# NMR Study of the Solution Structures of $TcO_2F_3$ and $ReO_2F_3$

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Both $TcO_2F_3$ and $ReO_2F_3$ are infinite chain, fluorine-bridged polymers in the solid state. Their solution structures have been studied by $^{19}F$ and $^{99}Tc$ NMR spectroscopy in $SO_2ClF$ solution and shown to exhibit cyclic $(MO_2F_3)_3$ (M = Tc, Re) and $(ReO_2F_3)_4$ structures that have been confirmed by simulation of the $^{19}F$ NMR spectra. The trimers dominate in both the technetium and rhenium systems, with both the tetramer and trimer existing in equilibrium in the rhenium system. A low concentration of a higher, possibly pentameric, cyclic rhenium polymorph is also present in equilibrium with the trimer and tetramer.

## Introduction

The transition metal pentafluorides, oxide tetrafluorides, and dioxide trifluorides complete their inner sphere six-coordination in the solid state by the formation of cis-fluorine bridges. The $VF_5$ type,[1] which includes $CrF_5$, $TcF_5$, and $ReF_5$ and consists of infinite chains of $MF_6$ units linked by cis-fluorine bridges, is the structure type found for the infinite chain oxide fluorides $MoOF_4$,[2] $TcOF_4$,[3] $ReOF_4$,[4] $TcO_2F_3$,[5] $ReO_2F_3$,[6] and $OsO_3F_2$[7] and have oxygen atoms trans to their fluorine bridges. Compounds of the $NbF_5$-type structure, adopted by $TaF_5$, $MoF_5$, $WF_5$, and $SbF_5$ (an open-chain polymer as a liquid),[8] crystallize as cyclic tetramers with near-linear fluorine bridges.[1,9] The crystal structure of $WOF_4$ shows that $WOF_4$ adopts the latter structure type, comprising a cyclic tetrameric structure with bridging W−F−W angles of 173°.[10] The metastable modifications of $TcOF_4$, $ReOF_4$, and $MoOF_4$ occur as cyclic trimeric structures.[1] Other examples of cyclic trimeric oxofluorides include $(SbOF_4)_3^{3-}$, which consists of an oxygen-bridged cyclic trimer in the solid state,[11] and the $V_3O_3F_{12}^{3-}$ [12] and $Mo_3O_6F_9^{3-}$ [13] anions, which both adopt fluorine-bridged trimeric structures.

Although metal fluorides and oxofluorides are well characterized in the solid state, their solution structures in low basicity, nonionizing solvents have been considerably less studied. A $^{19}F$ NMR study of $WOF_4$ dissolved in toluene at −93 °C confirmed the cyclic tetrameric arrangement observed in the solid state but also indicated the presence of other polymeric forms.[14] The high solubility of $MoOF_4$ in $SO_2ClF$,[15,16] even at very low temperatures, suggests that the open-chain $MoOF_4$ polymer observed in the solid state[2] rearranges to more soluble cyclic polymorphs.[17] We have previously described the X-ray crystal structures of $(TcO_2F_3)_\infty$,[5] $XeO_2F_2\cdot(^1/_\infty)(TcO_2F_3)_\infty$,[18] and [K][$Re_2O_4F_7$]$\cdot(^1/_\infty)(ReO_2F_3)_\infty$[6] in which $MO_2F_3$ (M = Tc, Re) comprises the infinite chain polymer described above. This paper describes the solution structures of three new cyclic oxide fluoride polymorphs $(MO_2F_3)_3$ and $(ReO_2F_3)_4$ and their determination by NMR spectroscopy and confirmation of the structures by simulations of their $^{19}F$ NMR spectra.

## Results and Discussion

Both $TcO_2F_3$ and $ReO_2F_3$ have been shown to be moderately strong electron pair acceptors toward fluoride ion and $CH_3CN$, forming the pseudooctahedral complexes $MO_2F_4^-$ and $O_2F_3$-$MNCCH_3$.[6,19] Sulfurylchlorofluoride, $SO_2ClF$, was chosen as the solvent in this study because it shows no significant donor properties toward $TcO_2F_3$ or $ReO_2F_3$; it has a wide liquid range and is resistant to oxidative attack. The utility of $SO_2ClF$ as a solvent for the study of high-valent metal oxofluoride compounds has been previously demonstrated for the $KrF_2$[15] and $XeF_2$[16] adducts of $MoOF_4$ and $WOF_4$.

The low solubilities of $ReO_2F_3$ and $TcO_2F_3$ in $SO_2ClF$ at room temperature are consistent with the polymeric natures of both compounds. However, a fraction of the initially insoluble solid dissolves upon heating the mixtures to ca. 50 °C in sealed FEP tubes to form colorless and pale-yellow solutions for $ReO_2F_3$ and $TcO_2F_3$, respectively.

**$^{19}F$ NMR Spectrum of $ReO_2F_3$ in $SO_2ClF$.** Solutions of $ReO_2F_3$ in $SO_2ClF$ at −120 °C consist of equilibrium mixtures

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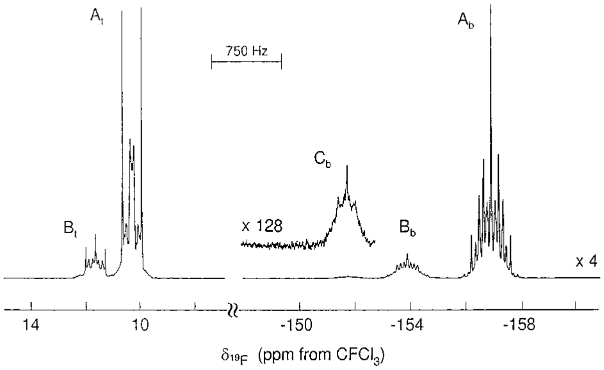
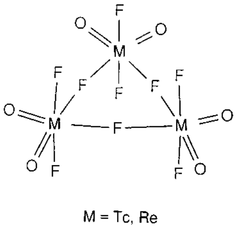
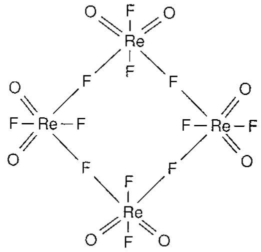


**Figure 1.** $^{19}F$ NMR spectrum (282.409 MHz, −120 °C in $SO_2ClF$ solvent) of $ReO_2F_3$. The labels A, B, and C denote the resonances of $(ReO_2F_3)_3$, $(ReO_2F_3)_4$, and $(ReO_2F_3)_5$, respectively, and subscripts t and b denote the terminal and bridging fluorine environments, respectively.

of the cyclic trimer (structure I) and cyclic tetramer (structure II) in a molar ratio of 5.0:1.0, as determined from the relative integrated intensities of their $^{19}F$ NMR resonances (Figure 1). This ratio remains relatively constant with increasing temperature, with a value of 5.3:1.0 at −40 °C. The $^{19}F$ NMR spectrum of $(ReO_2F_3)_3$ consists of two resonances at 10.3 and −156.9 ppm with relative integrated intensities of 2.0:1.0 that are assigned to the terminal and bridging fluorine environments, respectively. The other set of resonances, which also has relative integrated intensities of 2.0:1.0, occurs at 11.7 and −153.9 ppm and is assigned to the terminal and bridging fluorine environments of $(ReO_2F_3)_4$, respectively. A very weak resonance at −151.9 ppm was also observed and is tentatively assigned to the bridging fluorine environment in a higher cyclic polymorph, possibly a pentamer, although the corresponding terminal fluorine resonance was not detected and is assumed to be coincident with the terminal fluorine resonance of $(ReO_2F_3)_4$. The terminal fluorines of both polymorphs are significantly deshielded compared with that of $ReO_2F_3(CH_3CN)$ in $SO_2ClF$ (−23.8 and −25.8 ppm), whereas the chemical shifts of the bridging fluorines are highly shielded as is observed for other fluorine-bridged oxofluoro species, e.g., $W_2O_2F_9^-$,[20] $Mo_2O_2F_9^-$,[21] $Os_2O_4F_7^+$,[22] $Re_2O_4F_7^-$,[6] and $Re_2O_4F_5^+$.[18]



Structure I



Structure II

The complexity of the spectrum arises from the magnetic nonequivalence of the fluorine nuclei. A spin system that is closely related to the spin system of $(ReO_2F_3)_3$ is that of 1,3,5-trifluorobenzene, which is an AA′A″XX′X″ system consisting of two sets of three chemically equivalent but magnetically nonequivalent nuclei that spin−spin couple through four coupling paths: $^4J(^1H-^1H)$, $^4J(^{19}F-^{19}F)$, $^3J(^1H-^{19}F)$, and $^5J(^1H-^{19}F)$.[23] The resulting $^1H$ and $^{19}F$ NMR spectra each consist of 56 distinct transitions with the $^{19}F$ spectrum having features similar to the terminal fluorine resonance in the spectrum of $(ReO_2F_3)_3$.

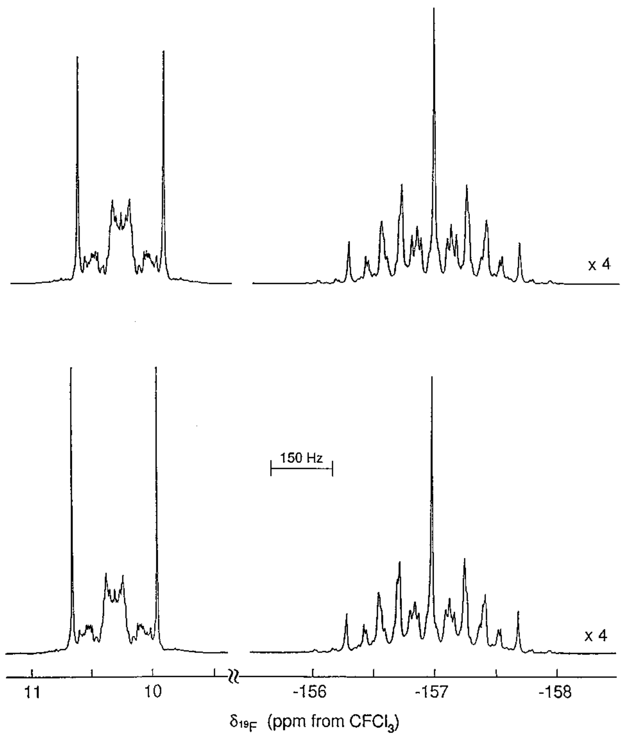


**Figure 2.** Simulated (upper trace, 2 Hz line broadening) and observed (lower trace) $^{19}F$ NMR spectra (282.409 MHz, −120 °C in $SO_2ClF$ solvent) of $ReO_2F_3$ showing the terminal and bridging fluorine environments of the cyclic trimer $(ReO_2F_3)_3$.

**Table 1.** $^{19}F$ NMR Parameters of $(ReO_2F_3)_3$, $(ReO_2F_3)_4$, and $(TcO_2F_3)_3$ Derived from Spectral Simulations

| NMR parameters[a] | $(ReO_2F_3)_3$ | $(ReO_2F_3)_4$ | $(TcO_2F_3)_3$ |
|---|---|---|---|
| Chemicals Shifts (ppm) | | | |
| $\delta(F_t)$ | 10.3 | 11.7 | 76.2 |
| $\delta(F_b)$ | −156.9 | −153.9 | −148.6 |
| Couplings (Hz)[a] | | | |
| $^2J(^{19}F_t-^{19}F_b)$ | 98 | 102 | 105 |
| $^2J(^{19}F_b-^{19}F_b)$ | 65 | 105 | 48 |
| syn-$^4J(^{19}F_t-^{19}F_t)$ | 12 | 12 | |
| anti-$^4J(^{19}F_t-^{19}F_t')$ | 2 | 2 | |
| $^2J(^{19}F_t-^{19}F_t)$ | ≥15 | ≥15 | 15 |

[a] The $^4J$ couplings are syn or anti with respect to the fluorine bridge.

Simulation of the $^{19}F$ NMR spectrum of $(ReO_2F_3)_3$ was accomplished by using nine magnetically nonequivalent fluorines (six terminal ($F_t$) and three bridging ($F_b$)) and required two chemical shifts and five coupling constants (Figure 2, Table 1). The dominant features of the spectrum were first simulated by refining the larger two-bond coupling constants, $^2J(^{19}F_t-^{19}F_b) = 98$ Hz and $^2J(^{19}F_b-^{19}F_b) = 65$ Hz. The secondary features of the spectrum were simulated by the introduction and refinement of the four-bond coupling constants syn-$^4J(^{19}F_t-^{19}F_t) = 12$ Hz and anti-$^4J(^{19}F_t-^{19}F_t') = 2$ Hz (coupling between fluorines syn and anti with respect to a fluorine bridge). The value of the last coupling constant to be introduced, $^2J(^{19}F_t-$

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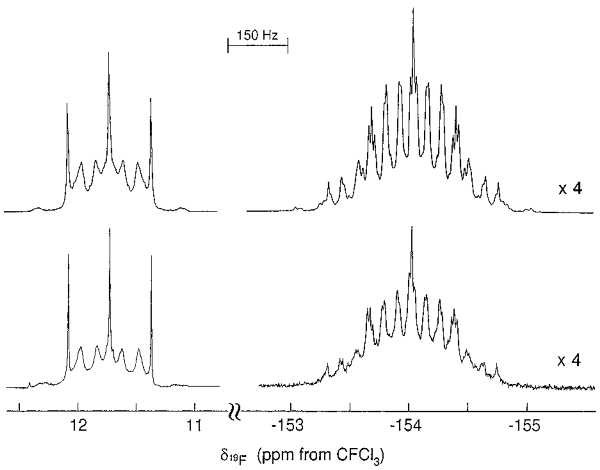

**Figure 3.** Simulated (upper trace, 2 Hz line broadening) and observed (lower trace) $^{19}F$ NMR spectra (282.409 MHz, −120 °C in $SO_2ClF$ solvent) of $ReO_2F_3$ showing the terminal and bridging fluorine environments of the cyclic tetramer $(ReO_2F_3)_4$.

$^{19}F_t$), could not be determined because acceptable simulated spectra were obtained for any value above 15 Hz but was set to 15 Hz based on the results obtained for the simulations of $(ReO_2F_3)_4$ and $(TcO_2F_3)_3$ (vide infra).

The $^{19}F$ NMR spectrum of $(ReO_2F_3)_4$ was simulated using a similar procedure and required 12 magnetically nonequivalent fluorine nuclei (8 terminal and 4 bridging) (Figure 3). The final coupling constants were $^2J(^{19}F_t-^{19}F_b) = 102$ Hz, $^2J(^{19}F_b-^{19}F_b) = 105$ Hz, syn-$^4J(^{19}F_t-^{19}F_t) = 12$ Hz, anti-$^4J(^{19}F_t-^{19}F_t') = 2$ Hz, and $^2J(^{19}F_t-F_t) = 15$ Hz. The significant increase in the magnitude of $^2J(^{19}F_b-^{19}F_b)$ in going from the trimer to the tetramer suggests that the $F_b-Re-F_b$ angle may be more open in the tetramer.[24]

The spectra of $(ReO_2F_3)_3$ and $(ReO_2F_3)_4$ were simulated without invoking chemical nonequivalences that arise from mixtures of conformers or from within a conformer. It may therefore be concluded that the cycles are conformationally labile at temperatures as low as −120 °C or that the rings have rigid conformations in which the metals and bridge fluorines are coplanar, or in the case of the tetramer, the $Re-F_b-Re$ angles are less than 180° with the bridging fluorines alternating above and below the plane defined by the four rhenium atoms.

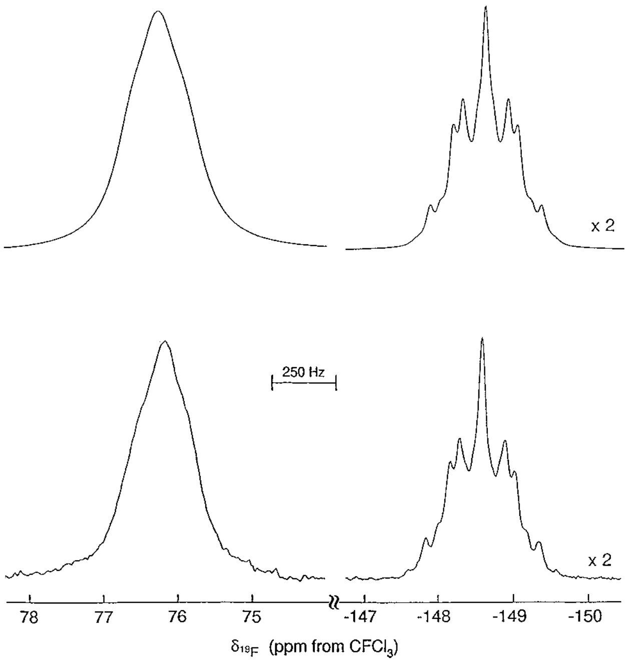

**Figure 4.** Simulated (upper trace; line broadenings, 130 Hz ($F_t$) and 30 Hz ($F_b$)) and observed (lower trace) $^{19}F$ NMR spectra (282.409 MHz, −120 °C in $SO_2ClF$ solvent) of $TcO_2F_3$ showing the terminal ($F_t$) and bridging ($F_b$) fluorine environments of the cyclic trimer $(TcO_2F_3)_3$.

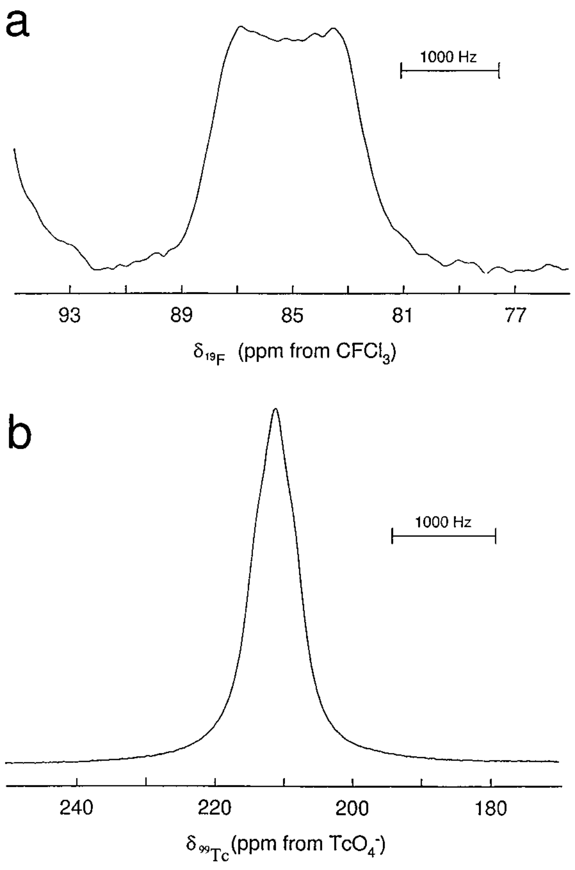

**Figure 5.** NMR spectra of $TcO_2F_3$ in $SO_2ClF$ recorded at 30 °C showing coupling between the terminal fluorine environments and $^{99}Tc$ in $(TcO_2F_3)_3$: (a) $^{19}F$ (282.409 MHz) spectrum; (b) Gaussian resolution enhanced $^{99}Tc$ (67.555 MHz) spectrum.

**$^{19}F$ and $^{99}Tc$ NMR Spectra of $TcO_2F_3$ in $SO_2ClF$.** The $^{19}F$ NMR spectrum of $TcO_2F_3$ in $SO_2ClF$ was recorded at −120 °C in order to quadrupole-collapse the $^{99}Tc-^{19}F$ couplings and is shown in Figure 4. The spectrum comprises two resonances at 76.2 and −148.6 ppm having relative integrated intensities of 2.0:1.0. The spectrum is consistent with structure I and was simulated employing the method used for $(ReO_2F_3)_3$, resulting in the coupling constants $^2J(^{19}F_b-^{19}F_t) = 105$ Hz, $^2J(^{19}F_b-^{19}F_b) = 48$ Hz and $^2J(^{19}F_t-^{19}F_t) = 15$ Hz. The broadness of the resonances in the experimental spectrum result from residual spin−spin coupling of both fluorine environments to the quadrupolar ($I = {}^9/_2$) $^{99}Tc$ nucleus and precluded refinement of the smaller four-bond coupling constants. Line-broadening factors of 130 and 30 Hz in the simulation of the terminal and bridging resonances, respectively, were required in order to account for the residual coupling between $^{99}Tc$ and the fluorine nuclei, which is expected to follow the order $^1J(^{19}F_t-^{99}Tc) > {}^1J(^{19}F_b-^{99}Tc)$. The $^{19}F$ NMR spectrum at 30 °C shows that the $^{99}Tc$ relaxation time has been significantly reduced owing to a lowering of the solvent viscosity (Figure 5a), resulting in a partially quadrupole-collapsed saddle-shaped resonance for the terminal fluorines at 85.1 ppm ($\Delta\nu_{1/2} = 1570$ Hz), and is

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**Table 2.** Raman Frequencies, Assignments, and Mode Descriptions for $MO_2F_3$ (M = Tc, Re) Recovered from an $SO_2ClF$ Solution Compared with Those of Their Open-Chain Polymers

| Frequencies ($cm^{-1}$)[a] | | | | assignments[b] |
|---|---|---|---|---|
| $ReO_2F_3$ from $SO_2ClF$[c] | $(ReO_2F_3)_\infty$[d] | $TcO_2F_3$ from $SO_2ClF$[e] | $(TcO_2F_3)_\infty$[f] | $C_{2v}$ point symmetry |
| 1025 (100) | 1026 (100) | 973 (100) | 974 (100) | $A_1$, $\nu_s(MO_2)$ |
| 1001 (29) | 994 (33) | 961 (29) | 963 (27) | $B_1$, $\nu_{as}(MO_2)$ |
| 997 (29) | 990 (11) | 958 (17), sh | 956, sh | |
| 688 (5), sh | 713 (2) | 685 (1) | 685 (3)* | $A_1$, $v_s(MF_{2t})$ |
| | 700 (14) | 669 (2) | 670 (7)* | |
| 677 (10) | 670 (1), sh | 648 (7) | 650 (16)* | $B_2$, $\nu_{as}(MF_{2t})$ |
| 665 (11) | 664 (4) | 631 (19) | 632 (36)* | |
| 404 (19) | 412 (17) | 414 (8), sh | 416, sh | $A_1$, $\delta(MO_2)$ |
| | | 409 (13) | 411 (19) | |
| 345 (4), sh | 349 (6) | | | $A_1$, $\delta(MF_{2t})$ |
| 328 (16) | 332 (11) | | | |
| 323 (15), sh | 326 (6), sh | 319 (19) | 320 (22)* | $B_2$, $\rho_w(MO_2)$ |
| 318 (10), sh | 319 (5) | | | |
| 298 (10) | 288 (1) | 292 (25) | 295 (30)* | $B_1$, $\delta(MF_{2t})$ |
| 292 (8), sh | | | | |
| 280 (9) | 276 (2) | 281 (21) | 284 (24)* | $A_2$, $\rho_t(MO_2)$ |
| 268 (5) | 270 (4) | 275 (15), sh | 278, sh | |
| | 251 (3) | | 264 (2) | |
| 226 (3) | 223 (<1) | 228 (4) | 231 (3)* | $B_2$, $\rho_w(MF_{2b})$ |
| | 213 (<1) | | 215 (<1) | |
| | 204 (<1) | | | |
| 158 (3) | 159 (1) | 172 (2) | 175 (<1)* | $A_1$, $\delta(MF_{2b})$ |
| 139 (4) | 136 (4) | 146 (4) | 148 (2)* | $B_1$, $\rho_r(MO_2)$ |
| 114 (4) | 114 (<1) | | 122 (2) | |
| 106 (4) | 101 (2) | 110 (3) | 111 (2) | |
| 81 (4) | 87 (<1) | | | |
| 75 (6) | 75 (1) | 75 (8) | | $A_2$, $\rho_t(MF_{2b})$ |
| | 55 (4) | | | |

[a] Values in parentheses denote relative intensities, and sh denotes shoulder. [b] Assignments and approximate mode descriptions are for the isolated cis-$F_{2t}O_2MF_{2b}$ group. Abbreviations: $\nu$, stretching; $\delta$, in-plane bending; $\rho_t$, twisting; $\rho_r$, rocking; $\rho_w$, wagging; $F_t$, terminal fluorines; $F_b$, bridging fluorines. [c] Spectrum recorded on microcrystalline solid in Pyrex glass capillary at 23 °C using 514.4 nm excitation. [d] From ref 6. [e] Spectrum recorded on microcrystalline solid in an FEP sample tube at 23 °C. [f] From ref 5. Several bands have been reassigned or assigned for the first time (denoted by asterisks) on the basis of those of $(ReO_2F_3)_\infty$.

consistent with the larger coupling between $^{99}Tc$ and the terminal fluorines. The bridging fluorine resonance could not be observed at this temperature presumably because of its low intensity and quadrupolar broadening. As in the case of the rhenium analogue, $(TcO_2F_3)_3$ appears to be either a rigid cycle of technetium and fluorine bridge atoms or conformationally labile on the NMR time scale down to −120 °C.

The $^{99}Tc$ NMR spectrum of $TcO_2F_3$ in $SO_2ClF$ recorded at 30 °C shows a single resonance at 211.0 ppm ($\Delta\nu_{1/2} = 500$ Hz) with partially resolved coupling to the terminal fluorines of $(TcO_2F_3)_3$. After resolution enhancement by Gaussian multiplication of the free-induction decay (Figure 5b), the one-bond $^{99}Tc-^{19}F_t$ coupling constant was estimated at $^1J(^{99}Tc-^{19}F_t) \approx 160$ Hz, which is significantly smaller than the value of 235 Hz observed for $[N(CH_3)_4][TcO_2F_4]$ in $CH_3CN$.[19] The $^{99}Tc$ chemical shift of $(TcO_2F_3)_3$ in $SO_2ClF$ is more shielded than that of $TcO_2F_3$ in $CH_3CN$ (267.4 ppm at 30 °C), $[N(CH_3)_4]$-$[TcO_2F_4]$ in $CH_3CN$ (343.2 ppm at 45 °C), and $[Cs][TcO_2F_4]$ in HF (247.4 ppm at 30 °C).[19]

**Raman Spectroscopy.** Attempts to grow crystals of $(ReO_2F_3)_3$ and $(ReO_2F_3)_4$ from $SO_2ClF$ solutions for single crystal X-ray diffraction were unsuccessful. However, the Raman spectrum of the colorless material recovered from these solutions (figure in Supporting Information) shows significant shifts in a number of bands when compared with the spectrum of the open-chain polymer $(ReO_2F_3)_\infty$ (Table 2). The bands assigned to the antisymmetric Re−O stretching mode are shifted from 990 and 994 $cm^{-1}$ in $(ReO_2F_3)_\infty$ to 997 and 1001 $cm^{-1}$, the bands assigned to the symmetric terminal Re−F stretching mode are shifted from 700 and 713 $cm^{-1}$ to 688 $cm^{-1}$, and the band assigned to the $ReO_2$ bending mode is shifted from 412 to 404 $cm^{-1}$. Although the exact origin of these frequency shifts is not apparent, they indicate that the structure of the material recovered from $SO_2ClF$ differs structurally from that of $(ReO_2F_3)_\infty$.[6] The Raman frequencies and intensities of the material recovered from a solution of $TcO_2F_3$ in $SO_2ClF$ (figure in Supporting Information) are not shifted significantly from those of polymeric $(TcO_2F_3)_\infty$,[5] and it may be concluded that only the open-chain polymeric form of $TcO_2F_3$ is recovered.

## Conclusion

Simulation of the $^{19}F$ NMR spectrum of $ReO_2F_3$ in $SO_2ClF$ shows that the solution contains an equilibrium mixture of a cyclic trimer, a cyclic tetramer, and possibly a cyclic pentamer. The cyclic trimer dominates in the rhenium case and is observed exclusively for technetium. The solution structures of $(MO_2F_3)_3$ and $(ReO_2F_3)_4$ contrast with the open-chain structures observed in the solid state for $(TcO_2F_3)_\infty$, $XeO_2F_2\cdot(^1/_\infty)(TcO_2F_3)_\infty$, and $[K][Re_2O_4F_7]\cdot(^1/_\infty)(ReO_2F_3)_\infty$. As in the solid state, the cyclic polymorphs also have cis-dioxo arrangements and are fluorine-bridged with the fluorine bridges occurring trans to the oxygens.

## Experimental Section

All operations were conducted in laboratories that were monitored routinely by the McMaster University Health Physics Group for radioactive contamination. All work involving $^{99}Tc$ was licensed and performed according to the regulations and recommendations of the Canadian Atomic Energy Control Board.[25]

**Apparatus and Materials.** Volatile materials were handled in vacuum lines constructed of Pyrex and FEP, and nonvolatile materials were handled in the dry nitrogen atmosphere of a drybox as previously described.[18]

The methods for the preparation of $TcO_2F_3$[5] and $ReO_2F_3$[6] have been described previously. The standard literature method was used for the purification of $SO_2ClF$ solvent[26] (Columbia Organic Chem. Co.).

**Nuclear Magnetic Resonance Spectroscopy.** Nuclear magnetic resonance spectra were recorded unlocked (field drift less than 0.1 Hz $h^{-1}$) on a Bruker AC-300 (7.0463 T) spectrometer equipped with an Aspect 3000 computer. The $^{19}F$ spectra were acquired with a 5 mm $^1H/^{13}C/^{31}P/^{19}F$ combination probe. The $^{99}Tc$ spectra were obtained with a 10 mm broadband VSP probe (tunable over the range 23−202 MHz). The $^{19}F$ (282.409 MHz) spectra were recorded using a ∼90° pulse width of 7 $\mu$s. A total of 200 transients were acquired in a 32 K memory using a spectral width setting of 25 kHz, acquisition time of 1.311 s, resolution of 0.77 Hz/data point, and line broadening of 1 Hz. The $^{99}Tc$ (67.555 MHz) spectra were recorded using a ∼90° pulse width of 9 $\mu$s. A total of 2000 transients were acquired in a 16K memory using a spectral width setting of 50 kHz, acquisition time of 0.164 s, resolution of 6.10 Hz/data point, and line broadening of 10 Hz. The $^{19}F$ and $^{99}Tc$ NMR spectra were referenced to external samples of neat $CFCl_3$ and 0.210 M aqueous $[NH_4][TcO_4]$, respectively, at 30 °C. The chemical shift convention used is that a positive (negative) sign indicates a chemical shift to high (low) frequency of the reference compound.

**Simulation of $^{19}F$ NMR Spectra.** The spectral simulations of $(ReO_2F_3)_3$ and $(TcO_2F_3)_3$ were carried out using an updated version of the program NUMARIT[27] called Xsim[28] on a Silicon Graphics INDY R5000 workstation. Coupling constants were introduced and perturbed one at a time until agreement between the simulated and the experimental spectrum was obtained. Iterative fitting by least-squares refinement was not possible because of the very large number of calculated transitions (>500 000). The estimated error for each coupling constant derived from the simulations is ±1 Hz. The spectral simulation of $(ReO_2F_3)_4$ was carried out in a similar manner using the PERCH NMR software package[29] on a 200 MHz PC equipped with a Pentium II processor.

**Raman Spectroscopy.** Raman spectra were recorded as previously described.[30] The holographic gratings used were 600 grooves $mm^{-1}$, blazed at 500 nm for the prefilter, and 1800 grooves $mm^{-1}$, blazed at 550 nm for the monochromator stages. The spectra were recorded at room temperature on samples that were sealed inside Pyrex melting point capillaries dried at 250 °C under vacuum ($ReO_2F_3$) or inside an FEP reactor tube ($TcO_2F_3$). The Raman spectrometer was frequency-calibrated using the 1018.3 $cm^{-1}$ line of neat indene. The laser power was approximately 300 mW at the sample (900 mW output power), and the monochromator slits were set to 200 $\mu$m corresponding to a resolution of 1 $cm^{-1}$. A total of 10 reads having 30 s integration times were summed for the Raman spectra.

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**Supporting Information Available:** Raman spectra of $TcO_2F_3$ and $ReO_2F_3$ recovered from $SO_2ClF$ solvent. This material is available free of charge via the Internet at http://pubs.acs.org.

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