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Hydrolysis of ammonium oxofluorotungstates: A ^{19}F, ^{17}O and ^{183}W NMR study

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ABSTRACT

Fluorine-19 and natural abundance ^{17}O and ^{183}W NMR spectroscopy were employed for the characterization of aqueous solutions of $(NH_4)_2WO_2F_4$ and $(NH_4)_3WO_3F_3$. Dissolution of the $(NH_4)_2WO_2F_4$ complex is accompanied by its partial acid hydrolysis to give the *trans*(*mer*)-dimer, $[W_2O_5F_6]^{4-}$, and unreacted *cis*-$[WO_2F_4]^{2-}$. The *cis*(*fac*)-$[W_2O_5F_6]^{4-}$ anion is the major soluble product resulting from the alkaline hydrolysis of $(NH_4)_2WO_2F_4$ along with the isolation of the solid $(NH_4)_2WO_3F_2$. In addition, the edge-bridging dimer, $[W_2O_6F_4]^{4-}$, and the cyclic trimer, $[W_3O_9F_6]^{6-}$, are also suggested as hydrolysis products. Decomposition of $(NH_4)_3WO_3F_3$ occurs in aqueous solution to give NH_4WO_3F.

1. Introduction

Ammonium oxofluorotungstates are the products that result when tungsten-containing minerals, including scheelite ($CaWO_4$), are fluorinated with ammonium hydrogen difluoride (NH_4HF_2), an effective fluorinating agent for the decomposition of natural raw materials [1]. Simple aqueous leaching of the cake obtained from fluorination at 150–200 °C has been used for separation of tungsten and calcium (as CaF_2), with the tungsten leaching into solution to form dioxofluorotungstate $[WO_2F_4]^{2-}$ [2].

The structure of the $[WO_2F_4]^{2-}$ anion in aqueous solutions has been previously investigated by ^{19}F NMR spectroscopy [3–5]. In accordance with the IR spectrum of $[WO_2F_4]^{2-}$, the *cis*-dioxo isomer was definitively established in solution by this method. The *cis*-structure of $[WO_2F_4]^{2-}$, as well as those of $[MoO_2F_4]^{2-}$ [6], OsO_2F_4 [7], $[TcO_2F_4]^-$ [8] and $[ReO_2F_4]^-$ [9], were characterized by two ^{19}F NMR resonances (two triplets) of equal intensity associated with an A_2X_2 spin system. In contrast, the *trans*-isomer would have all four fluorine ligands equivalent and the ^{19}F NMR spectrum would consist of a singlet. It should be noted that assignments of the high- and low-frequency triplets are reversed in the cases of W and Mo relative to those of Os, Tc, and Re. In the latter cases, ^{187}Os, ^{99}Tc and ^{17}O NMR spectra were recorded for OsO_2F_4 and $[TcO_2F_4]^-$, respectively. The corresponding ^{183}W and ^{17}O spectra have not been obtained for $[WO_2F_4]^{2-}$.

In the present work, aqueous solutions of $(NH_4)_2WO_2F_4$ and $(NH_4)_3WO_3F_3$ were investigated by ^{19}F, ^{17}O and ^{183}W NMR spectroscopy.

2. Results and discussion

Well-shaped, transparent prismatic crystals of $(NH_4)_2WO_2F_4$ were used for preparing concentrated (1.5 mol/L) aqueous solutions. The pH of this solution was ~3 indicating that partial hydrolysis had taken place. The ^{19}F NMR spectra of the solution are presented in Fig. 1. Two triplets of equal intensity at −76.6 (B) and −114.3 (F) ppm are readily assigned to *cis*-$[WO_2F_4]^{2-}$. The high-frequency triplet is assigned to the F-*trans*-to-F (F_c, *cis*-to-O) environment and the low-frequency triplet is assigned to the F-*trans*-to-O (F_t) environment, in agreement with the assignments of Buslaev and Petrosyants [4]. They found $^1J(^{183}W-^{19}F_t) = 50.0$ Hz to be significantly smaller than $^1J(^{183}W-^{19}F_c) = 118$ Hz and that the exchange processes involved only the more weakly bonded F_t ligands. In accordance with the smaller $^1J(^{183}W-^{19}F_t)$ coupling and the lability of the F_t ligands, the W–F_t bonds in the crystal structure of $(NH_4)_2WO_2F_4$ are longer [10]. In the present study, the room temperature F_t exchange was found to be slow on the NMR time scale.

The NMR ^{19}F spectra also contained a resonance at −156 ppm (G) which is assigned to HF_2^- [11,12]. Two triplets in Fig. 1b are broadened so that their splittings cannot be observed. The broadening is caused by ^{19}F exchange. The behavior of line-shape parameters upon lowering the temperature (Table 1) indicated that at the least four fluorine environments are involved in the

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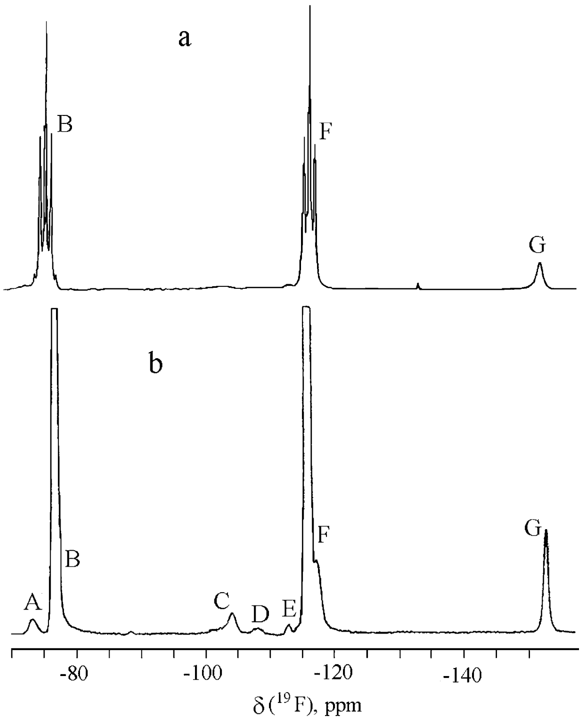


Fig. 1. The ^{19}F NMR spectra of aqueous $(NH_4)_2WO_2F_4$ at room temperature: (a) 75.5 MHz; (b) 376.5 MHz: (B and F) $[WO_2F_4]^{2-}$, (A and D) *trans*(*mer*)-$[W_2O_5F_6]^{4-}$, (C) edge-bridging dimer $[W_2O_6F_4]^{4-}$, (E) cyclic trimer, $[W_3O_9F_6]^{6-}$.

exchange (F^-, F^t, F^c, HF_2^-):

$$[WO_2F_2{}^cF_2{}^t]^{2-} \leftrightarrow [WO_2F_2{}^cF^t]^- + F^-, \tag{1}$$

$$[WO_2F_2{}^cF_2{}^t]^{2-} \leftrightarrow [WO_2F^cF_2{}^t]^- + F^-, \tag{2}$$

$$HF_2^- \leftrightarrow HF + F^-. \tag{3}$$

The F^- resonance (~ -120 ppm) is not directly observed, although the involvement of F^- in the exchange is implied from the observed exchange behavior [4]. The entries in Table 1 comprise the four-spin system involved in exchange, because F^- is common to Eqs. (1)–(3). Under slow, two-site exchange of F_c and F_t, lowering the temperature, i.e., increasing the lifetime of F_c and F_t in the anion, should result in a small increase in Δ and line narrowing due to a decreasing exchange contribution to the line width [13]. In fact, Δ for F_c and F_t actually increases, but the line widths increase. This means that the situation is not described by a two-site exchange but corresponds to multi-site exchange, and that the exchange is fast, in accordance with Eq. (3) [11,12]. The HF_2^- resonance actually narrows very significantly. The F^- concentration is unknown and therefore quantitative estimation of multi-site exchange rates is impossible. In addition, the spectrum contains the weak lines A, C, D, and E corresponding to the hydrolysis products.

The ^{183}W NMR spectrum of $[WO_2F_4]^{2-}$ is expected to be a superposition of two triplets with different splittings and a common spectral origin. In fact, the ^{183}W NMR spectrum of an aqueous solution of $(NH_4)_2WO_2F_4$ at 277 K (near the freezing point) displays a single triplet (Fig. 2) having a coupling constant of 114 Hz that corresponds to $^1J(^{183}W–^{19}F_c)$ found in Ref. [4]. Obviously, the faster exchange of F_t broadens this resonance, so that the splitting corresponding to $^1J(^{183}W–^{19}F_t) \approx 50$ Hz cannot be observed.

Table 1
Parameters that demonstrate ^{19}F exchange between $[WO_2F_4]^{2-}$ and HF_2^- of the exchanged lines.

T (K)	δ F_c, ppm ($\Delta\nu_{1/2}$, Hz)[a]	δ F_t ($\Delta\nu_{1/2}$)	Δ[b] (F_c–F_t)	δ HF_2^- ($\Delta\nu_{1/2}$)	Δ (F_t-HF_2)
297	−76.6 (125)	−114.3 (210)	37.7	−155 (1095)	40.7
277	−75.0 (270)	−114.1 (260)	39.1	−157.9 (240)	43.8

[a] $\Delta\nu_{1/2}$ is the NMR line width at half-height.
[b] Δ is the chemical shift difference for the indicated fluorine environments.

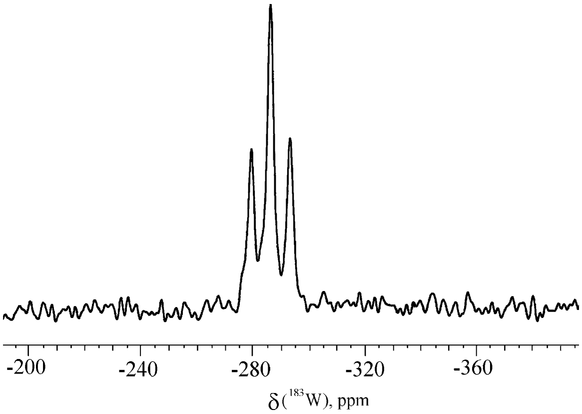


Fig. 2. The ^{183}W NMR spectrum (16.67 MHz) of aqueous $(NH_4)_2WO_2F_4$ at 277 K.

The ^{17}O NMR spectrum of an aqueous solution of $(NH_4)_2WO_2F_4$ is shown in Fig. 3. The line at 681 ppm is assigned to the $[WO_2F_4]^{2-}$ anion and lies in the range for terminal oxygen atoms O_t (W=O) whose chemical shifts are 550–760 ppm [12,14,15]. Much weaker signals at 657 (terminal oxygen atoms) and at 338 ppm are also present in the spectrum. The latter correspond to the bridging oxygen atoms (W–O–W) whose chemical shifts lie in the range 250–450 ppm [12,14]. The intensity ratio of terminal and bridging atoms is ca. 6:1 indicating that the tungsten octahedra are corner shared. Shifting of the terminal oxygen atom resonances to lower frequency is consistent with lengthening of the W=O bonds in this species relative to those in $[WO_2F_4]^{2-}$ [16].

Returning to the ^{19}F NMR spectrum, the compositions and structures of the bridging species are considered. As was noted above, acid hydrolysis takes place upon dissolution of $(NH_4)_2WO_2F_4$ in water. A broad singlet at −153 ppm (G, Fig. 1) is assigned to HF_2^- and the weak lines labeled A, C, D, and E correspond to the hydrolysis products. The hydrolysis was promoted by addition of $[Al(OH_2)_6]^{3+}$, in one case, and by addition of NH_3, in another (Fig. 4). The doublet at −72.1 (A) and the triplet at −106.5 (D) ppm, with relative integrated intensities of 2:1, were observed (Figs. 1b and 4a) and comprise a AX_2 spin system. It should be noted that a similar situation was observed in the ^{19}F NMR spectrum of a solution of WO_3 in concentrated aqueous HF (40%) [5]. The doublet at −68.8 and the triplet at −116.6 ppm with $^2J(^{19}F_c–^{19}F_t) = 70$ Hz (71 Hz in the present case) were assigned to the $[WO_2F_3{\cdot}H_2O]^-$ anion (two F_c and one F_t). It is clear that one is

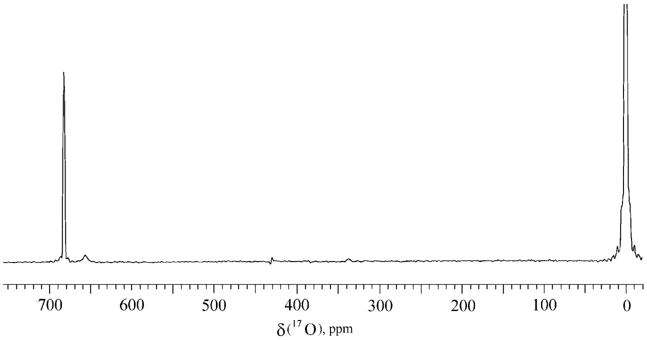


Fig. 3. The ^{17}O NMR spectrum (54.24 MHz) of aqueous $(NH_4)_2WO_2F_4$.

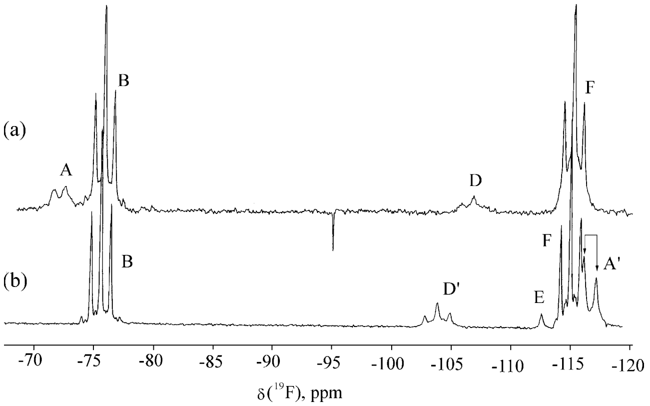
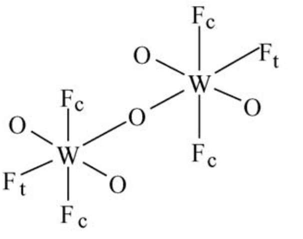


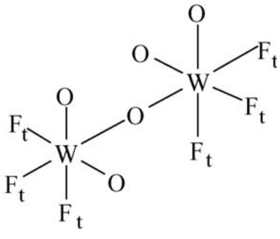
Fig. 4. The ^{19}F NMR (75.5 MHz) spectra of aqueous $(NH_4)_2WO_2F_4$: (a) acid hydrolysis by addition of Al_{aq}^{3+}, (b) alkaline hydrolysis by addition of NH_3.

dealing with the same species, but its previous assignment [5] was erroneous.

Alkaline hydrolysis of $(NH_4)_2WO_2F_4$ (Fig. 4b) also resulted in a doublet (A′) and in a triplet (D′). The first one appeared at lower frequency (−117.5 ppm) while the chemical shifts of the triplet remained essentially unchanged (−104.6 ppm). Chemically equivalent fluorine atoms corresponding to the triplet are assigned to fluorines trans to the bridging oxygen atom (F_t-*trans*-O_b). The one and only variant of AX_2 system in these cases is the dinuclear complex $[W_2O_5F_6]^{4-}$, which is referred to as a "dimer". In the first case (acid medium), it is a *trans*-dimer (or *mer*-isomer if the arrangement of the three oxygen atoms in the pseudo-octahedron is considered), and in the second case (alkaline medium), it is a *cis*-dimer (or *fac*-isomer with three oxygens located on an octahedral face):



trans (mer)-$[W_2O_5F_6]^{4-}$



cis (fac)-$[W_2O_5F_6]^{4-}$

It is known that the O atoms and F_t atoms in $[WO_2F_4]^{2-}$ are the most nucleophilic centers [17]. Most probably, a water molecule attacks a F_t atom with the formation of $F_t\cdots H{-}O{-}H\cdots F_t$ hydrogen bonds followed by HF elimination and the formation of the O-bridged dimer. In alkaline medium, F_c-OH exchange proceeds easily, leading to the corresponding isomer. Dimer formation is summarized by the following reactions:

$$2[WO_2F_4]^{2-} + H_2O = trans(mer)\text{-}[W_2O_5F_6]^{4-} + 2HF (pH \le 3) \tag{4}$$

$$2[WO_2F_4]^{2-} + 2OH^- = cis(fac)\text{-}[W_2O_5F_6]^{4-} + 2F^- + H_2O (pH \ge 6) \tag{5}$$

Indeed, in the latter case, a broad singlet at −119 ppm assigned to F^- (H, Fig. 5a) was observed in the ^{19}F NMR spectrum. The formation of *trans*(*mer*)-$[W_2O_5F_6]^{4-}$ by the addition of $Al(OH_2)_6^{3+}$ can be described as follows:

$$6[WO_2F_4]^{2-} + Al_{aq}^{3+} + 9H_2O = 3[W_2O_5F_6]^{4-} + [AlF_6]^{3-} + 6[H_3O]^+ \tag{6}$$

The presence of a singlet at −104 ppm (C, Fig. 1b) should be noted. If it is assumed that the F_t and F_c ligands of $[WO_2F_4]^{2-}$ octahedra are simultaneously attacked by a water molecule (the more electronegative F_t ligand is attacked by H^+ and the less electronegative F_c ligand is exchanged with OH^-), the dimer, $[W_2O_6F_4]^{4-}$, with edge-bridging octahedra is formed. Four equivalent fluorine atoms are opposite to two O_b atoms, and the W–F_t bond is somewhat strengthened relative to those in $[W_2O_5F_6]^{4-}$ because all four O_t atoms are in trans positions which leads to weakening of the W–O_t bond and to strengthening of the W–F_t bond, respectively.

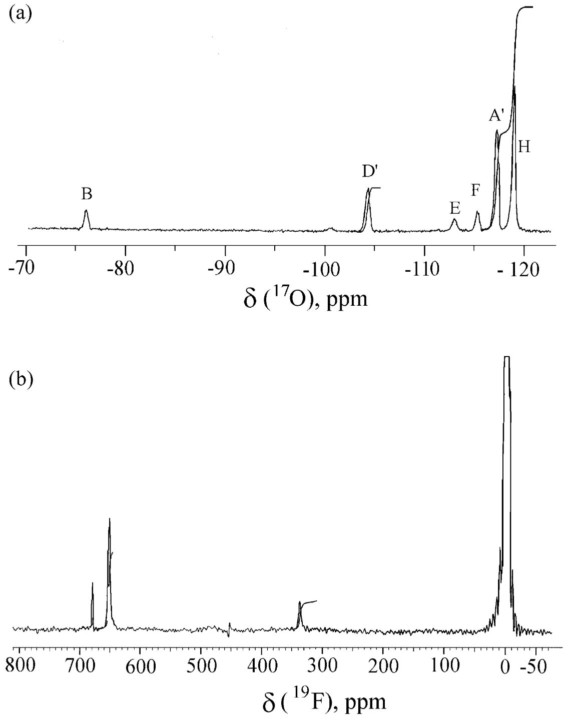
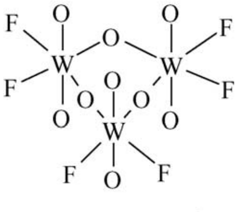


Fig. 5. NMR spectra of extensively hydrolyzed $(NH_4)_2WO_2F_4$ in alkaline medium: (a) ^{17}O NMR (54.24 MHz) spectrum at 295 K, (b) ^{19}F NMR (376.5 MHz) spectrum at 273 K.

More extensive oligomerization can proceed either in acid or alkaline solutions which can be associated with the presence of a singlet at −111 to −113 ppm in the ^{19}F NMR spectra (E; Figs. 1, 4b and 5a). The ^{19}F and ^{17}O NMR spectra of an extensively hydrolyzed $(NH_4)_2WO_2F_4$ solution (after separation of the solid phase) are shown in Fig. 5. It is clear that bridging species dominate in the solution. The O_t/O_b ratio in these forms is about 3:1 which requires the existence of species with the O_t/O_b = 2:1, because this ratio in the dimer is 4:1. Only the cyclic $[W_3O_9F_6]^{6-}$ trimer with the fluorine ligands trans to bridging oxygen atoms meets this requirement:



cyclo-$[W_3O_9F_6]^{6-}$.

It is clear that the W–F_t bond trans to O_b is stronger than the W–F_t bond trans to O_t, thus, the singlet at −113 ppm (E) is assigned to cyclic trimer because it occurs at higher frequency than δ(W–F_t) in $[WO_2F_4]^{2-}$.

The comparison of the integrated intensities of ^{19}F and ^{17}O NMR signals (Fig. 5) gives approximately $[W_2O_5F_6]^{4-}$, $0.33[W_3O_9F_6]^{6-}$

and 0.63$[WO_2F_4]^{2-}$ in the equilibrium. The composition of the solid phase resulting from alkaline hydrolysis corresponds to $(NH_4)_2WO_3F_2$ with the $O_t/O_b = 2:1$ in the infinite chain:

$$[WO_2F_4]^{2-} + 2OH^- = [WO_3F_2]^{2-} + H_2O + 2F^-. \quad (7)$$

The ^{19}F NMR spectrum of an aqueous solution of $(NH_4)_3WO_3F_3$ showed the presence of only free fluoride ion. This compound decomposes near quantitatively to insoluble NH_4WO_3F ($[WO_3F_3]^{3-} = [WO_3F]^- + 2F^-$). The composition of solid NH_4WO_3F was confirmed by X-ray powder data which are close to the pattern presented in [18] for this compound, by chemical analysis, and by vibrational spectroscopy. Its Raman spectrum (Fig. S1, Supporting information) contains a narrow band at 931 cm^{-1} which is assigned to the stretching vibration of the $W–O_t$ bond and a relatively broad band at 684 cm^{-1} which is assigned to the stretching vibration of $W–O_b–W$ in the layered structure of NH_4WO_3F (NH_4AlF_4 structural type). The solution pH (or filtrate) consisting of aqueous NH_4F was about 8. In alkali medium, the equilibrium: $2F^- + H_2O = HF_2^- + OH^-$ is shifted to the left side. One could assume the following mechanism for the hydrolytic decomposition of $(NH_4)_3WO_3F_3$. In accordance with our structural data [19], two O atoms in the octahedron with shorter W–O distances than the third W–O bond are attacked by water molecules (by protons) and the F atoms opposite to these two O atoms (with longer W–F distances) are easily substituted by OH^-. As a result of a polycondensation process, the layered structure with four O_b atoms in the WO_5F octahedron is formed.

3. Concluding remarks

The use of $(NH_4)_2WO_2F_4$ in crystalline form as the starting material for the preparation of its aqueous solutions permitted the detection of partial hydrolysis of the anion to give two isomers, *trans*-$[W_2O_5F_6]^{4-}$ and *cis*-$[W_2O_5F_6]^{4-}$. It is clear that the observation of only two triplets from *cis*-$[WO_2F_4]^{2-}$ in the ^{19}F NMR spectrum of $(NH_4)_2WO_2F_4$ [4] results from an excess of fluoride ion in these solutions. Firstly, hydrolysis of the complex is accompanied by the formation of two dimers, *trans*(*mer*)-$[W_2O_5F_6]^{4-}$ and *cis*(*fac*)-$[W_2O_5F_6]^{4-}$, depending on the pH of medium. It should be noted that the *mer*-isomer of $[WO_3F_3]^{3-}$ is not observed for this anion but is observed for the $[W_2O_5F_6]^{4-}$ anion. The hydrolysis process of $(NH_4)_2WO_2F_4$ is complex because it gives rise to additional species in solution such as the edge-bridging dimer, $[W_2O_6F_4]^{4-}$, or the cyclic trimer, $[W_3O_9F_6]^{6-}$. Nevertheless, oligomerization in the case of d^0 transition metal fluoride compounds is common. For example, the fluorine-bridged species $[W_2O_2F_9]^-$ [11,20], $[Mo_2O_2F_9]^-$ [21], $[Re_2O_4F_7]^-$, $[Re_3O_6F_{10}]^-$ [9], and possibly $[Tc_2O_4F_7]^-$ [8] have been observed in $(CH_3O)_2SO$ and CH_3CN. In all cases, the fluorine bridges are trans to oxygens in these anions. In the $[W_2O_5F_6]^{4-}$ dimers, the oxygen bridges are also trans to fluorines. The assignment of the signals in the ^{19}F NMR spectra of these species is unambiguous based on the multiplicities of the resonances that show that the fluorine ligands trans to oxygens are shifted to lower frequency relative to the fluorines cis to oxygens. The same ^{19}F chemical shift trend remains for *cis*-$[WO_2F_4]^{2-}$. An ambiguity exists for the assignment of the F_c and F_t environments in the *cis*-OsO_2F_4, *cis*-$[TcO_2F_4]^-$, *cis*-$[ReO_2F_4]^-$ anions which were assigned in reverse order [7–9] to those in *cis*-$[WO_2F_4]^{2-}$ [4] and in *cis*-$[ReO_2F_4]^-$ [22]. Most probably, all MO_2F_4 species are characterized by the higher frequency F_c-triplet relative to the F_t-triplet that is consistent with the higher frequency F_c-signals in the ^{19}F NMR spectra of $ReO_2F_3(CH_3CN)$ and $[Re_2O_4F_7]^-$ which was confirmed by a variable-temperature ^{19}F NMR exchange experiment between $[ReO_2F_4]^-$ and CsF in HF solvent [9]. Contrary to the $[WO_2F_4]^{2-}$ anion, the $[WO_3F_3]^{3-}$ anion does not exist in aqueous solution and decomposes hydrolytically giving the alkaline reaction.

4. Experimental

Well formed transparent prismatic crystals of $(NH_4)_2WO_2F_4$ were slowly crystallized from an aqueous solution of $(NH_4)_2WO_4$ obtained from tungsten oxide compounds and aqueous HF as previously described [10]. The crystals were washed with ethanol and air dried. The salt, 5 g, was dissolved in 10 mL of H_2O and filtered to remove small amounts of NH_4WO_3F. Aluminum chloride was added to the initial tungsten solution which was then filtered. Aqueous NH_3 was added to the initial tungsten solution until the first portion of $(NH_4)_2WO_3F_2$ was precipitated at pH = 6. The more extensive alkaline hydrolysis was accompanied by the appearance of a precipitate of $(NH_4)_2WO_3F_2$ which was filtered and ^{19}F NMR spectrum of the filtrate was recorded.

Small octahedral crystals of $(NH_4)_3WO_3F_3$ were synthesized as previously described [19]. The crystals of $(NH_4)_3WO_3F_3$, 4 g, were placed in 40 mL H_2O and stirred periodically. The light yellow product was filtered through a filter paper, washed with cold water several times and air dried. The product yield was 96%.

The solid hydrolysis products were analyzed by X-ray powder diffraction, elemental analyses, and by vibrational spectroscopy.

The NMR spectra were obtained using a Bruker MSL-400 spectrometer operating at 376.5 MHz (^{19}F), 54.24 MHz (^{17}O), and 16.67 MHz (^{183}W) at natural abundances and a WP-80 spectrometer operating at 75.5 MHz for ^{19}F NMR. The ^{19}F, ^{183}W, and ^{17}O NMR spectra were referenced to external samples of neat $CFCl_3$, 1.0 M aqueous Na_2WO_4, and H_2O, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.02.002.

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