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Article

Molybdenum Difluoride Dioxide, MoO$_2$F$_2$

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MoO$_2$F$_2$ is prepared by pyrolysis of (Na$^+$H$_2$O)$_2$ *cis*—MoO$_2$F$_4$$^{2-}$. A preliminary model of the structure is obtained from powder data: it has a triangular columnar structure with three fluorine bridges between the three molybdenum atoms and with oxygen bridges between the layers. (a = 1605, b = 384, c = 1395 pm, *Pnma*, Z = 12). The closest related structure is that of TiF$_4$, except that the orientation of the triangular columns is different.

Introduction

The theoretical interest on MoO$_2$F$_2$ is twofold. First, its molecular structure is expected to be different from main group compounds with similar composition, for example, SO$_2$F$_2$. 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$_2$F$_2$. 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 MoO$_2$F$_2$ molecular structure seem to be unknown, but the related MoO$_2$Cl$_2$ 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.
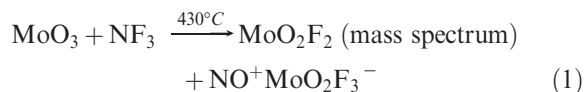
The solid state structure of MoO$_2$F$_2$ is also unknown. Certainly the molecule will undergo polymerization via ligand bridging, a coordination number of six with a close to octahedral structure is most likely, with two bridges between molybdenum atoms. Alternatively, a five coordinate polymer with one bridge could also occur. Among transition metal fluoride oxides bridging occurs usually through the F atoms; MoOF$_4$ is a prominent example out of very many known compounds.[5] If this behavior is applied to MoO$_2$F$_2$, then a model would result in which all fluorine atoms are in bridging positions, and the oxygen atom are terminal and in *cis* position to each other.

However, there are exceptions from these simple rules: Isoelectronic NbOF$_3$ and also TaOF$_3$ obviously have six coordinated metal atoms in a SnF$_4$ type structure, but there seems to be an O, F disorder with some oxygen atoms also in bridging positions.[6,7]

ReO$_3$F, 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] TcO$_3$F is isoelectronic to MoO$_2$F$_2$. 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]

MoO$_2$F$_2$ 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:

$$MoO_3 + NF_3 \xrightarrow{430°C} MoO_2F_2 \text{ (mass spectrum)}$$
$$+ NO^+MoO_2F_3{}^- \quad (1)$$

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(1) Hagen, K.; Cross, V. R.; Hedberg, K. *J. Mol. Struct.* **1978**, *44*, 187–193.

(2) Gillespie, R. J.; Robinson, E. A. *Angew. Chem.* **1996**, *108*, 539–560. Gillespie, R. J.; Robinson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495–514.

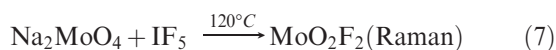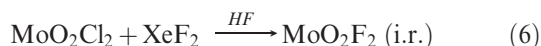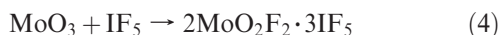(3) Kaupp, M. *Chem.—Eur. J.* **1999**, *5*, 3631–3643.

(4) Zasorin, I. M.; Spiridonov, E. Z.; Novikov, V. P.; Kupreev, G. I. *Koord. Khim.* **1975**, *1*, 574. Zasorin, I. M.; Spiridonov, E. Z.; Novikov, V. P.; Kupreev, G. I. *Coordination Chem.* (*Engl. Transl.*) **1975**, *1*, 473.

(5) Edwards, A. J.; Stevenson, B. R. *J. Chem. Soc. A* **1968**, 2503–2510. Edwards, A. J.; Stevenson, B. R. *J. Chem. Soc., Chem. Commun.* **1967**, 462–463.

(6) Köhler, J.; Simon, A.; van Wüllen, L.; Cordier, S.; Roisnel, T.; Poulain, M.; Somer, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2683–2690.

(7) Brink, F. J.; Withers, R. L.; Cordier, S.; Poulain, M. *J. Solid State Chem.* **2006**, *179*, 341–348.

(8) Supeł, J.; Marx, R.; Seppelt, K. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2979–2986.

(9) Supeł, J.; Abram, U.; Hagenbach, A.; Seppelt, K. *Inorg. Chem.* **2007**, *46*, 5591–5595.

(10) Glemser, O.; Wegener, J.; Mews, R. R. *Chem. Ber.* **1967**, *100*, 2474–2483.

(11) Ward, B. J.; Stafford, E. F. *Inorg. Chem.* **1968**, *7*, 2569–2573.

(12) Bartlett, N.; Robinson, P. L. *J. Chem. Soc.* **1961**, 3549–3550.

(13) Aynsley, E. E.; Nichols, R.; Robinson, P. L. *J. Chem. Soc.* **1953**, 623–626.

(14) Atherton, M. J.; Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 254–255.

(15) Ruff, O.; Eisner, F. *Chem. Ber.* **1907**, *40*, 2926–2935.

(16) Brisdon, A. K.; Holloway, J. H.; Hope, E. G. *J. Fluorine Chem.* **1998**, *89*, 35–37.

Table 1. Crystallographic Data for $Na_2MoO_2F_4 \cdot H_2O$, $MoO_2F_2 \cdot 2DMF$, and MoO_2F_2

	$Na_2MoO_2F \cdot H_2O$	$MoO_2F_2 \cdot 2DMF$	$MoO_2F_2{}^a$
chemical formula	$F_4H_2MoNa_2O_3$	$C_6F_2H_{14}MoN_2O_4$	F_2MoO_2
M_r	265.92	312.13	165.94
cryst. syst.	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$ (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)
ss/deg	90	98.982(3)	90
$V/10^6$ pm^3	598.86	1121.2	864.5(2)
Z	4	4	12
D_{calcd}/g 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_1)
parameters	93	75	35

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

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

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

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

$$MoO_2Cl_2 + HF \rightarrow MoO_2F_2 \quad (5)$$

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

$$Na_2MoO_4 + IF_5 \xrightarrow{120°C} MoO_2F_2 \text{(Raman)} \quad (7)$$

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 IF_5 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 (^{1}H at 399.65 MHz, ^{13}C at 100.4 MHz, and ^{19}F at 376.00 MHz). Chemical shift values are reported with respect to tetramethylsilane (TMS) (^{1}H, ^{13}C) and CCl_3F (^{19}F). 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 Kα 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 refinement[18]. 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 Kα 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 Kα 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° 2θ. 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.

$Na_2MoO_2F_4 \cdot 2H_2O$. $Na_2MoO_2F_4$ is obtained by dissolving 1 g of Na_2MoO_4 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 $Na_2MoO_2F_4 \cdot 2H_2O$ are grown by slow cooling from 50 °C to room temperature.

^{19}F-NMR (D$_2$O, RT): δ = 84.21 ppm, $w_{1/2} \cong 1000$ 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. $Na_2MoO_2F_4 \cdot 2H_2O$ 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

(17) Schumann, H.; Genthe, W.; Hahn, E.; Hossein, M.-B.; Helm, D. v. d. *J. Organomet. Chem.* **1986**, *28*, 2561–2567.

(18) Sheldrick, S. *Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1986; Sheldrick, S. *SHELXS*; Universität Göttingen: Göttingen, Germany, 1997.

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

	$Na_2MoO_2F_2 \cdot H_2O$	$MoO_2F_2 \cdot 2DMF$
Mo−O	168.5(5), 170.6(6)	169.5(1)
		223.5(1)[b]
Mo−F	ax[a] 192.8(5), 196.3(5)	189.9(1)
	eq[a] 206.4, 212.6(4)	
O−Mo−O	102.7(3)	103.3(1)
		78.38(6)[b]
F−Mo−F	ax 158.2(2)	155.19(8)
	eq 75.6(2)	

	MoO_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 MoO_2 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, $MoOF_4$), 1013 s, 852 s, br, 685 m, 450 w, br, 397 m, 280 m, 154 w, cm^{-1}.

Raman spectrum (white cryst.): 1085 (w, $MoOF_4$), 1014 m, 830 vs, 581 w, 396 w, 374 w, 353 w, 344, 281 m, 271 w, sh, 281 m, 271 w, sh, 202 w, 189 w, 117 w, cm^{-1}.
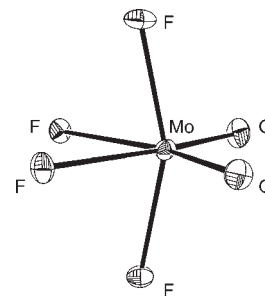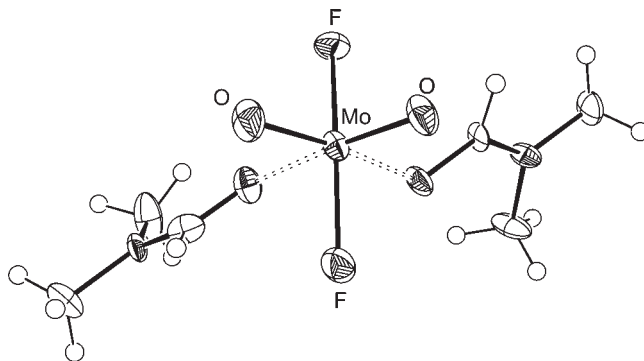
Mass spectrum, (EI rel to ^{98}Mo), m/z = 168 ($MoO_2F_2^+$, 100%), 149 (MoO_2F^+, 45%), 133 ($MoOF^+$, 10%), 130 (MoO_2^+, 10%), 114 (MoO^+, 5%), 98 (Mo^+, 5%).

$MoO_2F_2 \cdot 2DMF$. 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 × 10^6 pm^3 contains 12 molecular units, if a volume of 17−18 × 10^6 pm^3 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 TiF_4, 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 $(Na^+H_2O)_2$ $cis-MoO_2F_4^{2-}$, Ortep representation, 50% probability ellipsoids.

Figure 2. Structure of $MoO_2F_2 2 \cdot DMF$ 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 $Na_2MoO_2F_4 \cdot 2H_2O$ in pure form from Na_2MoO_4 and aqueous HF by a variation of the method for the preparation of $K_2MoO_2F_4$ (*cis*)[19]. It is important to work with an 13% HF concentration in H_2O. $NaHF_2$ 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 $Na^+ \cdot H_2O$ and $cis-MoO_2F_4^{2-}$ 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 HF_2^-), and also it shows the characteristic two strong Mo=O stretching vibrations close to 1000 cm^{-1} characteristic of the $cis-MoO_2$ configuration, see Experimental Section.

$Na_2MoO_2F_4 \cdot H_2O$ is then pyrolyzed 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 H_2O band at 3436 cm^{-1} in the IR spectrum. At 300 °C MoO_2F_2 sublimes out of the salt as a slightly yellow, glassy material. This is completely amorphous according to X-ray powder measurements.

$$Na_2MoO_2F_4 \xrightarrow{300°C} 2NaF + MoO_2F_2$$
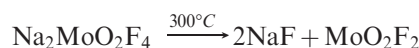
The vacuum pyrolysis has also been done in a mass spectrometer where the parent ion $MoO_2F_2^+$ as the one with highest mass has been identified.

(19) Chaminade, J. P.; Mouton, J. M.; Villeneuve, G.; Conzi, M.; Pouchard, M.; Hagenmüller, P. *J. Sol. State Chem.* **1986**, *65*, 27–39.
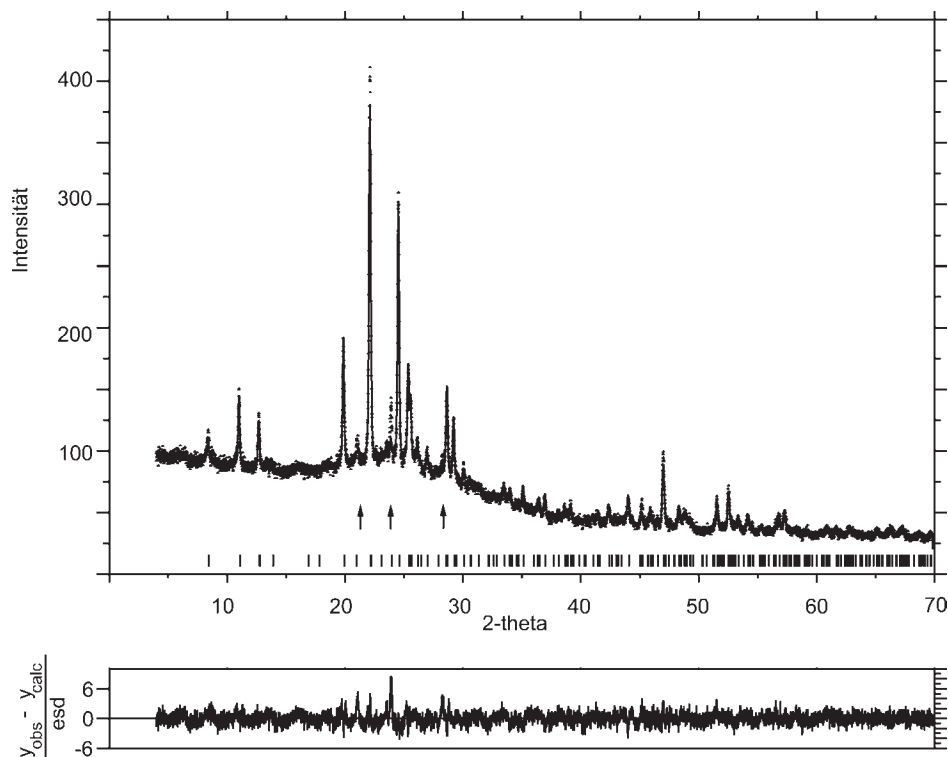
Figure 3. X-ray powder diagram of MoO_2F_2: Upper trace, dots: experimental intensity, line: calculated model. middle trace: position of calculated lines. lower trace difference experimental/calculation. Arrows: indicate strongest deviation.

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 $MoF_4NCl \cdot THF$, 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 $MoO_2Cl_2(CH_3)_3PO$ [21]. MoO_2F_2 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 TiF_4 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 $MoOF_4$, but the known X-ray data cannot be fitted to the impurity lines. But it is quite possible that $MoOF_4$ exists in other modifications than the one reported. (The structurally related ReO_2F_3 comes in four different modifications[8]).

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 MoO_3 (194.8 pm,[22] 198.0 pm[23]), or in ReO_3

(20) Riehl, M.; Wocadlo, S.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1195–1199.
(21) Davis, M. F.; Levason, W.; Ratnani, R.; Reid, G.; Rose, T.; Webster, M. *Eur. J. Inorg. Chem.* **2007**, 306–313.

(22) Kihlborg, L. *Ark. Kemi* **1963**, *21*, 357–364.
(23) Balerna, A.; Bernieri, E.; Burattini, E.; Kuzmin, A.; Lusis, A.; Purans, J.; Cikmach, P. *Nucl. Instrum. Methods Phys. Res.* **1991**, *A308*, 234–239.
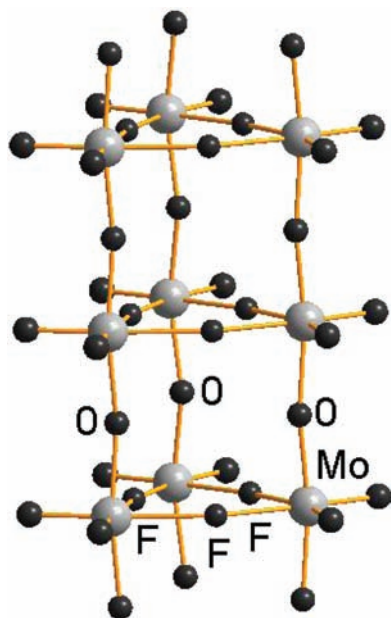
Figure 4. Structural model of MoO_2F_2 from X-ray powder data. Terminal atoms are fluorine and double bonded oxygen atoms, most likely in a disordered manner.

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.

(186.6 pm,[24] 187.8[25]) to name but a few examples. The $Mo\cdots Mo$ distances within the layers of 411 and 417 pm calls for a $Mo-F-Mo$ bridge. In $MoOF_4$ this (asymmetric and bent) bridge results in a $Mo\cdots Mo$ separation of 410.9 pm.[5] In MoO_2F_2 the $Mo-F-Mo$ bridges are essentially symmetric and slightly bent. The total structure resembles that of TiF_4.[26] As can be seen in Figure 4 and 5, only the relative orientation of the triangular columns are different in MoO_2F_2 and TiF_4. This may be due to the fact that the outer boundary of the TiF_4 columns are only fluorine atoms, but in MoO_2F_2 they are fluorine and oxygen atoms. The terminal oxygen and fluorine atoms in the MoO_2F_2 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 ReO_3F polymer, or the $MoO_2F_4^{2-}$ 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
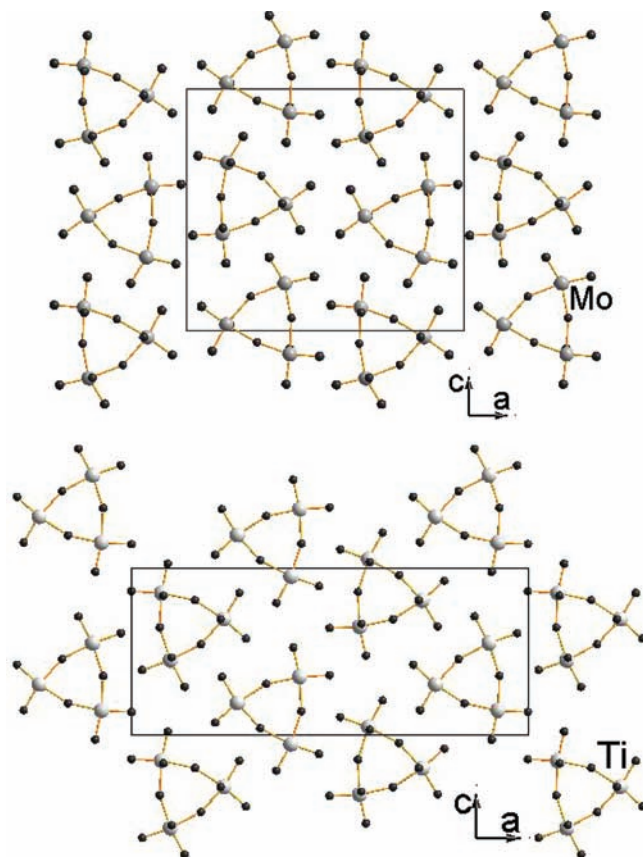
fluorine are quite similar, bond lengths ($Mo=O$ ca. 170 pm, $Mo-F$ ca. 190 pm) and bond angles are quite different.

The possible presence of both oxygen and fluorine bridges is paralleled in the structure of $NbOF_3$, where oxygen atoms seem to be disordered over all possible positions, and ReO_3F, where ordered oxygen and fluorine bridges occur in an ordered manner.

Conclusion

Crystalline MoO_2F_2 has a triangular columnar structure, similar to the TiF_4 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.

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

(24) Meisel, K. *Z. Anorg. Allg. Chem.* **1932**, *207*, 121–128.
(25) Jørgenson, J. E.; Jorgensen, D. J.; Batlogg, B.; Remeika, P.; Axe, J. D. *Phys. Rev. Ser 3* **1986**, *B 33*, 4793–4798.
(26) Bialowons, H.; Müller, M.; Müller, B. G. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1227–1231.