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Synthesis and Characterization of Cationic Technetium Complexes of 1,2-Bis(dimethylphosphino)ethane (DMPE). Structure Determinations of *trans*-$[Tc^{V}(DMPE)_2(OH)(O)](F_3CSO_3)_2$, *trans*-$[Tc^{III}(DMPE)_2Cl_2]F_3CSO_3$, and $[Tc^{I}(DMPE)_3]^+$ Using X-ray Diffraction, EXAFS, and ^{99}Tc NMR

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Three distinct cationic complexes of technetium, containing Tc(V), Tc(III), and Tc(I) centers, have been prepared by reduction of pertechnetate with bis(1,2-dimethylphosphino)ethane (DMPE). Careful control of reaction conditions allows the synthesis of any one of *trans*-$[Tc^{V}(DMPE)_2O_2]^+$, *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$, or $[Tc^{I}(DMPE)_3]^+$ in greater than 90% yield. All complexes have been characterized by visible–UV and IR spectrophotometry, elemental analyses, and high-performance liquid chromatography. The Tc(I) complex has been additionally characterized by ^{31}P and ^{99}Tc NMR, as well as by a new type of EXAFS (extended X-ray absorption fine structure) analysis, which show that this is an octahedral species with a Tc–P bond length of 2.40 Å. The Tc(V) and Tc(III) complexes have been additionally characterized by single-crystal X-ray analyses. The structure of the protonated technetium(V) salt, $[Tc[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2(OH)(O)](F_3CSO_3)_2$, formula weight 730.43, was refined to a conventional R factor of 0.051. Reddish orange needles of this salt crystallize in the monoclinic space group $P2_1/c$, with $a = 8.052$ (2) Å, $b = 11.527$ (2) Å, $c = 16.070$ (3) Å, $\beta = 101.96$ (2)°, and $Z = 2$. The technetium(V) center is approximately octahedrally coordinated with four equatorial P atoms at an average distance of 2.477 (5) Å surrounding a *trans*-$[O{=}Tc{-}OH]^{2+}$ core. Disorder in the trans oxygen ligands prevented crystallographic determination of the individual Tc–OH and Tc=O distances; the average technetium(V)–oxygen distance in this structure is 1.795 (3) Å. An EXAFS study of this complex gives a Tc=O distance of 1.66 Å and a Tc–OH distance of 1.96 Å. The structure of the technetium(III) salt $[Tc[(CH_3)_2PCH_2CH_2P(CH_3)_2]Cl_2]F_3CSO_3$, formula weight 613.43, has been refined to a conventional R factor of 0.056. Orange crystals of this salt grow in monoclinic space group $P2_1/c$, with $a = 8.076$ (2) Å, $b = 24.401$ (4) Å, $c = 13.435$ (4) Å, $\beta = 96.61$ (2)°, and $Z = 4$. The coordination geometry of the Tc(III) center is trans octahedral with four equatorial P atoms at an average distance of 2.436 (5) Å and two trans Cl atoms at 2.324 (4) Å.

Introduction

Bis(tertiary phosphine) and bis(tertiary arsine) ligands are known to stabilize transition metals in a variety of oxidation states and coordination geometries.[1,2] Cationic technetium complexes of bis(tertiary phosphine) ligands have been of particular interest because several of these species have been shown to be taken up by normal heart tissue and thus have potential utility in diagnostic nuclear medicine as myocardial imaging agents.[3-6] Specifically, the cationic complex *trans*-$[^{99}Tc(DMPE)_2Cl_2]^+$ provides heart images in several animal species and has recently been evaluated as a myocardial imaging agent in humans.[7-10] During the development of procedures for the synthesis of *trans*-$[^{99m}Tc(DMPE)_2Cl_2]^+$, high-performance liquid chromatographic analyses of reaction mixtures divulged the presence of several impurities, at least two of which are cationic ^{99m}Tc complexes of DMPE.[6] Since ^{99m}Tc is a short-lived isotope ($t_{1/2} = 6.1$ h), these three cationic ^{99m}Tc complexes have been identified via synthesis and conventional chemical characterization of their ^{99}Tc analogues ($t_{1/2}$ of ^{99}Tc $= 2.1 \times 10^5$ years). This paper reports the results of these studies. The structures of the three complexes have been determined by a combination of single-crystal X-ray analyses, EXAFS, and ^{99}Tc NMR. In the course of this work, a new approach to structure determination by EXAFS (extended X-ray absorption fine structure) has been developed.

Experimental Section

General Procedures. Unless otherwise noted, all chemicals were of reagent grade. Unless otherwise specified, the symbol Tc will refer to the technetium isotope of mass 99. Technetium-99 emits a low-energy (0.292 MeV) β particle with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it does not present a significant health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. Technetium-99, in the form of solid ammonium pertechnetate, was purchased from Oak Ridge National Laboratory and purified as previously described.[11]

The DMPE (1,2-bis(dimethylphosphino)ethane) ligand is not stable in the presence of air. Therefore all reactions were conducted under a blanket of inert gas with deoxygenated solvents. In some cases, the DMPE ligand was stabilized with respect to air oxidation by addition of a strong acid.[6] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or by Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada. DMPE was purchased from STREM Chemical Co. and used without further purification.

Synthesis. *trans*-Dioxobis(1,2-bis(dimethylphosphino)ethane)technetium(V) Trifluoromethanesulfonate, *trans*-$[Tc(DMPE)_2O_2]F_3CSO_3$. A 100.0-mg portion of $NH_4{}^{99}TcO_4$ (5.5×10^{-4}

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mol) was dissolved in 2.1 mL of 0.05M NaOH. To this solution was added 2.1 mL of 18% (v/v) DMPE in 95% ethanol dropwise with stirring, the reaction mixture turning orange almost immediately. After stirring for 10 min, the reaction solution was diluted to about 120 mL with 90/10 H_2O/ethanol and loaded onto a Sephadex SP C-25 cation-exchange column (5.0 × 2.0 cm) that had been equilibrated with H_2O and capped with 1 cm of clean sand. Excess DMPE ligand and ligand oxidation products were removed by washing the column with 80 mL of 3/1 0.005 M aqueous NaOH/95% ethanol. After the products were washed with 40 mL of H_2O to bring the pH of the eluant to ca. 7, the desired product band was eluted with 0.15 M LiF_3CSO_3 in a volume of about 10 mL. After removal of solvent by rotoevaporation, the solid mixture of LiF_3CSO_3 and technetium product was dissolved in 2 mL of acetone. Addition of 8 mL of 1/7 2-propanol/diethyl ether, followed by cooling to −4 °C, led to a yellow precipitate of *trans*-$[Tc(DMPE)_2O_2]F_3CSO_3$ in 75% yield. This material slowly decomposes on standing in light under ambient conditions. Visible–UV (H_2O) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 375 (135), 319 (2480), 254 (25 400). IR (ν, cm^{-1}): 775 (Tc=O). The protonated form of this complex cation was obtained by dissolving $[Tc(DMPE)_2O_2]F_3CSO_3$ in hot 2-propanol and adding several drops of concentrated F_3CSO_3H; addition of diethyl ether, followed by cooling to −4 °C, produced a dark orange precipitate of *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$. This material is stable on standing in light under ambient conditions. Crystals of this protonated complex suitable for X-ray diffraction analysis were obtained by slow cooling of a concentrated aqueous solution that had been brought to incipient precipitation by addition of 30/70 2-propanol/*tert*-butyl alcohol. Anal. Calcd for $[Tc(DMPE)(OH)(O)](F_3CSO_3)_2$: C, 23.02; H, 4.52; P, 16.96; F, 15.61. Found: C, 23.31;, H, 4.69; P, 17.93; F, 15.97.

***trans*-Dichlorobis(1,2-bis(dimethylphosphino)ethane)technetium(III) Trifluoromethanesulfonate, *trans*-$[Tc(DMPE)_2Cl_2]F_3CSO_3$.** The *trans*-$[Tc(DMPE)_2Cl_2]^+$ cation was prepared as previously described.[11] Single crystals of the $[F_3CSO_3]^-$ salt suitable for X-ray crystallography were grown by slow evaporation at room temperature of a saturated solution in 95% ethanol.

Tris(1,2-bis(dimethylphosphino)ethane)technetium(I) Salts, $[Tc(DMPE)_3]Y$ (Y = PF_6, ClO_4, F_3CSO_3, F). A 150-mg portion of pertechnetate (8.3×10^{-4} mol) was dissolved in 1.0 mL of H_2O. To this solution were added 10 mL of 11% (v/v) DMPE in 95% ethanol and 0.1 mL of 4 M NaOH, and the resulting mixture was heated in a sealed reaction vial for 1 h at 132 °C. After the reaction solution was cooled to room temperature, 0.2 mL of a saturated aqueous solution of either NH_4PF_6, $LiClO_4$, or LiF_3CSO_3 was added to yield a white precipitate that was removed by filtration and washed successively with cold 95% ethanol and diethyl ether. This material was purified by dissolution in acetonitrile, removal of an insoluble residue by centrifugation, and rotoevaporation to dryness; yield ca. 30%. Slower evaporation of the acetonitrile resulted in large crystals of a distorted-trigonal morphology. Anal. Calcd for $[Tc(DMPE)_3]PF_6$: C, 31.14; H, 6.97; P, 31.22; F, 16.42. Found: C, 30.69; H, 7.12; P, 33.53; F, 16.42. Calcd. for $[Tc(DMPE)_3]ClO_4$: C, 33.2; H, 7.46; P, 28.64; C, 5.46. Found: C, 33.48; H, 6.88; P, 28.49; Cl, 5.28. FAB MS, positive ion mode: parent peak at *m/e* 549. Visible–UV (three determinations in H_2O) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 253 (13 100 ± 500), 226 (11 700 ± 400). When pertechnetate was reduced with DMPE in the presence of HF/NaF, a salt was isolated that can be formulated as $[Tc(DMPE)_3]F \cdot 3H_2O$. This material was used in the EXAFS experiment. Anal. Calcd for $[Tc(DMPE)_3]F \cdot 3H_2O$: C, 34.76; H, 8.77; P, 29.87; F, 3.05. Found: C, 35.43; H, 8.15; P, 29.65; F, 2.76.

HPLC Analyses. High-performance liquid chromatography (HPLC) experiments were conducted on a Bioanalytical Systems apparatus equipped with a guard column containing ANSPEC pellicular C-8 packing material and a JONES reversed-phase C-8 analytical column (250 × 4.5 mm). Spectrophotometric detection was performed with a high-sensitivity Beckman Model 153 detector containing a 254 filter insert. The mobile phase consisted of 75/25 (v/v) methanol/water, the aqueous fraction containing 0.02 M sodium heptanesulfonate and 0.003 M phosphate buffer (pH 7.0). The pH of the mobile phase prepared in this fashion is ca. 8. The flow rate was 1.5 mL/min, and the pressure was ca. 1000 psi.

Equipment. Visible–UV spectra were recorded on either a Varian 624 or a Cary 210 spectrophotometer. IR spectra were obtained in KBr pellets or Nujol mulls using a Perkin-Elmer 224 grating infrared spectrometer. Fourier-transform NMR spectra (^{31}P, ^{99}Tc) were obtained on a Nicolet NT-300 instrument. X-ray diffraction measurements were made on a Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and a molybdenum target tube (λ = 0.710 73 Å).

X-ray Characterization of *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$. A reddish orange crystal in the shape of a rectangular prism (approximate dimensions 0.75 × 0.25 × 0.25 mm) was mounted on a glass fiber, with the fiber nearly parallel to the long axis of the crystal. Cu Kα radiation was used to obtain *h0l*, *h1l*, *hk0*, and *hkl* precession photographs. Systematic absences for *0k0*, *k* odd, and for *h0l*, *l* odd, indicated the space group $P2_1/c$.

Least-squares analysis of 15 intense reflections measured at both their $+2\theta$ and -2θ values yielded the monoclinic cell constants a = 8.052 (2) Å, b = 11.527 (2) Å, c = 16.070 (3) Å, β = 101.96 (2)°, V = 1459.09 Å^3, and Z = 2. The density calculated from the data is 1.653 g cm^{-3}, and that measured by neutral buoyancy in $CHBr_3$/diethyl ether is 1.66 g cm^{-3}. Intensities were measured[13] for 2712 reflections of the type $h,k,\pm l$ in the region 2.6° ≤ 2θ ≤ 56°. From these, 2364 unique, observed reflections ($|F| \geq 2\sigma(F)$) were obtained[13] by averaging. The calculated absorption coefficient is 9.139 cm^{-1}. Empirical absorption corrections were applied. The corrections (for I) ranged from 1.00 to 1.07. Five standard reflections were monitored after every 36 reflections to account for crystal stability and long-term drift. The drift correction varied in a random manner from 1.00 to 1.04. Other details of data collection were as follows: scan method $2\theta/\theta$; scan rate 1–8° min^{-1}; scan range 0.7° below Kα_1 peak to 0.8° above Kα_2 peak in 2θ; maximum h, 23; maximum k, 11; extreme l, ±16.

Structure Solution and Refinement of *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$. A Patterson vector map was computed, and from this the positions of the technetium and sulfur atoms were deduced. The technetium atom was placed at an inversion center (0, 0, 0) in the space group $P2_1/c$, giving rise to disorder between the trans OH and O ligands. In an attempt to resolve this disorder problem, the crystal was assigned to the acentric space group $P2_1$, which was also consistent with the vector map. A total of 11 atoms were located, yielding R_1 = 35%. This model could not be further developed. Therefore, all remaining calculations were conducted in $P2_1/c$, treating both Tc–O bonds as equivalent. The remaining atoms of the structure were located by difference Fourier techniques. All hydrogen atoms were arbitrarily assigned an isotropic[14] temperature parameter, B, of 4.0 Å^2.[13] Refinement of the positional parameters and anisotropic thermal parameters for the non-hydrogen atoms led to a final convergence at R_1 = 0.051 and R_w = 0.069. A final difference map was essentially featureless, the highest peak occurring near the sulfur atom and representing less than 0.21 e Å^{-3}. Zerovalent scattering curves from Cromer[15] were used for Tc, P, F, C, S, and O. Those for hydrogen were taken from Stewart.[16] The values of F_o and F_c are given in Table A.[17]

X-ray Characterization of *trans*-$[Tc(DMPE)_2Cl_2]F_3CSO_3$. Data collection and structure solution were similar to that for the Tc(V) compound given above. The crystal of dimensions 0.16 × 0.19 × 0.33 mm was shown via intensity measurements to conform to the monoclinic space group $P2_1/c$ with cell constants a = 8.076 (2) Å, b = 24.401 (4) Å, c = 13.435 (4) Å, β = 96.61 (2)°, and Z = 4. The density calculated from these data is 1.56 g cm^{-3}, and the density measured by neutral buoyancy in hexane/bromotrichloromethane is 1.56 g cm^{-3}. Intensities were measured for 4648 reflections of type $h,k,\pm l$ with $2\theta \leq 47.6°$ as follows: maximum h, 8; maximum k, 25; extreme l, ±13. Of these, 4025 were unique, with 3331 having $|F_o| > 2\sigma(F_o)$. Since the maximum relative error in F for this crystal was less than 2%, no absorption corrections were included. The drift correction varied from 0.99 to 1.03 in a random manner. Structure solution was by standard heavy-atom techniques. No hydrogen atoms were used in the calculations, which converged with refinement of all positional and anisotropic thermal parameters (244 variables) to R_1 = 0.056 and R_w = 0.047. The largest peaks on a final difference map (0.8–0.5 e A^{-3}) were in the vicinity of the carbon atoms but not

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Table I. Results of EXAFS Analysis on Tc-P Complexes

complex	retransformation range, Å	EXAFS[a] *r*, Å	EXAFS[a] *N*	crystallography *r*, Å	crystallography *N*
$[Tc(DMPE)_3]F$	1.23-2.34	Tc-P = 2.40	6.0[b]		
$[Tc(DMPE)_2(O)(OH)](F_3CSO_3)_2$	1.04-2.43	Tc-P = 2.46	4.1	Tc-P(av) = 2.48	4[c]
		Tc-O = 1.66	0.9	Tc-O = 1.795	2
		Tc-O = 1.96	0.7		
$[Tc(DMPE)_2Cl_2]Cl$	1.21-2.35	Tc-P = 2.45	4.7	Tc-P(av) = 2.44	4[c]
		Tc-Cl = 2.31	1.8	Tc-Cl(av) = 2.32	2
$[Tc(DMPE)_2Br_2]Br$	1.48-2.57	Tc-P = 2.44	4.0		
		Tc-Br = 2.51	1.6		
$[Tc(DPPE)_2Cl_2]Cl$	1.20-2.50	Tc-P = 2.50	4.0	Tc-P(av) = 2.50	4[d]
		Tc-Cl = 2.30	2.4	Tc-Cl = 2.32	2
$[Tc(DPPE)_2Br_2]Br$	1.39-2.62	Tc-P = 2.47	3.8	Tc-P(av) = 2.50	4[e]
		Tc-Br = 2.44	2.9	Tc-Br = 2.44	2

[a] EXAFS curve fitting used k^3 weighting. All fits except as noted were by empirical methods. [b] Theoretical amplitudes and phases were used for this fit. [c] This work. [d] Elder, R. C.; Nalesnik, T.; Whittle, R., unpublished work; DPPE is an abbreviation for bis(diphenylphosphino)ethane. [e] Reference 11.

at reasonable positions for hydrogen atoms. Values of F_o and F_c are in Table B.[17]

pK_a Determination. The pK_a of *trans*-$[Tc(DMPE)_2(OH)(O)]^{2+}$ was spectrophotometrically determined by using a standard nonlinear least-squares analysis of absorbance-$[H^+]$ data.[18] A total of 12 solutions of constant ionic strength 0.50 M (maintained with $LiClO_4$) were prepared at regularly spaced $[H^+]$ values in the range $[H^+]$ = 0.01-0.39 M. The spectrum of each solution was determined over the range 290-450 nm (Figure 1), and the absorbance of each solution was measured at both 319 and 375 nm. The extinction coefficients of the unprotonated species *trans*-$[Tc(DMPE)_2O_2]^+$ at these wavelenghths are 2490 and 140 M^{-1} cm^{-1}, respectively. The extinction coefficient of the protonated species (calculated by a nonlinear least-squares technique) at 375 nm is 1323 ± 50 M^{-1} cm^{-1}. Data obtained at each wavelength were analyzed independently, and the two resulting pK_a values were the same.

EXAFS. The extended X-ray absorption fine structure (EXAFS) spectra were collected at the Stanford Synchrotron Radiation Laboratory by using synchrotron radiation generated in the SPEAR ring. The monochromator (Si 220, double-crystal type) and transmission mode ionization chambers (N_2 filled) are standard and have been described previously.[19a] Incident beam intensity was measured by passing the monochromated radiation (vertical slit, 1.0 mm) through a first ionization chamber. Continuation of the beam through the sample chamber (He filled) to the second ionization chamber allowed the measurement of the transmitted intensity. In some cases wavelength calibration was obtained by passing the transmitted intensity through a calibration standard (powdered, yellow uranium oxide, UO_3) and into a third ionization chamber. Fluorescence data were concurrently collected with a detector of the Stern, Heald type[19b] purchased from F. Lytle of EXAFS Co., Seattle, WA. The usual range for data collection was 20.6-22.1 KeV, which encompasses the K absorption edge of technetium. In most cases 340 steps were recorded beyond the absorption edge, with integration time varying from 1 to 8 s/point, the longer times being used for regions most removed from the edge. All EXAFS spectra were obtained at ambient temperature on powdered solid samples diluted with dextrose or Li_2CO_3 in a cell of ca. 1.0-mm path length (μx_{max} = 0.2).

EXAFS Data Analysis. The extraction of EXAFS from the absorption spectrum (calculated from log (I_0/I) for transmission measurements and (F/I_0) for fluorescence measurements) followed the technique of Hodgson.[20,21] The computer programs used were local modifications of programs originating with Hodgson and coworkers.[22,23] Modifications include a new optimization routine utilizing the theoretical amplitude and phase functions of Teo and Lee.[24]

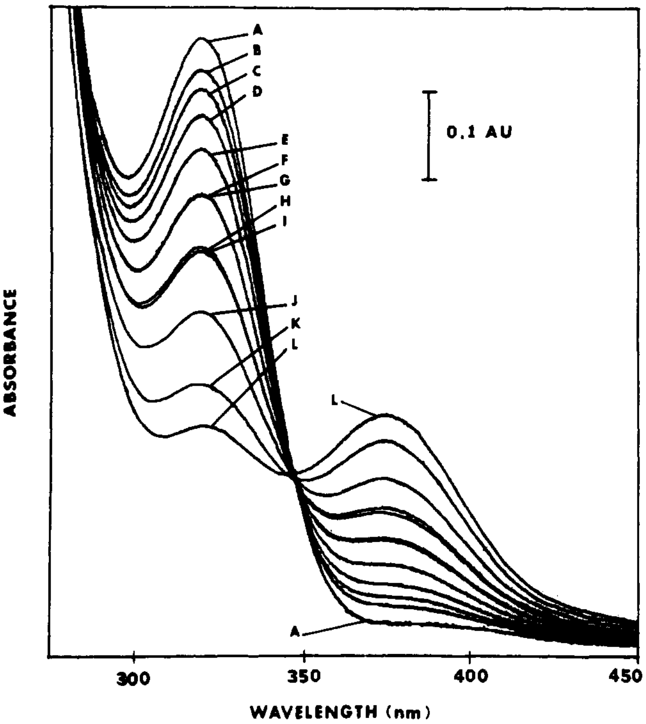

Figure 1. Visible-UV spectra recorded during spectrophotometric K_a determination for $[Tc(DMPE)_2(OH)(O)]^{2+}$ (μ = 0.50 M ($LiClO_4$)). $[H^+]$: (A) no added H^+ (pH 6); (B) 0.010 M; (C) 0.016 M; (D) 0.025 M; (E) 0.040 M; (F) 0.064 M; (G) 0.064 M; (H) 0.098 M; (I) 0.10 M; (J) 0.16 M; (K) 0.22 M; (L) 0.39 M.

Fourier filtering techniques were used for all spectra, with a square window function over the ranges indicated in Table I.

Structural parameters were extracted from the reduced EXAFS data by either a theoretical or an empirical approach. In the former, the EXAFS data points for a particular sample were fit to the theoretical equation[24]

$$\chi(\mathbf{k}) = \sum_j \frac{N_j}{\mathbf{k}r_j^2}(F_j(\mathbf{k}))e^{-2\theta_j^2\mathbf{k}^2} \sin(2\mathbf{k}r_j + \phi_j(\mathbf{k})) \qquad (1)$$

where N represents the number of atoms of the jth type at a distance r contributing to the backscattering; **k**, the photoelectron wave vector; $F_j(\mathbf{k})$, the calculated amplitude; θ_j, the Debye-Waller factor; and $\phi(\mathbf{k})$, the calculated phase. The functions for $F_j(\mathbf{k})$ and $\phi_j(\mathbf{k})$ used herein were those of Teo and Lee.[24] For each type of backscattering atom at a specific distance, four parameters were varied: E_0, N, r, and θ.

In the empirical approach, a complex containing a single type of first coordination sphere atoms with known N and r was used as a

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model and the filtered EXAFS data were fit to the standard functional form

$$\chi(\mathbf{k}) = \frac{C_1 e^{C_2 \mathbf{k}^2}}{\mathbf{k}^{C_3}} \sin (C_4 + C_5\mathbf{k} + C_6\mathbf{k}^2) \qquad (2)$$

where C_2, C_3, C_4, and C_6 are transferable parameters, useful for the description of the EXAFS modulations caused by that specific absorber–backscatterer pair in other complexes. To fit an unknown spectrum, C_1 and C_5 are allowed to vary for each set of backscattering atoms (shells) contributing to the filtered EXAFS data. The absorber–scatterer distance is calculated from $r_{\mathrm{unk}} = r_{\mathrm{model}} + [C_{5(\mathrm{unk})} - C_{5(\mathrm{model})}]/2$, and the number of backscattering atoms is estimated from $N_{\mathrm{unk}} = N_{\mathrm{model}}[C_{1(\mathrm{unk})}r_{\mathrm{unk}}{}^2]/[C_{1(\mathrm{model})}r_{\mathrm{model}}{}^2]$.

Results

Syntheses. The technetium(V) complex *trans*-$[Tc(DMPE)_2O_2]^+$ can be prepared at ambient temperature from pertechnetate and excess DMPE ligand under mildly alkaline conditions. Addition of the DMPE ligand to a millimolar solution of TcO_4^- yields within 2 min a yellow color that is characteristic of the desired product. HPLC and visible–UV spectrophotometric analysis of this reaction solution show that greater than 95% of the technetium is in the chemical form *trans*-$[Tc(DMPE)_2O_2]^+$. The synthesis of the technetium(III) complex *trans*-$[Tc(DMPE)_2Cl_2]^+$ from a number of technetium starting materials has been reported already.[6,11] In addition, this complex can also be prepared by the addition of DMPE ligand and HCl to *trans*-$[Tc(DMPE)_2O_2]^+$ under the same reaction conditions used to convert TcO_4^- to *trans*-$[Tc(DMPE)_2Cl_2]^+$.[25] This reaction can be represented by the following equation in which DMPE reduces Tc(V) to Tc(III):

$$Tc^{V}(DMPE)_2O_2^+ + {}^1/{}_2DMPE + 2HCl \rightarrow {}^1/{}_2(DMPE)O_2 + Tc^{III}(DMPE)_2Cl_2^+$$

Reduction also occurs when HCl is replaced by HBr, HI, or LiSCN, yielding the corresponding $[Tc(DMPE)_2X_2]^{+/0}$ complexes (in either the Tc(III) or Tc(II) oxidation state depending on the identity of X).

The technetium(I) complex $[Tc(DMPE)_3]^+$ can be prepared from pertechnetate and excess DMPE in alkaline media, employing fairly rigorous reaction conditions (150 °C, 1 h). This synthetic reaction, in which DMPE reduces Tc(VII) to Tc(I), proceeds in greater than 95% yield (by HPLC analyses) and may be represented as

$$TcO_4^- + DMPE\ (excess) \rightarrow Tc(DMPE)_3^+ + DMPE(O)_2$$

The $[Tc(DMPE_3]^+$ complex can also be synthesized from either of the Tc(III) *trans*-$[Tc(DMPE)_2Cl_2]^+$, or the Tc(V) *trans*-$[Tc(DMPE)_2O_2]^+$, complexes by employing the same reaction conditions used in the synthesis from pertechnetate. In all of these synthetic procedures, DMPE functions as both a reducing agent and a ligand.

Characterization. Relevant spectrophotometric parameters for *trans*-$[Tc^{V}(DMPE)_2O_2]^+$, *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$, and $[Tc^{I}(DMPE)_3]^+$ are noted in the Experimental Section. The intense charge-transfer band occurring in the visible region for *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$ and related complexes has been previously discussed.[11] *trans*-$[Tc(DMPE)_2O_2]^+$ and $[Tc(DMPE)_3]^+$ exhibit charge-transfer bands in the ultraviolet region of the spectrum. The IR spectra of *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$ and *trans*-$[Tc(DMPE)_2O_2]F_3CSO_3$ exhibit bands at 965 and 810 cm^{-1}, respectively, which are assigned as arising from the Tc=O stretch.[12] Elemental analyses of several salts of these complexes give results (vide supra) that are in agreement with the proposed formulations. Fast atom bombardment mass spectrometry (FAB-MS) shows that the parent peak of the Tc(I) complex occurs at *m/e* 549, consistent with the $[Tc^{I}(DMPE)_3]^+$ formulation. HPLC analyses of these complexes indicate that each complex is greater than 95% pure. Under the conditions delineated in the Experimental Section, the HPLC retention times of *trans*-$[Tc(DMPE)_2O_2]^+$, *trans*-$[Tc(DMPE)_2Cl_2]^+$, and $[Tc(DMPE)_3]^+$ are 4.1, 5.4, and 13.7 min, respectively.

Table II. Fractional Atomic Positional Parameters[a,b] for *trans*-$[Tc(DMPE)_2(O)(OH)](F_3CSO_3)_2$

atom	*x*	*y*	*z*
Tc[c]	0.0	0.0	0.0
P(1)	−0.0599 (1)	0.2106 (1)	−0.0044 (1)
P(2)	0.1233 (1)	0.0521 (1)	−0.1242 (1)
O(1)	0.2000 (4)	0.0262 (3)	0.0708 (2)
O(2)	0.4426 (6)	0.2240 (4)	0.0966 (3)
O(3)	0.6724 (4)	0.2568 (4)	0.2140 (3)
O(4)	0.3841 (5)	0.2776 (3)	0.2309 (3)
C(1)	0.0692 (6)	0.2042 (4)	−0.1501 (3)
C(2)	0.0760 (6)	0.2761 (4)	−0.0715 (4)
C(3)	−0.0163 (6)	0.2939 (4)	0.0921 (4)
C(4)	−0.2769 (7)	0.2452 (6)	−0.0552 (4)
C(5)	0.3510 (6)	0.0458 (6)	−0.1024 (4)
C(6)	0.0483 (9)	−0.0230 (5)	−0.2243 (4)
C(7)	0.5033 (8)	0.4325 (5)	0.1484 (5)
S	0.5015 (1)	0.2814 (1)	0.1758 (1)
F(1)	0.3552 (6)	0.4664 (4)	0.1077 (5)
F(2)	0.6107 (7)	0.4588 (5)	0.0998 (4)
F(3)	0.5558 (11)	0.4940 (4)	0.2159 (5)
H(1A)[d]	−0.054 (5)	0.209 (3)	−0.190 (3)
H(1B)	0.138 (5)	0.233 (4)	−0.176 (3)
H(2A)	0.177 (5)	0.276 (4)	−0.046 (3)
H(2B)	0.040 (5)	0.361 (4)	−0.086 (3)
H(3A)	0.068 (5)	0.265 (4)	0.140 (3)
H(3B)	−0.116 (5)	0.281 (3)	0.106 (3)
H(3C)	0.009 (5)	0.407 (3)	0.074 (3)
H(4A)	−0.278 (5)	0.310 (4)	−0.053 (3)
H(4B)	−0.322 (6)	0.209 (4)	−0.097 (3)
H(4C)	−0.356 (5)	0.224 (3)	−0.014 (3)
H(5A)	0.394 (5)	0.046 (4)	−0.154 (3)
H(5B)	0.408 (6)	−0.022 (4)	−0.089 (3)
H(5C)	0.409 (5)	0.078 (4)	−0.060 (3)
H(6A)	−0.060 (6)	−0.003 (3)	−0.254 (4)
H(6B)	0.174 (5)	0.010 (3)	−0.249 (3)
H(6C)	0.068 (5)	−0.101 (3)	−0.205 (3)

[a] The estimated error in the last digit is given in parentheses. This form is used throughout. [b] The numbering scheme for the cation is shown in Figure 2. [c] This atom lies on a symmetry-fixed position. [d] Hydrogen atom H(*n*) is bound to C(*n*).

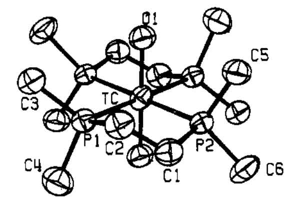

Figure 2. Perspective view of the *trans*-$[Tc(DMPE)_2(OH)(O)]^{2+}$ cation with hydrogen atoms omitted for clarity.

Crystal Structure. ***trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$.** Final fractional atomic positional parameters and their estimated standard deviations are given in Table II. The corresponding anisotropic thermal parameters may be found in Table C,[17] the derived root-mean-square displacements are in Table D, and the associated ellipsoids for the complex cation are shown in Figure 2. Selected bond lengths and bond angles are found in Table III with the remainder in Table E.[17]

The technetium(V) center is six-coordinate with an approximately octahedral coordination environment. The donor phosphorus atoms of the two bidentate DMPE ligands occupy the four equatorial coordination sites, forming two five-membered rings. The oxygen atoms occupy mutually trans positions related by the inversion center of space group $P2_1/c$. Since

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(25) Vanderheyden, J.-L., unpublished results.

Table III. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[$Tc(DMPE)_2(O)(OH)](F_3CSO_3)_2$

Lengths

Tc-P(1)	2.473 (1)	P(1)-C(4)	1.813 (5)
Tc-P(2)	2.480 (1)	P(2)-C(1)	1.833 (4)
Tc-O(1)	1.795 (3)	P(2)-C(5)	1.796 (5)
P(1)-C(2)	1.848 (6)	P(2)-C(6)	1.817 (6)
P(1)-C(3)	1.796 (5)		

Angles

P(1)-Tc-P(2)	81.20 (4)	C(3)-P(1)-Tc	119.86 (16)
P(1)-Tc-O(1)	89.83 (10)	C(1)-P(2)-C(5)	105.55 (26)
P(2)-Tc-O(1)	90.74 (12)	C(1)-P(2)-C(6)	103.57 (24)
C(2)-P(1)-C(4)	106.23 (27)	C(1)-P(2)-Tc	107.40 (17)
C(2)-P(1)-C(3)	104.58 (23)	C(5)-P(2)-C(6)	106.91 (30)
C(2)-P(1)-Tc	106.39 (15)	C(5)-P(2)-Tc	113.39 (20)
C(4)-P(1)-C(3)	105.59 (27)	C(6)-P(2)-Tc	118.83 (23)
C(4)-P(1)-Tc	113.14 (21)		

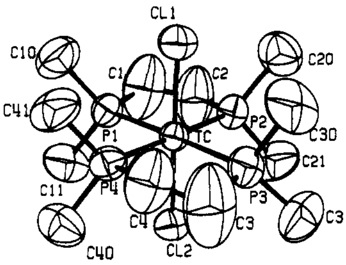

Figure 3. Perspective view of the *trans*-[$Tc(DMPE)_2Cl_2]^+$ cation with hydrogen atoms omitted for clarity.

one oxygen atom is protonated and the other is not, there must be a disorder in the crystal structure. However, refinement with a single type of oxygen atom proceeds smoothly to give an average Tc–O distance of 1.795 (3) Å. The maximum root-mean-square (rms) displacement of the oxygen atom (0.26 Å) is approximately perpendicular to the Tc–O bond as may be seen in Figure 2. The other two rms displacements for the oxygen atom are 0.24 and 0.20 Å (Table D).[17] This oxygen atom appears weakly hydrogen bonded to one of the oxygen atoms of the trifluoromethanesulfonate anion (O–O separation of 2.97 Å).

***trans*-[$Tc(DMPE)_2Cl_2]F_3CSO_3$.** Final fractional atomic positional parameters and their estimated standard deviations are given in Table IV. The corresponding anisotropic thermal parameters may be found in Table F,[17] rms displacements are given in Table G,[17] and the associated ellipsoids for the complex cation are shown in Figure 3. Selected bond lengths and bond angles are presented in Table V; those remaining are given in Table H.[17]

The structure of the [$Tc(DMPE)_2Cl_2]^+$ cation shows the trans octahedral geometry that is typical for Tc(III) [$TcD_2X_2]^+$ cations (D = chelating bis(tertiary phosphine or arsine), X = halogen or pseudohalogen).[11,26] The phosphorus atoms of the two bidentate DMPE ligands occupy four equatorial coordination sites with the two trans Cl^- ions completing the six-coordinate ligation.

FT-NMR Characterization of [$Tc^I(DMPE)_3]^+$. Figure 4 shows the ^{99}Tc NMR and ^{31}P NMR spectra of [$Tc^I(DMPE)_3]^+$. In the ^{99}Tc NMR spectrum the seven-line splitting pattern is consistent with one technetium atom being bonded to six equivalent phosphorus atoms of spin $^1/_2$. In the ^{31}P NMR spectrum, the 10-line pattern is consistent with the formulation of one type of phosphorus atom being bonded to ^{99}Tc that has a $^9/_2$ spin. In both spectra J_{Tc-P} = 574 Hz. The observation of sharp spectral lines strongly implies that the complex is diamagnetic.

Table IV. Fractional Atomic Positional Parameters[a] for *trans*-[$Tc(DMPE)_2Cl_2]F_3CSO_3$

atom	*x*	*y*	*z*
Tc	0.47576 (8)	0.12381 (3)	0.21891 (4)
Cl(1)	0.6868 (3)	0.0757 (1)	0.1532 (2)
Cl(2)	0.2666 (3)	0.1725 (1)	0.2846 (1)
P(1)	0.6228 (3)	0.1142 (1)	0.3864 (1)
P(2)	0.6429 (3)	0.2074 (1)	0.2233 (2)
P(3)	0.3216 (3)	0.1339 (1)	0.0534 (1)
P(4)	0.3096 (3)	0.0404 (1)	0.2175 (2)
C(1)	0.7664 (17)	0.1694 (5)	0.4009 (7)
C(2)	0.7546 (17)	0.2149 (5)	0.3417 (7)
C(3)	0.1583 (19)	0.0839 (6)	0.0428 (8)
C(4)	0.1973 (16)	0.0298 (4)	0.0928 (7)
C(10)	0.7401 (13)	0.0510 (4)	0.4137 (7)
C(11)	0.4970 (13)	0.1187 (4)	0.4900 (5)
C(20)	0.7967 (13)	0.2134 (4)	0.1319 (7)
C(21)	0.5390 (14)	0.2740 (4)	0.2103 (8)
C(30)	0.4468 (16)	0.1236 (5)	−0.0517 (6)
C(31)	0.2159 (14)	0.1978 (4)	0.0168 (6)
C(40)	0.1534 (12)	0.0354 (4)	0.3036 (6)
C(41)	0.4099 (13)	−0.0251 (4)	0.2344 (7)
S	−0.0183 (3)	0.3716 (1)	0.2326 (2)
O(1)	0.0099 (9)	0.4173 (3)	0.2966 (4)
O(2)	0.0223 (10)	0.3214 (3)	0.2810 (5)
O(3)	−0.1677 (8)	0.3742 (3)	0.1684 (4)
C(5)	0.1370 (15)	0.3773 (4)	0.1550 (7)
F(1)	0.2935 (8)	0.3792 (3)	0.1962 (4)
F(2)	0.1172 (9)	0.4222 (3)	0.0949 (4)
F(3)	0.1342 (8)	0.3363 (3)	0.0875 (5)

[a] The numbering scheme for the cation is shown in Figure 3.

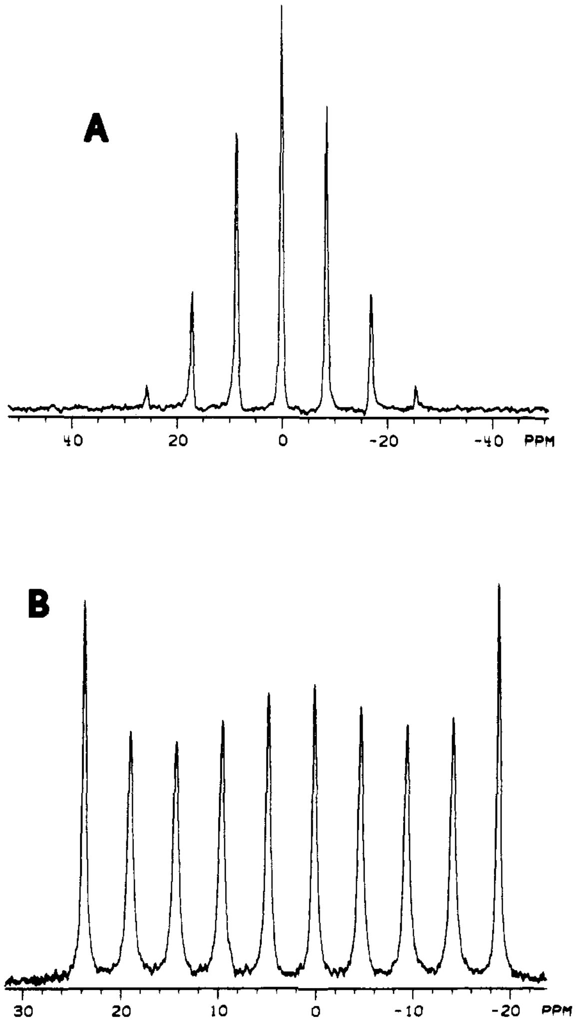

Figure 4. (a) ^{99}Tc NMR spectrum of [$Tc(DMPE)_3]^+$. On this scale an external standard of TcO_4^- (pertechnetate) is located as a single sharp peak at +13 ppm. (b) ^{31}P NMR spectrum of [$Tc(DMPE)_3]^+$.

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(26) Elder, R. C.; Whittle, R.; Glavan, K. A.; Johnson, J. F.; Deutsch, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1662.

Table V. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$[Tc(DMPE)_2Cl_2]CF_3SO_3$

	Lengths		
Tc-P(1)	2.431 (2)	Tc-P(3)	2.432 (2)
Tc-P(2)	2.443 (2)	Tc-P(4)	2.436 (2)
Tc-Cl(1)	2.326 (2)	Tc-Cl(2)	2.321 (2)
P(1)-C(1)	1.773 (13)	P(2)-C(2)	1.746 (10)
P(3)-C(3)	1.789 (15)	P(4)-C(4)	1.829 (10)
C(1)-C(2)	1.364 (16)	C(3)-C(4)	1.499 (17)
P(1)-C(10)	1.824 (10)	P(1)-C(11)	1.819 (9)
P(2)-C(20)	1.849 (11)	P(2)-C(21)	1.830 (9)
P(3)-C(30)	1.846 (11)	P(3)-C(31)	1.819 (10)
P(4)-C(40)	1.811 (10)	P(4)-C(41)	1.795 (9)
	Angles		
P(1)-Tc-P(2)	81.29 (7)	P(3)-Tc-P(4)	81.57 (8)
P(1)-Tc-P(4)	97.84 (7)	P(2)-Tc-P(3)	99.28 (8)
P(1)-Tc-Cl(1)	90.07 (7)	P(1)-Tc-Cl(2)	89.83 (7)
P(2)-Tc-Cl(1)	90.22 (8)	P(2)-Tc-Cl(2)	89.33 (8)
P(3)-Tc-Cl(1)	91.39 (8)	P(3)-Tc-Cl(2)	88.71 (8)
P(4)-Tc-Cl(1)	90.12 (8)	P(4)-Tc-Cl(2)	90.33 (8)

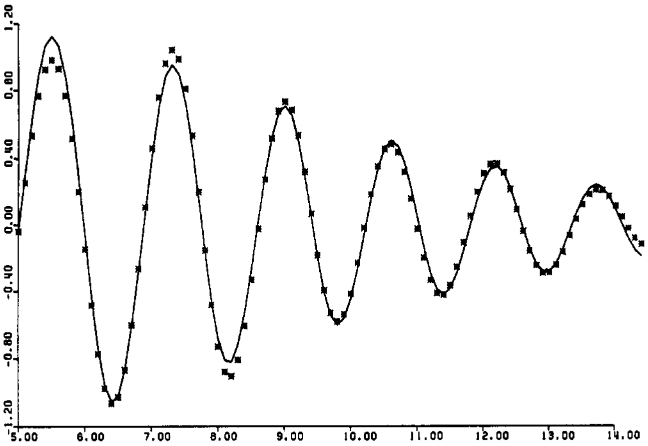

Figure 5. Plot of observed (points) and calculated (lines) EXAFS data over the indicated **k** range vs. $\chi(\mathbf{k})^2$ for $[Tc(DMPE)_3]^+$.

EXAFS. A Fourier transform of the EXAFS data for $[Tc(DMPE)_3]F$ in R (Å) space gave rise to a single, somewhat asymmetric, peak at 1.90 Å, suggesting that only one type of atom (phosphorus) was present in the coordination sphere. The entire peak (from 1.23 to 2.34 Å) is retransformed into K space, and a good fit (Figure 5) is obtained from theoretical phases and amplitudes to describe only a Tc–P interaction. Thus, there is no need to include atoms other than phosphorus bonded to technetium. The resulting structural parameters are R = 2.40 Å, N = 6.0, and θ = 0.05 Å, where θ is the Debye–Waller disorder parameter in eq 1. With the bond distance of 2.40 Å and coordination number of 6.0, the EXAFS data for $[Tc(DMPE)_3]F$ were fit to parameters of the empirical form given in eq 2. These transferable parameters describing the Tc–P bond were combined with the comparable parameters describing Tc–O, Tc–Cl, and Tc–Br bonds (derived from EXAFS data on TcO_4^-, $TcCl_6^{2-}$, and $TcBr_6^{2-}$, respectively) to fit EXAFS data on five other, previously characterized, technetium–phosphine complexes containing both Tc–P and Tc–X (X = O, Cl, Br) bonds. The results of these fits are summarized in Table I, and the fits are graphically displayed in Figure 6.

Discussion

Syntheses. When pertechnetate is brought into reaction with excess DMPE, a series of complexes containing technetium in oxidation states VII, V, III, and I can be observed: $[Tc^{VII}O_4]^-$, *trans*-$[Tc^{V}(DMPE)_2O_2]^+$, *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$, $[Tc^{I}(DMPE)_3]^+$. This series nicely illustrates the variety of oxidation states available to technetium and their successive generation by the action of a 2-equiv reductant (DMPE). In this system the technetium(II) oxidation state, either as *trans*-$[Tc^{II}(DMPE)_2Cl_2]$ or $[Tc^{II}(DMPE)_3]^{2+}$, does not appear to be a predominant component. However, this qualitative observation is merely a manifestation of the reduction potentials of the DMPE complexes and the conditions employed in the chromatographic analysis of these systems. Detailed electrochemical studies[27] show that both *trans*-$[Tc^{II}(DMPE)_2Cl_2]$ and $[Tc^{II}(DMPE)_3]^{2+}$ can be quantitatively produced at the appropriate applied potentials. No evidence has yet been obtained for bis(phosphine) complexes of either technetium(IV) or technetium(VI).

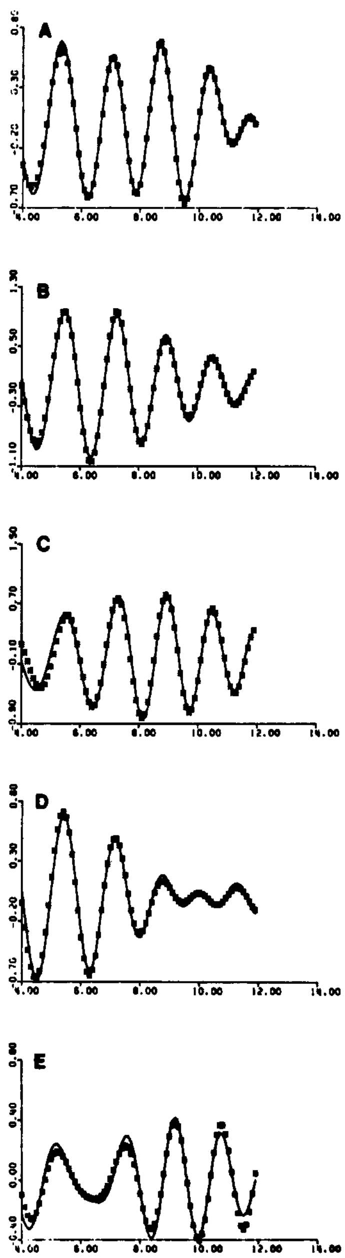

Figure 6. Plot of observed (points) and calculated (lines) EXAFS data over the indicated **k** range vs. $\chi(\mathbf{k})^2$ for several previously characterized technetium–phosphine complexes having both Tc–P and Tc–X (X = O, Cl, Br) bonds: (A) *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$; (B) *trans*-$[Tc(DMPE)_2Cl_2]Cl$; (C) *trans*-$[Tc(DMPE)_2Br_2]Br$; (D) *trans*-$[Tc(DPPE)_2Cl_2]Cl$; (E) *trans*-$[Tc(DPPE)_2Br_2]Br$.

In the presence of excess DMPE, $[Tc^{I}(DMPE)_3]^+$ is the thermodynamically stable product of the above series and either of the technetium(V) or technetium(III) intermediates

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[27] Ichimura, A.; Heineman, W. R.; Vanderheyden, J.-L.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 1272.

can be readily converted to it. Isolation of technetium(V) and technetium(III) complexes thus involves trapping relatively unstable reaction intermediates and requires careful control of reaction conditions. The *trans*-$[Tc^{V}(DMPE)_2O_2]^+$ cation is obtained at alkaline pH under mild reaction conditions and short reaction times; at longer reaction times, $[Tc^{I}(DMPE)_3]^+$ is produced. The *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$ cation is obtained under stringent reaction conditions in the presence of HCl; the amount of acid must be carefully controlled since too little promotes formation of $[Tc^{I}(DMPE)_3]^+$ and too much inactivates DMPE by converting it to the protonated form. In this latter situation, or if the reaction conditions are not sufficiently stringent, *trans*-$[Tc^{V}(DMPE)_2O_2]^+$ is produced rather than the desired *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$. This intricate interplay among reaction conditions and reaction products is the main source of past difficulties encountered in synthesizing the ^{99m}Tc analogue *trans*-$[^{99m}Tc(DMPE)_2Cl_2]^+$ for evaluation as a potential myocardial imaging agent.[6]

The complicated synthetic chemistry involved in the production of *trans*-$[Tc(DMPE)_2Cl_2]^+$ and related complexes can be simplified by isolating the precursor technetium(V) complex from the reaction mixture. Reaction of isolated *trans*-$[Tc^{V}(DMPE)_2O_2]^+$ with a halide (or pseudohalide) readily yields *trans*-$[Tc(DMPE)_2X_2]^{+/0}$ complexes that are otherwise difficult to obtain.[25] In these reactions, technetium(V) is reduced either by the halide (or pseudohalide) or by addition of a reductant. The oxidation state of the final product (Tc(II) or Tc(III)) is determined by reaction conditions and the nature of the halide or pseudohalide.

Characterization. In addition to the EXAFS and single-crystal X-ray studies described below, the three cationic complexes presented in this work have been characterized by a variety of techniques. HPLC analysis shows that each complex is greater than 95% pure, and elemental analyses of isolated salts give results consistent with the proposed formulations. The visible–UV spectra of the technetium(V) and technetium(I) complexes are relatively uninformative, while the visible spectrum of *trans*-$[Tc(DMPE)_2Cl_2]^+$ is dominated by the halogen-to-technetium charge-transfer band that has previously been discussed in detail.[11] The $[Tc^{I}(DMPE)_3]^+$ complex is colorless, as expected for a low-spin, d^6 complex of π-back-bonding ligands (e.g., the isoelectronic $Mo(CO)_6$ is also colorless), while the yellow color of the *trans*-$[Tc(DMPE)_2O_2]^+$ complex results from tailing of the intense ligand-to-metal charge-transfer band ($\lambda_{max} = 319$ nm) from the ultraviolet into the visible region.

The *trans*-$[Tc(DMPE)_2O_2]^+$ cation is characterized by an IR absorption band at 775 cm^{-1}, which is at the limit of the range (780–900 cm^{-1}) observed for complexes containing the *trans*-$[TcO_2]^+$ core.[12] That this technetium(V) complex contains the *trans*-$[TcO_2]^+$ entity rather than a TcO^{3+} core is consistent with a previously noted generalization based on charge neutralization.[12] Neutral ligands such as DMPE promote the *trans*-$[TcO_2]^+$ core wherein two oxo groups neutralize the high formal charge on technetium(V), whereas anionic ligands such as Cl^- or $EDTA^{4-}$ promote the monooxo TcO^{3+} core. Other technetium(V) complexes having the *trans*-$[TcO_2]^+$ core include *trans*-$[Tc(cyclam)O_2]^+$,[28] *trans*-$[Tc(en)_2O_2]^+$,[29] *trans*-$[Tc(py)_4O_2]^+$,[30] and *trans*-$[Tc(diars)_2O_2]^+$.[26] Protonation of *trans*-$[Tc(DMPE)_2O_2]^+$ to yield *trans*-$[Tc^{V}(DMPE)_2(OH)(O)]^{2+}$ causes the Tc=O stretch to shift to higher frequencies, but the 920–980-cm^{-1} region is obscured by bands arising from the DMPE ligand and thus the exact Tc=O stretching frequency cannot be assigned. At ionic strength 0.5 M, 25 °C, the pK_a of *trans*-$[Tc(DMPE)_2(OH)(O)]^{2+}$ is 0.80 ± 0.05 ($K_a = 6.3 \pm 0.05$), indicating that this is a relatively strong acid. For comparison, the pK_a of *trans*-$[Tc(cyclam)(OH)(O)]^{2+}$ is 2.5 ± 0.1 at ionic strength 2.0 M, 25 °C,[28] and that for *trans*-$[Re(en)_2(OH)(O)]^{2+}$ is 3.26 ± 0.02, 25 °C, at ionic strength 0.02 M.[31] These data show that, as expected, amine ligands donate more negative charge to the metal(V) center, making the $[M(O)_2(amine)_4]^+$ complexes considerably more basic than the $[M(O)_2(phosphine)_4]^+$ complex; correspondingly, the protonated phosphine complex is considerably more acidic than the amine analogues.

The ^{99}Tc and ^{31}P NMR spectra of $[Tc(DMPE)_3]^+$ shown in Figure 4 provide compelling evidence in favor of the proposed formulation of this complex. First, the splitting patterns demonstrate that the complex contains six equivalent phosphorus atoms bonded to one unique technetium atom (J_{Tc-P} = 574 Hz). Second, the observance of sharp spectral lines strongly implies that the complex is diamagnetic. In the presence of strong-field ligands, only spin-paired d^2 or d^6 configurations can reasonably be diamagnetic. Since the preparative chemistry and elemental analyses detailed above virtually eliminate the d^2 possibility, the complex then contains a spin-paired, d^6 center and is thus a technetium(I) species. To our knowledge, the ^{99}Tc NMR spectrum in Figure 4 constitutes the first reported for a Tc(I) complex. ^{99}Tc NMR spectra of Tc(VII) and Tc(V) complexes have recently been presented by Lock and co-workers.[32] Presumably it is the near octahedral symmetry of $[Tc(DMPE)_3]^+$ that permits observance of the ^{99}Tc NMR despite the large quadrupole moment of this nucleus. The chemical shift of ^{99}Tc in $[Tc(DMPE)_3]^+$, relative to TcO_4^-, is 13 ppm, considerably less than the shifts observed by Lock and co-workers for Tc(V) and Tc(VII) complexes.[32]

EXAFS. Two different approaches have been used by others in fitting EXAFS data. One method that depends on the transferability of parameters found for model compounds has been developed by Hodgson and co-workers.[20] The other from Teo and Lee[24] utilizes transferable phases and amplitudes derived from theoretical calculations. Each method has its drawbacks. The model, or empirical, approach in practice requires a "single-shell" compound whose crystal structure is known (that is, a complex in which all the ligating atoms are of the same type, are bound at the same distance, and have equal bond strengths). A model compound must be available and characterized both by X-ray diffraction and EXAFS analysis for every possible central atom, ligating atom pair. The theoretical approach may be applied to a single-shell compound without a prior crystal structure, as evidenced by our fit of data for $[Tc(DMPE)_3]F$ (Figure 5), which gives a bond distance of 2.40 Å and a coordination number of 6.0. The difficulty with the theoretical approach is that more parameters are treated as variables (r, N, θ, and E_0, which is the energy at which $k = 0$) than in the empirical approach. The increased number of variables, at least in our hands, makes it extremely difficult to fit multishell complexes. Since most complexes of interest are in fact multishell, this difficulty limits the utility of the theoretical approach to EXAFS. In an attempt to utilize the best features of each approach we have used a hybrid technique that appears to work extremely well.

The need for the new approach to EXAFS analysis arose because, in our hands, none of the crystals of a variety of salts of $[Tc(DMPE)_3]^+$ were suitable for single-crystal diffraction analyses[33] and thus we had no single-shell model for the Tc–P

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distance nor did we know the structure of $[Tc(DMPE)_3]^+$, although NMR evidence indicated both Tc–P bonding and equivalence of all of the phosphorus atoms. The Fourier transform of the EXAFS data suggested only one type of atom in the technetium coordination sphere, and the shape of the EXAFS envelope indicated that the ligating atom was indeed phosphorus. Given this information, we then fit the Fourier-filtered data with theoretical phases and amplitudes. Subsequently we fit this same data to eq 2 used in the empirical approach, varying parameters C_1–C_6. The transferability of C_2, C_3, C_4, and C_6 plus the new "known" r and N for $[Tc(DMPE)_3]^+$ allowed us to apply the empirical approach to several multishell complexes containing phosphorus and some other ligating atom(s). Since many of these complexes have known crystal structures, we are able to check the validity of the hybrid approach. There are four compounds in Table I with known crystal structures. The worst agreement is for *trans*-$[Tc(DPPE)_2Br_2]Br$[11] where, from EXAFS, the Tc–P bond length is 2.47 Å and from the crystal structure it is 2.50 Å. Since this agreement is as good as was found for an extensive series of multishell fits using molybdenum complexes,[21] it is clear that the hybrid approach is sound and the results as reliable as those from the empirical approach alone. On the basis of this evidence we feel a conservative assignment of the esd for the Tc–P bond in the single-shell complex $[Tc(DMPE)_3]^+$ is 0.02 Å; thus, Tc–P is 2.40 (2) Å.

Thus, in the case of $[Tc(DMPE)_3]^+$, EXAFS provides information that was unavailable to us from X-ray crystallography. A somewhat more subtle case is that of *trans*-$[Tc(DMPE)_2(OH)(O)]F_3CSO_3$. Here, the crystal structure refined easily (vide supra) to describe a complex with one type of Tc–P bond and also only one type of Tc–O bond, although chemical evidence indicates that two types of oxygen atoms are present. The crystallographic Tc–O value, 1.80 Å, is out of line with reported technetium to oxygen single- or double-bond lengths[34] but agrees moderately well with the numerical average (1.84 Å) expected from one single bond (2.02 Å) and one double bond (1.65 Å). Thus, the crystal structure may be interpreted as not disagreeing with the *trans*-$[Tc(OH)(O)]^{2+}$ core formulation; however, it does not require such an interpretation nor can it provide any information about the actual technetium to oxygen distances. The EXAFS data, on the other hand, do not suffer from such an ambiguity. The best model is a three-shell fit with one short Tc═O distance, 1.66 Å, and one longer Tc–O bond of 1.96 Å with coordination numbers of 0.9 and 0.7, respectively. The diminished value calculated for the coordination number of the longer Tc–O bond is a phenomenon seen frequently in EXAFS analysis and seems to reflect the significantly lower rigidity of the longer and weaker bond.[35,36]

Single-Crystal X-ray Structures. The trans octahedral geometries observed for *trans*-$[Tc^{III}(DMPE)_2Cl_2]^+$ and *trans*-$[Tc^V(DMPE)_2(OH)(O)]^{2+}$ are entirely as expected on the basis of previously reported structures of *trans*-$[Tc^{III}(diars)_2Cl_2]^+$,[26] *trans*-$[Tc^{III}(DPPE)_2Br_2]$,[11] *trans*-$[Tc^V(cyclam)O_2]^+$,[28] *trans*-$[Tc^V(en)_2O_2]^+$,[29] and *trans*-$[Tc^V(diars)_2O_2]^+$.[33] This geometry is universally observed for $[M(diars)_2X_2]^{n+}$ complexes[1,2] and is expected to be common for $[MD_2X_2]^{n+}$ species where D is either a chelating bis(tertiary phosphine or arsine) ligand.[11]

Several technetium(V) complexes, prepared by the reduction of pertechnetate in aqueous media, have been structurally characterized.[34] These complexes contain either the TcO^{3+} core of the *trans*-$[TcO_2]^+$ core, the former being favored by ancillary ligands that donate significant negative charge to the technetium center and the latter being favored by neutral ancillary ligands. In *trans*-$[Tc(DMPE)_2(OH)(O)]^{2+}$ the *trans*-$[TcO_2]^{2+}$ core has been protonated to yield the *trans*-$[Tc(OH)(O)]^{2+}$ core. A second protonation yields the *trans*-$[Tc(H_2O)(O)]^{3+}$ core (which has been recently structurally characterized in a different system[33]), and this is just the aquated form of the TcO^{3+} core.

The Tc(III)–Cl bond length in *trans*-$[Tc(DMPE)_2Cl_2]^+$ (2.323 (3) Å) is essentially the same as the Tc(III)–Cl bond lengths observed in salts of the related *trans*-$[Tc(diars)_2Cl_2]^+$ cation (2.329 (1) Å for the chloride salt, 2.318 (6) Å for the perchlorate salt).[26] Tc–Cl distances of 2.32–2.36 Å are reported[34] for a variety of six-coordinate complexes wherein (i) the Tc oxidation state is mixed II/III, III, IV or V, and (ii) the trans situated atom is either chloride, singly bonded oxygen, or singly bonded nitrogen.

The three structures described here provide a remarkable illustration of the importance of π back-bonding between phosphorus and technetium. Generally, as the metal oxidation state increases, the radius of the metal is expected to decrease and thus, for ionic systems, the M–X bond length is expected to decrease with increasing metal oxidation state. Exactly the reverse behavior is found for the three types of Tc–P bonds studied here, i.e. Tc(V)–P = 2.48 (1) Å, Tc(III)–P = 2.44 (1) Å, and Tc(I)–P = 2.40 (2) Å. π back-bonding interactions between Tc and P are expected to increase with decreasing technetium oxidation state. Thus, the decrease of the Tc–P bond length by 0.08 Å on going from Tc(V) to Tc(I) provides clear evidence for the importance of π back-bonding in determining the Tc–P bond length in phosphine complexes.

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Registry No. *trans*-$[Tc(DMPE)_2O_2]F_3CSO_3$, 91602-33-4; *trans*-$[Tc(DMPE)_2(OH)(O)](F_3CSO_3)_2$, 91491-90-6; *trans*-$[Tc(DMPE)_2Cl_2]F_3CSO_3$, 91491-91-7; $[Tc(DMPE)_3]PF_6$, 91491-92-8; $[Tc(DMPE)_3]ClO_4$, 91491-93-9; $[Tc(DMPE)_3]F$, 91491-94-0; $[Tc(DMPE)_2Cl_2]Cl$, 80537-73-1; $[Tc(DMPE)_2Br_2]Br$, 80529-07-3; $NH_4{}^{99}TcO_4$, 34035-97-7; P, 7723-14-0; Tc, 7440-26-8; O_2, 7782-44-7.

Supplementary Material Available: Tables A–H, showing F_c and F_o values, anisotropic thermal parameters, root-mean-square displacements, and bond lengths and angles for both *trans*-$[Tc(DMPE)_2(O)(OH)](CF_3SO_3)_2$ and *trans*-$[Tc(DMPE)_2Cl_2]F_3CSO_3$ (30 pages). Ordering information is given on any current masthead page.

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