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Chemical Applications of ^{99}Tc NMR Spectroscopy: Preparation of Novel Tc(VII) Species and Their Characterization by Multinuclear NMR Spectroscopy

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Abstract: The ^{99}Tc NMR parameters of a number of Tc(VII) and one Tc(V) species have been determined. The anion TcO_4^- ($\Xi = 22.508\,311$ MHz in H_2O) was chosen as the standard for ^{99}Tc NMR spectroscopy. A ^{99}Tc–^{17}O coupling constant of 131.4 Hz was obtained from a ^{17}O- and ^{18}O-enriched sample of TcO_4^- whose ^{99}Tc spectrum also showed an isotopic shift of 0.22 ppm/mass number arising from a statistical distribution of $^{16}O/^{17}O/^{18}O$ isotopic isomers. Technetium-99 and proton NMR provided definitive proof for the existence of the stereochemically nonrigid TcH_9^{2-} anion. Both TcO_3F and the novel TcO_3^+ cation were synthesized and characterized by ^{99}Tc, ^{17}O, and ^{19}F NMR spectroscopy. Preliminary results on two new technetium(VII) oxyfluorides tentatively identified as $F_2O_2TcOTcO_2F_2$ and TcO_2F_3 are also reported. The diamagnetic d^2 anion, $TcO_2(CN)_4^{3-}$, represents the most deshielded ^{99}Tc environment encountered in the present study.

Technetium chemistry is of considerable interest in medical diagnoses because of the extensive use of ^{99m}Tc complexes as scanning agents. Technetium-99 is the only NMR-active technetium isotope ($I = {}^9/_2$) possessing a significantly long half-life (0.29 MeV β, $t_{1/2} = 2.12 \times 10^5$ years). It is obtained in 100% abundance and has a receptivity relative to ^1H of 0.275. Technetium-99 is produced either by neutron bombardment of molybdenum followed by decay of ^{99m}Tc to ^{99}Tc or in the fission of ^{235}U or ^{239}Pu. Owing to the high NMR detection receptivity of ^{99}Tc and almost complete lack of reliable published data on ^{99}Tc NMR, we have undertaken a preliminary broad-ranging NMR study of this nucleus. With the exception of the observation of the TcO_4^- resonance,[1] this nuclide has been all but ignored as an NMR nucleus. In the present study we have established the ranges of ^{99}Tc NMR parameters of d^0 Tc(VII) and d^2 Tc(V) species. With the aid of ^{99}Tc, ^{17}O, ^{19}F, and ^1H NMR, we have significantly extended the number of known Tc(VII) species, which prior to this study was limited to TcO_4^-, Tc_2O_7, Tc_2S_7, TcO_3F, TcO_3Cl, and the report of the partially characterized TcH_9^{2-} anion.

Although ^{99}Tc possesses an appreciable quadrupole moment ($Q = -0.19\ (5) \times 10^{-28}\ m^2$),[2] the effect of quadrupole line broadening is attenuated by the large size of the spin, I, in the relaxation eq 1 ($\Delta\nu$ is the line width, T_2 the transverse relaxation time, T_1 the spin–lattice relaxation time, eq the electric field gradient at the ^{99}Tc nucleus, and τ_c the molecular correlation time).[3] The effect of I is substantial and yields line widths that are among the narrowest of all quadrupolar nuclei studied to date. Consequently, quadrupole line broadening does not appear to place a serious constraint on the observation of ^{99}Tc resonances for species of widely varying molecular symmetries.

$$\pi\Delta\nu = \frac{1}{T_2} \simeq \frac{1}{T_1} = \frac{3\pi^2}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2 \tau_c \quad (1)$$

Results and Discussion

TcO_4^-. The tetrahedral TcO_4^- anion has been chosen as the standard for ^{99}Tc NMR spectroscopy. Because of the high sensitivity of ^{99}Tc and narrow line width resulting from a cubic electric field at ^{99}Tc ($\Delta\nu = 2.7$ Hz), an acceptable spectrum of TcO_4^- can be obtained from a single transient (signal/noise ≈ 210, pulse width 35 μs at 2.114 T on a 9.1-mm column of 0.210 M $NH_4^+TcO_4^-$ in D_2O). The exact resonance frequency of ^{99}Tc in the aforementioned pertechnetate sample was determined to be $\Xi = 22\,508\,311 \pm 10$ Hz at 25 °C (quoted such that the protons in Me_4Si resonate at exactly 100 MHz). Consequently, all chemical shift data (Table I) are quoted relative to TcO_4^-. No concentration dependence for $NH_4^+TcO_4^-$ solutions between 210 and 9.33×10^{-5} M was detected.

Enrichment of TcO_4^- with ^{17}O (21.9% ^{17}O and 42.7% ^{18}O) by exchange with enriched H_2O at 100 °C for 1 week resulted in a ^{17}O NMR spectrum consisting of an equiintensity decet (Figure 1a) arising from spin–spin coupling of ^{17}O to ^{99}Tc (Table I). The ^{99}Tc spectrum yielded, in addition to a strong central line and couplings caused by $Tc^{17}OO_3^-$ and $Tc^{17}O_2O_2^-$ (lines caused by $Tc^{17}O_3O^-$ and $Tc^{17}O_4^-$ were too weak to be observed), a set of smaller splittings (8.8 Hz at 2.114 T) that appear on each of the main lines (Figure 1b). These splittings are attributed to primary isotopic shielding effects arising from a statistical distribution of $^{16}O/^{17}O/^{18}O$ isotopic isomers. The calculated intensity ratios agree with the observed intensities, and as anticipated, the more massive isotopic isomers occur at lower frequency. The isotopic shift per oxygen mass unit was 0.22 ppm.

TcH_9^{2-}. A hydride anion of technetium has been reported previously by Ginsberg[4] who obtained a ^1H NMR resonance that was compatible with the TcH_9^{2-} anion, consisting of a broad, partially quadrupole-collapsed line ($\Delta\nu \approx 189$ Hz) to high field of Me_4Si. We have repeated the preparation of the hydride by using the method of Ginsberg[4] and have obtained both the ^{99}Tc and ^1H NMR spectra (Figure 2 and Table I). The ^{99}Tc resonance was shifted 3672 ppm to high field of TcO_4^- and displayed partially resolved binominal decet fine structure with a ^{99}Tc–^1H coupling of 24 Hz. The coupling is also in agreement with the observed ^1H spectrum, which consisted of a partially quadrupole-collapsed decet having a line width of 224 Hz. The spectra are consistent with a hydride structure that is fluxional on the NMR time scale and provide definitive proof for the existence of TcH_9^{2-}. A significant low-frequency shift relative to TcO_4^- is anticipated for Tc(VII) bonded to electropositive centers such as hydridic protons. The observed ^{99}Tc chemical shift typifies hydride chemical shifts and represents the most shielded ^{99}Tc nucleus observed thus far. The low-frequency position of the ^1H resonance is also characteristic of protons of a hydridic nature bonded to technetium.

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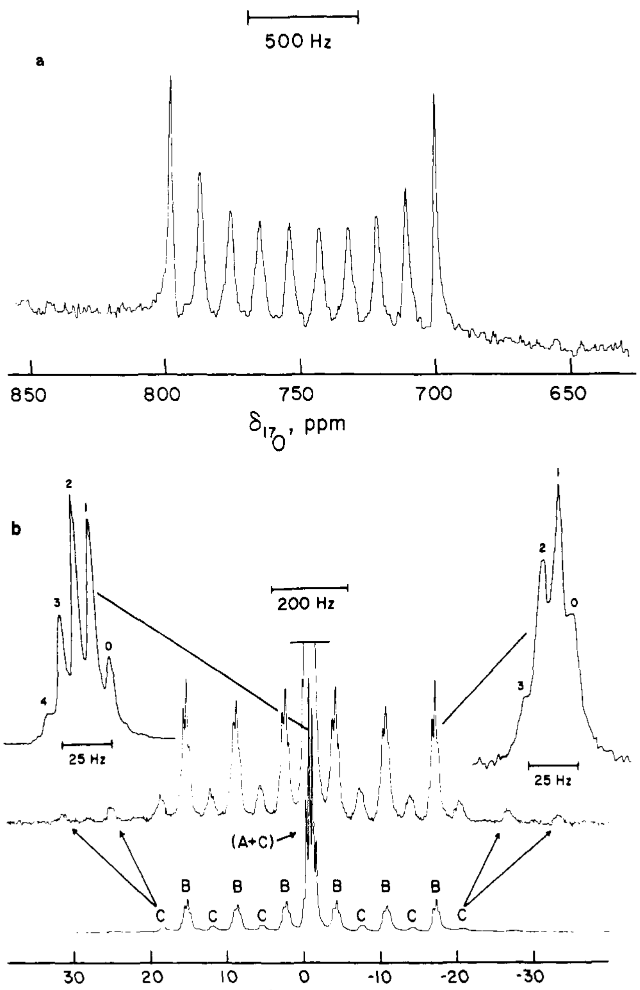

Figure 1. ^{17}O (a) and ^{99}Tc (b) NMR spectra of ^{17}O (21.9%) and ^{18}O (42.7%) enriched $KTcO_4$ in H_2O at 25 °C. Isotopic isomers are denoted by (A) TcO_4^-, (B) $Tc^{17}OO_3^-$, and (C) $Tc^{17}O_2O_2^-$, where a nonsuperscripted O represents ^{16}O and/or ^{18}O. Assignments for the insets corresponding to A and B are $Tc^{16}O_x{}^{18}O_{4-x}^-$ (A) and $Tc^{17}O^{16}O_x{}^{18}O_{3-x}^-$ (B), where x, the number of ^{16}O atoms, is indicated.

Technetium(VII) Oxyfluorides. Pertechnetate is known to undergo fluorination in anhydrous HF to yield TcO_3F.[5] Consequently, the ^{99}Tc and ^{17}O spectra of TcO_3F were recorded for ^{17}O-enriched TcO_4^- in anhydrous HF solution (Table I). The high-frequency shifts of both resonances relative to TcO_4^- are indicative of fluorination. The ^{99}Tc–^{17}O coupling is, however, similar to that of TcO_4^-, suggesting that there is little distortion from the tetrahedral O–Tc–O bond angle. Interestingly, no ^{19}F–^{99}Tc coupling or ^{19}F resonance could be observed, although Raman spectroscopy[5] of the sample showed that only TcO_3F was formed. It must be concluded that TcO_3F behaves as a weak fluoride ion base and undergoes exchange with HF according to eq 2. This was confirmed by acidification of a solution of TcO_4^-

$$TcO_3F + HF \rightleftarrows TcO_3^+ + HF_2^- \qquad (2)$$

in HF with excess AsF_5. Addition of AsF_5 to HF solutions of TcO_3F yielded new ^{99}Tc and ^{17}O resonances to high frequency of TcO_3F. Removal of HF and excess AsF_5 followed by redissolution in HF produced the same chemical shifts (Table I) and indicated that the salt, $TcO_3^+AsF_6^-$, was stable to pumping at room temperature. The new lines are consequently assigned to the hitherto unreported TcO_3^+ cation (D_{3h}).

Noble gas fluorides have been used previously to synthesize examples of high-oxidation-state species of the elements that were inaccessible by other means.[6] In the present preliminary work, KrF_2 and XeF_6 have been used to synthesize new examples of technetium(VII) oxide fluorides. The addition of excess XeF_6 to a HF solution of TcO_3F (containing H_2O from the solvolysis of TcO_4^-) yielded a new ^{99}Tc line to high frequency of both TcO_3F and TcO_3^+ that exhibited a 1:2:1 triplet arising from ^{99}Tc–^{19}F spin–spin coupling involving two equivalent fluorine atoms directly bonded to ^{99}Tc (Table I). The ^{17}O and ^{19}F NMR spectra consisted of partially quadrupole-collapsed decets arising from spin coupling to ^{99}Tc. Fluorination of TcO_3F with KrF_2 in HF also yielded the above product, which reacted further with this potent fluorinating agent to give a second new oxyfluoride in HF solution (Figure 3). The latter species, which has been studied by ^{99}Tc, ^{17}O, and ^{19}F NMR (Table I), yielded singlets in each instance.

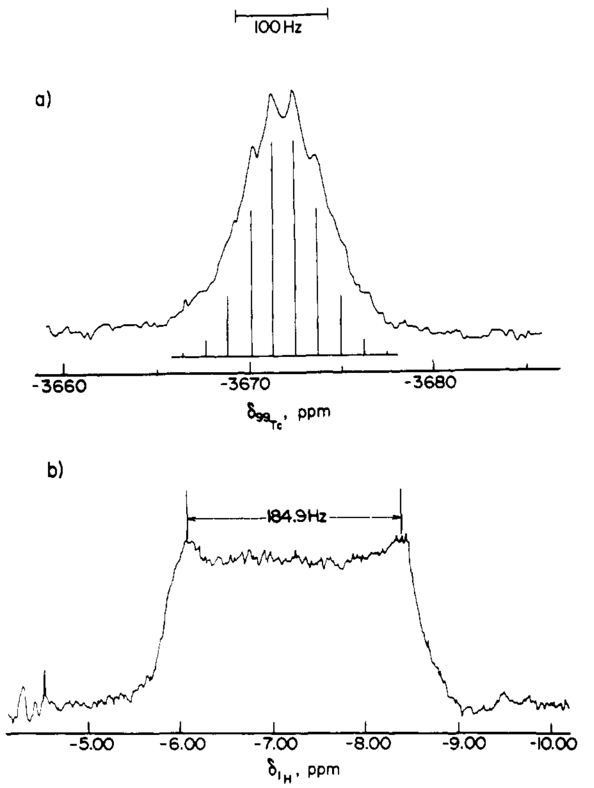

Figure 2. ^{99}Tc (a) and ^{1}H (b) NMR spectra of TcH_9^{2-} (K_2TcH_9 dissolved in 40% aqueous KOH) recorded at −12 °C.

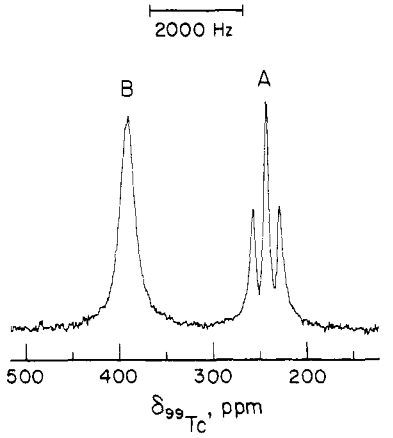

Figure 3. ^{99}Tc spectrum resulting from the incomplete reaction of KrF_2 with $KTcO_4$ in HF (TcO_3F). Triplet A ($Tc_2O_5F_4$) also results from the reaction of TcO_4^- with XeF_6 in HF and is the only technetium-containing product observed in the XeF_6 system. The broad singlet B (TcO_2F_3) results from the further reaction of $Tc_2O_5F_4$ with KrF_2.

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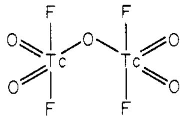
Table I. NMR Chemical Shifts and Coupling Constants for Some Tc(VII) and Tc(V) Species

	δ^{a}				*J*, Hz		
species	^{99}Tc	^{17}O^{b}	^{19}F	^{1}H	^{99}Tc–^{17}O	^{99}Tc–^{19}F	^{99}Tc–^{1}H
TcH_9^{2-} [c]	−3672 (22)			−7.22 (224)			24
TcO_4^-	0 (2.7)[d]	748.6 (23)[e]			131.4[e]		
TcO_3F [f,g]	43.7 (23)	1048 (108)			139.8		
TcO_3^+ [f,h]	160.7 (670)	1214 (720)[i]					
$Tc_2O_5F_4$ [f,j]	245.9 (135)	1234 (780)[k]	22.6 (25 °C, 2280)[k] 29.3 (−80 °C, 720)[l]		87 (±5)	259	
TcO_2F_3 [f,m]	396.3 (375)	1211 (~700)[i]	−6.5 (−47 °C, 370)[l]				
$[TcO_2(CN)_4]^{3-}$ [n]	806.0 (642)						

[a] Spectra were recorded and referenced externally at 25 °C unless indicated otherwise. The chemical shift convention is that outlined by IUPAC (*Pure Appl. Chem.* **1972**, *29*, 627; **1976**, *45*, 217): ^{99}Tc, aqueous $NH_4^+TcO_4^-$ (0.132 M); ^{17}O, H_2O; ^{19}F, $CFCl_3$. The values in parentheses denote the line width $\Delta\nu$ in hertz. [b] The spectra were obtained from samples containing 21.9% ^{17}O and 42.7% ^{18}O. [c] K_2TcH_9 was dissolved in 40% KOH in H_2O solvent at −19 °C and the spectra were recorded at -12 °C. The ^{99}Tc line width was measured from the ^{1}H-decoupled spectrum. [d] The $Tc^{16}O_4^-$ line is taken as the reference line, and $\Delta\nu$ is quoted for that line. [e] A previously reported ^{17}O NMR study of TcO_4^- yielded only a single ^{17}O resonance ($\Delta\nu \approx 1150$ Hz) from ^{17}O-enriched TcO_4^-; (Figgis, B. N.; Kidd, R. G; Nyholm, R. S. *Proc. R. Soc. London, Ser.* **1962**, *269*, 469. [f] Spectrum recorded in HF solvent. [g] TcO_3F was generated by dissolution of $KTcO_4$ in anhydrous HF. [h] Prepared by the reaction of excess AsF_5 with an HF solution of $KTcO_4$ (see text). [i] The line is a partially quadrupole-collapsed decet arising from coupling to ^{99}Tc and is "square-topped", i.e., no multiplet lines are resolved. [j] Prepared by the reaction of TcO_3F with XeF_6 or KrF_2 in HF solvent. Resonances due to $XeOF_4$ ($\delta_{^{19}F}$ 93.8, $\delta_{^{17}O}$ 315.7, $J_{^{129}Xe-^{19}F} = 1202$ Hz, and $J_{^{129}Xe-^{17}O} = 696$ Hz) and XeF_4 ($\delta_{^{19}F}$ −24.1, $J_{^{129}Xe-^{19}Fe} = 3870$ Hz) were also observed (−80 °C) in the reaction of TcO_3F with XeF_6. [k] The line is partially quadrupole-collapsed arising from ^{99}Tc coupling and is saddle shaped with the two outer lines being clearly resolved. The line width refers to the entire envelope. [l] The line is a nearly completely quadrupole-collapsed decet (due to ^{99}Tc coupling) and is Lorentzian in shape. [m] Prepared by the reaction of excess KrF_2 with $Tc_2O_5F_4$ in HF solvent. [n] Spectrum recorded in H_2O solvent.

The low-frequency ^{99}Tc triplet (Figure 3) is tentatively assigned to $Tc_2O_5F_4$ (structure I) and the broad ^{99}Tc singlet to TcO_2F_3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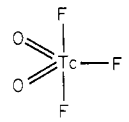
II

(structure II). Xenon oxide tetrafluoride is observed in addition to xenon tetrafluoride and O_2 gas in reactions with XeF_6 (eq 3).

$$2TcO_3F + XeF_6 \rightarrow I + XeF_4 + 0.5O_2 \tag{3}$$

Xenon oxide tetrafluoride arises from the reaction of XeF_6 with H_2O formed by HF solvolysis of TcO_4^-. Oxygen and krypton gases are liberated in reactions of TcO_3F with KrF_2 (eq 4 and 5). In

$$2TcO_3F + KrF_2 \rightarrow I + Kr + 0.5O_2 \tag{4}$$

$$I + KrF_2 \rightarrow 2II + Kr + 0.5O_2 \tag{5}$$

the case of KrF_2 oxidations, water generated in the solvolysis of TcO_4^- is quantitatively oxidized to yield O_2 and HF.

Chemical exchange of fluorines among solvent and TcO_2F_3 sites accounts for our failure to observe ^{99}Tc–^{19}F coupling in this case as well as our observation of only a single broad ^{19}F environment at low temperature (Table I). The broad ^{17}O resonance for TcO_2F_3 is attributable to partial collapse of the ^{99}Tc–^{17}O coupling brought about by quadrupole relaxation of ^{99}Tc in the asymmetric electric field of a trigonal bipyramid and by fluctuating electric field gradients arising from chemical exchange of fluorine ligands. We can rule out the possibility that $TcOF_5$ is formed in the oxidation of Tc_2O_5F by excess KrF_2. Unlike the substance identified as TcO_2F_3, which is coordinately unsaturated, $TcOF_5$ (C_{4v}) should behave like the related pseudooctahedral $ReOF_5$ and IOF_5 molecules and would not be expected to exhibit chemical exchanged among its axial and equatorial fluorine environments and HF solvent. Our failure to observe two nonlabile fluorine environments as well as the observed exchange behavior attributed to TcO_2F_3 is consistent with the proposed formulation of the latter oxyfluoride and inconsistent with $TcOF_5$ formation.

The observation of ^{99}Tc–^{19}F coupling for $Tc_2O_5F_4$ indicates the rate of fluorine exchange is slow. Only one oxygen environment could however be observed for the oxygen-bridged structure proposed for $Tc_2O_5F_4$. The partially resolved ^{99}Tc–^{17}O coupling is consistent with the lowered symmetry around ^{99}Tc. Failure to observe a unique bridging ^{17}O environment can be attributed to the effects of two ^{99}Tc nuclei spin–spin coupled to one ^{17}O. This would give rise to a broad, partially quadrupole-collapsed 19-line multiplet (relative intensity ratios 1:2:3:4:5:6:7:8:9:10:9:8:7:6-:5:4:3:2:1) having one-fourth the intensity of the terminal oxygen environment. The line width and low intensity of the line presumably preclude observation of the bridging environment of $Tc_2O_5F_4$ with the present instrumentation and level of ^{17}O enrichment.

Table II. ^{99}Tc Longitudinal Relaxation Times for Technetium(VII) Species

species	solvent	T_1, s[a]
TcH_9^{2-}	40% KOH in H_2O	0.023
TcO_4^- [b]	D_2O	0.139
	Me_2SO-d_6	0.139
	acetonitrile-d_3	0.132
	acetone-d_6	0.111
	methanol-d_4	0.091
TcO_3F	HF	0.018
TcO_3^+	HF	<0.001
TcO_2F_3	HF	0.003
$Tc_2O_5F_4$	HF	<0.001

[a] All T_1 values were obtained at 25 °C with the exception of that for TcH_9^{2-}, which was obtained at -16 °C. [b] NH_4TcO_4, 0.24 M; $T_1(^{17}O) = 0.202$ s for TcO_4^- in H_2O.

Further studies of these new oxyfluoro species of technetium(VII) and $TcO_3^+AsF_6^-$ are currently in progress.

$[TcO_2(CN)_4]^{3-}$. The ^{99}Tc NMR spectrum of *trans*-dioxotetracyanotechnetate(V) represents the only Tc(V) compound characterized thus far by ^{99}Tc NMR spectroscopy. The spectrum consists of a broad line in H_2O solvent and is the highest frequency ^{99}Tc chemical shift observed thus far. The deshielding of Tc(V) with respect to Tc(VII) is contrary to the trend anticipated on the basis of oxidation states alone. The valence shell in Tc(VII) compounds is mainly of s and p origin; there are no low-lying excited states created by ligand field splitting of the d orbitals. Consequently, the paramagnetic contribution to ^{99}Tc shielding will be small in Tc(VII) compounds compared to that for diamagnetic d^2 Tc(V) species such as $[TcO_2(CN)_4]^{3-}$.

T_1 Relaxation Times. The ^{99}Tc and ^{17}O spin–lattice relaxation times, T_1, of technetium(VII) species are summarized in Table II.

Kidd[1b] has reported a line width of $\Delta\nu = 29$ Hz for aqueous TcO_4^-, a value that is substantially greater than that reported in our study. From eq 1, our value of 2.7 Hz yields a value of 0.118 s for T_1 and is in good agreement with the T_1 value of 0.139 s determined by the inversion–recovery method in the present study.

Line widths of ^{99}Tc resonance are mainly due to the direct quadrupolar relaxation $\Delta\nu = 1/(\pi T_2)$. In the short correlation time limit for such an interaction, the transverse and longitudinal relaxation times, T_2 and T_1, are equal according to eq 1, and nuclear quadrupole relaxation dominates the spin–lattice relaxation time T_1. This is corroborated by a correlation between spin–lattice relaxation times and electric field gradients for the series TcO_4^-, TcO_3F, TcO_3^+ in which T_1 and $1/(\pi\Delta\nu)$ decrease from left to right. In general, there is a good correlation among T_1, $\Delta\nu$, and the electric field gradient at ^{99}Tc. Even though ^{99}Tc should possess an electric field gradient of zero in TcO_4^-, the efficient relaxation of ^{99}Tc is presumably also brought about by quadrupolar relaxation. The electric field gradient can be modulated by mixing the asymmetric molecular vibrations. This theory, first originated by Valiev,[7] has more recently been extended to the case of a quadrupolar nucleus at the center of a molecule belonging to a cubic point group.[8] The effective electric field gradient at ^{99}Tc in aqueous TcO_4^- estimated from eq 1 with $T_1 = 0.139$ s and $\tau_c = 8.1 \times 10^{-12}$ s is $eq = -0.15 \times 10^{15}$ esu. Kidd[1b] has reported a value of 0.33×10^{15} esu based on a T_1 value estimated from an inaccurate line width (29 Hz) and quadrupole moment (0.3×10^{-28} m^2). The quadrupole moment value we have chosen to use (-0.19 (5) $\times 10^{-28}$ M^2) agrees with the predictions of the single-particle nuclear shell model. Both calculations assume $\tau_c = 8.1 \times 10^{-12}$ s.

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 performed according to the regulations and recommendations of the Canadian Atomic Energy Control Board.

Apparatus and Materials. All manipulations involving air-sensitive materials were carried out under anhydrous conditions in a dry box or, in the case of volatile fluorides, on a vacuum line constructed from 316 stainless steel, nickel, Teflon, and FEP. All preparative work involving XeF_6 and KrF_2 was carried out in 7-mm or 3.5-mm o.d lengths of FEP tubing. The tubing was heat sealed at one end and connected through a 45° SAE flare to a Teflon (Du Pont) valve to form the reaction vessel.

NH_4TcO_4 (Oak Ridge National Laboratories) was purified by recrystallization from 30% hydrogen peroxide. $KTcO_4$ was prepared from crude NH_4TcO_4 by crystallization from H_2O_2 solution containing a stoichiometric amount of KOH. Pertechnetate salts were dried under dynamic vacuum for 24 h prior to use. Water enriched in ^{17}O (21.9%) and ^{18}O (42.7%) (Office de Rayonnements Ionisants, Saclay, France) was used to prepare enriched samples of TcO_4^- by heating 0.75 g of $KTcO_4$ with 1 mL of enriched water in a sealed tube for 1 week at 100 °C.

K_2TcH_9 was synthesized according to the method of Ginsberg.[4] Commercial samples of the solvents D_2O, acetone-d_6, dimethyl-d_6 sulfoxide (Stohler Isotope Chemicals), acetonitrile-d_3 and methanol-d_4 (Merck) were used without further purification.

KrF_2,[9] XeF_6,[10] and AsF_5[11] were prepared as described elsewhere. Commercial anhydrous HF (Matheson) was dried by storage under 6 atm of F_2 gas for 1 month in a nickel vessel prior to use.

Sample Preparations. With the exception of samples containing HF solvent, all NMR samples were prepared in 8- or 10-mm o.d. standard wall tubing and attached by means of 0.25 in. Teflon nuts and ferrules to Teflon diaphragm valves. All samples were degassed and sealed under vacuum. Samples containing HF solvent were prepared by heat sealing their respective 3.5- and 7-mm o.d. reaction vessels under vacuum and inserting them into 5-mm (^{19}F) and 10-mm (^{17}O and ^{99}Tc) precision glass NMR tubes.

Hydrogen fluoride solutions of TcO_3F were prepared by condensing anhydrous HF onto $KTcO_4$ in FEP reaction tubes at −196 °C (0.030 g of $KTcO_4$, 0.20 g of HF, in 3.5-mm tubes; 0.090 g of $KTcO_4$, 1.0 g of HF, in 7-mm tubes). $KTcO_4$ rapidly dissolved in HF upon warming to room temperature, yielding colorless to very pale yellow solutions. The resulting solutions of TcO_3F were treated with a fivefold excess of AsF_5 condensed into the sample at −196 °C to yield solutions of $TcO_3^+AsF_6^-$ and $H_3O^+AsF_6^-$[13] at room temperature. The latter solutions were pumped to dryness and maintained under dynamic vacuum for 2 h. Upon redissolution in HF, no changes in the ^{99}Tc and ^{17}O chemical shifts or line widths were observed, demonstrating that $TcO_3^+AsF_6^-$ is stable to pumping at room temperature.

Solutions of TcO_3F prepared as described above were treated with either a twofold excess of XeF_6 to yield $Tc_2O_5F_4$ or a sixfold excess of KrF_2 to yield TcO_2F_3. Both XeF_6 and KrF_2 react rapidly with TcO_3F (and H_2O liberated in the solvolysis of TcO_4^- by HF) to give $Tc_2O_5F_4$. The reaction of $Tc_2O_5F_4$ with KrF_2 at room temperature is slow, requiring several hours to go to completion. The slow competing autodecomposition of KrF_2 to Kr and F_2 in HF requires that large excesses of KrF_2 be used to ensure complete reaction.

Nuclear Magnetic Resonance Spectroscopy. Fluorine-19, technetium-99, and oxygen-17 spectra were obtained on Bruker WH-90 and proton spectra on Bruker WP-80 Fourier-transform spectrometers. All spectra were accumulated in 16K memories with the exception of proton spectra, which were accumulated in an 8K memory. Fluorine-19 spectra were ^{2}H-locked by using an external D_2O lock sample located in the probehead. Technetium-99 and oxygen-17 spectra were either locked to the deuterated solvent or to D_2O placed in the annular cavity formed by a 7-mm FEP tube or 8-mm precision glass tube contained in a 10-mm precision glass tube. Proton spectra were run at 80.00 MHz in a 5-mm precision glass tube containing an acetone-d_6 capillary for locking and accumulated in 80 scans by using a spectral width of 2.5 kHz (0.61 Hz/data point; acquistion time, 1.64 s) and a pulse width of 7.4 μs. Oxygen-17 spectra on ^{17}O-enriched samples were obtained at 12.20 MHz in 30 000–50 000 scans with a spectral width of 50 kHz (6.1 Hz/data point; acquistion time, 0.163 s) and a pulse width of 35 μs. Technetium-99 spectra were obtained at 20.27 MHz in 500–2000 scans with a spectral width of 25 kHz (3.0 Hz/data point; acquistion time, 0.327 s) and a pulse width of 20 μs for multiple scan spectra. For single-pulse spectra of TcO_4^-, the data point resolution was 0.048 Hz (spectral width, 400 Hz; acquistion time, 20.48 s) with a pulse width of 35 μs. Fluorine-19 spectra were recorded at 84.66 MHz in 300–400 scans with use of a spectral width of 30 kHz (3.7 Hz/data point; acquistion time, 0.270 s) and a pulse width of 2 μs.

Spin–lattice relaxation limes, T_1, were measured in degassed, vacuum sealed samples by the standard (π–τ–$\pi/2$) sequence with accumulation of the free-induction decay after the $\pi/2$ pulse.

Variable-temperature studies were carried out with use of Bruker temperature controllers. Temperatures were measured with a thermocouple inserted directly into the sample region of the probe and were accurate to ±1 °C.

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Note Added in Proof. Recently, we have observed ^{99}Tc signals for the lower oxidation states I and III: $Tc(R_3CNC)_6^+$, R = H, CH_3 ($\delta_{^{99}Tc}$ −1908, $\omega_{1/2}$ = 74 Hz); $Tc(CN)_7^{4-}$ ($\delta_{^{99}Tc}$ −1329, $\omega_{1/2}$ = 5000 Hz).

Registry No. ^{99}Tc, 14133-76-7; K_2TcH_9, 60950-18-7; $KTcO_4$, 13718-33-7; TcO_3F, 42246-22-0; $TcO_3^+AsF_6^-$, 82555-95-1; $Tc_2O_5F_4$, 82555-96-2; TcO_2F_3, 82555-97-3; $K_3[TcO_2(CN)_4]$, 73466-61-2; ^{17}O, 13698-48-4; ^{18}O, 14797-71-8.

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