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Synthesis, Characterization, and Electrochemical Properties of Technetium Complexes Containing both Tetradentate Schiff Base and Monodentate Tertiary Phosphine Ligands: Single-Crystal Structure of *trans*-(*N*,*N*′-Ethylenebis(acetylacetone iminato))bis(triphenylphosphine)technetium(III) Hexafluorophosphate[1]

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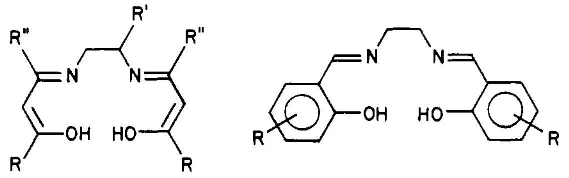
A series of nine technetium(III) complexes of the type *trans*-$[\mathrm{Tc^{III}LY_2}]^+$, where L represents a tetradentate Schiff base ligand and Y represents a monodentate tertiary phosphine ligand, has been synthesized and characterized. This series includes the five Schiff base ligands *N*,*N*′-ethylenebis(acetylacetone iminato) ((acac)$_2$en), *N*,*N*′-ethylenebis(*tert*-butyl acetoacetate iminato), *N*,*N*′-ethylenebis(benzoylacetone iminato), *N*,*N*′-ethylenebis(3-bromoacetylacetone iminato), and *N*,*N*′-ethylenebis(salicylideneaminato). These complexes are prepared by reaction of the corresponding technetium(V) Schiff base complex, *trans*-$[\mathrm{Tc^{V}L(O)OH_2}]^+$, with excess phosphine, which concomitantly reduces and coordinates to the technetium center. The hexafluorophosphate salt of the title complex, with L = (acac)$_2$en and Y = PPh$_3$ (molecular formula $\mathrm{TcP_3F_6N_2O_2C_{48}H_{48}}$, formula weight 990.83), has been characterized by single-crystal X-ray structural analysis refined to a conventional *R* factor of 0.109. Further refinement was precluded by severe disorder in the $\mathrm{PF_6}^-$ anions. Rectangular crystals of this salt crystallize in the triclinic space group $P\bar{1}$, with $a = 19.037$ (5) Å, $b = 16.339$ (3) Å, $c = 15.454$ (4) Å, $\alpha = 95.37$ (2)°, $\beta = 96.47$ (2)°, $\gamma = 91.32$ (2)°, and $Z = 4$. The technetium(III) center is approximately octahedrally coordinated with the two N and two O donor atoms of the tetradentate Schiff base ligand in the equatorial plane and the two phosphine P atoms in the trans apical positions with an average Tc–P bond length of 2.51 (2) Å. Other complexes in this series have been characterized by some combination of elemental analyses, IR and visible–UV spectrophotometry, thin-layer and column chromatography, and cyclic voltammetry (CV). All complexes exhibit characteristic charge-transfer bands in the visible region of the spectrum. The position of the lowest energy metal-to-ligand charge-transfer (MLTCT) band is a function of both the nature of the Schiff base ligand and the nature of the substituents bonded to the donor P atoms. CV shows that in acetonitrile, with use of a glassy-carbon electrode, every technetium(III) complex in this series exhibits a reduction to Tc(II) and an oxidation to Tc(IV). The $E^{\circ\prime}$ values of these Tc(IV)/Tc(III) and Tc(III)/Tc(II) redox couples also depend upon the nature of the Schiff base ligand and on the nature of the substituents bonded to the donor P atoms. For both couples the values of $E^{\circ\prime}$ are linearly related to the energies of the MLTCT bands.

Introduction

Transition-metal complexes containing tetradentate Schiff base ligands of the type



have been known and studied for many years.[4,5] The magnetic,[4] electronic,[4] and electrochemical[6] properties of these complexes depend markedly on the nature of the substituents on the backbone of the Schiff base ligand.[4,7] The synthesis and characterization of a series of technetium(V) complexes containing these tetradentate Schiff base ligands and having the formulation *trans*-$[\mathrm{Tc^{V}L(O)X}]^+$ (L = Schiff base ligand and X = H$_2$O, Cl) have recently been reported.[8] Investigation of the reactivity of these Tc(V) complexes with a series of monodentate tertiary phosphine ligands led to the synthesis of new monocationic technetium(III) complexes containing coordinated phosphines. These new complexes are of special interest in light of recent developments in the field of nuclear medicine.[9] The tendency of the heart to accumulate unit positively charged metal ions is well documented,[10] and thallium-201 as $[\mathrm{Tl_{aq}}]^+$ is the heart scanning agent currently used in hospitals around the country. For the past several years we have been interested in the development of robust *cationic* technetium complexes for potential use as heart imaging agents[9,11,12] and have recently reported on the inorganic chemistry,[13,14] pharmaceutical preparation,[15] and biological properties[16,17] of several monocationic diphosphine–technetium(III) complexes. These studies indicate that the human heart can be successfully imaged with monocationic technetium(III) complexes and that a clinically useful agent is likely

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to be found within this class of compounds. In this paper we thus report on the synthesis and characterization of a new series of monocationic phosphine–technetium(III) complexes which may eventually yield a useful heart imaging agent. This series also provides a useful framework for evaluating the effect of systematic variations in ligand structure on the electronic properties of the technetium(III) center.

Acronyms and Abbreviations

$(acac)_2en$ = *N,N'*-ethylenebis(acetylacetone iminato), $[CH_3{-}C(O^-){=}CH{-}C(CH_3){=}N{-}CH_2{-}]_2$

$(buac)_2en$ = *N,N'*-ethylenebis(*tert*-butyl acetoacetate iminato), $[(CH_3)_3CO{-}C(O^-){=}CH{-}C(CH_3){=}N{-}CH_2{-}]_2$

$(bzac)_2en$ = *N,N'*-ethylenebis(benzoylacetone iminato), $[C_6H_5{-}C(O^-){-}CH{-}C(CH_3){=}N{-}CH_2{-}]_2$

$(brac)_2en$ = *N,N'*-ethylenebis(3-bromoacetylacetone iminato), $[CH_3{-}C(O^-){=}C(Br){-}C(CH_3){=}N{-}CH_2{-}]_2$

$(sal)_2en$ = *N,N'*-ethylenebis(salicylideneaminato), $[o\text{-}(O^-)C_6H_4{-}CH{=}N{-}CH_2{-}]_2$

TEAP = tetraethylammonium perchlorate

DPPE = 1,2-bis(diphenylphosphino)ethane

acac = acetylacetonato

PPh_3 = triphenylphosphine

Et = ethyl

Ph = phenyl

MTLCT = metal-to-ligand charge transfer

CV = cyclic voltammetry

TLC = thin-layer chromatography

Experimental Section

General Considerations. Syntheses were performed with technetium-99. This isotope emits a low-energy (0.292-MeV) β particle with a half-life of 2.12×10^5 y. When handled in milligram amounts, ^{99}Tc does not present a serious 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.

All common laboratory chemicals were of reagent grade. The tetradentate Schiff base ligands were available from a previous study.[8] All phosphine ligands were purchased from Strem Chemical and used without further purification.

TEAP, labeled "suitable for polarography", was purchased from G. F. Smith Chemicals, Inc. The acetonitrile used in the electrochemistry experiments was labeled "suitable for use in pesticide analyses, spectrometry, liquid chromatography and gas chromatography" and was purchased from Burdick & Jackson Laboratories, Inc. Technetium-99 was purchased from Oak Ridge National Laboratory as solid ammonium pertechnetate and purified as previously described.[13] Silica gel was purchased from Whatman (LPS-2, 37-53 micrometer). Silica gel TLC plates were purchased from Eastman Kodak (# 13181 with fluorescent indicator, No. 6060). Elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada, or Galbraith Laboratories, Inc., Knoxville, TN.

Tetrabutylammonium hexafluorophosphate, $[(n\text{-}C_4H_9)_4N]PF_6$, was prepared by a literature method[18] and recrystallized three times from hot absolute ethanol; mp 242–244 °C. **Tetrabutylammonium tetrachlorooxotechnetate(V)** was synthesized by the method of Davison et al.[19] and shown to exhibit the same visible–UV spectrophotometric parameters as reported.[19]

Bis(phosphine)(Schiff base)technetium(III) Complexes, *trans*-$[Tc^{III}LY_2]^+$ (L = $(acac)_2en$, $(buac)_2en$, $(bzac)_2en$, $(brac)_2en$, $(sal)_2en$; Y = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3). A typical preparation employing tetrabutylammonium tetrachlorooxotechnetate(V) as the starting material was conducted as follows. A 0.15-g (0.3-mmol) amount of $(Bu_4N)[TcOCl_4]$ was dissolved in 10 mL of methanol, and 0.074 g (0.32 mmol) of $(acac)_2en$ was added. The solution became an intense red-brown color and was stirred for ca. 15 min. A 0.26-mL (0.93-mmol) quantity of diphenylethylphosphine was added. The solution was stirred for 15 min at ambient temperature and then filtered to remove two common side products: $[TcCl_3(PR_nR'_{3-n})_3]$ as a bright orange precipitate or $[TcCl_4(PR_nR'_{3-n})_2]$ as an emerald green precipitate. The desired *trans*-$[TcLY_2]^+$ salts were purified from this filtrate by procedures involving rotavaporation followed by either extraction and/or column chromatography. For the PF_6^- salts of the cations *trans*-$[Tc((acac)_2en)Y_2]^+$ (Y = $PEtPh_2$, PEt_2Ph, PEt_3) and *trans*-$[TcL(PEtPh_2)_2]^+$ (L = $(acac)_2en$, $(brac)_2en$, $(sal)_2en$), the purification sequence was as follows. The filtrate was rotaevaporated to dryness, dissolved in a minimum (5–10 mL) of dichloromethane, and loaded onto a chromatography column prepared by slurrying silica in dichloromethane. Elution with dichloromethane, followed by acetone, removed excess ligand and undesired side products. Elution with methanol removed the desired blue-green technetium(III) complex. After filtration of this fraction, 0.1 g of Bu_4NPF_6 was added and the solution was concentrated and cooled in the freezer to yield crystals of the desired product. These were collected, washed with distilled water, and dried over P_2O_5 in vacuo. The PF_6^- salts of the cations *trans*-$[Tc((acac)_2en)(PPh_3)_2]^+$ and *trans*-$[Tc((buac)_2en)Y_2]^+$ (Y = $PEtPh_2$, PEt_2Ph) required modifications in the above procedure for complete purification. After rotavaporation of the filtrate, an extraction with ether removed an undesired olive green species. The remaining oily residue was dissolved in a minimum of methanol. For *trans*-$[Tc((acac)_2en)(PPh_3)_2]^+$ and *trans*-$[Tc((buac)_2en)(PEt_2Ph)_2]^+$ this solution was loaded onto a silica chromatography column that had previously been prepared in methanol. The desired blue-green product comprised the first fraction eluted with methanol. The remainder of the purification procedure was as outlined above. Purification of *trans*-$[Tc((buac)_2en)(PEt_2Ph)_2]^+$ did not require chromatography. A 0.1-g amount of Bu_4NPF_6 and 1–2 mL of distilled water were added to the original filtrate, which was then rotavaporated to precipitate the desired blue-green product. After filtration to remove the orange supernatant, the desired product was dissolved in a minimum volume of methanol, and crystals were generated by the concentration and cooling procedure outlined above. For all complexes, overall yields based on $[TcOCl_4]^-$ were in the range 20–40%.

A typical preparation using the appropriate technetium(V) Schiff base complex as the starting material was conducted as follows. A 0.051-g (0.12-mmol) amount of *trans*-$[TcO(OH_2)((acac)_2en)]Br$ was dissolved in ca. 10 mL of methanol, and 0.093 mL (0.35 mmol) of diphenylethylphosphine was added. The reaction solution became an intense blue-green and was stirred at room temperature for ca. 15 min. TLC analysis on silica gel showed the presence of only one product. Tetrabutylammonium hexafluorophosphate (0.1 g) was added, and the solution was filtered and then concentrated to about 5 mL with use of an aspirator. After the mixture was cooled overnight in the freezer, 0.103 g of *trans*-$[Tc((acac)_2en)(PEtPh_2)_2]PF_6$ was collected by filtration, washed with distilled water, and dried over P_2O_5 in vacuo: yield 98%; TLC R_f (dichloromethane) 0.19, R_f (methanol) 0.48.

Visible–UV and IR spectral data of all complexes are given in Tables I and II, respectively. Elemental analyses of selected complexes are in Table III.

Physical Measurements. Visible–UV spectra were recorded on a Varian 634 or a Cary 210 spectrophotometer at ambient temperature. The infrared (IR) spectra were recorded at KBr pellets on a Perkin-Elmer 599 spectrophotometer. Electrochemical data were obtained with a Bioanalytical Systems CV-5 voltammograph apparatus and VC-2 cell with 0.1 M TEAP in acetonitrile as the electrolytic medium. Cyclic voltammograms were obtained under anaerobic conditions vs. a Ag/AgCl reference electrode (filling solution 3.0 M NaCl; the

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Table I. Visible–UV Spectrophotometric Parameters for Technetium Complexes Containing Schiff Base and Phosphine Ligands[a]

complex	color	λ_{max} (ϵ)
$[Tc((acac)_2en)(PEt_3)_2]^+$	reddish green	577 (1380), 416 (4460), 368 (2640), 286 sh (6790), 263 (8000)
$[Tc((acac)_2en)(PEt_2Ph)_2]^+$	blue-green	592 (2310), 413 (6100), 365 (4950), 288 (17 100), 240 sh (24 800)
$[Tc((acac)_2en)(PEtPh_2)_2]^+$	blue-green	595 (1730), 405 (5300), 362 (4450), 294 (12 900), 244 sh (21 100)
$[Tc((acac)_2en)(PPh_3)_2]^+$	olive green	605 (1460), 519 (1630), 399 (6000), 351 (4500), 259 (23 700)
$[Tc((buac)_2en)(PEt_2Ph)_2]^+$	blue-green	615 (660), 374 (2400), 295 (4350)
$[Tc((buac)_2en)(PEtPh_2)_2]^+$	bluish purple	608 (1850), 537 (2260), 379 (7980), 255 (25 000)
$[Tc((bzac)_2en)(PEtPh_2)_2]^+$	olive green	617 (2100), 449 (9000), 365 (7300), 285 sh (21 400), 235 sh (33 900)
$[Tc((brac)_2en)(PEtPh_2)_2]^+$	mint green	632 (2500), 412 (7000), 296 (13 700), 245 sh (30 000)
$[Tc((sal)_2en))(PEtPh_2)_2]^+$	Kelly green	635 (3860), 453 (11 500), 402 (10 200), 342 (11 200), 306 (14 900), 255 sh (42 600)

[a] λ_{max} in nm, ϵ in M^{-1} cm^{-1}. All spectra were obtained in methanol solution.

Table II. Infrared Spectral Parameters for Technetium Complexes Containing Schiff Base and Phosphine Ligands[a]

complex	C=N	P–C	PF_6^-	Ph
$[Tc((acac)_2en)(PEt_3)_2]PF_6$	1560	1400–1500	840	
$[Tc((acac)_2en)(PEt_2Ph)_2PF_6$	1540–1560	1400–1500	835	680–760
$[Tc((acac)_2en)(PEtPh_2)_2]PF_6$	1545	1380–1500	835	690–750
$[Tc((acac)_2en)(PPh_3)_2]PF_6$	1550–1600	1360–1470	840	700–750
$[Tc((buac)_2en)(PEt_2Ph)_2]PF_6$	1500–1600	1360–1470	840	700–750
$[Tc((buac)_2en)(PEtPh_2)_2]PF_6$	1520	1400–1500	835	690–740
$[Tc((bzac)_2en)(PEtPh_2)_2]PF_6$	1550	1400–1500	840	690–760
$[Tc((brac)_2en)(PEtPh_2)_2]PF_6$	1545	1380–1490	835	690–740
$[Tc((sal)_2en)(PEtPh_2)_2]PF_6$	1590	1400–1500	840	690–760

[a] Frequencies given in cm^{-1}. All spectra were obtained in KBr pellets, polystyrene reference.

Table III. Elemental Analyses for Selected Technetium(III) Complexes Containing Schiff Base and Phosphine Ligands

complex		% C	% H	% N	% P	% F
$[Tc((acac)_2en)(PEtPh_2)_2]PF_6$	calcd	53.69	5.37	3.13	10.40	12.75
	exptl	53.14	5.30	2.88	11.00	12.86
$[Tc((bzac)_2en)(PEtPh_2)_2PF_6$	calcd	58.94	5.11	2.75	9.14	11.20
	exptl	58.29	5.34	2.88	10.31	12.24
$[Tc((buac)_2en)(PEtPh_2)_2PF_6$	calcd	54.65	5.94	2.77	9.21	11.29
	exptl	53.26	5.97	2.64	8.84	11.09
$[Tc((sal)_2en)(PEtPh_2)_2]PF_6$	calcd	56.29	4.69	2.90	9.91	12.15
	exptl	56.38	4.80	2.92	9.71	12.11

Table IV. Crystal Data and Selected[a] Details of the Structure Determinations of $[Tc((acac)_2en)(PPh_3)_2]PF_6$

mol formula	$TcP_3F_6N_2O_2C_{48}H_{48}$
a/Å	19.037 (5)
b/Å	16.339 (3)
c/Å	15.454 (4)
α/deg	95.37 (2)
β/deg	96.47 (2)
γ/deg	91.32 (2)
Z	4
space group	$P\bar{1}$
μ(Mo Kα)/cm^{-1}	3.88
cryst size/mm	0.40 × 0.28 × 0.22
no. of data in refinement[b]	7899
R[c]	0.109
R_w[d]	0.117

[a] Further information is available in Table F.[21] [b] Intensity measurements were made on a Philips PW1100 diffractometer, equipped with a graphite monochromator, using Mo Kα radiation. For both structures unique data with $F > 6\sigma(|F_o|)$ were used in the refinement. [c] The function minimized was $w(|F_o| - |F_c|)^2$ where $w = 1/(\Sigma(F_o))^2$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table V. Energies of MTLCT Transitions, and $E^{\circ\prime}$ Values for Technetium Complexes Containing Schiff Base and Phosphine Ligands[a,b]

complex	E_{MTLCT}	$E^{\circ\prime}$ Tc-(III/II)	$E^{\circ\prime}$ Tc-(IV/III)
$[Tc((acac)_2en)(PEt_3)_2]^+$	2.15	−1.050	0.690
$[Tc((acac)_2en)(PEt_2Ph)_2]^+$	2.09	−0.990	0.710
$[Tc((acac)_2en)(PEtPh_2)_2]^+$	2.08	−0.890	0.740
$[Tc((acac)_2en)(PPh_3)_2]^+$	2.05	−0.840	0.790
$[Tc((buac)_2en)(PEt_2Ph)_2]^+$		−0.890	0.600
$[Tc((buac)_2en)(PEtPh_2)_2]^+$	2.04	−0.810	0.650
$[Tc((bzac)_2en)(PEtPh_2)_2]^+$	2.01	−0.800	0.820
$[Tc((brac)_2en)(PEtPh_2)_2]^+$	1.96	−0.750	0.830
$[Tc((sal)_2en)(PEtPh_2)_2]^+$		−0.670	0.845

[a] Conditions: cyclic voltammetry in acetonitrile, 0.1 M TEAP; glassy-carbon working electrode; Ag/AgCl reference electrode; Pt auxiliary electrode. [b] E_{MTLCT} values in eV, E° values in V.

potential of this electrode is −35 mV relative to SCE[20]) with a glassy-carbon working electrode.

X-ray Characterization of *trans*-$[Tc((acac)_2en)(PPh_3)_2]PF_6$. The structure was determined with a Philips PW1100 four-circle diffractometer. A summary of crystal data and details of the structure refinement are given in Table IV. The structure was solved and refined in the space group $P\bar{1}$, the triclinic unit cell having been established by Delauney reduction. The positions of the two independent technetium atoms were determined from a Patterson synthesis. The remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The asymmetric unit contains two independent complex cations, partially related by pseudosymmetry. The coordination sphere of the first independent Tc atom and the atoms of its tetradentate ligand are related to those of the second Tc atom by the approximate operation $^1/_2 + x, y, {}^1/_2 - z$. This relationship does not apply to the phenyl rings of the phosphine ligands, which have slightly different conformations in the two cations as can be seen in Figure 1. The parameters of the two complex cations were refined in separate blocks. The two PF_6^- ions show the severe disorder that frequently occurs for highly symmetrical counterions of this type. Difference Fourier syntheses calculated without the atoms of the anions showed extended regions of electron density corresponding to the positions of the fluorine atoms. For the first PF_6^- anion (containing P(a), Figure 2[21]) two sets of equatorial fluorine atoms were identified. Atoms in each set were assigned a common site occupation factor. In the initial stages these two parameters were refined subject to the constraint that their total was 1.0, with a fixed isotropic thermal parameter of 0.08 Å^2 for these atoms. The electron density corresponding to the second PF_6^- anion was resolved into two completely

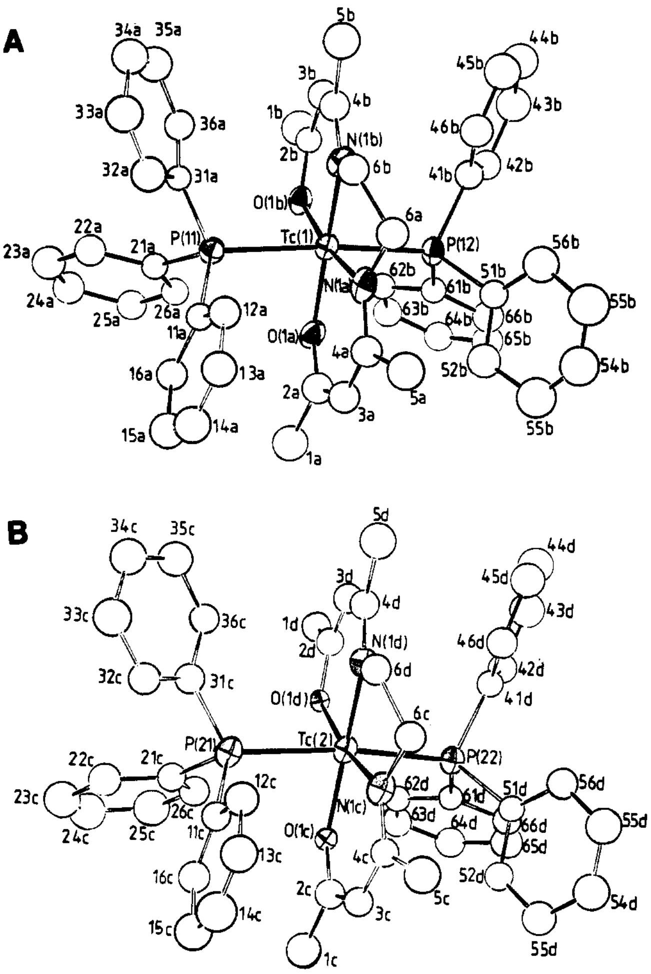

Figure 1. Structures of two crystallographically independent cations (A and B) of *trans*-$[\mathrm{Tc((acac)_2en)(PPh_3)_2}]^+$ showing the atom labels used in all tables.

separate sets of atoms of partial occupancy. Site occupation factors of 0.55 and 0.45 were assigned to these two sets (anions containing P(b) and P(c), Figure 3[21]) on the basis of the mean relative peak heights in the Fourier synthesis. In the final stages of refinement the site occupancy factors for all the disordered atoms were fixed and anisotropic thermal parameters were assigned to the Tc, P, O, and N atoms. Blocked full-matrix refinement resulted in $R = 0.109$ and $R_w = 0.117$. Values of $|F_o|$ and F_c are listed in Table A.[21]

Results

Syntheses of the *trans*-$[\mathrm{TcLY_2}]^+$ Complexes. These mixed-ligand (tetradentate Schiff base and monodentate phosphine) technetium(III) complexes can be prepared directly from the oxotechnetium(V) Schiff base analogue:

$$\mathrm{Tc^{V}L(O)OH_2^+ + 3Y \rightarrow Tc^{III}LY_2^+ + YO} \qquad (1)$$

This reaction involves the two equivalent reduction of Tc(V) to Tc(III) with the concomitant coordination of two monodentate phosphine ligands to the reduced technetium center. When the ratio of phosphine ligand to technetium(V) starting material is 3, the reaction is virtually quantitative with yields >98%. The mixed-ligand technetium(III) complexes can be prepared more conveniently, albeit in lower yields, from the general technetium(V) starting material $\mathrm{TcOCl_4}^-$:[19]

$$\mathrm{Tc^{V}OCl_4^- + L + 3Y \rightarrow Tc^{III}LY_2^+ + YO + 4Cl^-} \qquad (2)$$

The 20–40% product yields that are characteristic of this reaction arise from the fact that the precursor *trans*-$[\mathrm{Tc^{V}L(O)OH_2}]^+$ complexes are generated from $[\mathrm{TcOCl_4}]^-$ in less than 50% yields.[8]

Characterization. In addition to the single-crystal structural determination of the title complex, the mixed-ligand technetium(III) complexes are characterized by (1) elemental analyses of representative compounds, which are in agreement with the proposed formulations (Table III, (2) thin-layer and column chromatography, which show the presence of only one complex, and (3) visible–UV (vide infra) and IR spectrophotometry (Tables I and II). The infrared spectra of the technetium(III) complexes exhibit an intense absorption at ca. 840 cm^{-1} which is characteristic of the $\mathrm{PF_6}^-$ anion and an absorbance in the 1500–1600-cm^{-1} region, which is assigned as the C=N stretch characteristic of the imine group of the Schiff base ligand. Absorptions in the 1350–1500-cm^{-1} region are assigned as P–C stretches and are typical for phosphines.

Cyclic Voltammetry. The $E^{\circ\prime}$ values listed in Table V are calculated as the average of the potentials of the reduction and corresponding oxidation waves for each CV process. These data show that the $E^{\circ\prime}$ of both the Tc(III) → Tc(II) and Tc(III) → Tc(IV) processes are sensitive to (a) the substituents on the Schiff base ligand and (b) the substituents on the *trans*-situated phosphine ligands. When complexes having the same Schiff base ligands are compared, the difference in $E^{\circ\prime}$ values between the bis(triphenylphosphine) and the bis(triethylphosphine) complexes is about 200 mV for the II/III couple and about 100 mV for the III/IV couple ($E^{\circ\prime}_{\mathrm{Ph}} - E^{\circ\prime}_{\mathrm{Et}}$). When complexes having the same phosphine ligand are compared, varying the substituents on the Schiff base ligand causes $E^{\circ\prime}$ to range over 150 mV for the II/III couple and over about 100 mV for the III/IV couple.

Visible–UV Spectra. All the *trans*-$[\mathrm{Tc^{III}LY_2}]^+$ complexes are intensely colored, and the visible–UV spectra show multiple absorbances. The spectrophotometric data presented in Tables I and V show that the energies of specific absorbance maxima are a function of both the Schiff base and phosphine ligands. Variation of the substituents on either the trans phosphines or on the equatorial Schiff base ligand leads to changes in the energies of these transitons of up to 0.1 eV.

Crystal Structure. The X-ray diffraction analysis of *trans*-$[\mathrm{Tc((acac)_2en)(PPh_3)_2}]\mathrm{PF_6}$ shows that the asymmetric unit contains two independent complexes, the $\mathrm{Tc((acac)_2en)}$ components of which are related by pseudosymmetry, and that both $\mathrm{PF_6}^-$ ions show serious disorder. Final fractional atomic positional parameters and their estimated standard deviations are given in Table VI. The corresponding anisotropic thermal parameters are found in Table B,[21] and the associated ellipsoids for the complex cations are shown in Figure 1. Selected bond lengths and angles are found in Table VII, with the remainder found in Table C.[21] Intermolecular distances less than 3.5 Å are found in Table D,[21] and intramolecular distances less than 4.2 Å are found in Table E.[21] Both technetium(III) cations have octahedral geometries, and there is reasonable agreement between bond lengths of similar donor atoms. Averaging the lengths of chemically equivalent bonds gives the following data: Tc–N, 2.06 (2) Å; Tc–O, 2.02 (1) Å; Tc–P, 2.51 (1) Å.

Discussion

Synthesis. Synthesis of the mixed-ligand (tetradentate Schiff base and monodentate phosphine) technetium(III) complexes involves reduction of the parental technetium(V) Schiff base complex with 1 equiv of phosphine and concomitant substitution of two phosphine ligands onto the technetium center. A plausible mechanism for this complex reaction invovles coordination of a phosphine to the labile site of the technetium(V) complex (i.e., trans to the yl oxygen atom[8]), followed by induced oxygen atom transfer to a second phosphine with simultaneous coordination of the third phosphine ligand. This is illustrated in Scheme I.

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(21) All tables designated by alphabetic characters, and Figures 4 and 5, have been deposited as supplementary material.

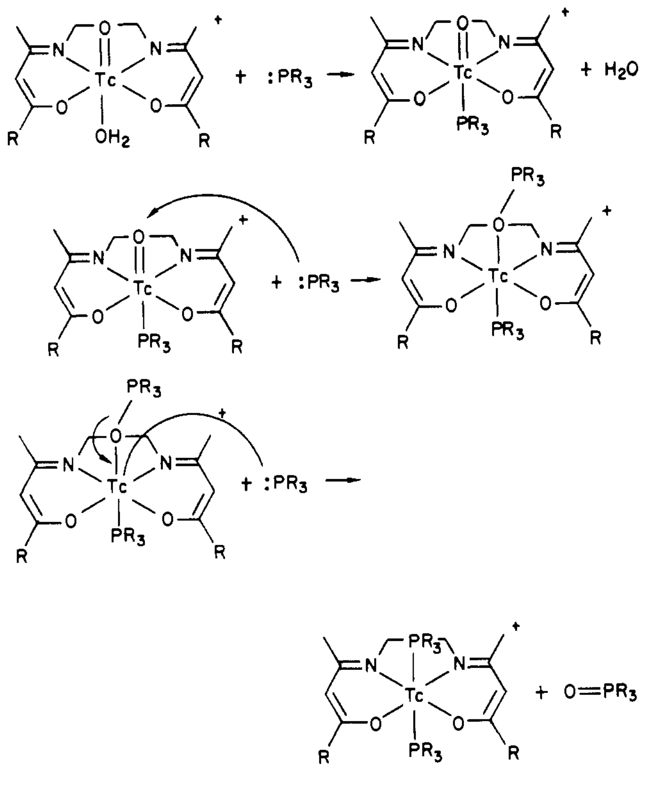
Table VI. Fractional Atomic Coordinates and Thermal Parameters (Å^2) for [Tc((acac)$_2$en)(PPh$_3$)$_2$]PF$_6$

atom	x	y	z	U_{iso} or U_{eq}, Å^2	atom	x	y	z	U_{iso} or U_{eq}, Å^2
Tc(1)	0.26201 (6)	0.22940 (6)	0.51071 (7)	0.0406 (6)	F(a4)[c]	0.6931 (18)	0.3714 (22)	0.4522 (22)	0.191 (11)
P(11)	0.3778 (2)	0.2972 (2)	0.4928 (2)	0.043 (2)	F(a5)[c]	0.7366 (19)	0.3036 (18)	0.5699 (19)	0.095 (10)
P(12)	0.1494 (2)	0.1486 (2)	0.5183 (2)	0.048 (2)	F(a6)[c]	0.7938 (18)	0.4090 (20)	0.4239 (20)	0.165 (10)
N(1a)	0.2045 (6)	0.3159 (7)	0.4443 (9)	0.059 (8)	F(a3')[d]	0.7181 (20)	0.4308 (22)	0.4395 (22)	0.117 (11)
N(1b)	0.2514 (6)	0.3093 (7)	0.6178 (8)	0.054 (7)	F(a4')[d]	0.7979 (24)	0.3034 (23)	0.5566 (25)	0.157 (12)
O(1a)	0.2693 (5)	0.1657 (6)	0.3947 (6)	0.062 (6)	F(a5')[d]	0.8104 (21)	0.3590 (27)	0.4199 (26)	0.177 (14)
O(1b)	0.3094 (5)	0.1510 (5)	0.5904 (6)	0.050 (6)	F(a6')[d]	0.6946 (24)	0.3649 (27)	0.5544 (29)	0.195 (15)
P(a)	0.7639 (4)	0.3617 (3)	0.4930 (3)	0.087 (4)	C(1c)	0.8497 (10)	0.0648 (11)	−0.2004 (13)	0.092 (5)
Tc(2)	0.76133 (6)	0.20915 (6)	0.00879 (7)	0.0401 (6)	C(2c)	0.8046 (8)	0.1284 (9)	−0.1587 (10)	0.063 (4)
P(21)	0.8788 (2)	0.2859 (2)	0.0168 (2)	0.048 (2)	C(3c)	0.7669 (8)	0.1841 (9)	−0.2085 (9)	0.057 (4)
P(22)	0.6537 (2)	0.1163 (2)	−0.0070 (2)	0.043 (2)	C(4c)	0.7236 (7)	0.2484 (8)	−0.1788 (9)	0.053 (3)
N(1c)	0.7190 (6)	0.2684 (7)	−0.0962 (8)	0.053 (7)	C(5c)	0.6823 (9)	0.2946 (11)	−0.2492 (12)	0.082 (5)
N(1d)	0.7183 (6)	0.3038 (6)	0.0791 (7)	0.049 (7)	C(6c)	0.6725 (8)	0.3373 (9)	−0.0704 (10)	0.061 (4)
O(1c)	0.8036 (5)	0.1275 (5)	−0.0750 (6)	0.034 (5)	C(6d)	0.6979 (8)	0.3720 (9)	0.0237 (10)	0.061 (4)
O(1d)	0.7915 (4)	0.1604 (5)	0.1233 (6)	0.029 (5)	C(5d)	0.6792 (10)	0.3889 (11)	0.2097 (13)	0.087 (6)
P(b)[a]	0.2170 (4)	0.3886 (4)	1.0194 (5)	0.091 (5)	C(4d)	0.7109 (8)	0.3121 (9)	0.1645 (10)	0.064 (4)
P(c)[b]	0.4451 (8)	0.4163 (8)	−0.0039 (7)	0.055 (9)	C(3d)	0.7368 (8)	0.2463 (9)	0.2203 (10)	0.064 (4)
C(1a)	0.2789 (10)	0.1294 (12)	0.2464 (13)	0.087 (6)	C(2d)	0.7696 (8)	0.1817 (9)	0.1985 (10)	0.057 (4)
C(2a)	0.2518 (9)	0.1885 (10)	0.3167 (11)	0.068 (4)	C(1d)	0.7932 (8)	0.1216 (9)	0.2646 (10)	0.064 (4)
C(3a)	0.2137 (9)	0.2557 (10)	0.2984 (11)	0.067 (4)	C(11c)	0.8923 (7)	0.3196 (8)	−0.0909 (9)	0.055 (3)
C(4a)	0.1903 (9)	0.3120 (10)	0.3553 (11)	0.067 (4)	C(12c)	0.8511 (9)	0.3907 (10)	−0.1150 (11)	0.067 (4)
C(5a)	0.1386 (10)	0.3827 (12)	0.3196 (13)	0.092 (6)	C(13c)	0.8552 (10)	0.4127 (11)	−0.2018 (12)	0.080 (5)
C(6a)	0.1752 (9)	0.3771 (10)	0.5061 (11)	0.071 (4)	C(14c)	0.8896 (11)	0.3723 (13)	−0.2532 (14)	0.103 (6)
C(6b)	0.2281 (8)	0.3896 (10)	0.5928 (11)	0.069 (4)	C(15c)	0.9312 (10)	0.2957 (11)	−0.2359 (13)	0.084 (5)
C(5b)	0.2660 (11)	0.3707 (12)	0.7761 (14)	0.099 (6)	C(16c)	0.9289 (8)	0.2768 (9)	−0.1469 (10)	0.065 (4)
C(4b)	0.2700 (9)	0.3005 (10)	0.6994 (11)	0.066 (4)	C(21c)	0.9559 (7)	0.2205 (9)	0.0412 (9)	0.057 (4)
C(3b)	0.2947 (9)	0.2234 (10)	0.7301 (11)	0.069 (4)	C(22c)	1.0245 (9)	0.2579 (10)	0.0474 (11)	0.077 (5)
C(2b)	0.3103 (7)	0.1566 (8)	0.6778 (10)	0.050 (3)	C(23c)	1.0853 (11)	0.2081 (12)	0.0613 (13)	0.097 (6)
C(1b)	0.3339 (11)	0.0758 (13)	0.7115 (14)	0.096 (6)	C(24c)	1.0745 (11)	0.1288 (13)	0.0767 (14)	0.101 (6)
C(11a)	0.3710 (7)	0.3498 (8)	0.3931 (9)	0.049 (3)	C(25c)	1.0067 (11)	0.0909 (13)	0.0746 (14)	0.104 (6)
C(12a)	0.3342 (8)	0.4225 (9)	0.3906 (11)	0.063 (4)	C(26c)	0.9465 (8)	0.1395 (9)	0.0522 (10)	0.067 (4)
C(13a)	0.3251 (9)	0.4609 (11)	0.3113 (12)	0.074 (5)	C(31c)	0.9000 (8)	0.3766 (9)	0.0931 (10)	0.058 (4)
C(14a)	0.3484 (10)	0.4243 (11)	0.2403 (13)	0.081 (5)	C(32c)	0.9374 (8)	0.4458 (9)	0.0737 (10)	0.067 (4)
C(15a)	0.3839 (10)	0.3535 (12)	0.2384 (13)	0.087 (5)	C(33c)	0.9541 (10)	0.5095 (12)	0.1404 (13)	0.090 (5)
C(16a)	0.3963 (8)	0.3108 (9)	0.3190 (11)	0.060 (4)	C(34c)	0.9331 (10)	0.5100 (11)	0.2247 (13)	0.089 (5)
C(21a)	0.4486 (7)	0.2273 (8)	0.4813 (9)	0.049 (3)	C(35c)	0.8951 (9)	0.4380 (11)	0.2446 (12)	0.080 (5)
C(22a)	0.5189 (9)	0.2578 (10)	0.4970 (11)	0.072 (4)	C(36c)	0.8794 (8)	0.3735 (9)	0.1793 (10)	0.058 (4)
C(23a)	0.5746 (10)	0.2019 (11)	0.4876 (12)	0.084 (5)	C(41d)	0.5989 (7)	0.1353 (8)	0.0826 (9)	0.048 (3)
C(24a)	0.5609 (10)	0.1173 (11)	0.4634 (12)	0.082 (5)	C(42d)	0.5877 (8)	0.0710 (9)	0.1366 (10)	0.065 (4)
C(25a)	0.4887 (9)	0.0908 (10)	0.4437 (11)	0.067 (4)	C(43d)	0.5505 (11)	0.0897 (12)	0.2079 (11)	0.095 (6)
C(26a)	0.4347 (8)	0.1426 (9)	0.4570 (10)	0.059 (4)	C(44d)	0.5272 (11)	0.1648 (13)	0.2312 (13)	0.097 (6)
C(31a)	0.4165 (7)	0.3728 (7)	0.5824 (8)	0.041 (3)	C(45d)	0.5336 (10)	0.2301 (11)	0.1731 (13)	0.089 (5)
C(32a)	0.4359 (9)	0.4541 (11)	0.5718 (12)	0.076 (5)	C(46d)	0.5736 (8)	0.2073 (10)	0.0997 (11)	0.069 (4)
C(33a)	0.4640 (10)	0.5070 (10)	0.6434 (13)	0.087 (6)	C(51d)	0.5953 (7)	0.1221 (8)	−0.1082 (9)	0.046 (3)
C(34a)	0.4731 (10)	0.4782 (12)	0.7274 (13)	0.086 (5)	C(52d)	0.6212 (8)	0.0859 (8)	−0.1854 (10)	0.054 (4)
C(35a)	0.4609 (10)	0.3932 (11)	0.7363 (13)	0.087 (5)	C(53d)	0.5830 (9)	0.0906 (10)	−0.2676 (11)	0.081 (5)
C(36a)	0.4314 (8)	0.3408 (9)	0.6612 (10)	0.061 (4)	C(54d)	0.5192 (10)	0.1387 (11)	−0.2738 (13)	0.084 (5)
C(41b)	0.1227 (8)	0.1442 (9)	0.6312 (10)	0.057 (4)	C(55d)	0.4943 (10)	0.1732 (11)	−0.1986 (13)	0.088 (5)
C(42b)	0.1107 (9)	0.0669 (10)	0.6595 (11)	0.071 (4)	C(56d)	0.5328 (8)	0.1656 (9)	−0.1146 (10)	0.066 (4)
C(43b)	0.0902 (11)	0.0700 (13)	0.7497 (14)	0.095 (6)	C(61d)	0.6721 (7)	0.0067 (8)	−0.0081 (8)	0.046 (3)
C(44b)	0.0843 (11)	0.1408 (14)	0.7984 (15)	0.100 (6)	C(62d)	0.7356 (7)	−0.0194 (8)	0.0275 (9)	0.052 (3)
C(45b)	0.0965 (12)	0.2140 (13)	0.7681 (15)	0.099 (6)	C(63d)	0.7500 (9)	−0.1048 (10)	0.0347 (11)	0.075 (5)
C(46b)	0.1157 (9)	0.2172 (11)	0.6810 (12)	0.081 (5)	C(64d)	0.6957 (9)	−0.1599 (10)	0.0050 (11)	0.076 (5)
C(51b)	0.0718 (8)	0.1844 (9)	0.4526 (10)	0.058 (4)	C(65d)	0.6280 (10)	−0.1346 (11)	−0.0332 (12)	0.080 (5)
C(52b)	0.0732 (10)	0.1675 (11)	0.3618 (13)	0.086 (5)	C(66d)	0.6165 (8)	−0.0516 (9)	−0.0391 (10)	0.066 (4)
C(53b)	0.0081 (12)	0.2025 (14)	0.3075 (16)	0.108 (7)	F(b1)[a]	0.20639	0.44887	0.94100	0.1366 (67)
C(54b)	−0.0364 (12)	0.2432 (14)	0.3493 (14)	0.107 (7)	F(b2)[a]	0.29493	0.37363	0.99905	0.1513 (75)
C(55b)	−0.0382 (13)	0.2609 (14)	0.4316 (17)	0.112 (8)	F(b3)[a]	0.24518	0.46288	1.08599	0.1327 (70)
C(56b)	0.0207 (11)	0.2299 (12)	0.4893 (13)	0.091 (6)	F(b4)[a]	0.23046	0.33025	1.09465	0.1290 (70)
C(61b)	0.1511 (7)	0.0418 (8)	0.4770 (9)	0.049 (3)	F(b5)[a]	0.18958	0.31322	0.95209	0.1571 (80)
C(62b)	0.2146 (8)	−0.0001 (9)	0.4881 (10)	0.057 (4)	F(b6)[a]	0.13836	0.40621	1.04097	0.1740 (94)
C(63b)	0.2131 (9)	−0.0888 (10)	0.4609 (11)	0.073 (5)	F(c1)[b]	0.47440	0.36814	0.06307	0.1497 (140)
C(64b)	0.1509 (9)	−0.1287 (10)	0.4317 (11)	0.071 (5)	F(c2)[b]	0.44826	0.33975	−0.05057	0.1201 (106)
C(65b)	0.0906 (10)	−0.0911 (11)	0.4200 (12)	0.085 (5)	F(c3)[b]	0.43575	0.50083	0.05724	0.1573 (144)
C(66b)	0.0870 (9)	−0.0008 (11)	0.4446 (12)	0.079 (5)	F(c4)[b]	0.40047	0.45294	0.91560	0.0963 (90)
F(a1)	0.7828 (8)	0.4370 (10)	0.5586 (11)	0.151 (5)	F(c5)[b]	0.51620	0.43820	−0.03860	0.2201 (205)
F(a2)	0.7487 (15)	0.2811 (18)	0.4341 (19)	0.250 (11)	F(c6)[b]	0.37430	0.37020	0.02240	0.2532 (251)
F(a3)[c]	0.8454 (12)	0.3403 (14)	0.5355 (14)	0.112 (7)					

[a] These atoms have an occupation factor of 0.65 [b] These atoms have an occupation factor of 0.35. [c] These atoms have an occupation factor of 0.55. [d] These atoms have an occupation factor of 0.45.

While this synthetic reaction is straightforward, the purification of the product complex is time consuming. As was true for the parental technetium(V) Schiff base complexes,[8] product purification is the crucial step in the isolation of these compounds. For the technetium(III) complexes described in this paper, the unreacted phosphine and technetium-containing

Scheme I



byproducts (vide infra) must be removed in order to allow isolation of the desired product. This purification is most readily effected by chromatography on silica.

Crystal Structure. This complex exhibits an approximately octahedral coordination geometry with the tetradentate Schiff base ligand defining the equatorial plane and the two triphenylphosphine ligands occupying axial positions. Within the two equivalent cations of the asymmetric unit cell, agreement between analogous bond lengths is good. Averaging the lengths of the four Tc(III)–P bonds gives a value of 2.51 (1) Å. This compares favorably with the Tc(III)–P bond distance found in *trans*-$[\mathrm{Tc(DPPE)_2Br_2}]^+$ (i.e. 2.50 (1) Å),[13] a complex that also contains a technetium(III) center and phenyl-substituted phosphine ligands. Comparison of the Tc(III)–O and Tc(III)–N bond lengths of the title complex to equivalent bond lengths in similar, or even related, structures is more difficult. Very few known technetium complexes containing Tc in oxidation states lower than IV even contain Tc–O or Tc–N bonds. Those that do also have some special ligand feature that stabilizes lower valent technetium in the presence of these nominally "hard" donor atoms. The Tc(III)–O bonds in *trans*-$[\mathrm{Tc(acac)_2(PPh_3)Cl}]$[22] have an average value of 2.01 Å, which is in good agreement with the average value of 2.02 Å for the Tc–O bonds found in the title complex (Table VIIII). The Tc(III)–N bond length listed in Table VIII is also in good agreement with the two Tc(III)–N distances observed in hexakis(isothiocyanato)technetium(III) (2.06 (2) Å vs. 2.04 (2) and 2.05 (2) Å[23]). The data in Table VIII also show that the Tc–O and Tc–N distances in two comparable Tc(III) and Tc(V) Schiff base complexes are remarkably similar. An interpretation of this observation in terms of the π-back-bonding ability of the central metal will have to await the acquistion of more structural data.

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) in *trans*-$[\mathrm{Tc((acac)_2en)(PPh_3)_2}]\mathrm{PF_6}$

Bond Lengths (Å)			
Tc(1)-P(11)	2.499 (4)	Tc(2)-P(21)	2.524 (4)
Tc(1)-P(12)	2.511 (4)	Tc(2)-P(22)	2.496 (3)
Tc(1)-O(1a)	2.007 (10)	Tc(2)-O(1c)	2.016 (9)
Tc(1)-O(1b)	2.017 (9)	Tc(2)-O(1d)	2.038 (9)
Tc(1)-N(1a)	2.084 (12)	Tc(2)-N(1c)	2.062 (12)
Tc(1)-N(1b)	2.041 (11)	Tc(2)-N(1d)	2.046 (10)
Bond Angles (deg)			
P(11)-Tc(1)-P(12)	173.9 (1)	P(21)-Tc(2)-P(22)	172.1 (1)
O(1a)-Tc(1)-O(1b)	99.3 (4)	O(1c)-Tc(2)-O(1d)	99.6 (4)
O(1a)-Tc(1)-N(1a)	88.4 (5)	O(1c)-Tc(2)-N(1c)	89.2 (4)
N(1a)-Tc(1)-N(1b)	83.3 (5)	N(1c)-Tc(2)-N(1d)	82.8 (4)
O(1b)-Tc(1)-N(1b)	89.2 (4)	O(1d)-Tc(2)-N(1d)	88.6 (4)
P(11)-Tc(1)-O(1a)	86.5 (3)	P(21)-Tc(2)-O(1c)	84.4 (3)
P(11)-Tc(1)-N(1a)	92.7 (3)	P(21)-Tc(2)-N(1c)	92.4 (3)
P(11)-Tc(1)-N(1b)	90.8 (3)	P(21)-Tc(2)-N(1d)	92.5 (3)
P(11)-Tc(1)-O(1b)	91.9 (3)	P(21)-Tc(2)-O(1d)	91.4 (3)
P(12)-Tc(1)-O(1a)	88.0 (3)	P(22)-Tc(2)-O(1c)	88.1 (3)
P(12)-Tc(1)-N(1a)	89.8 (3)	P(22)-Tc(2)-N(1c)	90.1 (3)
P(12)-Tc(1)-N(1b)	95.0 (3)	P(22)-Tc(2)-N(1d)	95.3 (3)
P(12)-Tc(1)-O(1b)	86.4 (3)	P(22)-Tc(2)-O(1d)	92.5 (3)

Table VIII. Selected Tc-O and Tc-N Bond Lengths (Å)

compd	Tc oxidn state	Tc-O	Tc-N
$[n\text{-}\mathrm{C_4H_9N}]_3[\mathrm{Tc(NCS)_6}]$[a]	III		2.04
trans-$[\mathrm{Tc((acac)_2en)(PPh_3)_2}]\mathrm{PF_6}$[b]	III	2.02	2.06
trans-$[\mathrm{Tc(acac)_2(PPh_3)Cl}]$[c]	III	2.01	
$[\mathrm{Tc((acac)_2en)O(H_2O)}]\mathrm{Br_{0.25}Cl_{0.75}}$[d]	V	2.02	2.00
$[\mathrm{Tc((sal)_2en)OCl}]$[d]	V	1.99	2.04

[a] Reference 23. [b] This work. [c] Reference 22. [d] Reference 8.

Visible–UV Spectra. The *trans*-$[\mathrm{TcLY_2}]^+$ complexes exhibit intense bands in the visible region of the spectrum. The position of the band at lowest energy (550–650 nm, ε ca. 10^3 $\mathrm{M^{-1}\ cm^{-1}}$) follows two general trends (Table I). (a) When L is held constant ($\mathrm{(acac)_2en}$ or $\mathrm{(buac)_2en}$ in Table I), this band moves to higher energy as the phosphine ligands become better σ donors (i.e. as phenyl substituents are replaced by ethyl substituents). (b) For a constant phosphine ligand ($\mathrm{PEtPh_2}$ in Table I), this band also moves to higher energy as the substituents on the Schiff base ligand become more electron donating. These two trends, combined with the intensity of the absorbances, suggest that this lowest energy band arises from a metal-to-ligand charge-transfer (MTLCT) transition. Transfer from Tc(III) to either the phosphine (Y) or Schiff base (L) ligand is possible, and the data in Tables I and VIII are not sufficient to distinguish between the two possibilities. The energy of the MTCLT band is affected to approximately the same extent (≃ 0.1 eV) regardless of whether L or Y is varied. However, since the π orbitals of the Schiff base ligand are inherently more capable of accepting and delocalizing electron density, this MTLCT band is tentatively assigned as arising from a Tc(III) to L transition.

Cyclic Voltammetry. The *trans*-$[\mathrm{Tc^{III}LY_2}]^+$ complexes undergo both a chemically reversible oxidation and a chemically reversible reduction. A cyclic voltammetry study of some of these complexes[24] in propylene carbonate using a platinum working electrode shows that under these experimental conditions both redox processes are also electrochemically reversible. However, under the conditions used in this study (acetonitrile, glassy-carbon electrode) the redox processes do not fulfill the technical requirements for electrochemical reversibility. For example, the separation between corresponding

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(22) (a) Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1977**, 1837. (b) Bandoli, G.; Clemente, D. A.; Mazzi, U.; Roncari, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3359.

(23) Trop, H. S.; Davison, A.; Jones, A. G.; Davison, M. A.; Szalda, D. J.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 1105.

(24) Ichimura, A.; Deutsch, E.; Heineman, W. R., manuscript in preparation.

oxidation and reduction peaks for a given process is on the order of 150–200 mV, rather than the expected theoretical value of 59 mV. This indicates that, at a graphite electrode in acetonitrile, electron transfer in these systems is slow. The two redox processes observed in this work are formulated as a Tc(III) → Tc(II) reduction and a Tc(III) → Tc(IV) oxidation on the basis of (a) spectroelectrochemical studies of some of these complexes[24] showing that $n = 1.0$ for each process and (b) the following observations made for each complex reported herein. When the current is initiated at the start of each CV experiment at 0.0 V vs. Ag/AgCl, only a small charging current is observed. If, however, the CV is initiated at a potential more positive than that of the Tc(III) → Tc(IV) oxidation or more negative than that of the Tc(III) → Tc(II) reduction, a large Faradaic current is observed. This current is generated in both cases by the conversion of the technetium species in the immediate vicinity of the electrode to the oxidation state dictated by the applied potential. If, however, the technetium species is already in the oxidation state demanded by the potential (e.g. Tc(III) at 0.0 V), only the small charging current is observed.

The data of Table V show that the substituents on both Y and L affect the $E^{\circ\prime}$ values of the Tc(III)/Tc(II) and Tc(IV)/Tc(III) couples. As the phosphine ligands (Y) become better reductants (i.e., as phenyl substituents are replaced by ethyl substituents), the technetium(III) center becomes more difficult to reduce but easier to oxidize. This is consistent with the generalization that phosphines with alkyl (rather than aryl) groups are better σ donors than π acceptors and thus stabilize technetium in higher oxidation states. For example, in the $(acac)_2en$ series (Table V), the triethylphosphine complex is ca. 200 mV more difficult to reduce to Tc(II) than is the analogous triphenylphosphine complex but is easier to oxidize to Tc(IV) by ca. 100 mV.[25]

The substituents on the Schiff base ligand (L) also affect the redox potentials of the technetium center. The data in Table V show that, for the *trans*-$[TcL(PEtPh_2)_2]^+$ series, as the substituents on L become more electron withdrawing (Bz, Br) the Tc(III) center becomes more difficult to oxidize and easier to reduce. Contrariwise, the electron-donating substituents (alkyl) render more difficult the reduction to Tc(II) and facilitate the oxidation to Tc(IV). These CV results are consistent with the generalization that addition of electronegative or electron-delocalizing moieties causes a Schiff base ligand to function as a better π acceptor. Thus, by delocalizing electron density from the metal center, L can promote reduction and inhibit oxidation of the metal. Of all the *trans*-$[TcL(PEtPh_2)_2]^+$ complexes studied, *trans*-$[Tc((sal)_2en)(PEtPh_2)_2]^+$ is the easiest to reduce and the most difficult to oxidize, and thus the $(sal)_2en$ ligand appears to provide the maximum amount of charge delocalization in these systems. Remarkably, for this complex the Tc(III) oxidation state is stable over an excursion of more than 1.5 V (from −0.67 to +0.85 V). The effect of ligand substituents on the Tc(III)/Tc(II) couple of *trans*-$[TcLY_2]^+$ complexes can be compared to the effect of these same substituents on the Tc(III)/Tc(II) couple of *trans*-$[TcD_2Cl_2]^+$ complexes, where D represents a chelating tertiary diphosphine ligand.[13] When the substituent bonded directly to the phosphorus donor atom is changed from phenyl to ethyl, the magnitudes of the effects in the two sets of complexes are remarkably similar. Thus, *trans*-$[Tc(R_2PCH_2CH_2PR_2)_2Cl_2]^+$ is 0.25 V more difficult to reduce, and *trans*-$[Tc(acac_2en)(PR_3)_2]^+$ is 0.21 V more difficult to reduce, when R is ethyl. As expected, this effect of changing a phenyl substituent to an alkyl substituent is significantly decreased when the substituent is one atom removed from the donor atom. Thus, when *trans*-$[Tc((bzac)_2en)(PEtPh_2)_2]^+$ vs. *trans*-$[Tc((acac)_2en)(PEtPh_2)_2]^+$ is considered, a $Tc–O–C–C_6H_5$ linkage is compared to a $Tc–O–C–CH_3$ linkage, and it is seen (Table V) that the methyl derivative is only 0.1 V more difficult to reduce than is the phenyl derivative.

Plots of $E^{\circ\prime}$ values for the *trans*-$[TcLY_2]^+$ complexes vs. the Hammett substituent parameter values[1,26] are linear when either variations in L or Y are considered. However, the resultant ρ values are relatively small (ranging from +0.21 to +0.51), indicating that the $E^{\circ\prime}$ values governing redox at the technetium center are not nearly as sensitive to variations in the electron-donating properties of the ligands as are typical organic reactions involving the ligands themselves.

Relationship between MTLCT and $E^{\circ\prime}$. The effects influencing the energies of the lowest energy MTLCT bands and the redox potentials of the technetium(III) center appear to be related. The energy of the MTLCT band increases as the metal becomes more difficult to reduce (i.e. as the ligands become better σ donors). This relationship is apparent from the data of Table V and can be illustrated by plotting Tc(III/II) and Tc(IV/III) $E^{\circ\prime}$ values vs. the energy of the lowest energy MTLCT band (in eV) for four related *trans*-$[Tc((acac)_2en)Y_2]^+$ complexes where Y is varied from PEt_3 to PPh_3. A similar plot can be generated[1] in the same fashion by holding the trans Y ligands constant and varying the substituents on L. For both series, the relationships are close to linear with slopes that approach unity. In contrast to results of a related study,[13] the similarity of the slopes in both series would appear to indicate that neither Y nor L dominates determination of redox potential or of energy of the MTLCT band. The equatorial Schiff base ligand and the two axial phosphine ligands appear to contribute equally to determining the values of these parameters.

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Registry No. $[Tc((acac)_2en)(PEt_3)_2]PF_6$, 93426-98-3; $[Tc((acac)_2en)(PEt_2Ph)_2]PF_6$, 93427-00-0; $[Tc((acac)_2en)(PEtPh_2)_2]PF_6$, 93427-02-2; $[Tc((acac)_2en)(PPh_3)_2]PF_6$, 93427-04-4; $[Tc((buac)_2en)(PEt_2Ph)_2]PF_6$, 93453-70-4; $[Tc((buac)_2en)(PEtPh_2)_2]PF_6$, 93453-72-6; $[Tc((buac)_2en)(PEtPh_2)_2]PF_6$, 93427-06-6; $[Tc((brac)_2en)(PEtPh_2)_2]PF_6$, 93427-08-8; $[Tc((sal)_2en)(PEtPh_2)_2]PF_6$, 93427-10-2; $(Bu_4N)[TcOCl_4]$, 71341-65-6.

Supplementary Material Available: Tables A–F, showing F_c and F_o values, anisotropic thermal parameters, complete bond lengths and angles, intermolecular distances (<3.5 Å), and intramolecular distances (<4.2 Å), and Figures 2 and 3, showing the hexafluorophosphate anion (61 pages). Ordering information is given on any current masthead page.

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[25] In comparisons of the effect of substituents on the value of $E^{\circ\prime}$, it is generally true that for analogous complexes the species with the more negative $E^{\circ\prime}$ for the III/II process will also exhibit the more negative $E^{\circ\prime}$ for the IV/III process. The $(buac)_2en$ systems are exceptions to this observation. The reasons for this anomalous behavior are not currently understood.

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