Technetium(II) complexes of potentially heptadentate Schiff base ligands: synthesis and characterization. X-ray crystal structure of [Tc(tren-py₃)](PF₆)₂

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Abstract

The synthesis and characterization of structural isomers of tris[4-(2-pyridyl)-3-aza-3-butenyl]-aminetechnetium(II) tetraphenylborate are described. Two other structural isomers, tris[4-(2-(6-methyl-pyridyl))-3-aza-3-butenyl]aminetechnetium(II) tetraphenylborate and tris[4-(2-pyridyl)3-aza-3-pen-tenyl]aminetechnetium(II) tetraphenylborate, are also reported. Fast atom bombardment mass spectra, electron spin resonance spectra, cyclic voltammetry and conductivity studies of the new, Tc(II) complexes of potentially heptadentate ligands are discussed. The X-ray crystallographic structure of the PF_6^- salt of the major isomer of tris[4-(2-pyridyl)-3-aza-3-butenyl]aminetechnetium(II) shows a pseudo seven coordinate capped octahedral geometry. The mean Tc–imine nitrogen distance is 2.071 Å, and the mean Tc–pyridine nitrogen distance is 2.109 Å. The Tc-tertiary amine nitrogen distance is 2.933(7) Å, but this nitrogen's lone pair is directed toward the Tc atom (the average Tc–N–C angle is 102°). Crystal data for $C_{24}H_{27}F_{12}N_7P_2Tc$: monoclinic space group $P2_1/c$, $a = 15.082(1)$, $b = 10.7455(8)$, $c = 19.777(1)$ Å, $\beta = 110.29(1)°$, $V = 3006.2(8)$ Å³ to give $Z = 4$ and $R = 0.061$.

Introduction

Several technetium complexes of multidentate, chelating ligands have recently been reported. Hepta-coordinate technetium compounds such as the tech-netium xanthate complexes [1] and the technetium dioxime complexes [2] show potential as radiophar-maceuticals with the short-lived, γ-emitting isotope ^{99m}Tc. A Tc(IV) complex of the potentially heptad-entate ligand, tris[2-(2'-hydroxybenzylidene-ethyl)]amine, has been synthesized and may have potential application to myocardial imaging [3]. New Tc complexes with a chelating, tetradentate 'umbrella' ligand have also been structurally characterized [4]. First-row transition metal complexes of the potentially heptadentate, 'umbrella-type' ligand, tris[1-(2-pyri-dyl)-2-azabuten-4-yl]amine (tren-py₃, see Fig. 1), have been synthesized and characterized crystallograph-ically [5, 6]. Some new Tc(II) compounds of tren-py₃ and two of its methyl derivatives are reported here. These water soluble species may have future application in diagnostic nuclear medicine.

Experimental

Caution: Technetium-99 is a weak β^--emitter ($E = 292$ keV, $t_{1/2} = 2.12 \times 10^5$ years). All experiments have been done in laboratories approved for low-level radioactive materials following precautions de-tailed elsewhere [7].

Ammonium pertechnetate was obtained as a gift from Du Pont/Biomedical Products. Solvents and reagents were used as received unless otherwise indicated. Tris(2-aminoethyl)amine (tren), 2-pyri-dinecarboxaldehyde, 6-methyl-2-pyridinecarboxal-dehyde, 2-acetylpyridine, sodium tetraphenylborate (NaBPh₄), triphenylphosphine (PPh₃), and sodium hexafluorophosphate (NaPF₆) were obtained from Aldrich Chemical Company. Column chromato-graphy was performed with ICN Biomedicals Alumina N, Activity I. The starting materials, [(C₄H₉)₄N][TcOCl₄] [8], [TcCl₄(PPh₃)₂] [9] and [TcCl₃(PPh₃)₂(NCCH₃)] [10] were prepared as de-tailed elsewhere. Methylene chloride was distilled over calcium hydride.

Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. UV–Vis spectra were

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measured on a Hewlett Packard 8451A photodiode array spectrophotometer. Fast atom bombardment mass spectra (FAB-MS) were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun, that produced a beam of 6–8 keV Xenon neutrals. The samples were dissolved in a *p*-nitrobenzyl alcohol matrix. ESR spectra were recorded in the X-band ($\nu = 9.41$ GHz) on a Bruker ESP 300 ESR spectrometer and simulations of ESR spectra were performed with EPR-SIM [11]. Cyclic voltammetry was performed on N_2-purged CH_2Cl_2 solutions of the metal complexes with 0.1 M tetrabutylammonium perchlorate (TBAP, recrystallized from acetone and water, GFS Chemicals) as supporting electrolyte. Experiments were conducted using a one-compartment cell with a Pt disk as the working electrode (Bioanalytical Systems), a Pt wire as the auxiliary electrode, and a Ag/AgCl reference electrode (Bioanalytical Systems). $E_{1/2}$ values were calculated from the average of the anodic (E_a) and cathodic (E_c) peak potentials, $E_{1/2} = (E_a + E_c)/2$. $E_{1/2}$ values were measured relative to Ag/AgCl and are uncorrected for junction potentials. The potentiostat employed was a PAR model 174 polarographic analyzer and the data were plotted with a Hewlett Packard 7044A XY recorder. The ferrocene/ferrocenium couple in CH_2Cl_2 solution with 0.1 M TBAP as supporting electrolyte occurs at +0.45 V versus Ag/AgCl on this set-up. Routine IR spectra were recorded on a Mattson Cygnus 100 FT spectrophotometer. Conductivity data were measured on a Beckman-Altex conductivity bridge (RC-16C) with a Beckman conductivity cell.

Preparation of tris[4-(2-pyridyl)-3-aza-3-butenyl]aminetechnetium(II) tetraphenylborate, [Tc(L1)](BPh₄)₂

To [TcCl₃(PPh₃)₂(NCCH₃)] (80 mg, 0.10 mmol) was added 2.1 ml of a methanolic solution of tren (24 mg, 0.16 mmol) and 2-pyridinecarboxaldehyde (53 mg, 0.50 mmol). The mixture was refluxed for 1 h, during which time the initial orange slurry became a purple solution which was chromatographed on an alumina column with 80% dichloromethane/20% methanol. A dark purple band eluted, followed by a magenta fraction which was washed from the top of the column with methanol. After collecting and concentrating the purple and magenta fractions, NaBPh₄ (106 mg, 0.31 mmol) dissolved in methanol was added to each, causing the precipitation of purple and magenta solids. The products were filtered onto fritted glass funnels, washed with diethyl ether and dried *in vacuo*. Yield of the dark purple solid ([Tc(L1)](BPh₄)₂·3H₂O), 41 mg (34%). Yield of the magenta solid ([Tc(L1)](BPh₄)₂·2.5H₂O), 15 mg (13%).

Dark purple solid

Anal. Calc. for C₇₂H₇₃B₂N₇O₃Tc: C, 71.76; H, 6.11; N, 8.14; Cl, 0. Found: C, 71.52; H, 5.73; N, 8.82; Cl, 0%. UV–Vis (MeCN) (λ_{max}, nm (ϵ, 1 M^{-1} cm^{-1})): 212 (35 300); 272 (9000); 526 (3500); 658 (3000). FAB-MS(+), m/z (abundance %): 512 (100%), $(M)^+$; 436 (83%), $(M - py)^+$. Conductivity (acetone, 25 °C, 9.1×10^{-5} M) 101 cm² ohm^{-1} equiv^{-1}.

Magenta solid

Anal. Calc. for C₇₂H₇₂B₂N₇O₂.₅Tc: C, 72.31; H, 6.07; N, 8.20. Found: C, 72.27; H, 6.10; N, 7.99%. UV–Vis (MeCN) (λ_{max}, nm (ϵ, 1 M^{-1} cm^{-1})): 214 (20 740); 276 (5040); 484 (sh); 530 (2100); 656 (300). FAB-MS(+), m/z (abundance %): 512 (72%), $(M)^+$; 422 (100%), $(M - C - py)^+$. Conductivity (acetone, 25 °C, 9.0×10^{-5} M) 134 cm² ohm^{-1} equiv^{-1}.

Preparation of tris[4-(2-pyridyl)-3-aza-3-butenyl]aminetechnetium(II) hexafluorophosphate, [Tc(L1)](PF₆)₂

To [TcCl₃(PPh₃)₂(NCCH₃)] (121 mg, 0.16 mmol) was added 4.2 ml of a methanolic solution of tren (49 mg, 0.33 mmol) and 2-pyridinecarboxaldehyde (109 mg, 1.0 mmol). The reaction conditions and chromatography were identical to those described above. To the purple fraction, NaPF₆ (56 mg, 0.33 mmol) dissolved in 0.5 ml of water was added. Within two days at room temperature, purple, prismatic, X-ray quality crystals had grown in the roundbottom flask. Yield of the purple crystals, 26 mg (21%). The electronic spectrum of the purple crystals was identical to that of the purple isomer of [Tc(L1)](PF₆)₂. To the magenta fraction, NaPF₆ (53 mg, 0.32 mmol) dissolved in 0.5 ml of water was added, but no solid precipitated.

Preparation of tris[4-(2-(6-methylpyridyl))-3-aza-3-butenyl]aminetechnetium(II) tetraphenylborate, [Tc(L2)](BPh₄)₂

To [TcCl₃(PPh₃)₂(NCCH₃)] (74 mg, 0.10 mmol) was added 2.1 ml of a methanolic solution of tren (21 mg, 0.14 mmol) and 6-methyl-2-pyridinecarboxaldehyde (55 mg, 0.46 mmol). The mixture was refluxed for 1 h, during which time the initial orange slurry became a deep blue solution which was chromatographed on alumina with 80% dichloromethane/20% methanol. The desired material eluted as a blue band and was completely washed off the column with methanol. After collecting and concentrating the fraction, NaBPh₄ (105 mg, 0.31 mmol) dissolved in methanol was added, causing the precipitation of a deep blue solid. The product was filtered onto a fritted glass funnel, washed with diethyl ether and

dried *in vacuo*. Yield of the deep blue solid ([Tc(L2)](BPh$_4$)$_2$·2H$_2$O), 74 mg (60%).

Anal. Calc. for C$_{75}$H$_{68}$B$_2$N$_7$O$_2$Tc: C, 73.84; H, 5.62; N, 8.04. Found: C, 73.00; H, 6.15; N, 8.44. UV–Vis (MeCN) (λ_{max}, nm (ϵ, l M^{-1} cm^{-1}) l): 218 (77 400); 278 (30 700); 360 (7600); 554 (12 000); 662 (12 800). FAB-MS(+), *m/z*: 554, (*M*)$^+$. Conductivity (acetone, 25 °C, 8.9×10^{-5} M) 104 cm^2 ohm^{-1} equiv^{-1}.

Preparation of tris[4-(2-pyridyl)-3-aza-3-pentenyl]aminetechnetium(II) tetraphenylborate, [Tc(L3)](BPh$_4$)

To [TcCl$_3$(PPh$_3$)$_2$(NCCH$_3$)] (58 mg, 0.08 mmol) was added 1.6 ml of a methanolic solution of tren (19 mg, 0.13 mmol) and 2-acetylpyridine (51 mg, 0.42 mmol). The mixture was refluxed for 5 h, during which time the initial orange slurry became a red–purple solution which was chromatographed on an alumina column with 80% dichloromethane/20% methanol. A red–purple band eluted and was removed completely from the column with methanol. After collecting and concentrating the red–purple fraction, NaBPh$_4$ (93 mg, 0.27 mmol) dissolved in methanol was added, causing the precipitation of a red–purple solid which was filtered onto a fritted glass funnel, washed with diethyl ether and dried *in vacuo*. Yield of the red–purple solid ([Tc(L3)](BPh$_4$)$_2$·3H$_2$O), 27 mg (27%).

Anal. Calc. for C$_{75}$H$_{70}$B$_2$N$_7$O$_3$Tc: C, 72.76; H, 5.70; N, 7.92. Found: C, 70.40; H, 5.97; N, 8.11%. UV–Vis (MeCN) (λ_{max}, nm (ϵ, l M^{-1} cm^{-1})): 218 (77 700); 268 (22 700); 528 (7200). FAB-MS(+), *m/z*: 554, (*M*)$^+$; 482, (*M*−py)$^+$; 450, (*M*−py−CCH$_3$)$^+$. Conductivity (acetone, 25 °C, 9.0×10^{-5} M) 112 cm^2 ohm^{-1} equiv^{-1}.

Results and discussion

The reactions of the potentially heptadentate ligands described above with [TcCl$_3$(PPh$_3$)$_2$(NCCH$_3$)] were expected to yield Tc(III) complexes. However, the reactions in methanol give dicationic Tc(II) complexes; the methanol may serve as a reducing agent. Reactions of the ligands with technetium precursors in higher oxidation states, such as [Tc^{IV}Cl$_4$(PPh$_3$)$_2$], [(C$_4$H$_9$)$_4$N][Tc^{V}OCl$_4$] and NH$_4$[Tc^{VII}O$_4$], yield the same dicationic Tc(II) complexes.

Figure 1 shows the structures of the potentially heptadentate, Schiff base ligands used in this study. The ligands are based on tren-py$_3$ [6a] and are formed by the condensation reaction between tren and 2-pyridinecarboxaldehyde or one of its derivatives. Two methyl derivatives of tren-py$_3$ (L1) have been prepared. Tren-(pyMe)$_3$, (L2), in which a methyl group is bound to the sixth position of each pyridine

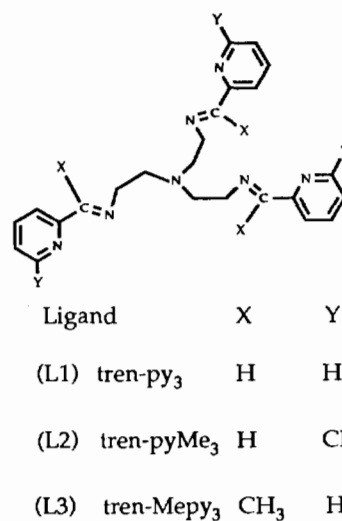| Ligand		X	Y
(L1)	tren-py$_3$	H	H
(L2)	tren-pyMe$_3$	H	CH$_3$
(L3)	tren-Mepy$_3$	CH$_3$	H

Fig. 1. Schematic representation of the ligands used in this study.

ring, and tren-(Mepy)$_3$, (L3), in which the methyl group is bound to the imine carbon, are structural isomers whose metal complexes show that subtle variations in ligand structure result in quite different spectroscopic and electrochemical results.

The reaction of [TcCl$_3$(PPh$_3$)$_2$(NCCH$_3$)] and tren-py$_3$ (L1) results in a purple solution. Chromatography of the reaction mixture on alumina gives two fractions. The major, purple product is eluted first with CH$_2$Cl$_2$/CH$_3$OH. The minor product (the more polar, magenta fraction) is eluted with methanol. The assignment of the 2+ oxidation state for the technetium is determined by elemental analyses which allow for two tetraphenylborate anions per Tc(II) complex; the waters of hydration assigned in the analyses exhibited characteristic stretches in the IR spectra. The UV–Vis spectra of the complexes are similar, but the absorbance of the minor product at 656 nm is much less intense than the corresponding absorbance of the major product. FAB-MS show identical parent peaks at 512 *m/z*. These peaks correspond to Tc(I) species; the Tc(II) complexes are reduced in the *p*-nitrobenzyl alcohol matrix. The fragmentation patterns for the complexes are different. The purple compound loses pyridine. A prominent peak at 422 *m/z* shows that the magenta product loses pyridine plus a carbon, presumably the imine carbon. The above observations lead us to conclude that the purple and magenta complexes are structural isomers.

The cyclic voltammetry for all compounds is summarized in Table 1. The interpretation of the cyclic voltammetry is based in part on previous work with similar compounds such as [Tc(bpy)$_3$]$^{2+}$ [12, 13]. The purple isomer of [Tc(L1)]$^{2+}$ is oxidized irreversibly to a Tc(III) species at +0.17 V versus Ag/

TABLE 1. Cyclic voltammetry results for presented compounds

Complex	$E_{1/2}$ (V vs. Ag/AgCl)
[TcL1](BPh$_4$)$_2$ (major, purple)	$+0.17^a$, -0.05^b, -0.45, -0.88^c, -1.36
[TcL1](BPh$_4$)$_2$ (minor, magenta)	$+1.02^a$, -0.10^b, -0.40, -0.99, -1.34^a
[TcL2](PF$_6$)$_2$	$+0.62^a$, $+0.18^b$, -0.33, -0.93^c
[TcL3](BPh$_4$)$_2$	$+1.10^a$, $+0.62^b$, -0.64^c, -1.14, -1.34^a

Experiments were performed in CH$_2$Cl$_2$ solution with 0.1 M TBAP as supporting electrolyte. Scan rate was 100 mV/s. $E_{1/2}$ values correspond to reversible processes, unless noted otherwise. Reversible couples have ΔE values equal to 140 mV. Ferrocene showed similar behavior on this set-up. The ΔE deviation from 59 mV is attributed to iR drop. ^{a}Irreversible peak potential, E_a. ^{b}Irreversible peak potential, E_c. ^{c}Quasi-reversible $E_{1/2}$. Quasi-reversible couples have ΔE greater than 140 mV.

AgCl. The Tc(III) species generated electrochemically is reduced irreversibly at -0.05 V. The E_c at -0.05 V is not observed unless the oxidized species at $+0.17$ V has been generated. The reversible Tc(II)/Tc(I) couple occurs at -0.45 V. At more negative potentials, the quasi-reversible couples at -0.88 and -1.36 V probably correspond to electrochemistry on the (L1) ligand. Cyclic voltammetry of the minor, magenta product is different from that of the major, purple product. The irreversible Tc(II)/Tc(III) oxidation at $+1.02$ V occurs at a significantly higher potential than for the purple isomer. The irreversible Tc(II)/Tc(III) oxidation at -0.1 V is only observed if the oxidized species at $+1.02$ V has been generated. The reversible Tc(II)/Tc(I) couple at -0.40 V shows that the magenta isomer is slightly easier to reduce than the purple isomer. The more negative peaks most likely correspond to electrochemistry on the ligand.

The two products give identical ESR spectra at 130 K in acetonitrile/toluene glass. None of the compounds in this study show ESR signals at room temperature. The unpaired electron's signal is coupled to the technetium nucleus (nuclear spin of ^{99}Tc $= 9/2$) as evidenced by the ten line splitting pattern. The spectra have been simulated [11] as axial with $gx = gy = 2.12$, $gz = 2.17$, $ax = ay = 0.01$ cm^{-1} and $az = 0.0015$ cm^{-1}; an axial spectrum is expected for the C$_3$ molecule, [Tc(L1)]$^{2+}$.

The conductivity data of the two products are comparable. The major product shows a conductivity of 101 cm^2 ohm^{-1} equiv^{-1} in acetone at a concentration of 9.1×10^{-5} M and that for the minor, magenta product is 134 cm^2 ohm^{-1} equiv^{-1} at a concentration of 9.0×10^{-5} M. For comparative purposes, the tetraphenylborate salt of [Mn(L1)]$^{2+}$ was synthesized [5], and its conductivity is 109 cm^2 ohm^{-1} equiv^{-1} at 8.6×10^{-5} M. The conductivities of the compounds are similar, establishing that the Tc species are two to one electrolytes.

The X-ray crystallographic structure determination (Table 2) of the purple isomer of [Tc(L1)](PF$_6$)$_2$ corroborates the information obtained from the ESR and mass spectra, elemental analyses and conductivity studies of [Tc(L1)](BPh$_4$)$_2$. An ORTEP diagram of [Tc(L1)](PF$_6$)$_2$, viewed along the molecule's C$_3$ axis of symmetry, is shown in Fig. 2. Selected bond distances and bond angles in [Tc(L1)](PF$_6$)$_2$ are given in Tables 3 and 4.

The [Tc(L1)]$^{2+}$ cation is pseudo seven coordinate. The mean imine nitrogen–Tc distance is 2.071 Å and the mean pyridine nitrogen–Tc distance is 2.109 Å. These metal nitrogen distances are compared in Table 5 to those of the other [M(L1)]$^{2+}$ complexes (where M is Mn, Fe, Co, Ni, Cu and Zn; see Table 5). The Tc–tertiary nitrogen distance is 2.933(7) Å, which is significantly longer than the other Tc–N distances in the complex, but this is one of the shorter metal–tertiary nitrogen distances in the [M(L1)]$^{2+}$ series of compounds. Considering that the covalent radius and van der Waals radius of Tc^{2+} is larger than that of the dications of the first-row transition metals referred to above, the Tc–tertiary N distance may indicate a stronger metal–tertiary N interaction in the Tc complex than evidenced in the other complexes of the tren-py$_3$ ligand.

The angles around N7 demonstrate the 'interaction' between the N7 and Tc atoms. If the Tc and N7 were at the point of maximum repulsion, the Tc–N7–C angle would be 90°. However, the average Tc–N7–C angle is 102° which shows that the lone pair of N7 points to the Tc. The bridgehead C–N7–bridgehead C angles would be 120° when repulsion between Tc and N7 is greatest. The actual C–N7–C angles, C71–N7–C73, C71–N7–C75 and C73–N7–C75, are 116.6(8), 113.4(7) and 116.2(8)°, respectively.

On examining the coordination of N1–N6 to Tc, the geometry of this set of atoms is best regarded as a trigonally distorted octahedron. The cis N–Tc–N bond angles, which vary from 74.7(3)–103.7(3)°, fall

TABLE 2. X-ray data for the structure determination of the purple isomer [Tc(tren-py₃)](PF₆)₂

Empirical formula	$C_{24}H_{27}N_7P_2F_{12}Tc$
Formula weight (g mol⁻¹)	802.45
Crystal color, habit	blue–black, prism
Crystal dimensions (mm)	$0.150 \times 0.150 \times 0.240$
Crystal system	monoclinic
a (Å)	15.082(1)
b (Å)	10.7455(8)
c (Å)	19.777(1)
β (°)	110.29(1)
V (Å³)	3006.2(8)
Space group	$P2_1/c$ (No. 14)
Z	4
D (calc.) (g/cm³)	1.773
μ (cm⁻¹)	6.65
Diffractometer	Enraf-Nonius CAD-4
Radiation (λ, Å) (graphite monochromated)	Mo Kα (0.71069)
Temperature (°C)	23
No. reflections used for unit cell determination (2θ range (°))	25 (17.0–30.0)
Scan type	ω–2θ
Scan width (°)	$(0.80 + 0.35 \tan\theta)$
Scan rate (°/min)	0.9–8.0
Max 2θ (°)	54.9
No. reflections measured	
total	7522
unique	7264
Data collected	$+h + k \pm l$
Reflections collected	$h0l$: $l \neq 2n$
	$0k0$: $k \neq 2n$
R_{int}	0.048
T_{max}, T_{min}	0.74, 1.06
Correction (Lorentz–polarization)	empirical absorption using DIFABSᵃ
Structure solution	direct methodsᵇ
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(|F_o| - |F_c|)^2$
Least-squares, wt.	$4F_o^2/\sigma^2(F_o^2)$
Atomic scattering factorsᶜ	neutral atom scattering factors
Anomalous dispersionᵈ	all non-H atoms
Extinction effects	not observed
Criterion, no. observations	$I > 3.00\sigma(I)$, 7786
No. variables	415
R, R_w	0.061, 0.057
Goodness of fit	1.34
Max. shift/error in final cycle	0.01
Max. peak in final difference map (e Å⁻³)	0.52
Min. peak in final difference map (e Å⁻³)	−0.83

ᵃRef. 14. ᵇStructure solution methods: MITHRIL [15] and DIRDIF [16]. ᶜRef. 17. ᵈRef. 18.

into three groups. Each arm forms a strained five-membered chelate ring which results in bond angles that are smaller than the ideal 90°. The bite angles N2–Tc–N6, N1–Tc–N4 and N3–Tc–N5 are 74.7(3), 75.5(3) and 75.5(3)°, respectively. The
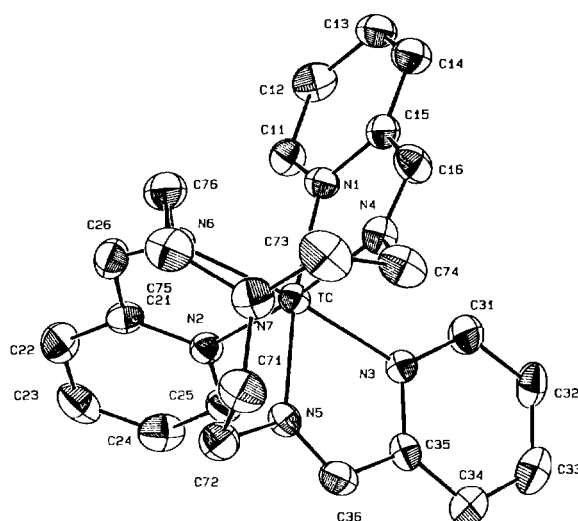
Fig. 2. ORTEP [19] diagram of [Tc(L1)](PF₆)₂ showing 35% probability ellipsoids.

TABLE 3. Bond lengths (Å) for the purple isomer of [Tc(tren-py₃)](PF₆)₂

Tc–N1	2.112(6)	N3–C35	1.37(1)
Tc–N2	2.117(6)	N4–C16	1.30(1)
Tc–N3	2.097(7)	N4–C74	1.46(1)
Tc–N4	2.058(7)	N5–C36	1.30(1)
Tc–N5	2.072(7)	N5–C72	1.47(1)
Tc–N6	2.083(7)	N6–C26	1.27(1)
Tc–N7	2.933(7)	N7–C71	1.47(1)
N1–C15	1.35(1)	N7–C73	1.43(1)
N2–C21	1.35(1)	N7–C75	1.49(1)
C15–C16	1.44(1)	C21–C26	1.42(1)
C35–C36	1.41(1)		

TABLE 4. Selected bond angles (°) for the purple isomer of [Tc(tren-py₃)](PF₆)₂

N1–Tc–N2	96.1(3)	N2–Tc–N6	74.7(3)
N1–Tc–N3	95.8(2)	N3–Tc–N4	85.6(3)
N1–Tc–N4	75.5(3)	N3–Tc–N5	75.5(3)
N1–Tc–N5	171.4(3)	N3–Tc–N6	170.6(3)
N1–Tc–N6	86.3(3)	N4–Tc–N5	103.0(3)
N2–Tc–N3	96.0(3)	N4–Tc–N6	103.7(3)
N2–Tc–N4	171.6(3)	N5–Tc–N6	102.2(3)
N2–Tc–N5	85.4(2)	C71–N7–C73	116.6(8)
C73–N7–C75	116.2(8)	C71–N7–C75	113.4(7)

N(imine)–Tc–N(imine) angles, N5–Tc–N4, N6–Tc–N5 and N6–Tc–N4, are 103.0(3), 102.2(3) and 103.7(3)°, respectively, and demonstrate the tetragonal distortion along the C_3 axis. The six remaining cis N–Tc–N angles comprise the third group and vary from 85.4(2)–96.1(3)°. These angles are the least distorted from the ideal 90° among the three groups.

The 'height to bite' and twist angle measurements, defined in ref. 5, indicate that the geometry of the

complex is best described as distorted octahedral. For trigonal prisms, the ideal 'height to bite' ratio is 1.0, and for octahedra, it is 0.816. The 'height to bite' ratio of $[Tc(L1)]^{2+}$ is 0.77. For trigonal prisms, the ideal twist angle is 0°, and for octahedra, it is 60°. In $[Tc(L1)]^{2+}$, the twist angle is 52°. If N7 is included in the coordination sphere, the complex is best described as capped octahedral. A summary of these numbers and a comparison with other $[M(L1)]^{2+}$ complexes are given in Table 5.

The reaction of $[TcCl_3(PPh_3)_2(NCCH_3)]$ with tren(pyMe)$_3$, (L2), in which a methyl group is bound to the sixth position of each pyridine ring, gives a deep blue complex in high yield. The FAB-MS(+) shows a molecular ion peak at 554 m/z which corresponds to $[Tc(tren(pyMe)_3)]^+$; no fragmentation is observed. Elemental analyses of the tetraphenylborate salt of the compound indicate its formulation to be $[Tc(L2)](BPh_4)_2 \cdot 2H_2O$. The conductivity of the BPh$_4^-$ salt of the complex is 104 cm^2 ohm^{-1} equiv^{-1} at a concentration of 8.9×10^{-5} M; this falls in the range for a two to one electrolyte. The complex is stable in wet solvents and its PF$_6^-$ salt can be prepared in a similar manner as the BPh$_4^-$ salt.

Cyclic voltammetry on $[Tc(L2)](PF_6)_2$ follows the pattern described above for the purple and magenta isomers. $[Tc(L2)](PF_6)_2$ is irreversibly oxidized to a Tc(III) species at +0.62 V versus Ag/AgCl. The irreversible Tc(III)/Tc(II) reduction at +0.18 V is not observed unless the species generated at +0.62 V has been produced. The reversible Tc(II)/Tc(I) couple occurs at −0.33 V. The quasi-reversible couple at −0.93 V most likely corresponds to electrochemistry associated with the ligand.

The ESR spectrum at 130 K in acetonitrile/toluene glass is a ten line spectrum that indicates the unpaired electron's signal is split by the technetium nucleus. The spectrum may be simulated [11] as rhombic with $gx = 1.92$, $gy = 2.28$, $gz = 2.50$, $ax = 0.0001$ cm^{-1}, $ay = 0.006$ cm^{-1} and $az = 0.0001$ cm^{-1}, which indicates that at 130 K there is a distortion from the compound's ideal, axial C_3 geometry.

A structural isomer of $[Tc(L2)]^{2+}$ is synthesized by the reaction of $[TcCl_3(PPh_3)_2(NCCH_3)]$ with (L3) (tren(Mepy)$_3$), where the methyl group is bound to the imine carbon. The FAB-MS(+) spectrum of the red–purple complex, $[Tc(L3)]^{2+}$, shows a molecular ion peak at 554 m/z which represents $[Tc(L3)]^+$. The mass spectrum shows fragmentation peaks that represent loss of pyridine, and pyridine plus CCH$_3$; the latter must correspond to the imine carbon and methyl groups bound to it. Although the elemental analysis is low for carbon, the analytical results for the BPh$_4^-$ salt of the complex most closely correspond to $[Tc(L3)](BPh_4)_2 \cdot 3H_2O$. Since the complex ana-

TABLE 5. Comparison of structural parameters of M(L1)$^{2+}$ series of complexes; distances are in Å, angles are in °

	MnL1(BF$_4$)$_2$	FeL1(BF$_4$)$_2$	CoL1(BF$_4$)$_2$	NiL1(BF$_4$)$_2$	NiL1(PF$_6$)$_2$	CuL1(BF$_4$)$_2$	ZnL1(BF$_4$)$_2$	TcL1(PF$_6$)$_2$
M–N(7)	2.794(2)	3.439(4)	2.870(2)	3.227(4)	3.235(4)	3.110(2)	3.013(2)	2.933(7)
Mean M–N(imine)	2.201	1.942	2.093	2.087	2.081	2.102	2.128	2.071
Mean M–N(pyridine)	2.317	1.967	2.200	2.100	2.105	2.143	2.226	2.109
Bite (b)	2.672	2.544	2.642	2.654	2.639	2.664	2.684	2.55
Height (h)	2.256	2.047	2.156	2.202	2.138	2.222	2.257	1.970
Height/bite (h/b)	0.844	0.805	0.816	0.830	0.810	0.834	0.841	0.77
Twist angle (ϕ)	42.96	53.97	48.67	49.14	50.88	47.69	45.9	52.0
Reference	5	5, 6b	5	5	5, 6a	5	5	this work

lyzes correctly for nitrogen and hydrogen, the low carbon result may be attributed to incomplete combustion and the formation of technetium carbides [20]. The conductivity of the BPh_4^- salt of the complex is 112 cm^2 ohm^{-1} equiv^{-1} at a concentration of 9.0×10^{-5} M. The complex, $[Tc(L3)]^{2+}$, hydrolyzes in water and wet solvents to yield an orange–brown solution that was not characterized.

The ESR spectrum of $[Tc(L3)]^{2+}$ at 130 K in acetonitrile/toluene glass corroborates the technetium in the 2 + oxidation state. The ten line spectrum may be simulated [11] as a rhombic system with $gx = 1.92$, $gy = 2.14$, $gz = 2.37$, $ax = 0$ cm^{-1}, $ay = 0.008$ cm^{-1} and $az = 0.0008$ cm^{-1}. This ESR spectrum is quite different from that of $[Tc(L2)]^{2+}$ discussed above. Although the ligands L2 and L3 differ only in the position of the methyl groups, this structural perturbation results in different ESR spectra of the two complexes, $[Tc(L2)]^{2+}$ and $[Tc(L3)]^{2+}$.

The cyclic voltammetry study of $[Tc(L3)](BPh_4)_2$ shows that this complex is the most difficult to oxidize and reduce among all the compounds discussed above. The irreversible Tc(II)/Tc(III) oxidation occurs at + 1.10 V versus Ag/AgCl and the irreversible Tc(III)/Tc(II) reduction is at + 0.62 V. These potentials are the most positive of the complexes presented in this work. The quasi-reversible Tc(II)/Tc(I) couple at − 0.64 V shows that $[Tc(L3)]^{2+}$ is the most difficult to reduce among all the compounds in this series. The reversible couple at − 1.14 V and the irreversible anodic peak at − 1.34 V correspond to electrochemistry on the ligand.

Conclusions

Novel, dicationic Tc(II) complexes of potentially heptadentate ligands have been synthesized. Structural isomers of $[Tc(tren-py_3)]^{2+}$ have been characterized and the isomer formed in greater yield is a pseudo seven coordinate capped octahedron, as shown by X-ray crystallography. $[Tc(tren-(Mepy)_3)]^{2+}$ and $[Tc(tren-(pyMe)_3)]^{2+}$ illustrate that the tren-py$_3$ ligand can be subtlely fine-tuned to give Tc(II) complexes which show very different ESR spectra and cyclic voltammetry.

Acknowledgements

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