Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Disorder in crystals of dioxofluorotungstates, $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$

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Received 2 April 2008
Accepted 13 October 2008

Dioxotetrafluorotungstates $(NH_4)_2WO_2F_4$ [(I) at 297 K and (II) at 133 K] and $Rb_2WO_2F_4$ (III) were synthesized in a single-crystal form and their structures were determined by X-ray diffraction. Two independent states of the *cis*-WO_2F_4 octahedron are characteristic of static and dynamic disorder in structure (I). Dynamically disordered W2 is displaced from the symmetry axis producing four possible orientations of anion that permits O and F atoms to be identified in separate orientations owing to the inherent differences between W—O and W—F bonding. After the phase transition at lower temperature (201 K), (I) transforms into the twin structure (II) with complete O/F ordering. Structure (III) is characterized by full O/F static disorder without any phase transitions at lower temperature.

1. Introduction

One of the important strategies for synthesizing new polar materials with a range of useful physical properties including pyroelectricity, ferroelectricity, piezoelectricity and second harmonic generation (SHG) is to use inherently polar, or non-centrosymmetric, anions, such as *fac*-$[MO_3F_3]^{n-}$, *cis*-$[MO_2F_4]^{n-}$ or $[MOF_5]^{n-}$ anions (M = d^0 transition metal; Withers *et al.*, 2007; Maggard *et al.*, 2003; Marvel *et al.*, 2007). The crystallographic order of the oxofluoride anions provides an opportunity to synthesize a noncentrosymmetric solid-state structure, which is a potential candidate for use in new SHG materials (Heier *et al.*, 1999). Out-of-center octahedral distortions are responsible for SHG properties. Thus, oxofluoride anions themselves are an attractive component for the design and synthesis of new SHG active materials (Heather *et al.*, 2005). Two different nitrogen-containing cations, tetrakis(pyridine)copper(II) ($[Cu(py)_4]^{2+}$) and pyridinum (pyH^+), or $[Cu(py)_4]^{2+}$ and 5-hydroxy-2-methylpyridinum ($[HNC_6H_6OH]^+$) were employed to discern the oxide and fluoride positions on the $[MO_2F_4]^{2-}$ (M = Mo, W) anions (Heier *et al.*, 1999; Welk *et al.*, 2002; Maggard *et al.*, 2002; Welk *et al.*, 2001; Norquist *et al.*, 1998; Heier *et al.*, 1998). The fully ordered $[WO_2F_4]^{2-}$ anion has only been observed in $[HNC_6H_6OH]_2Cu(py)_4(WO_2F_4)_2$ (Welk *et al.*, 2001) and in $Na_2WO_2F_4$ (Vlasse *et al.*, 1982; Chaminade *et al.*, 1986). In other cases studied it is completely or partially disordered as a consequence of static orientational disorder (12 possible orientations of a distorted *cis*-$[WO_2F_4]^{2-}$ octahedron in a crystal; Heier *et al.*, 1998, 1999). Among the series of $A_2WO_2F_4$ (A = alkali cation or ammonium), $Cs_2WO_2F_4$ displays the anion in a completely disordered orientation (Srivastava & Ackerman, 1992). Crystal structures of $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$ have not been determined until now in spite of the

doi:10.1107/S0108768108033053

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$F_4O_2W{\cdot}2H_4N$	$F_4O_2W{\cdot}2H_4N$	$F_4O_2W{\cdot}2Rb$
M_r	327.93	327.93	462.79
Cell setting, space group	Orthorhombic, *Cmcm*	Triclinic, $P\bar{1}$	Trigonal, $P\bar{3}m1$
Temperature (K)	297 (2)	133 (2)	297 (2)
a, b, c (Å)	5.9410 (4), 14.4206 (10), 7.1456 (5)	5.9013 (4), 14.1993 (9), 7.7162 (5)	6.0056 (3), 6.0056 (3), 4.8636 (5)
α, β, γ (°)	90.00, 90.00, 90.00	90.022 (2), 112.466 (2), 89.999 (2)	90.00, 90.00, 120.00
V (Å^3)	612.18 (7)	597.50 (7)	151.91 (2)
Z	4	4	1
D_x (Mg m^{-3})	3.558	3.645	5.059
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	18.77	19.36	34.94
Crystal form, color	Sphere, colorless	Sphere, colorless	Plate, colorless
Crystal size (mm)	$r = 0.13$	$r = 0.13$	0.12 × 0.12 × 0.03
Data collection			
Diffractometer	Bruker Smart 1000 CCD	Bruker Smart 1000 CCD	Bruker Smart 1000 CCD
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan	Multi-scan	Integration
$T_{\min}$	0.089	0.086	0.011
$T_{\max}$	0.089	0.086	0.183
No. of measured, independent and observed reflections	8105, 1012, 937	15 611, 6355, 6066	1232, 216, 208
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.034	0.035	0.035
$\theta_{\max}$ (°)	39.0	39.4	31.4
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.045, 1.13	0.039, 0.092, 1.06	0.020, 0.047, 1.01
No. of reflections	1012	6355	216
No. of parameters	41	165	13
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.6776P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0P)^2 + 17.957P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.656P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.045	0.027	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.58, −1.52	10.21, −7.77	0.95, −1.90
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.0201 (3)	0.00027 (10)	0.169 (3)

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

fact that the former has been known for more than 140 years (it was first described by Marignac, 1862, 1863).

In this work structural analysis of $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$ was undertaken to distinguish between static and dynamic disorder of the structural units forming crystals of these compounds.

2. Experimental

2.1. Synthesis

Reagent-grade tungsten oxide compounds, aqueous hydrofluoric acid (45% HF by weight) and ammonium hydrogen difluoride were used. Two methods were employed for preparing diammonium dioxotetrafluorotungstate. The first was the fluoridation of tungstates with concentrated HF. We used ammonium *para*-tungstate. The other method was the fluoridation of tungsten trioxide WO_3, ammonium or calcium tungstate (scheelite, $CaWO_4$) with NH_4HF_2. The initial components were mixed in a stoichiometric ratio and heated to 473 K, producing $(NH_4)_3WO_2F_5$. $CaWO_4$ as a starting material was preferable because of its faster interaction with NH_4HF_2

$$CaWO_4 + 3.5NH_4HF_2 = CaF_2 + (NH_4)_3WO_2F_5 + 0.5NH_3 + 2H_2O.$$

The cake was leached by water (solid:liquid = 1:4), and the mother liquor was filtered and slowly evaporated in air. $(NH_4)_2WO_2F_4$ crystallized from the saturated solution. High-quality differently shaped single crystals (thick plates, prisms, isometric polyhedra) of this salt were obtained through $(NH_4)_3WO_3F_3$ which was precipitated from a hot solution of $(NH_4)_2WO_2F_4$ in excess NH_4F, followed by the addition of aqueous NH_3 until a white product appeared during the process of stirring. The solid was dissolved in HF aqueous solution, filtered and slowly evaporated in air at room temperature.

$Rb_2WO_2F_4$ was synthesized in accordance with the reaction

$$(NH_4)_2WO_2F_4 + Rb_2CO_3 = Rb_2WO_2F_4 + 2NH_3 + CO_2 + H_2O.$$

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

W1—O1	1.689 (2)	W2—F1	2.004 (2)	O1—*X*2	2.699 (2) ×4
W1—F1	2.079 (2)	W2—F2*A*	1.890 (1)	F1—*X*2	2.626 (2) ×4
W1—*X*2†	1.897 (1) ×4	W2—F2*B*	2.070 (1)	*X*2—*X*2*A*	2.623 (2) ×2
W2—O1	1.782 (2)	W2—F2*C*	1.903 (1)	*X*2—*X*2*C*	2.695 (2) ×2
W2—O2	1.705 (1)				
O1—W1—F1	180	F1—W2—F2*A*	84.75 (4)	O1—W2—F2*B*	88.61 (4)
O1—W1—*X*2	97.46 (4) ×4	F1—W2—F2*B*	80.24 (4)	O1—W2—F2*C*	94.11 (4)
F1—W1—*X*2	82.54 (4) ×4	F1—W2—F2*C*	84.42 (4)	O2—W2—F2*A*	96.99 (7)
*X*2—W1—*X*2*A*	87.50 (7) ×2	O1—W2—F1	168.84 (2)	F2*A*—W2—F2*B*	82.82 (7)
*X*2—W1—*X*2*C*	90.57 (7) ×2	O1—W2—O2	101.38 (5)	F2*B*—W2—F2*C*	85.34 (7)
F1—W2—O2	89.76 (5)	O1—W2—F2*A*	94.55 (4)	F2*C*—W2—O2	93.11 (8)

† X2 = F(O).

The reactants were mixed in a stoichiometric ratio, thoroughly ground and heated on a hot plate (at~ 573 K) until the Rb fully displaces the NH_4 (no green coloring of a wet indicator paper in vapors of the gaseous products). Polycrystalline $Rb_2WO_2F_4$ was then water-dissolved with the addition of a small amount of HF, filtered and slowly evaporated in air at room temperature. Hexagonal plates or needles were crystallized which were suitable for X-ray determinations.

Anal.: calc. for $(NH_4)_2WO_2F_4$: NH_4 11.0, W 56.1, F 23.2; found: NH_4 10.9, W 55.9; F 23.5. $Rb_2WO_2F_4$ was checked only with regard to the Rb content (calc. Rb 36.9, found Rb, 36.6). Ammonia was determined by the Kjeldahl method with a precision of ± 0.3 mass %. Pyrohydrolysis at 673 K was used for the simultaneous determination of fluorine and tungsten. 0.2–0.4 g of the sample placed in a Pt boat were hydrolyzed in superheated steam for 2 h. HF was absorbed by water followed by titration with $Th(NO_3)_4$, and tungsten was analyzed gravimetrically by weighing WO_3. The precision of fluorine and tungsten determination was ± 0.5 mass %. Rubidium was determined by atomic absorption spectrometry.

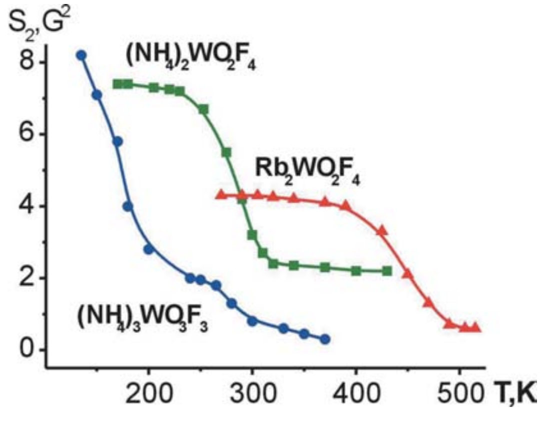

Figure 1
Second moment of ^{19}F NMR spectra *versus* temperature for the compounds under study. $(NH_4)_3WO_3F_3$ is presented for comparison to emphasize the reorientational anionic motion at the lowest temperature of the experiment (no plateau is observed).

2.2. Crystallographic determination

Single crystals of $(NH_4)_2WO_2F_4$ in the spherical form and a hexagonal plate of $Rb_2WO_2F_4$ were chosen for the X-ray structure investigations. The crystals were mounted on glass needles with epoxy resin. Data collections were carried out at 297 and 133 K 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 2θ = −31 and −50° 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 method with anisotropic approximation of the non-H atoms. H atoms were not localized in the crystal structure of $(NH_4)_2WO_2F_4$. Information about the structure determination is gathered in Table 1.[1] Selected bond distances and angles for (I), (II) and (III) are given in the corresponding tables (see text).

2.3. Solid-State ^{19}F NMR spectroscopy

^{19}F NMR spectra of polycrystalline samples (the first derivatives of absorption signals) were recorded on a modified Bruker SWL 3-100 CW wide-line spectrometer (84.66 MHz) in the temperature range (135–510) ± 2 K. The error in measuring the second moments S_2 of the NMR spectra was no more than 5–8% and the error in the determination of the half-widths δB was no more than 2%. The second moments for $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$ crystals were calculated by the Van Vleck formula.

2.4. Spectroscopic measurements

Mid-IR (400–4000 cm^{-1}) spectra were collected using a Shimadzu FTIR Prestige-21 spectrometer at ambient temperature operating at a resolution of 2 cm^{-1}. The *cis*-WO_2 symmetric and asymmetric stretches were visible at 957 and 889 cm^{-1} and at 949 and 897 cm^{-1} in the spectra of $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$, respectively.

The Raman spectra of samples were recorded with a Triplemate, SPEX spectrometer equipped with a multichannel detector, LN-134PB, Princeton Instruments, in backscattering geometry. The spectral resolution was 1 cm^{-1}. The 488 nm, 100 mW line of an Ar ion laser was used for the spectral excitation. For the low-temperature measurements the sample was fixed on a cold finger of a helium cryostat (APD Cryogenic Inc). The temperature was measured with an accuracy of 0.1 K.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5013). Services for accessing these data are described at the back of the journal.

3. Results and discussion

The crystal structures of both compounds investigated consist of isolated $[WO_2F_4]^{2-}$ octahedra and the corresponding cations. It should be taken into consideration that the tungsten octahedron reorientates dynamically in $(NH_4)_2WO_2F_4$ at room temperature in accordance with the ^{19}F NMR data (Fig. 1), while it forms a rigid sublattice in $Rb_2WO_2F_4$. To a first approximation, the crystal structure (I) was solved with R_1 equal to 0.0398 by location of the W atom in the $(0, y, \frac{1}{4})$ position of the space group *Cmcm*. Owing to the relatively large R_1 value that was probably due to the reorientational motion of the $[WO_2F_4]^{2-}$ anions around a twofold (or pseudo fourfold) axis (Voit *et al.*, 2006), an additional refinement of structure (I) was carried out by the displacement of the W atom from the special 4(*c*) position into the 16(*h*) position that reduced R_1 to 0.0289. According to the Raman spectra of this compound (Fig. 2), two states of the *cis*-$[WO_2F_4]^{2-}$ octahedron can be observed. Thus, the W atom was distributed between special W1 and general W2 sites at the next step of the structural refinement which finished with a low R_1 value of 0.0200. The occupation parameters were refined for the W1 and W2 sites, and the occupation parameters for the F2 and O2 atoms were determined from a ratio of 3:1.

A similar structural refinement was carried out in two other possible groups, *Cmc*2_1 and *Ama*2, that gave the somewhat higher *R* values of 0.022 and 0.033, respectively, and unreasonable distances in the octahedron. Thus, the choice of the centrosymmetric space group *Cmcm* seemed to be correct, which was confirmed by the absence of a second harmonic generation (SHG) response in the $(NH_4)_2WO_2F_4$ crystal.

Fig. 3 represents the crystal structure of (I) consisting of two crystallographycally independent ammonium groups and disordered $[WO_2F_4]$ octahedra (Fig. 4*a*). In these octahedra, axial ligands (O1 and F1) are ordered while three fluorine atoms and one oxygen equatorial atom occupy statistically one general 16(*h*) position, and the W atom is distributed on two 4(*c*) and 16(*h*) positions with probabilities of 0.143 (6) and 0.214 (2), respectively. In the $[W1O_2F_4]$ octahedron, four vertexes are situated in an equatorial plane at equal distances of 1.897 Å from the central W1, while all the interatomic distances differ from each another in the asymmetric $[W2O_2F_4]$ (Table 2) that enables F and O atoms to be identified from their W2—*X* distances (Fig. 4*b*).

However, an appreciable difference should be noted in the W—O distances compared with 1.75 Å for $Na_2WO_2F_4$ (Vlasse *et al.*, 1982). The W1 and W2 atomic coordinates probably cannot be determined with very high accuracy since the two electron clouds overlap, owing to the short W—W distance of 0.203 Å. A separate refinement of the structural states gives W1—O1 = 1.750 (7) and W—F1 = 2.013 (7) Å for the first one, and W2—O1 = 1.761 (4), W2—O2 = 1.732 (2) and W2—F1 = 2.023 (4) Å for the second one. Somewhat different W2—O distances in the $[W2O_2F_4]$ octahedron are probably due to the influence of hydrogen bonds. Most likely, $[W2O_2F_4]$ octahedra rotate stepwise around the **b** axis between their own positions, while $[W1O_2F_4]$ octahedra are statically disordered.

It should be noted that it is not so very rare that static and dynamic disorder are present simultaneously in a crystal lattice. An electron paramagnetic resonance (EPR) study of $(NH_4)_3VO_2F_4$ (Rao *et al.*, 1982) showed that the anions in this compound are both dynamically and statically disordered at room temperature. The crystal structure determination of $(NH_4)_3VO_2F_4$ (Leimkuhler & Mattes, 1986) indicated the presence of two crystallographically non-equivalent $[VO_2F_4]$ octahedra in the structure. In spite of some inaccuracies published, such as the *trans* structure of $[VO_2F_4]^{3-}$ (Rao *et al.*, 1982) or unreasonably short hydrogen-bridged N···O and N···F bonds of 2.00–2.02 Å (Leimkuhler & Mattes, 1986), the

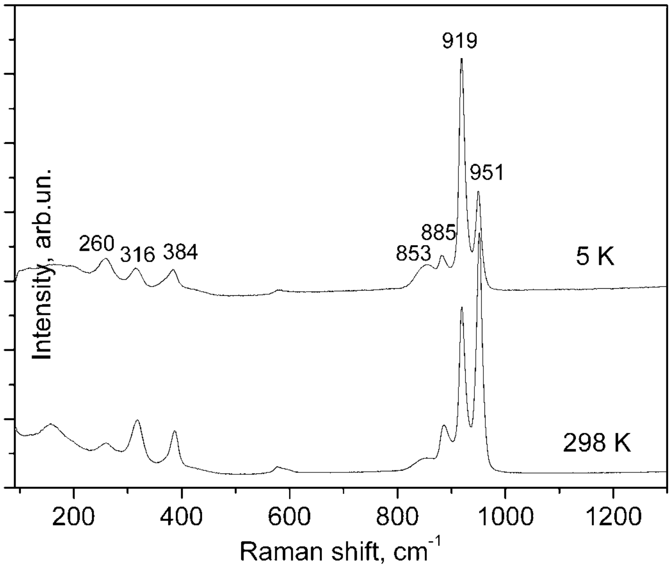

Figure 2
Raman spectra of $(NH_4)_2WO_2F_4$ (488 nm laser beam).

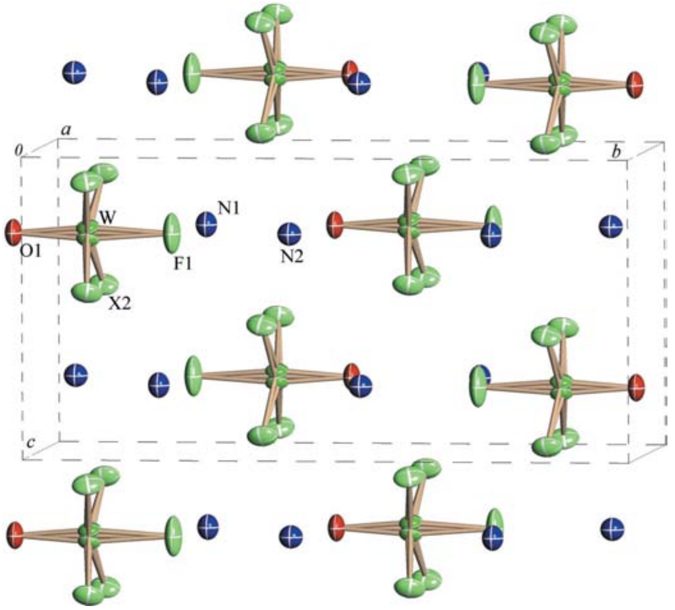

Figure 3
Disordered crystal structure of $(NH_4)_2WO_2F_4$ (I) at 297 K.

Table 3

Unit-cell transformations for the $(NH_4)_2WO_2F_4$ (II) twin crystal (see also Table 1).

	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
Basis	**a**, **b**, **c**	−**a**, **b**, −**c**	**a**, −**b**, −**a** − **c**	−**a**, −**b**, **a** + **c**	**a**, **b**, **a** + 2**c**
a (Å)	5.9013	5.9013	5.9013	5.9013	5.9013
b (Å)	14.199	14.199	14.199	14.199	14.199
c (Å)	7.716	7.716	7.716	7.716	14.261
α (°)	90.02	89.97	90.02	89.98	90.02
β (°)	112.47	112.49	112.49	112.49	89.98
γ (°)	90.00	90.02	90.02	89.98	90.00

main feature concerning the existence of two disordered octahedral states (static and dynamic) does not seem to be in doubt.

H atoms in the structure of (I) were not localized. Ten and eight O(F) atoms are close to N1 and N2, respectively. The ammonium groups are therefore not in tetrahedral environments, which means that they are disordered by rotation (reorientation). On decreasing the temperature the compound undergoes two phase transitions (PT) at 201 and 160 K with the entropy changes $\Delta S_1 = 19.0 \pm 1.1$ J mol^{-1} K^{-1} and $\Delta S_2 = 1.40 \pm 0.07$ J mol^{-1} K^{-1}, respectively (Flerov *et al.*, 2006). The first one, which is a PT of the order–disorder type, was presumably mainly a result of the ordering of ammonium groups because no crystal data of the low-temperature phase were available. Nevertheless, a polarization–optical study of $(NH_4)_2WO_2F_4$ revealed that the phase transition at low temperature is connected with the symmetry change *Cmcm* ↔ $\bar{1}$ and the formation of a twin structure (Mel'nikova *et al.*, 2006).

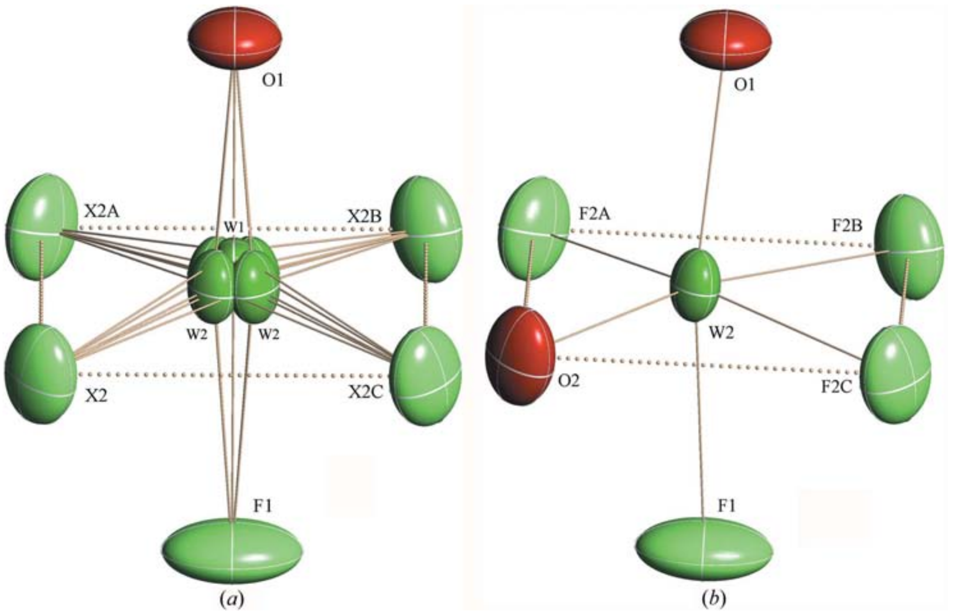

Figure 4

Superposition of the static and dynamic states of $[WO_2F_4]$ octahedra (*a*) and the real geometry of the $[W2O_2F_4]$ octahedron (*b*) in the structure of (I).

A phase transition of crystal (I) into the twinned state (II) was confirmed as a result of the structure determination and refinement of (II), which was performed with R_1 equal to 0.195 in the triclinic unit cell $P\bar{1}$ proposed by the *INDEX* procedure. Alternatively, a pseudo-orthorhombic supercell may be found whose 222/*mmm* pseudo-symmetry defines a four-component twin with the twin rules shown in Table 3. A similar case has been published in detail (Bolotina *et al.*, 2005). Structure (II) was refined in several models either as a two- or four-component twin using different combinations of the twin rules. The corresponding procedures of *SHELXTL* were used which were connected either with *HKL*4 or *HKL*5 data formats. The following results were obtained in three two-component twin models:

(i) Cell 1–Cell 2 (TWIN/$\bar{1}$00; 010; 00$\bar{1}$/): $R_1 = 0.0392$; twin ratio 0.52 (1):0.48 (1); positive-definite displacement ellipsoids were determined for all the atoms.

(ii) Cell 1–Cell 3 (TWIN/100; 0$\bar{1}$0; $\bar{1}$0$\bar{1}$/): $R_1 = 0.141$; twin ratio 0.50 (3):0.50 (3); all atoms were determined to have nonpositive-definite ellipsoids; bond lengths seemed to be unreasonable.

(iii) Cell 1–Cell 4 (TWIN/$\bar{1}$00; 0$\bar{1}$0; 101): $R_1 = 0.0394$; twin ratio 0.52 (1):0.48 (1); some ellipsoids were nonpositive-definite.

The structure refinement in a four-component twin model finished with $R_1 = 0.0354$. Four twin parts were refined as approximately equal in volume, however, the displacement ellipsoids of some F and O atoms were negatively determined. However, all variants of structural refinement with relatively low *R* values resulted in equal values of all the atomic coordinates within the error limits. The two-component twin model formed by Cell 1 and Cell 2 was chosen as the final result.

The structure (II) is ordered (Fig. 5) with two kinds of $[WO_2F_4]$ octahedra which are geometrically close to $[W2O_2F_4]$ in the structure of (I) (Table 4). The analysis of the nitrogen environment shows that the ammonium groups in (II) still rotate. It is clear that the changes in the motions of the octahedra (to *R*ln4 from *R*ln10) are the main contributors to ΔS_1 at the phase transition. This conclusion is in accordance with the ^{19}F NMR data.

$Rb_2WO_2F_4$ (III) crystallizes in the space group *Pm*1 and it is isostructural with $Cs_2WO_2F_4$ (Srivastava & Ackerman, 1992). Its structure is fully disordered (Fig. 6). The W—*X* distances are averaged and the $[WO_2F_4]$ octahedra are almost regular (Table 5). As in $Cs_2WO_2F_4$, each oxide or fluoride ion of (III) is surrounded by four equidistant

Table 4
Selected distances (Å) and angles (°) for (II).

W1—O1	1.732 (3)	F1—O2	2.708 (5)	F5—O4	2.699 (6)
W1—O2	1.770 (4)	F1—F2	2.583 (5)	F5—F6	2.646 (6)
W1—F1	2.053 (4)	F1—F3	2.532 (5)	F5—F7	2.541 (6)
W1—F2	1.915 (3)	F1—F4	2.656 (5)	F5—F8	2.582 (5)
W1—F3	1.996 (4)	O1—O2	2.709 (5)	O3—O4	2.697 (6)
W1—F4	1.923 (4)	O1—F2	2.705 (5)	O3—F6	2.759 (5)
W2—O3	1.727 (4)	O1—F3	2.676 (6)	O3—F7	2.696 (5)
W2—O4	1.755 (4)	O1—F4	2.756 (6)	O3—F8	2.708 (6)
W2—F5	2.053 (3)	O2—F2	2.683 (5)	O4—F6	2.724 (6)
W2—F6	1.923 (3)	F2—F3	2.702 (5)	F6—F7	2.573 (5)
W2—F7	2.024 (4)	F3—F4	2.654 (5)	F7—F8	2.712 (5)
W2—F8	1.923 (3)	F4—O2	2.712 (6)	F8—O4	2.672 (5)

O1—W1—O2	101.4 (2)	F3—W1—F4	81.7 (2)	F5—W2—F6	83.4 (2)
O1—W1—F2	95.6 (2)	F4—W1—O2	94.4 (2)	F5—W2—F7	77.1 (2)
O1—W1—F3	91.5 (2)	O1—W1—F1	168.5 (2)	F5—W2—F8	80.9 (2)
O1—W1—F4	97.6 (2)	O2—W1—F3	167.0 (2)	O4—W2—F6	95.5 (2)
F1—W1—O2	89.9 (2)	F2—W1—F4	163.0 (2)	F6—W2—F7	81.3 (2)
F1—W1—F2	81.2 (2)	O3—W2—O4	101.5 (2)	F7—W2—F8	86.8 (2)
F1—W1—F3	77.4 (2)	O3—W2—F6	98.1 (2)	F8—W2—O4	93.1 (2)
F1—W1—F4	83.8 (2)	O3—W2—F7	91.6 (2)	O3—W2—F5	168.3 (2)
O2—W1—F2	93.4 (2)	O3—W2—F8	95.6 (2)	O4—W2—F7	166.9 (2)
F2—W1—F3	87.4 (2)	F5—W2—O4	89.9 (2)	F6—W2—F8	162.0 (2)

rubidium cations so that each ligand is in an identical coordination environment and the anion is disordered. Such an explanation was given by Marvel *et al.* (2007). Thus, in contrast to (I), disorder in (III) has a static character with 12 possible orientations of the [WO_2F_4] anion. Compound (III) does not undergo any phase transition at lower temperatures. However, it shows a yellow luminescence at room temperature as does $Cs_2WO_2F_4$ (Srivastava & Ackerman, 1992). This phenomenon is scheduled to be the subject of a future paper. An attempt was undertaken to refine structure (III) by displacing the W atom from the (0, 0, 0) position by analogy with (I), but the atomic coordinates returned to their initial values.

4. Conclusions

The structures of $(NH_4)_2WO_2F_4$ and $Rb_2WO_2F_4$ are characterized by orientational disorder of a different nature. In the rubidium complex, indistinguishable positions of O and F atoms appear to be statically disordered in their orientation which obscures the true geometry of the [WO_2F_4] octahedron. A similar phenomenon is also observed in the structure of the ammonium complex for [$W1O_2F_4$] octahedra. However, in the case of [$W2O_2F_4$] octahedra we were able to suggest the reorientational motion model of these octahedra and identify the O and F atoms on the local scale owing to the dynamic nature of the disorder. Phase transitions of the order–disorder type at decreasing temperatures are connected with dynamic orientational disorder in $(NH_4)_2WO_2F_4$ but are absent in the case of the static disorder in $Rb_2WO_2F_4$.

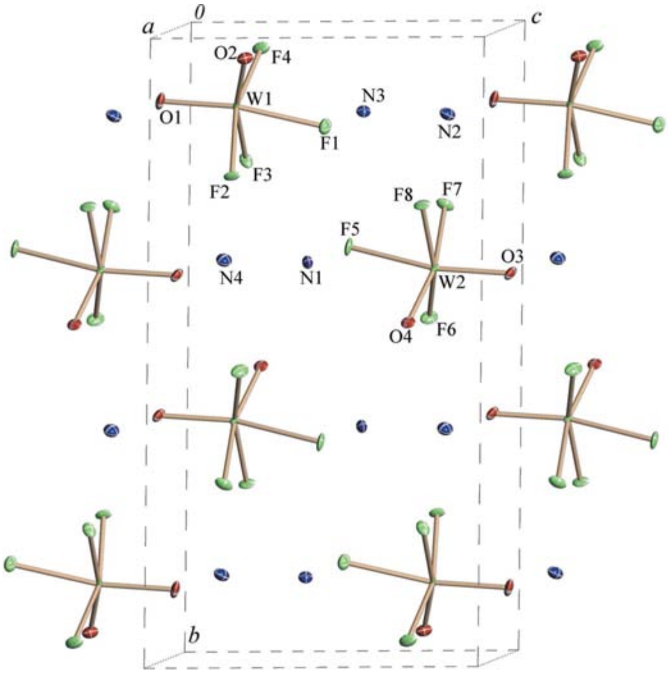

Figure 5
Structure of $(NH_4)_2WO_2F_4$ (II) at 133 K.

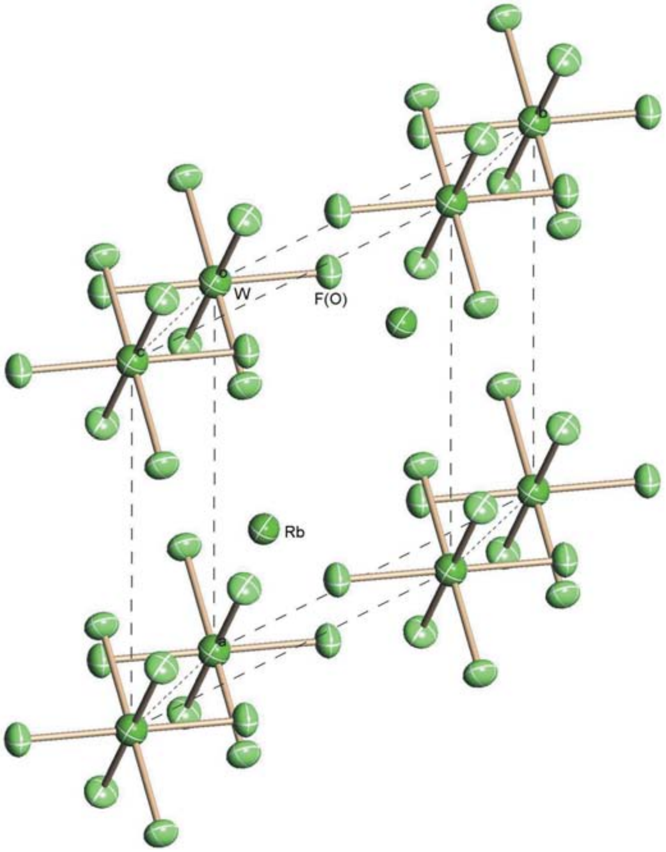

Figure 6
Statically disordered structure of $Rb_2WO_2F_4$ at 297 K.

Table 5
Selected distances (Å) and angles (°) for (III).

$W-X$†	1.887 (2) ×6	$X-X''$	2.705 (4) ×6	$Rb-X'$	3.043 (1) ×6
$X-X'$	2.631 (4) ×6	$Rb-X$	2.973 (2) ×3		
$X-W-X'$	91.6 (1) ×6	$X-W-X''$	88.4 (1) ×6	$X-W-X'''$	180.0 (1) ×3

† X = F(O).

We thank S. V. Mel'nikova for SHG measurement of $(NH_4)_2WO_2F_4$, V. Ya. Kavun for the ^{19}F NMR data and T. V. Basova for recording the Raman spectra of $(NH_4)_2WO_2F_4$. We deeply appreciate N. B. Bolotina's valuable advice and help with the text editing.

References

Bolotina, N., Kirschbaum, K. & Pinkerton, A. A. (2005). *Acta Cryst.* B**61**, 577–584.

Bruker (1998). *SMART*, Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SAINT*, Version 6.02*a*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chaminade, J. P., Moutou, J. M., Villeneuve, G., Couzi, M., Pouchard, M. & Hagenmuller, P. (1986). *J. Solid State Chem.* **65**, 27–39.

Flerov, I. N., Fokina, V. D., Gorev, M. V., Vasiliev, A. D., Bovina, A. F., Molokeev, M. S., Kocharova, A. G. & Laptash, N. M. (2006). *Phys. Solid State.* **48**, 759–764.

Heather, K., Kirsch, J. E., Stern, C. L. & Poeppelmeier, K. R. (2005). *Inorg. Chem.* **44**, 884–895.

Heier, K. R., Norquist, A. J., Halasyamani, P. S., Duarte, A., Stern, C. L. & Poeppelmeier, K. R. (1999). *Inorg. Chem.* **38**, 762–767.

Heier, K. R., Norquist, A. J., Wilson, C. G., Stern, C. L. & Poeppelmeier, K. R. (1998). *Inorg. Chem.* **37**, 76–80.

Leimkuhler, M. & Mattes, R. (1986). *J. Solid State Chem.* **65**, 260–264.

Maggard, P. A., Kopf, A. L., Stern, C. L. & Poeppelmeier, K. R. (2002). *Inorg. Chem.* **41**, 4852–4858.

Maggard, P. A., Nault, T. S., Stern, C. L. & Poeppelmeier, K. R. (2003). *J. Solid State Chem.* **175**, 27–33.

Marignac, M. C. (1862). *C. R. Acad. Sci.* **55**, 888–892.

Marignac, M. C. (1863). *Ann. Chim. Phys.* **69**, 61–86.

Marvel, M. R., Lesage, J., Baek, J., Halasyamani, P. S., Stern, C. L. & Poeppelmeier, K. R. (2007). *J. Am. Chem. Soc.* **129**, 13963–13969.

Mel'nikova, S. V., Fokina, V. D. & Laptash, N. M. (2006). *Russ. Phys. Solid State*, **48**, 117–121.

Norquist, A. J., Heier, K. R., Stern, C. L. & Poeppelmeier, K. R. (1998). *Inorg. Chem.* **37**, 6495–6501.

Rao, U. R. K., Venkateswarke, K. S. & Wani, B. R. (1982). *Mol. Phys.* **47**, 637–645.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Srivastava, A. M. & Ackerman, J. F. (1992). *J. Solid State Chem.* **98**, 144–150.

Vlasse, M., Moutou, J. M., Cervera-Marzal, M., Chaminade, J.-P. & Hagenmuller, P. (1982). *Rev. Chim. Miner.* **19**, 58–64.

Voit, E. I., Voit, A. I., Mashkovsky, A. A., Laptash, N. M. & Kavun, V. Ya. (2006). *Russ. J. Struct. Chem.* **47**, 642–650.

Welk, M. E., Norquist, A. J., Arnold, F. P., Stern, C. L. & Poeppelmeier, K. R. (2002). *Inorg. Chem.* **41**, 5119–5125.

Welk, M. E., Norquist, A. J., Stern, C. L. & Poeppelmeier, K. R. (2001). *Inorg. Chem.* **40**, 5479–5480.

Withers, R. L., Brink, F. J., Liu, Y. & Norén, L. (2007). *Polyhedron*, **26**, 290–299.