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Synthesis and Characterization of Technetium(III) Complexes with Nitrogen Heterocycles by O Atom Transfer from Oxotechnetium(V) Cores. Crystal Structures of *mer*-$[Cl_3(pic)_3Tc]$ and *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ (pic = 4-Picoline). Electrochemical Parameters for the Reduction of Tc^{II}, Tc^{III}, and Tc^{IV}

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The combination of pyridine ligands, $[OCl_4Tc]^-$, and O atom acceptors of different cone angles, such as PMe_2Ph or PPh_3, results in Tc^{III} complexes that vary in the coordination of the phosphine ligand. The compounds *mer*-$[Cl_3(4\text{-picoline})_3Tc]$ and *mer*-$[Cl_3(4\text{-picoline})(PMe_2Ph)_2Tc]$ have been obtained in good yield and have been characterized spectroscopically and by single-crystal X-ray diffraction. The former crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 13.328$ (2) Å, $b = 8.902$ (1) Å, $c = 18.019$ (4) Å, $\beta = 103.25$ (1)°, and $Z = 2$. The latter forms crystals in $P\bar{1}$ (triclinic) with the cell parameters $a = 12.35$ (1) Å, $b = 13.890$ (5) Å, $c = 7.949$ (3) Å, $\alpha = 97.29$ (3)°, $\beta = 101.56$ (6)°, $\gamma = 71.14$ (6)°, and $Z = 2$. Linear correlations of technetium reduction potentials in DMF with electrochemical ligand additivity parameters (E_L's) have been obtained for the $Tc^{II,I}$, $Tc^{III,II}$, and $Tc^{IV,III}$ couples. The slope and intercept (S_M, I_M) pairs for each technetium oxidation–reduction couple, respectively, are (1.39, −2.07), (1.29, −0.91), and (1.00, 0.65).

The chemistry of technetium often depends on minor differences in the ligands or subtle changes in reaction conditions.[1,2] In an effort to both understand and develop preparative reactions of this element in its mid oxidation states, we have been systematically studying the reactions of oxotechnetium(V) complexes in aqueous and nonaqueous solvents.[3-5] When complexes such as $[OCl_4Tc]^-$ are heated in neat pyridine or in organic solvents with high pyridine concentrations, O atom transfer to the pyridine occurs to yield mixed-valent compounds of the type $[X(py)_3XTc\text{–}O\text{–}Tc(py)X_3(py)]$ and $[X(py)_4Tc\text{–}O\text{–}Tc(py)X_4]$, in which the Tc atoms can be thought of as being in the 3.5 oxidation state.[6]

Reduction of $[Tc{=}O]^{3+}$ by O atom transfer to phosphines has been used to prepare bis(diphosphine) chelates that have shown promise as potential myocardial imaging $^{99m}Tc^{III}$ radiopharmaceuticals.[7] In general, the use of a good oxygen atom acceptor, such as phosphines,[8] brings the metal all the way down to the Tc^{III} oxidation state without the formation of isolable mixed-valent compounds;[9,10] however, one μ-oxo complex has recently been prepared by phosphine reduction.[11] In many of these reactions, a mixture of complexes with varying numbers of halide, pyridine, and phosphine ligands probably results with the relative abundance of each complex depending on the nature and concentration of the ligands and other reaction conditions. In the present study, where only the phosphine ligand is varied, it has been possible to obtain two of these complexes, *mer*-$[Cl_3(pic)_3Tc]$ and *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ (pic = 4-methylpyridine), in good yields and characterize them by X-ray crystallography and an array of spectroscopic methods. The $Tc^{III,II}$ reduction potentials of these complexes are sufficiently negative that a broad range of $Tc^{III,II}$ $E°$'s can now be correlated with Lever's ligand additivity electrochemical parameters[12] to yield metal ion parameters that allow new $Tc^{III,II}$ couples to be estimated.

Experimental Section

Syntheses. The compound *mer*-$[Cl_3(pic)_3Tc]$ was prepared dissolving 60 mg of $[n\text{-}Bu_4N][TcOCl_4]$ in 3 mL of 4-picoline to which was added 200 mg of PPh_3 or $P(4\text{-}MeOPh)_3$ dissolved in 2 mL of picoline. The mixture was refluxed for 2 h and cooled to room temperature. A yellow precipitate was collected after addition of 100 mL of hexane, washed thoroughly with 1:1 hexanes/diethyl ether and hexanes. After drying, the solid was dissolved in a minimum of chloroform and the solution was loaded onto a silica gel chromatography column, which was eluted with chloroform. The major band was collected and dried by rotary evaporation. Yield: ~60%. Anal. Calcd for $Cl_3C_{18}H_{21}N_3Tc$: H, 4.37; C, 44.61; N, 8.67; Cl, 21.95; Tc, 20.41. Found: H, 4.29; C, 44.75; N, 8.82; Cl, 21.76; Tc, 20.3. UV–visible peaks in $CHCl_3$, λ, nm (ϵ, $M^{-1}\,cm^{-1}$): 245 (12 300), 285 (9900), 331 (sh), 405 (4200). $\mu_{eff} = 2.81\ \mu_B$. ^1H NMR ($CDCl_3$), δ (ppm): 30.3 [CH_3 (x)], 24.2 [H_β (x)], 21.5 [CH_3 (z)], 17.1 [H_β (z)], −6.1 [H_α (x)], −21.0 [H_α (z)]. IR: 1621 (s), 1501 (s), 1441 (s), 1428 (s), 1209 (s), 1028 (s), 812 (vs), 756 (s), 745 (vs), 497 (vs). For the NMR assignments, the 2-fold axis was assigned as Z, the Cl–Tc–Cl axis is y, and the pic–Tc–pic axis is x. A corresponding labeling system is used for the two other complexes.

The compound *mer*-$[Cl_3(py)_3Tc]$ was made by an analogous method. Yield: 75%. Anal. Calcd for $Cl_3C_{15}H_{15}N_3Tc$: H, 3.42; C, 40.71; N, 9.49; Cl, 24.03; Tc, 22.35. Found: H, 3.39; C, 40.89; N, 9.46; Cl, 23.35; Tc, 22.5. UV–visible peaks in $CHCl_3$, λ, nm (ϵ, $M^{-1}\,cm^{-1}$): 240 (15 600), 288 (8250), 331 (sh), 413 (4500). $\mu_{eff} = 2.65\ \mu_B$. ^1H NMR ($CDCl_3$), δ (ppm): 24.0 [H_β (x)], 17.1 [H_β (z)], −0.9 [H_γ (x)], −2.3 [H_γ (z)], −6.95 [H_α (x)], −18.2 [H_α (z)]. IR (cm^{-1}): 1604 (s), 1498 (s), 1444 (s), 1430 (s), 1219 (s), 1025 (s), 812 (vs), 756 (s), 695 (vs).

mer-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ was prepared in an identical fashion except that PMe_2Ph was used as the O-atom acceptor. Yield: 65%. Anal. Calcd for $Cl_3P_2C_{22}H_{29}NTc$: H, 5.09; C, 45.98; N, 2.44; Cl, 18.51; P, 10.78; Tc, 17.21. Found: H, 5.14; C, 45.76; N, 2.65; Cl, 18.82; Tc, 16.7. UV–visible peaks in methanol, λ, nm (ϵ, $M^{-1}\,cm^{-1}$): 237 (23 700), 281 (7200), 386 (3450). $\mu_{eff} = 2.58\ \mu_B$. ^1H NMR (acetone-d_6), δ (ppm): 29.7 [CH_3 (pic)], 24.5 [H_β (pic)], 22.6 [H_γ (Ph, x)], 21.6 [H_β (Ph, x)], 16.4 [H_γ (Ph, z)], 13.1 [H_β (z)], 7.4 (CH_3 (P, x)], 2.9 [CH_3 (P, x)], −4.7 [H_α (pic, y)], −20.2 [H_α (P, x)], −22.5 [H_α (P, z)]. IR (cm^{-1}): 1637 (m), 1433 (s), 1103 (m), 948 (s), 948 (s), 910 (vs), 740 (s), 709 (s), 695 (s), 491 (s).

Compound Characterization. All elemental analyses (except for ^{99}Tc) were performed by Galbraith Laboratories, Knoxville, TN. Technetium analyses were performed in this laboratory.[6] Magnetic susceptibility studies were performed on a Cahn Model 7500 electrobalance equipped with a 14 502-G permanent magnet at 25 °C. UV–visible spectra were

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Table I. Crystallographic Data for *mer*-[Cl_3(pic)$_3$Tc] and *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]

formula	$TcC_{18}H_{21}N_3Cl_3$	$TcC_{22}H_{29}NP_2Cl_3$
fw	484.64	574.69
cryst dimens, mm	0.03 × 0.06 × 0.10	0.10 × 0.25 × 0.25
color	yellow	yellow, rectangular
radiation source (λ, Å)	Cu Kα (1.541 78) graphite monochromated	Mo Kα (0.710 69)
μ, cm^{-1}; rel transm factors	92.89; 0.63–1.0	10.02
space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
cell constants, Å and deg	a = 13.328 (2) b = 8.902 (1) c = 18.019 (4) β = 103.25 (1)	a = 12.35 (1) b = 13.890 (5) c = 7.949 (3) α = 97.29 (3) β = 101.56 (6) γ = 71.14 (6)
V, Å^3	2081.0 (7)	1261 (3)
Z	4	2
d_{calcd}, g/cm^3	1.547	1.513
F_{000}	976	584
tot. no. of unique observns	3278	5823
no. of obsd reflcns^a	2005	5080
scan mode	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$, deg	119.3	55.2
scan rate, deg/min in Ω	16	32
scan width, deg	[0.79 + 0.30 tan θ]	[1.26 + 0.30 tan θ]
no. of variables in least squares	226	262
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.033	0.034
$R_w{}^b = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert w(F_o)^2\rvert]^{1/2}$	0.043	0.054
goodness of fit = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)_2/(N_{observns}\ N_{params})]^{1/2}$	1.0	1.57

^{a} T = 20 (1) °C. Reflections with $F_o > 3\sigma(F_o)$ were retained as observed and used in the solution and refinement of the structure. Three standard reflections were monitored with a limit of 0.2% variation. Function minimized: $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$. ^{b} Weighting scheme: $w = 4(F_o)^2[\sigma^2/(F_o)^2]^2$.

obtained on a Cary Model 2400 spectrophotometer. IR spectra were determined on KBr pellets in a Nicolet Model 510 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian 300 XL Fourier transform spectrometer. NMR assignments were based on comparison of the resonances present in the spectra of *mer*-[Cl_3(pic)$_3$Tc] and *mer*-[Cl_3(py)$_3$Tc] to determine the methyl and H_γ peaks, relative line widths to discriminate between H_α and H_β peaks, and relative intensities to distinguish those lying along the x or z axes. These assignments were, in turn, used to assign the picoline proton resonances in *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]. The resonances of the PMe_2Ph's along the x and z axes were distinguished on the basis of their shifts relative to those of the x and z picolines in *mer*-[Cl_3(pic)$_3$Tc].

Electrochemical measurements were performed by cyclic or square-wave voltammetry in 0.1 M tetraethylammonium perchlorate (TEAP) in DMF on a versatile electrochemical apparatus constructed in this laboratory.[13] A carbon paste or platinum button working electrode, Ag/AgCl reference electrode, and platinum-wire auxiliary electrode were used in all measurements. Reduction potentials were determined as the peak potential in square-wave voltammetric scans and by the average of the anodic and cathodic peak potentials from cyclic voltammetric scans. All potentials were internally referenced against the ferrocene couple (400 mV vs NHE).[14]

Table II. Positions of Atoms in the Technetium Coordination Sphere in *mer*-[Cl_3(pic)$_3$Tc]

atom	x	y	z
Tc1	0.26817 (3)	0.40156 (6)	0.88668 (3)
Cl1	0.2831 (1)	0.3072 (2)	0.7653 (1)
Cl2	0.1112 (1)	0.5211 (2)	0.83187 (9)
Cl3	0.4234 (1)	0.2898 (2)	0.9497 (1)
N1	0.3511 (3)	0.6014 (6)	0.8709 (3)
N2	0.1877 (3)	0.2015 (5)	0.9034 (3)
N3	0.2507 (3)	0.4824 (5)	0.9945 (2)

Table III. Positions of Atoms in the Technetium Coordination Sphere in *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]

atom	x	y	z
Tc1	0.65748 (2)	0.18379 (1)	0.47522 (2)
Cl1	0.76324 (7)	0.07576 (7)	0.2534 (1)
Cl2	0.64116 (7)	0.04193 (6)	0.5814 (1)
Cl3	0.67158 (7)	0.33203 (6)	0.3830 (1)
P1	0.54194 (6)	0.28400 (6)	0.6860 (1)
P2	0.84191 (6)	0.16708 (5)	0.6647 (1)
N1	0.5005 (2)	0.1922 (2)	0.2823 (3)

Table IV. Bond Distances (Å) Surrounding the Tc atom in *mer*-[Cl_3(pic)$_3$Tc] and *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]

	mer-[Cl_3(pic)$_3$Tc]	[Cl_3(pic)(PMe_2Ph)$_2$Tc]
Tc–Cl1	2.460 (2)	2.393 (2)
Tc–Cl2	2.320 (1)	2.353 (2)
Tc–Cl3	2.340 (1)	2.342 (2)
Tc–N1	2.148 (5)	2.198 (3)
Tc–N2	2.136 (5)	
Tc–N3	2.135 (4)	
Tc–P1		2.421 (2)
Tc–P2		2.425 (3)

Table V. Bond Angles (deg) Surrounding the Tc atom in *mer*-[Cl_3(pic)$_3$Tc] and *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]

	mer-[Cl_3(pic)$_3$Tc]	*mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc]
Cl1–Tc1–Cl2	91.57 (7)	91.01 (5)
Cl1–Tc1–Cl3	92.56 (7)	92.10 (5)
Cl2–Tc1–Cl3	175.87 (7)	176.74 (3)
N1–Tc1–Cl1	91.0 (1)	85.36 (9)
N1–Tc1–Cl2	90.3 (1)	90.42 (8)
N1–Tc1–Cl3	89.5 (1)	90.84 (8)
N1–Tc1–N2	179.2 (2)	
N1–Tc1–N3	90.5 (2)	
N2–Tc1–N3	89.4 (2)	
N2–Tc1–Cl1	89.2 (1)	
N2–Tc1–Cl2	90.5 (1)	
N2–Tc1–Cl3	89.6 (1)	
N3–Tc1–Cl1	178.3 (1)	
N3–Tc1–Cl2	87.6 (1)	
N3–Tc1–Cl3	88.3 (1)	
N1–Tc1–P1		91.17 (9)
N1–Tc1–P2		174.18 (7)
Cl2–Tc1–P1		86.37 (5)
Cl2–Tc1–P2		90.91 (6)
Cl3–Tc1–P1		90.59 (5)
Cl3–Tc1–P2		88.14 (6)
P1–Tc1–P2		94.57 (7)
P1–Tc1–Cl1		175.64 (3)
P2–Tc1–Cl1		88.95 (7)

Crystal Structure Determinations. A yellow single crystal of *mer*-[Cl_3(pic)$_3$Tc] suitable for X-ray diffraction was grown by slow solvent diffusion of hexanes into a chloroform solution of the compound and mounted on a glass fiber, which was placed in the beam of a Rigaku AFC5R diffractometer. Pertinent crystal data are given in Table I. Space group assignment was based on the systematic absence of $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. Intensities of three representative reflections, which were measured for every 150 reflections, remained constant throughout data collection so that no decay correction was necessary; however, an empirical absorption correction was applied. The Tc atom was located by direct methods and the structure solved from difference Fourier maps.[15,16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (C–H = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} value of the atom to which they were bonded. Refinement was by full-matrix least squares. Neutral-atom scattering factors[17] and anomalous dispersion effects were included in F_c;[18] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[12,19]

Solution of the structure of *mer*-[Cl_3(pic)(PMe_2Ph)$_2$Tc] were similarly performed, except that Mo Kα radiation was used. On the basis of

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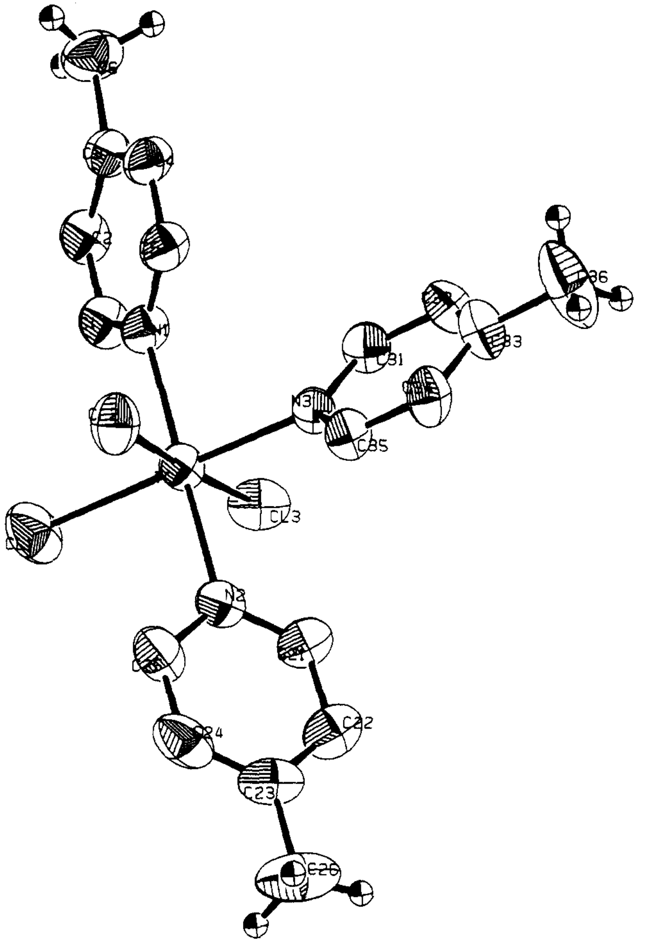

Figure 1. ORTEP diagram of *mer*-[$Cl_3(pic)_3Tc$]. Aromatic hydrogens have been removed for clarity.

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be P$\bar{1}$. No decay or absorption correction was applied.

Results

Synthesis. The compound *mer*-[$Cl_3(pic)_3Tc$] was obtained with PPh_3 or P(4-MeO-Ph)$_3$ as the reducing agent, while [Cl_3(pic)($PMe_2Ph)_2Tc$] was obtained with PMe_2Ph. At Tc/phosphine ratios greater than 1:4, the compound [Cl(pic)$_4$Tc–O–TcCl$_4$(pic)][6] was isolated from reaction mixtures by thin-layer chromatography and identified by its TLC R_f and UV–visible spectrum. Refluxing [Cl(pic)$_4$Tc–O–TcCl$_4$(pic)] with PMe_2Ph did not reduce the μ-oxo complex further.

Structures. The structure of *mer*-[$Cl_3(pic)_3Tc$] is shown in Figure 1, and that for *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$] is given in Figure 2. Table II contains the atomic coordinates of the atoms in the technetium coordination sphere of *mer*-[$Cl_3(pic)_3Tc$], and those for *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$] are listed in Table III. The bond distances and angles surrounding the essentially octahedral technetium atoms in both *mer*-[$Cl_3(pic)_3Tc$] and *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$] are listed in Tables IV and V, respectively.

Compound Characterization. The values of μ_{eff} for these compounds are significantly less than that calculated for strong spin–orbit coupling (μ_{eff} = 3.39 μ_B, λ = -495 cm^{-1})[20] in a Tc^{III} ion but are reasonably close to the spin-only value of 2.83 μ_B expected for a low-spin d^4 ion, suggesting little spin–orbit coupling. On the other hand, such a value could also arise from spin–orbit coupling in conjunction with a ligand field that departs appreciably from octahedral symmetry.[20] Some evidence for the former case is that the electron spin relaxation times are sufficiently short so as to not greatly broaden the ^{1}H NMR peaks, which is a feature of triply degenerate (T) ground states.[21]

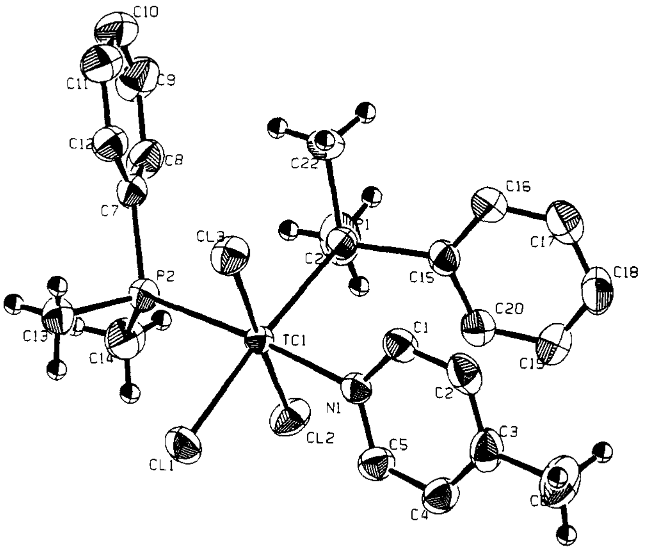

Figure 2. ORTEP diagram of *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$]. Aromatic hydrogens have been removed for clarity.

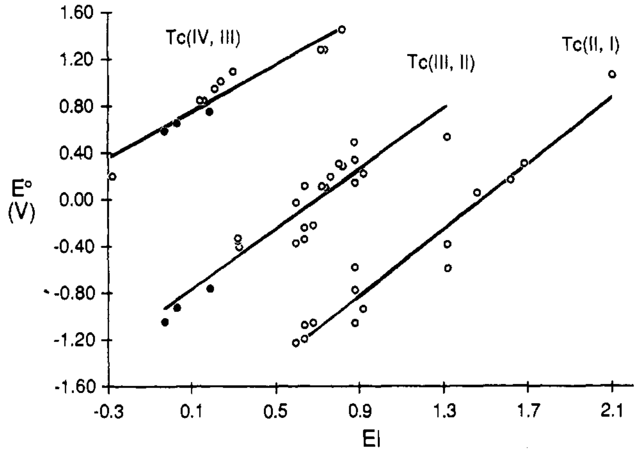

Figure 3. Plot of $E°$ values for Tc^{III,II} couples versus $\sum_{i=1}^{n} a_i E_L(i)$. Solid points (●) are from this work. Parameters and references for other points are given in the supplementary material.

The Tc^{II,III} reduction potentials for *mer*-[$Cl_3(pic)_3Tc$] and *mer*-[$Cl_3(py)_3Tc$] in 0.1 M ($Et_4N)ClO_4$ in DMF are 600 ± 12 and 660 ± 3 mV (vs NHE), respectively. The $E°$ values for the Tc^{III,II} couples for the same compounds are -1040 ± 20 and -921 ± 3 mV, respectively. The relative cyclic voltammetric peak heights (i_{pc}/i_{pc} = 1) and peak separations (80–90 mV) for both sets of couples were comparable with those of the ferrocene internal standard, indicating that the electron transfers are reversible on the cyclic voltammetric time scale. The Tc^{IV,III} reduction potential for *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$] is also reversible by the same criteria and occurs at 760 ± 12 mV; however, the Tc^{III,II} couple is irreversible, with almost no return oxidation wave, and occurs at an estimated potential of -760 mV. A new oxidation wave is apparent at -441 mV following the reduction of *mer*-[Cl_3(pic)($PMe_2Ph)_2Tc$].

A recent appoach to the estimation of metal ion reduction potentials assumes that the effect of ligands on $E°$ is invariant for each ligand, so that a parameter (E_L) can be assigned to individual ligands, and that these effects are additive over the ligands present.[12] In Figure 3, the reduction potentials reported here are correlated with other $E°$ values for which ligand parameters are available. Each line in Figure 3 represents the least-squares fit to the data for each of the three technetium oxidation–reduction couples indicated. The slope and intercept

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Table VI. Electrochemical Parameters for Oxidation–Reduction Couples of Octahedral Technetium Complexes in Organic Solvents

Tc couple	slope S_M	std dev	int I_M	std dev	corr coeff	$E^\circ(Tc^{n+}(aq))$, V
II–I	1.39	0.12	−2.07	0.10	0.95	−1.74
III–II	1.29	0.08	−0.91	0.11	0.88	−0.60
IV–III	1.00	0.10	0.64	0.09	0.92	0.89

of each line allows other E° values to be estimated according to the equation:[12]

$$E^\circ = S_M \sum_{i=1}^{n} a_i E_{L(i)} - I_M$$

where n is the coordination number, a_i is the dentacity of a given ligand, and S_M and I_M are the slope and intercept for each technetium couple as listed in Table VI.

Discussion

Synthesis. The occurrence of $[Cl(pic)_4Tc–O–TcCl_4(pic)]$ in reaction mixtures at Tc:phosphine ratios >0.25 is consistent with the report of μ-oxo formation in an analogous synthetic system.[11] Since $[Cl(pic)_4Tc–O–TcCl_4(pic)]$ was not reduced under the reaction conditions that yielded the Tc^{III} compounds, it appears that the formation of mixed-valent, μ-oxo compounds can occur in competition with the synthesis of the technetium(III) complexes by O atom transfer from oxotechnetium(V) cores to phosphines.

Mazzi and co-workers reported that refluxing alkyldiphenylphosphines with $NH_4[TcO_4]$ in 0.5 M HCl in ethanol for 1 h yields $[TcX_3L_3]$ and $[TcX_2L_4]$, where X = Cl and Br and L = $PMePh_2$ and $PEtPh_2$, with the former being obtained in 0.6 M $PMePh_2$ and the latter in $[PMePh_2]$ = 0.2 M.[22] With dialkylphenylphosphines, $[TcX_3L_3]$ and $[TcX_2L_4]$, L = PMe_2Ph and PEt_2Ph, were similarly obtained. When the larger PPh_3 was employed, only $[TcX_4(PPh_3)_2]$ was obtained owing to steric hindrance arising from the phenyl groups. It was also suggested that steric forces cause the alkyldiphenylphosphine complexes to decompose more quickly than the dialkylphenyl analogues. The crystal structure of *mer*-$[Cl_3(PMe_2Ph)_3Tc]$ revealed high steric hindrance, so that its stability has been attributed to electronic factors.[23] Pearlstein has prepared *mer*-$[Cl_3(CH_3CN)(PPh_3)_2Tc]$ through the reaction of (n-Bu_4N)$[OCl_4Tc]$ with PPh_3 in acetonitrile. The acetonitrile ligand in this complex is readily replaced by small molecules such as CO and NO, but they do not participate appreciably in back-bonding with the Tc^{III}.[10] Consequently, the lability of the acetonitrile is probably due to a combination of the Tc^{III}'s inability to back-bond with it, the poor σ-donor characteristics of acetontrile, and some steric repulsion by the PPh_3 groups.

The properties of the small and more basic PMe_2Ph (cone angle $\theta = 122°$; $pK_a = 6.5$; electronic parameter $\chi = 10.6$) in comparison with PPh_3 ($\theta = 145°$; $pK_a = 2.73$; $\chi = 13.25$)[24,25] allow the former to cross the energy threshold for facile coordination to the *mer*-Cl_3Tc moiety, while the latter fails to coordinate. The relative importance of the steric and electronic effects of these two ligands were evaluated by running the reaction with $P(4\text{-}MeO\text{-}Ph)_3$, which has a cone angle identical with that of PPh_3 but an electron-donor capacity ($pK_a = 4.59$; $\chi = 10.5$) similar to that of PMe_2Ph. Since coordination of $P(4\text{-}MeO\text{-}Ph)_3$ does not occur to any significant extent, it appears that the steric effect predominates in preventing either triphenylphosphine ligand from binding under these reaction conditions. Consequently, manipulating the size of the phosphine ligand can modulate the ratio of phosphine to pyridine ligands in complexes of this type. By analogy to Mazzi's work, the irreversible reduction of *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ is probably due to the loss of a chloride as a result of steric forces generated by the phosphines. This is consistent with the higher potential of the new wave that appears and the relative stability of the unhindered *mer*-$[Cl_3(pic)_3Tc]$ following reduction, even though picoline is less able than PMe_2Ph to delocalize the added charge off the metal.

Structure. In the structure of *mer*-$[Cl_3(pic)_3Tc]$, the Tc–N bond lengths are within the range (2.13 ± 0.05 Å) expected for Tc^{III} complexes.[9–11,26–28] The slight lengthening of the Tc–Cl1 bond relative to other Tc^{III}–Cl distances (2.36 ± 0.05 Å)[9,10,25,27] is due to a mild steric repulsion generated by the two adjacent cis chlorides, which are bent slightly away from Cl1. The analogous Tc–Cl1 bond in *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ is also slightly longer than those of the two chlorides opposite one another. Owing to a slight steric repulsion generated by the larger PMe_2Ph ligands, the Tc–N1 bond is slightly longer in this complex than analogous bonds in other Tc^{III} complexes. The Tc–P bonds are both within the expected range (2.44 ± 0.04 Å)[9,10,25–27] for complexes of this type.

Electrochemistry. The reduction potentials of these complexes are fairly negative relative to other $Tc^{III,II}$ couples[29] owing to the coordination of three halides. This fetaure is useful in determining the dependence of $Tc^{III,II}$ potentials as a function of E_L parameters over a wide range and in allowing the $Tc^{IV,III}$ reduction potentials to be determined. When these data are fitted in a linear fashion and compared to a similar plot for $Tc^{II,I}$ couples (cf. Figure 3), the lines approach being parallel, indicating that each technetium oxidation state is susceptible to a similar degree to the stabilization (or destabilization) effects exerted by a fairly broad cross section of ligands. The slopes from these analyses are among the highest of any couples yet reported in nonaqueous media, which verifies that the reduction potential of technetium are more readily modified by subtle changes in the ligands than most other transition-metal ions. Since the atomic size, Pauling electronegativity, and first ionization potential of Tc are similar to those of the metalloids and other elements exhibiting a broad range of oxidation states under nonforcing conditions, and Tc has well-extended 4d orbitals capable of multiply bonding in either a dative or retrodative fashion, which tends to stabilize both its higher and lower oxidation states, respectively, it seems reasonable that Tc should be fairly sensitive to changes in oxidation states as a function of its coordination sphere. While Re^{III} complexes similar to those reported here often exhibit E° values of approximatly 0.2 V less than those of Tc^{III},[30,31] this correspondency should not be taken as a generality, since the slope parameter for $Tc^{III,II}$ is probably higher than that for $Re^{III,II}$. Indeed, the S_M for $Tc^{IV,III}$ estimated here is higher than that for $Re^{IV,III}$ (S_M = 0.85 ± 0.05, I_M = 0.50 ± 0.13). A similar caveat holds for comparisons with Mn, which has S_M and I_M values of 0.81 ± 0.02 and −1.76 ± 0.08, respectively, for the $Mn^{II,I}$ couple.[12]

Since an electron added to either Tc^{II}, Tc^{III}, or Tc^{IV} goes into a nominal t_{2g} orbital in octahedral symmetry, it is not surprising that the slopes of the lines in Figure 3 are similar. Ligand effects altering the relative energies of these orbitals in adjacent oxidation states can be expected to be similar. However, lines parallel to those in Figure 3 should not be expected for couples, such as $Tc^{I,0}$, in which the electron is added to an e_g orbital or when the octahedral field is strongly distorted, as in complexes containing the $[Tc{\equiv}O]^{3+}$ or $[Tc{\equiv}N]^{2+}$ cores in C_{4v} symmetry. The electro-

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chemical parameters for Tc provide estimates of the reduction potentials of the putative aqua ions, $[Tc(H_2O)_6]^{n+}$ (n = 2-4), in *organic* media (see Table VI). These provide an indication of the *thermodynamic* stabilities of these ions, which suggest that (1) $[Tc(H_2O)_6]^+$ is probably unstable in any protic media, (2) $[Tc(H_2O)_6]^{2+}$ and $[Tc(H_2O)_6]^{3+}$ may be observable under inert atmosphere, and (3) $[Tc(H_2O)_6]^{4+}$ may be attainable in highly acidic media at Tc concentrations sufficiently low to inhibit polynuclear formation.

The synthetic reactions, steric effects, and electrochemical parameters quantified here confirm that the chemistry of technetium is somewhat more pliable than that of other transition metals. While its central position in the periodic table is often invoked as an explanation for this, the fundamentals of this question remain to be answered at the electronic level.

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Supplementary Material Available: For *mer*-$[Cl_3(pic)_3Tc]$ and *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$, tables of positions for all atoms, temperature factors for non-hydrogen atoms, bond distances and angles, least-squares planes, and electrochemical data (19 pages); listing of calculated and observed structure factor amplitudes (49 pages). Ordering information given on any current masthead page.

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Synthesis and Spectroscopy of Copper(II) Compounds of a Chelating Imidazole–Thioether Ligand. Molecular Structures of (1,5-Bis(4-imidazolyl)-3-thiapentane)dichlorocopper(II), (1,5-Bis(4-imidazolyl)-3-thiapentane)bis(thiocyanato-*N*)copper(II), and Bis[(μ-chloro)(1,5-bis(4-imidazolyl)-3-thiapentane)copper(II)] Bis(perchlorate)

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The synthesis and characterization of copper coordination compounds with the novel tridentate ligand 1,5-bis(4-imidazolyl)-3-thiapentane (abbreviated as bimtp) are described. The compounds are of the general formula $[Cu(bimtp)X_2]$ with X^- = Cl^-, Br^-, NO_3^-, and NCS^-. Also, compounds with mixed anions were isolated with general formula $[Cu(bimtp)X]Y$ with X^- = Cl^- and Y^- = ClO_4^- and BF_4^-. bimtp acts as a tridentate ligand in all compounds, both imidazole nitrogens and the thioether sulfur participating in the coordination of copper. All compounds of the formula $[Cu(bimtp)X_2]$ are five-coordinated in a distorted trigonal-bipyramidal or distorted square-pyramidal geometry. In the chloro-bridged dimer $[Cu(bimtp)Cl]_2(ClO_4)_2$, the copper ion is five-coordinated in a square pyramid. Single crystals of $[Cu(bimtp)Cl_2]$, $[Cu(bimtp)(NCS)_2]$, and $[Cu(bimtp)Cl]_2(ClO_4)_2$ were used for structure determinations, using heavy-atom techniques and refined by least-squares methods. $[Cu(bimtp)Cl_2]$: orthorhombic, space group $P2_12_12_1$, a = 7.605 (2) Å, b = 8.280 (1) Å, c = 22.644 (5) Å, Z = 4, T = 293 K; R = 0.032, R_w = 0.040 for 1605 reflections; Cu–N = 1.97 Å, Cu–Cl = 2.48 and 2.32 Å, Cu–S = 2.50 Å, in an almost ideal trigonal-bipyramidal geometry. $[Cu(bimtp)(NCS)_2]$: monoclinic, space group $P2_1/n$, a = 13.000 (2) Å, b = 16.400 (3) Å, c = 8.131 (1) Å, β = 105.9 (1)°, Z = 4, T = 293 K; R = 0.045, R_w = 0.047 for 3035 reflections; Cu–N = 1.96 and 1.98 Å, Cu–NCS = 1.99 and 2.00 Å, Cu–S = 2.60 Å, in a distorted trigonal-bipyramidal geometry. $[Cu(bimtp)Cl]_2(ClO_4)_2$: monoclinic, space group $P2_1/c$, a = 8.703 (2) Å, b = 13.776 (3) Å, c = 12.857 (2) Å, β = 97.47 (2)°, Z = 2, T = 293 K; R = 0.046, R_w = 0.057 for 3151 reflections; Cu–N = 1.95 Å, Cu–Cl = 2.31 Å, Cu–Cl′ = 2.86 Å, Cu–S = 2.42 Å, Cu–Cu = 3.55 Å, in a distorted square-pyramidal geometry. The compounds were characterized further by EPR and ligand field spectroscopy. Cyclic voltammetry of $[Cu(bimtp)Cl_2]$ and $[Cu(bimtp)Cl]_2(ClO_4)_2$ yielded quasi-reversible waves with $E^{\circ\prime}$ between 0.07 and 0.16 V (with respect to SCE).

Introduction

More than a decade ago the structure of plastocyanin was determined in the reduced as well as the oxidized form.[2,3] The active site of this and other blue copper proteins is constituted from two histidine nitrogens, one methionine thioether sulfur, and one thiolate sulfur of cysteine, surrounding the copper in a distorted tetrahedron. In the last decade the possible synthesis of model compounds has been studied extensively. So far, no compounds mimicking the particular properties of type I copper proteins could be prepared.

Recently a new method has been found, enabling the synthesis of a large variety of 4(5)-substituted imidazole and thioether-containing ligands.[4] In the resulting series of imidazole–thioether ligands, the coordination bite between the imidazole N and the thioether S atom is too small. Coordination compounds containing a five-membered chelate ring are obtained, with the N-metal–S coordination angle never exceeding 84.2°[5-7] A different series of imidazole–thioether ligands, containing a four-bond N-to-S bridge, was therefore synthesized. The longer N-to-S bridge enables the formation of a six-membered chelate ring, increasing the bite of the ligand. This paper describes the synthesis and characterization of coordination compounds of the ligand 1,5-bis(4-imidazolyl)-3-thiapentane (bimtp) with the transition metal copper and various anions. A schematic drawing of the ligand bimtp is shown in Figure 1. To investigate the binding in detail and to illustrate the chelating nature of the ligand, some X-ray

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