that of TiF₄, although the metric of the latter is quite different (with exception of the b axis and the cell volume). Setting the Mo atom in reasonable positions gave the starting model. First, refinements were done by the program LX15LS of WIF David, 1919 Science Division, Butterford Appleton Lab, Chilton, U.K. The program Topas [Topas v3, copyright 1999, 2000 Bruker AXS] was used to perform further Rietveld structure refinements on this structure model. At first displacement factors were not refined and arbitrarily set to unity for all atoms, and a single displacement factor was refined later for all atoms. The background was fitted using a second order Chebychev polynomial plus two pseudo-Voigt functions describing two broad bumps in the background. The peak shapes were described using the fundamental parameters approach, that is, an instrument function which was calculated from the known instrument parameters was numerically convoluted with the sample peaks function. The latter consisted of two Lorentzian contributions, one with a $1/\cos(\theta)$ and one with a $\tan(\theta)$ dependence.

Results

Our approach has been to obtain MoO_2F_2 in a reproducible and straightforward way. After testing the previously described reactions, we found that often the products have been $MoOF_4$, $H_3O^+Mo_2O_2F_9^-$, or mixtures of unclear compositions.



Figure 1. Anion cis $MoO_2F_4^{2-}$ in the crystal structure of $(Na^+H_2O)_2$ *cis*-MoO₂ F_4^{2-} , Ortep representation, 50% probability ellipsoids.



Figure 2. Structure of $MoO_2F_22 \cdot DMF$ in the crystal, Ortep representation, 50% probability ellipsoids.

We assumed, as it turned out correctly, that MoO_2F_2 is a very coordinatively unsaturated compound, so that presence of any basic material has to be avoided.

At first we isolated Na₂MoO₂F₄·2H₂O in pure form from Na₂MoO₄ and aqueous HF by a variation of the method for the preparation of K₂MoO₂F₄(*cis*)¹⁹. It is important to work with an 13% HF concentration in H₂O. NaHF₂ as a side product can be separated by fractional crystallization. The identity of this salt is established by its single crystal structure which shows isolated Na⁺·H₂O and *cis*-MoO₂F₄²⁻ units, see Figure 1. Bond lengths and angles, see Table 1, have the expected values. The Raman spectrum serves as a test for the purity (absence of the symmetric stretching mode 628 cm⁻¹ and the lattice mode at 144 cm⁻¹ of HF₂⁻), and also it shows the characteristic two strong Mo=O stretching vibrations close to 1000 cm⁻¹ characteristic of the *cis*-MoO₂ configuration, see Experimental Section.

Na₂MoO₂F₄·H₂O is then pyrolized in vacuum. Till 260 °C only the crystal water is liberated, as is evidenced by the DTA measurement and the almost complete disappearance of the broad H₂O band at 3436 cm⁻¹ in the IR spectrum. At 300 °C MoO₂F₂ sublimes out of the salt as a slightly yellow, glassy material. This is completely amorphous according to X-ray powder measurements.

$$Na_2MoO_2F_4 \xrightarrow{300^\circ C} 2NaF + MoO_2F_2$$

The vacuum pyrolysis has also been done in a mass spectrometer where the parent ion $MoO_2F_2^+$ as the one with highest mass has been identified.

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Figure 3. X-ray powder diagram of MoO_2F_2 : Upper trace, dots: experimental intensity, line: calculated model. middle trace: position of calculated lines. lower trace difference experimental/calculation. Arrows: indicate strongest deviation.

 MoO_2F_2 is a very reactive species. Organic solvents usually cause reduction under formation of blue deposits. Only from a dimethylformamide solution have we been able to grow single crystals. These contain two DMF molecules attached to the molybdenum atom via their oxygen atoms, trans positioned to the Mo=O bonds, so that the coordination of the molybdenum atom is now distorted octahedral, see Figure 2. A similar compound, $MoO_2F_2 \cdot 2THF$ has been accidentally found, possibly by hydrolysis of MoF₄NCl· THF, and also has been characterized by a single crystal structure determination ²⁰. Recently $MoO_2F_2 \cdot 2(R_3)PO$ $(R = CH_3, C_6H_5)$ have been obtained by a chlorine-fluorine exchange reaction from MoO₂Cl₂(CH₃)₃PO⁻²¹. MoO₂F₂ dissolves in anhydrous HF under partial oxygen fluorine exchange. The resulting mixture could not be fully analyzed. A part of crystalline material seems to be H_3O^+ - $Mo_2O_2F_9^-$ according to an imperfect single crystal structure determination. So any preparative method in presence of HF should be useless. All in all it seems impossible to find a suitable solvent for preparation of single crystals of neat MoO_2F_2 .

Structural Model for MoO_2F_2 . Similar to ReO_3F^8 annealing of amorphous MoO_2F_2 resulted in crystallization. But still there are shortcomings: At the necessary temperature of 290 °C MoO_2F_2 starts to decompose, which is indicated by the appearance of a blue color. If the sample is kept in quartz tubes under a mild pressure (a few bar) of oxygen, the decomposition seems to be slowed down. Glassy yellow MoO_2F_2 then changes into white, extremely thin needles like cotton wool. This material is by far too fine for a single crystal structure determination.

X-ray data from the powder could be obtained, however, and lattice constants and the space groups *Pnma* or *Pna2*₁, can be secured. To minimize the number of parameters and in analogy to the TiF₄ structure, the centrosymmetric space group *Pnma* was chosen for further refinement. As can be seen in Figure 3, the powder data are far from perfect. There seems to be a strong background, possibly from residual amorphous material. Also some lines do not belong to the bulk material. Their intensity varies, so there must be an impurity present. Raman data indicate the presence of MoOF₄, but the known X-ray data cannot be fitted to the impurity lines. But it is quite possible that MoOF₄ exists in other modifications than the one reported. (The structurally related ReO₂F₃ comes in four different modifications⁸).

Rietveld refinement in space group *Pnma* produced the position of three independent molybdenum atoms in the cell. These form triangular columns, see Figure 4. The Mo····Mo separation between the layers of the columns is 386 pm, the separations within one triangle are 406, 410, and 414 pm, and between columns the shortest separations are 499, 500, and 502 pm.

The *Rietveld* refinement also provides the positions of bridging atoms between layers and within the triangles. The bridging atoms between layers are equidistant from the Mo atoms, with slightly bent bridge angles. The resulting bond distances of about 195 pm are typical for a Mo–O–Mo bridge, as in MoO₃ (194.8 pm,²² 198.0 pm²³), or in ReO₃

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Figure 4. Structural model of MoO_2F_2 from X-ray powder data. Terminal atoms are fluorine and double bonded oxygen atoms, most likely in a disordered manner.

(186.6 pm,²⁴ 187.8²⁵) to name but a few examples. The Mo···Mo distances within the layers of 411 and 417 pm calls for a Mo–F–Mo bridge. In MoOF₄ this (asymmetric and bent) bridge results in a Mo···Mo separation of 410.9 pm.⁵ In MoO₂F₂ the Mo–F–Mo bridges are essentially symmetric and slightly bent. The total structure resembles that of TiF₄.²⁶ As can be seen in Figure 4 and 5, only the relative orientation of the triangular columns are different in MoO₂F₂ and TiF₄. This may be due to the fact that the outer boundary of the TiF₄ columns are only fluorine atoms, but in MoO₂F₂ they are fluorine and oxygen atoms. The terminal oxygen and fluorine atoms in the MoO₂F₂ structure were difficult to locate in the *Rietveld* refinement, but the vibrational spectra can help somewhat.

The Raman spectrum changes considerably upon annealing. The amorphous product has only one distinct Mo=O stretching vibration at 1013 cm⁻¹ and a very broad feature between 800 and 950 cm⁻¹. After annealing the distinct vibration remains at 1014, but the broad feature narrows to a vibration at 830 cm⁻¹. If the two oxygen atoms would be both terminal, then two sharp vibrations in the 1000 cm⁻¹ area should be observed. A good example for this is the Raman spectra of the ReO₃F polymer, or the MoO₂F₄²⁻ anion, see Experimental Section. In agreement with the arguments from the *Rietveld* refinement there is obviously only one terminal oxygen atom and then, as a consequence, one terminal fluorine atom. The strong Raman vibration at 830 cm⁻¹ could derive from the Mo–O–Mo bridge.

The two terminal atoms are expected to conclude the distorted octahedral coordination of the molybdenum atoms. The difficulty in locating is almost certainly an O/ F disorder. While the electron densities of oxygen and



Figure 5. Comparison of the MoO_2F_2 (above) and the known TiF_4 (below) structure, view in both cases along the *b* axis. Note that the orientation of the triangular columns to each other is different.

fluorine are quite similar, bond lengths (Mo=O ca. 170 pm, Mo-F ca. 190 pm) and bond angles are quite different.

The possible presence of both oxygen and fluorine bridges is paralleled in the structure of NbOF₃, where oxygen atoms seem to be disordered over all possible positions, and ReO₃F, where ordered oxygen and fluorine bridges occur in an ordered manner.

Conclusion

Crystalline MoO_2F_2 has a triangular columnar structure, similar to the TiF₄ structure. The whisker type of the crystal shape is understandable with this structure model. More precise information about the oxygen and fluorine positions might be obtainable from synchrotron and neutron powder measurements, which are planned. But even then severe disorder of the terminal oxygen and fluorine atoms could hamper these efforts, as is indicated by a first experiment with synchrotron radiation.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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