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Orientational disorder and phase transitions in crystals of dioxofluoromolybdate, $(NH_4)_2MoO_2F_4$

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Dioxotetrafluoromolybdate, $(NH_4)_2MoO_2F_4$, was synthesized in a single-crystal form and its structures [(I) at 297 K and (II) at 223 K] were determined by X-ray diffraction. Two independent states of a *cis*-MoO_2F_4 octahedron are characteristic of static and dynamic disorder in structure (I). The dynamically disordered Mo atom is displaced from the symmetry axis producing four possible orientations of an anion that allow O and F atoms to be identified in separate orientations owing to the inherent differences between the Mo—O and Mo—F bonding. After the phase transition at lower temperature, (I) transforms into the statically disordered structure (II) with three possible orientations of the *cis*-MoO_2F_4 octahedron. In this case, it also seemed possible to distinguish between O and F atoms on a local scale. H atoms of two independent NH_4 groups in (II) which form bifurcated N—H···F(O) hydrogen bonds were localized.

1. Introduction

The *cis*-$[MoO_2F_4]^{2-}$ anion is inherently centrosymmetric and contains polarizable Mo—O bonds, making it a potential candidate for second-harmonic generation (SHG). The strategy of crystallizing the $[MoO_2F_4]^{2-}$ anion with two different cations, tetrakis(pyridine)copper(II) ($[Cu(py)_4]^{2+}$) and pyridinum (pyH^+), was capable of ordering two Mo—O bonds (Heier *et al.*, 1998). Another general structural principle is evident in the example of $M(pyz)(H_2O)_2MoO_2F_4$ (M = Zn, Cd), where close-packed helical chains linked by pyrazine led to the formation of a three-dimensional chiral structure (Maggard *et al.*, 2001, 2002, 2004). The *cis*-directing nature of the $[MoO_2F_4]^{2-}$ anions is very important for helical chain formation, while the *trans*-directing $[WO_2F_4]^{2-}$, its group 6 analog, favors the formation of a one-dimensional chain (Welk *et al.*, 2001). Despite similar out-of-center distortions of the metal, the tungsten anion has longer M—O bonds than the molybdenum anion, and the relative nucleophilicities of the corresponding ligands around the M atom in $[MoO_2F_4]^{2-}$ and $[WO_2F_4]^{2-}$ are different. The most negatively charged, or nucleophilic, ligands on the $[MoO_2F_4]^{2-}$ anion, as determined by bond-valence analysis, are the two F positions opposite the *cis*-O atoms, while O1 in $[WO_2F_4]^{2-}$ is highly nucleophilic, closely followed by the fluorides *trans* to the oxides (Welk *et al.*, 2001). This difference should probably be reflected in the crystal structures of $(NH_4)_2WO_2F_4$ and $(NH_4)_2MoO_2F_4$. Recently we have reported the crystal structures of the former compound (Udovenko & Laptash, 2008), but the crystal structure of the latter has not been determined until now. Our optical properties (Mel'nikova & Laptash, 2008*a*,*b*) and calorimetric (Fokina *et al.*, 2010; Gorev *et al.*, 2010) studies of $(NH_4)_2MoO_2F_4$ revealed that there is a significant difference

Table 1
Experimental details.

For all structures: $MoO_2F_4{\cdot}2H_4N$, M_r = 240.02, Z = 4. Experiments were carried out with Mo $K\alpha$ radiation using a Bruker Smart 1000 CCD diffractometer. Absorption was corrected for by multi-scan methods, *SADABS* (Bruker, 1999). Refinement was with 0 restraints.

	(I)	(II)
Crystal data		
M_r	240.02	240.02
Crystal system, space group	Orthorhombic, *Cmcm*	Orthorhombic, *Pnma*
Temperature (K)	297	223
a, b, c (Å)	5.9672 (7), 14.4798 (17), 7.1105 (9)	7.1452 (4), 5.8979 (3), 14.2737 (7)
V (Å^3)	614.37 (13)	601.52 (5)
μ (mm^{-1})	2.16	2.21
Crystal size (mm)	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.30
Data collection		
$T_{\min}$, $T_{\max}$	0.564, 0.564	0.558, 0.558
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8355, 1276, 1202	15 861, 2362, 2237
$R_{\rm int}$	0.021	0.020
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.077, 1.30	0.023, 0.063, 1.22
No. of reflections	1278	2362
No. of parameters	41	60
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.55, −0.64	0.75, −1.56

Computer programs used: *SMART* (Bruker, 1998), *SAINT* (Bruker, 2000), *SHELXTL* (Sheldrick, 2008).

in the temperatures of phase transitions, the symmetry of the low-temperature phase, and the optical and dielectric properties between the two compounds.

In this work the orientational disorder of room- and low-temperature phases of $(NH_4)_2MoO_2F_4$ was investigated to suggest the mechanism of phase transitions in this compound compared with that in $(NH_4)_2WO_2F_4$.

2. Experimental

2.1. Synthesis

Large single crystals of $(NH_4)_2MoO_2F_4$ were synthesized through $(NH_4)_3MoO_3F_3$ obtained from a mixture of ammonium molybdate aqueous solution with a concentrated solution of NH_4F. The resulting excess white precipitate of $(NH_4)_3MoO_3F_3$, which can contain an impurity of $(NH_4)_2MoO_3F_2$, was dissolved in an aqueous solution of HF. The transparent solution was then slowly evaporated in air, and well shaped single crystals of $(NH_4)_2MoO_2F_4$ in the form of prisms or thick plates were obtained.

Anal.: calc. for $(NH_4)_2MoO_2F_4$: NH_4 15.0, Mo 40.0, F 31.7; found: NH_4 15.0, Mo 40.2, F 31.4. Ammonia was determined by the Kjeldahl method with a precision of ± 0.3 mass %. Pyrohydrolysis at 670–700 K was used for the simultaneous determination of fluorine and molybdenum. The sample (0.2–0.4 g) was placed in a Pt boat and hydrolyzed in superheated steam for 2 h. HF was absorbed by water followed by titration with $Th(NO_3)_4$, and molybdenum was analyzed gravimetrically by weighting MoO_3. The precision of fluorine and molybdenum determination was ± 0.5 mass %.

2.2. Crystallographic determination

For the X-ray structure investigations a single crystal of $(NH_4)_2MoO_2F_4$ was prepared in spherical form by dissolving the crystal in water. The crystal was mounted on a glass needle with epoxy resin. Data collections were carried out at 297 (phase I) and 223 K (phase II) with Mo $K\alpha$ radiation (λ = 0.71073 Å) on a Bruker SMART-1000 CCD diffractometer. 0.2° ω scans for (I) and (II) were performed at three φ settings with $2\theta = -31$ and $-60°$ at a detector distance of 45 mm with an exposure time of 20 s per frame. The structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique with an anisotropic approximation of the non-H atoms. H atoms were localized only in the crystal structure of (II) and their positions were not refined. Information on the structure determination is shown in Table 1.[1] Selected bond distances and angles for (I) and (II) are given in Tables 2 and 3. Parameters of hydrogen bonds for (II) are presented in Table 4.

3. Results and discussion

The crystal structures of both phases of $(NH_4)_2MoO_2F_4$ consist of isolated $[MoO_2F_4]^{2-}$ octahedra and ammonium cations. To a first approximation, the crystal structure of (I) was solved with R_1 equal to 0.0502 by location of the Mo atom in the $(0, y, \frac{1}{4})$ position of the space group *Cmcm*. Owing to the relatively large R_1 value and the similarity of crystal structures of (I) and $(NH_4)_2WO_2F_4$ (Udovenko & Laptash, 2008), an additional refinement of structure (I) was carried out by the displacement of the Mo atom from the special 4*c* position into the 16*h* position that reduced R_1 to 0.0362. The electron-density section of the Mo atom in the octahedron (Fig. 1*a*) supports our assumption of the displacement of the Mo atom from the symmetry axis. Thus, the Mo atom was distributed between special Mo1 and general Mo2 sites at the next step of the structural refinement with R_1 = 0.0254. The occupation parameters were refined for the Mo1 and Mo2 sites, and the occupation parameters for the F2 and O2 atoms were assumed to have a ratio of 3:1.

Fig. 2 represents the crystal structure of (I) consisting of two crystallographically independent ammonium groups and disordered $[MoO_2F_4]$ octahedra (Fig. 3*a*). In these octahedra

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5027). Services for accessing these data are described at the back of the journal.

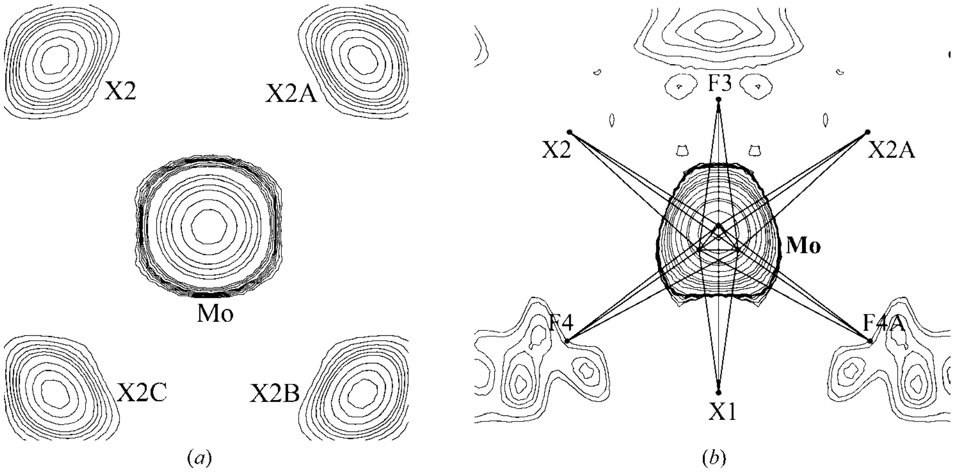
Table 2
Selected distances (Å) and angles (°) for (I).

Mo1—O1	1.681 (3)	Mo2—F1	2.001 (4)	O1—*X*2	2.686 (2) ×4
Mo1—F1	2.060 (3)	Mo2—F2*A*	1.892 (3)	F1—*X*2	2.629 (2) ×4
Mo1—*X*2†	1.901 (1) ×4	Mo2—F2*B*	2.111 (5)	*X*2—*X*2*A*	2.632 (2) ×2
Mo2—O1	1.766 (5)	Mo2—F2*C*	1.921 (4)	*X*2—*X*2*C*	2.706 (2) ×2
Mo2—O2	1.678 (5)				
O1—Mo1—*X*2	96.9 (1) ×4	F1—Mo2—F2*A*	84.9 (2)	O2—Mo2—F2*A*	98.4 (3)
F1—Mo1—*X*2	83.1 (1) ×4	F1—Mo2—F2*B*	79.5 (1)	F2*A*—Mo2—F2*B*	82.0 (2)
*X*2—Mo1—*X*2*A*	87.6 (1) ×2	F1—Mo2—F2*C*	84.2 (1)	F2*B*—Mo2—F2*C*	84.2 (2)
*X*2—Mo1—*X*2*C*	90.7 (1) ×2	O1—Mo2—O2	102.5 (1)	F2*C*—Mo2—O2	93.8 (2)
O1—Mo1—F1	180	O1—Mo2—F2*A*	94.4 (2)	O1—Mo2—F1	166.7 (3)
*X*2—Mo1—*X*2*B*	166.1 (2) ×2	O1—Mo2—F2*B*	87.2 (3)	O2—Mo2—F2*B*	170.2 (3)
F1—Mo2—O2	90.8 (3)	O1—Mo2—F2*C*	93.4 (2)	F2*A*—Mo2—F2*C*	163.8 (2)

† *X*2 = F(O).

Table 3
Selected distances (Å) and angles (°) for (II).

Mo1—O2	1.711 (1) ×2	Mo2—O1	1.708 (1)	Mo2—F3	2.074 (1)
Mo1—F1	1.903 (1)	Mo2—O2	1.724 (1)	Mo2—F4	1.910 (1)
Mo1—F3	1.914 (1)	Mo2—F2*A*	1.917 (1)	Mo2—F4*A*	2.089 (1)
Mo1—F4	2.096 (1) ×2	F3—O2	2.697 (1) ×2	O2—O2*A*	2.683 (2)
F1—O2	2.717 (1) ×2	F3—F4	2.600 (1) ×2	O2—F4	2.653 (1) ×2
F1—F4	2.652 (1) ×2	F4—F4*A*	2.727 (2)		
F1—Mo1—O2	97.3 (1) ×2	F3—Mo1—F4	80.7 (1) ×2	F4—Mo1—F4*A*	81.2 (1)
F1—Mo1—F4	82.9 (1) ×2	O2—Mo1—F4	87.8 (1) ×2	F1—Mo1—F3	158.4 (1)
F3—Mo1—O2	96.0 (1) ×2	O2—Mo1—O2*A*	103.3 (1)	O2—Mo1—F4*A*	168.8 (1) ×2
O1—Mo2—F4	94.1 (1)	F3—Mo2—F4	81.4 (1)	O2—Mo2—F2*A*	94.8 (1)
O1—Mo2—O2	104.7 (1)	F3—Mo2—O2	90.0 (1)	F2*A*—Mo2—F4*A*	82.8 (1)
O1—Mo2—F2*A*	96.9 (1)	F3—Mo2—F2*A*	84.9 (1)	F4—Mo2—F4*A*	85.9 (1)
O1—Mo2—F4*A*	88.0 (1)	F3—Mo2—F4*A*	77.3 (1)	F4—Mo2—O2	93.7 (1)
O1—Mo2—F3	164.9 (1)	O2—Mo2—F4*A*	167.3 (1)	F4—Mo2—F2*A*	163.9 (1)



(*a*) (*b*)

Figure 1
Electron-density section of the Mo atom in (*a*) (I) and (*b*) (II).

axial ligands (O1 and F1) are ordered while three F atoms and one equatorial O atom statistically occupy one general 16*h* position. The Mo atom is distributed on two 4*c* and 16*h* positions with probabilities of 0.43 (4) and 0.14 (1). In the [Mo1O_2F_4] octahedron, four vertices are situated in an equatorial plane at equal distances of 1.901 (1) Å from the central Mo1, while all the interatomic distances differ from one another in the asymmetric [Mo2O_2F_4] (Table 2) that enables F and O atoms to be identified from their Mo2—*X* distances (Fig. 3*b*). These distances are found to be in good agreement with those for crystallographically ordered [MoO_2F_4] octahedra (Heier *et al.*, 1998; Maggard *et al.*, 2002, 2004; Grandjean & Weiss, 1967).

However, appreciable differences should be noted in the Mo—O distances (Table 2). The Mo1 and Mo2 atomic coordinates probably cannot be determined with very high accuracy since the two electron clouds overlap, owing to the short Mo—Mo distance of 0.229 Å. A separate refinement of the structural states gives Mo1—O1 = 1.709 (3) Å for the first refinement, and Mo2—O1 = 1.722 (3), Mo2–O2 = 1.730 (2) Å for the second. Most likely, [Mo2O_2F_4] octahedra rotate stepwise around the ***b*** axis between their own positions, while [Mo1O_2F_4] octahedra are statically disordered similarly to those in $(NH_4)_2WO_2F_4$.

H atoms in (I) were not localized owing to its reorientational disorder. There are 11 O(F) atoms located around the N1 and N2 atoms with distances 3.006 (1)–3.130 (3) and 2.787 (3)–3.356 (3) Å, respectively.

On decreasing the temperature the compound undergoes two phase transitions at 269.8 and 180 K with the entropy changes ΔS_1 = 18.2 ± 1.3 J mol^{-1} K^{-1} and ΔS_2 = 1.70 ± 0.25 J mol^{-1} K^{-1}, respectively (Fokina *et al.*, 2010). The first transition with a rather large ΔS value (*ca R*ln9) means that it is of order–disorder type.

Structure (II) was determined in two possible space groups, *Pnma* and *Pna*2$_1$. We preferred the former centrosymmetric space group, since in *Pna*2$_1$ one H atom was not found, but the structural geometries and R_1 values (0.0233 and 0.0224) were close for these two groups. To a first approximation, the crystal structure of (II) was solved with R_1 = 0.0555 with the Mo atom in the ($x, \frac{1}{4}, z$) position of the space group *Pnma*. Owing to the relatively large R_1 value and the presence of three high electron-density peaks around the Mo atom forming an almost regular triangle, the electron-density section through these peaks was constructed (Fig. 1*b*).

Table 4
Hydrogen-bond parameters (Å, °) in (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F4$^{\rm i}$	0.85	2.25	2.948 (1)	139
N1—H1···F4$^{\rm ii}$	0.85	2.25	2.948 (1)	139
N1—H2···F3$^{\rm iii}$	0.85	2.31	2.978 (1)	136
N1—H2···X2$^{\rm iv}$	0.85	2.47	3.116 (2)	133
N1—H3···F4$^{\rm v}$	0.83	2.28	2.923 (1)	134
N1—H3···F4$^{\rm iii}$	0.83	2.28	2.923 (1)	134
N2—H4···F4$^{\rm vi}$	0.88	2.05	2.844 (1)	150
N2—H5···X2$^{\rm vii}$	0.83	2.37	3.003 (1)	133
N2—H5···X2$^{\rm viii}$	0.83	2.37	3.003 (1)	133
N2—H6···F4$^{\rm ix}$	0.89	2.45	3.166 (1)	138
N2—H6···F4$^{\rm x}$	0.89	2.45	3.166 (1)	138

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, y+1, -z+\frac{1}{2}$; (vii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x-\frac{1}{2}, y+1, -z+\frac{1}{2}$; (ix) $x, -y+\frac{1}{2}, z$; (x) $x, y+1, z$.

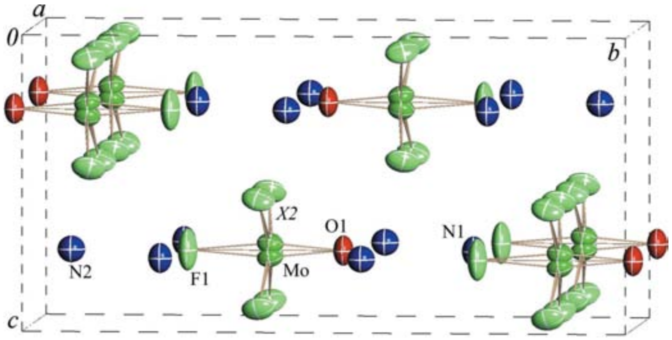


Figure 2
The disordered crystal structure of $(NH_4)_2MoO_2F_4$ at room temperature (I).

Analysis of this section showed two independent Mo atoms in the structure (Mo1 in the special 4c position and Mo2 in the general 8d position), which form three orientations of $[MoO_2F_4]$ around the pseudo-threefold axis. The subsequent refinement of the structure led to $R_1 = 0.0233$. The occupation parameters were refined for the Mo1 and Mo2 sites and the corresponding occupation parameters for the disordered O and F atoms were estimated.

The crystal structure of (II) (Fig. 4) consists of two crystallographically independent ordered NH_4 groups and disordered $[MoO_2F_4]$ octahedra with one F atom and two O atoms statistically occupying the special X1 position and the general X2 position (Fig. 5a). The Mo atom displaced from the octahedral center is randomly distributed on 4c and 8d positions with probabilities of 0.41 (1) and 0.29 (1). In the $[Mo1O_2F_4]$ and $[Mo2O_2F_4]$ octahedra (Figs. 5b and 5c) the O and F atoms were identified from the Mo—X distances (Table 3). The O atoms in the Mo1 environment occupy one general X2 position, while one O atom in the Mo2 environment is situated in the general X2 position and the other one is located in the special X1 position.

The H atoms of both NH_4 groups in (II) are localized. The hydrogen bonds of the type N—H···F(O) (except one) are bifurcated (Table 4) and connect the $[MoO_2F_4]$ octahedra into the frame. This framework structure is rigid and the $[MoO_2F_4]$ disorder in (II) is static. Considering the spatial orientations of the NH_4 tetrahedra in (II) and environments of the N1 and N2 atoms in (I), it can be concluded that the tetrahedra $[N1H_4]$ and $[N2H_4]$ are disordered in (I) on two equivalent orientations connected by the 90° rotation around the local twofold axis of the tetrahedron or by the 180° rotation around the twofold structural axis. During the phase transition, the orientational equivalency of the NH_4 tetrahedra is disturbed owing to atomic displacements, and the NH_4 groups acquire only one orientation. It should be noted that the atomic pairs N1—O1 (3.130 Å) and N2—F1 (2.787 Å) in (I), located on the twofold axis, do not form hydrogen bonds, *i.e.* the H atoms are not situated on the structural axes. First, the hydrogen bonds are formed by the F atoms (Table 4) opposite the O atoms in the octahedron in accordance with the highest nucleophilicities of these ligands. The formation of these hydrogen bonds ensures the transition from the dynamic disorder of structural units to the rigid lattice with static disorder of the $[MoO_2F_4]$ octahedra.

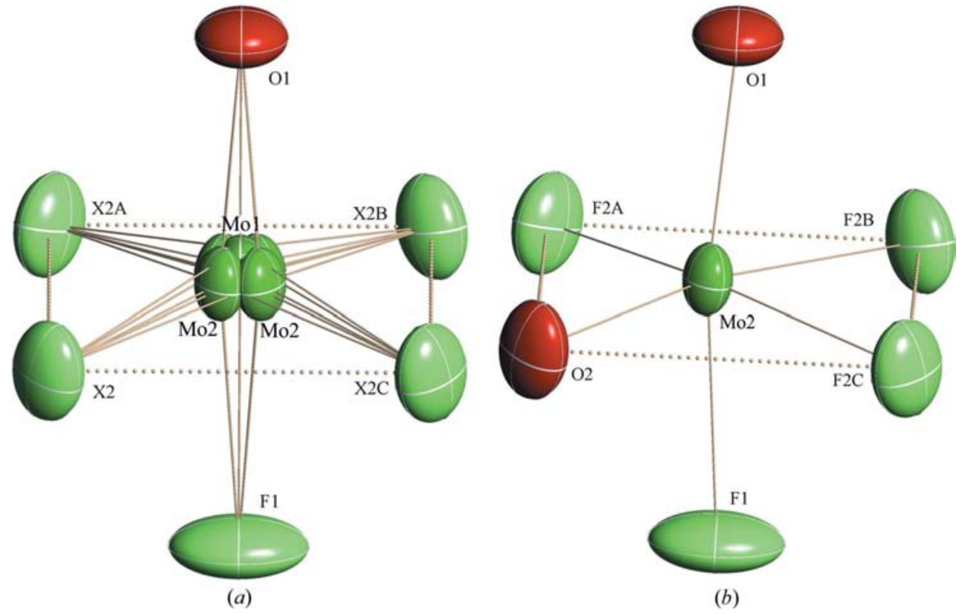


Figure 3
Superposition of static and dynamic states of (a) $[MoO_2F_4]$ octahedra and the real geometry of (b) the $[Mo2O_2F_4]$ octahedron in structure (I).

It is now possible to calculate ΔS at phase transitions from different structural units. Taking into account two orientations of the [N1H$_4$] groups and two orientations of the [N2H$_4$] tetrahedra, and also the fact that only dynamically disordered Mo2O$_2$F$_4$ octahedra participate in the phase transition, ΔS can be expressed as: $\Delta S = R\ln 2.2 + R\ln 2 + R\ln 2 = R\ln 8.8$, which is very close to the $R\ln 9$ observed experimentally. The first component of the sum means that only 56% of all Mo atoms (in accordance with position probabilities) rotate and contribute to ΔS at the phase transition (*i.e.* $R\ln 2.2$ from a possible $R\ln 4$). In the case of $(NH_4)_2WO_2F_4$, this part is equal to $R\ln 3.3$, while two NH$_4$ groups should give $R\ln 3$ in accordance with position probabilities of the dynamically disordered W atom (86%) and the value of ΔS ($R\ln 10$). These data reveal that the octahedra and the ammonium groups in both complexes reorient independently at room temperature. The absence of strong N—H···F(O) bonds in the *Cmcm* phase of $(NH_4)_2WO_2F_4$ was confirmed by the coincidence of the phase transition temperature (T_1) and the pressure coefficient dT_1/dp of $(NH_4)_2WO_2F_4$ (Flerov *et al.*, 2006*a*,*b*) and $(ND_4)_2WO_2F_4$ (Flerov *et al.*, 2007*a*,*b*). After the phase transition the anionic sublattice in the two complexes $(NH_4)_2WO_2F_4$ and $(NH_4)_2MoO_2F_4$ transform to the rigid state, but the octahedra are fully ordered in the former while they are statistically disordered in the latter case. Ammonium groups are fully ordered in the low-temperature phase of $(NH_4)_2MoO_2F_4$, while they partially move (reorient) in the low-temperature phase of $(NH_4)_2WO_2F_4$.

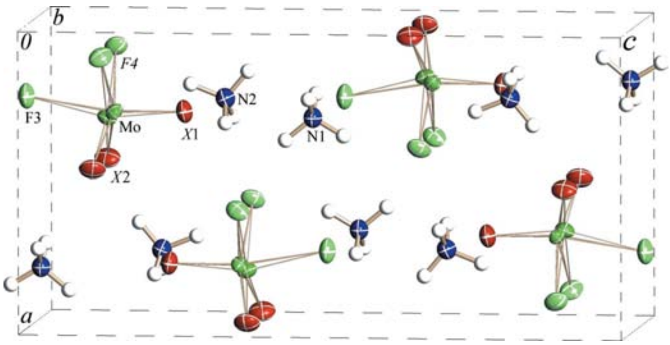


Figure 4
The statically disordered crystal structure of $(NH_4)_2MoO_2F_4$ (II) at 223 K after the phase transition.

4. Conclusions

The crystal structures of $(NH_4)_2MoO_2F_4$ and $(NH_4)_2WO_2F_4$ at room temperature are very similar and differ only by the ratio of the static and dynamic components of orientational disorder. At low temperature the two complexes undergo order–disorder phase transitions from dynamic states to static states. The *cis*-directing nature of the $[MoO_2F_4]^{2-}$ anions is probably responsible for the static disorder in the anionic sublattice and the order of all ammonium groups in $(NH_4)_2MoO_2F_4$, while the *trans*-directing property of $[WO_2F_4]^{2-}$ ensures anionic static ordering and partial order of the ammonium groups in $(NH_4)_2WO_2F_4$. It also seemed possible to discern the O and F atoms on a local scale under static disorder (not only under dynamic disorder) of the $[MoO_2F_4]^{2-}$ octahedron having three spatial orientations around its pseudo-threefold axis. The case is rare and similar to that of Na_2NbOF_5 (Stomberg, 1984) with two spatial anionic orientations.

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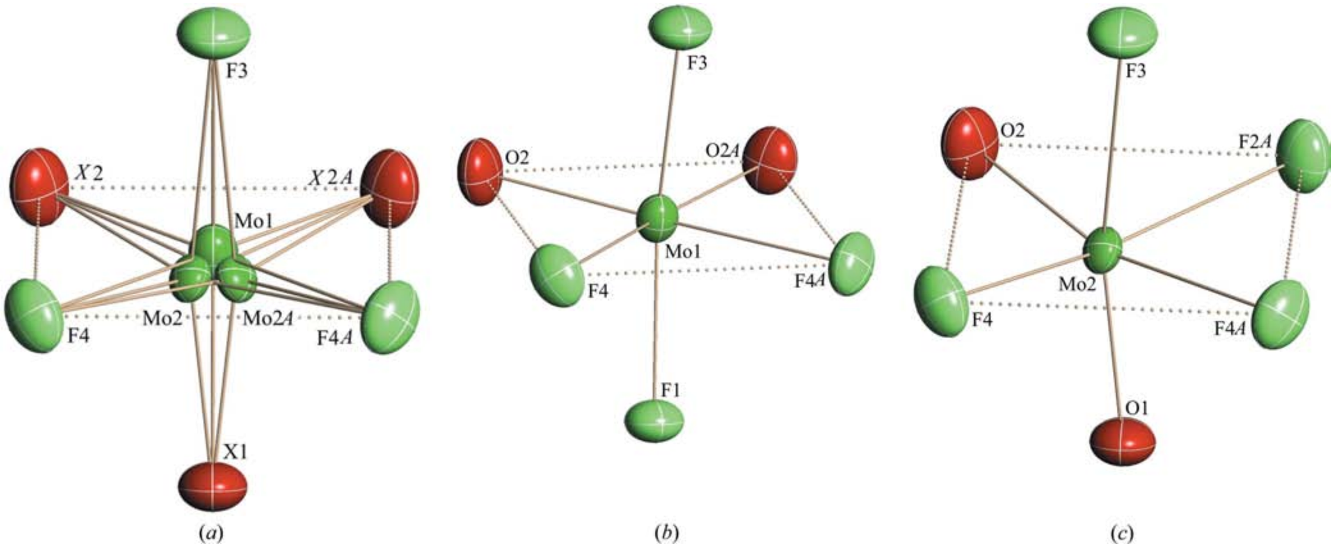

Figure 5
Some fragments of structure (II): (*a*) spatial orientations of [MoO$_2$F$_4$] octahedron; coordination polyhedra of (*b*) Mo1 and (*c*) Mo2.

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