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Synthesis, Characterization, and X-ray Structural Determinations of Technetium(V)-Oxo-Tetradentate Amine Oxime Complexes

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A number of neutral and lipophilic oxo(L)technetium(V) complexes have been synthesized, where L is a tetradentate amine oxime for which 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (Pn(AO)$_2$) is the prototype. These TcOL complexes have been characterized by their visible–UV spectra, IR spectra, ^{1}H and ^{13}C NMR spectra, fast atom bombardment (FAB) mass spectra, and X-ray diffraction studies. The X-ray crystal structures of four of these complexes show them to be mono(oxo)technetium(V) species with the oxo group situated at the apex of a square pyramid and the technetium lying an average of 0.68 Å above the plane defined by the four nitrogen atoms of the tetradentate amine oxime. In each case the tetradentate amine oxime ligand loses three protons on coordination to the technetium(V) center, resulting in an overall charge of zero for the complex, multiple bonding between the amide nitrogens and the technetium, and intramolecular hydrogen bonding between the oxime oxygens. *meso*-TcOPn(AO-CH$_3$)$_2$, TcO$_3$N$_4$C$_{11}$H$_{21}$, crystallizes in the orthorhombic system, space group $P2_12_12_1$, a = 8.607 (2) Å, b = 10.327 (2) Å, c = 16.345 (3) Å, and Z = 4; *dl*-TcO[(CH$_3$)$_2$Pn(AO-CH$_3$)$_2$], TcO$_3$N$_4$C$_{13}$H$_{25}$, crystallizes in the orthorhombic system, space group $P2_12_12_1$, a = 6.948 (2) Å, b = 12.460 (3) Å, c = 19.299 (4) Å, and Z = 4; *meso*-TcO[(CH$_3$)$_2$Pn(AO-CH$_3$)$_2$], TcO$_3$N$_4$C$_{13}$H$_{25}$, crystallizes in the monoclinic system, space group $P2_1/n$, a = 11.231 (3) Å, b = 24.238 (7) Å, c = 12.645 (7) Å, β = 93.90 (3)°, and Z = 8; TcOPn(AO)(AO-CH$_3$), TcO$_3$N$_4$C$_{12}$H$_{23}$, crystallizes in the monoclinic system, space group $P2_1/n$, a = 13.048 (3) Å, b = 10.328 (2) Å, c = 12.984 (2) Å, β = 116.68 (2)°, and Z = 4.

Introduction

The use of single photon emission computerized tomography (SPECT) as a measure of regional cerebral blood flow has led to an increased interest in the development of technetium-99m complexes for imaging the brain.[1-3] Recently in our laboratories, technetium-99m was shown to form a stable, neutral, and lipophilic complex with 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (propylene amine oxime; Pn(AO)$_2$),[4] a tetradentate amine oxime ligand (see Table I). Biodistribution studies in laboratory test animals have shown this complex to diffuse across the intact blood brain barrier and be efficiently extracted by normal brain.[5] However, it is not sufficiently retained by the brain to image its cerebral distribution by using conventional SPECT instrumentation. A number of derivatives of Pn(AO)$_2$ have been synthesized[6] and their technetium-99m complexes evaluated.[6-8] They have been shown to have a high brain uptake but a much slower rate of cerebral clearance[6-8] than does ^{99m}TcPn(AO)$_2$.

The X-ray structural determination of the technetium-99 complex of Pn(AO)$_2$ showed it to be the five-coordinate mono(oxo)technetium(V) species TcOPn(AO)$_2$,[9] with Pn(AO)$_2$ occupying the basal plane of a square pyramid. Upon coordination the Pn(AO)$_2$ ligand loses three protons, resulting in a −3 charge on the ligand and a zero overall charge for the technetium(V) complex.

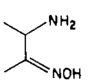
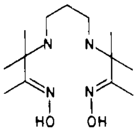
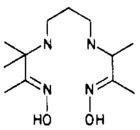
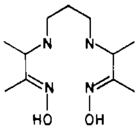
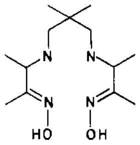
To better understand the chemistry of these potential brain agents, a number of technetium-99 complexes of derivatives of Pn(AO)$_2$ have been synthesized and characterized. Substituents on the amine oxime backbone were varied (Table I) to probe the effect(s) of these structural changes on the properties of the resultant technetium(V) complexes.

Experimental Section

General Data. Syntheses were performed with technetium-99, a low energy (0.292 MeV) β-particle emitter with a half-life of 2.12 × 10^5 years. When handled in milligram quantities, Tc-99 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 Pn(AO)$_2$ ligand was provided by R. K. Murmann and was synthesized and purified as previously described.[10-12] The Pn(AO)(AO-CH$_3$), Pn(AO-CH$_3$)$_2$ and (CH$_3$)$_2$Pn(AO-CH$_3$)$_2$ ligands (see Table I) were provided by Amersham International. Pn(AO-CH$_3$)$_2$ was a 50/50 mixture of the *dl* and meso isomers, while (CH$_3$)$_2$Pn(AO-CH$_3$)$_2$ was available in both the *dl* and meso isomer forms. All were used as received. Technetium-99, as a solution of ammonium pertechnetate, was obtained from Oak Ridge

Table I. Ligand Nomenclature

ligand	acronym	name
–CH$_2$CH$_2$CH$_2$–	Pn	propylene
	AO	3-amino-3-methyl-2-butanone oxime or amine oxime
	Pn(AO)$_2$ ≡ PnAO[a]	3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime
	Pn(AO)(AO-CH$_3$) ≡ PM-PAO[b]	3,3,9-trimethyl-4,8-diazaundecane-2,10-dione dioxime
	Pn(AO-CH$_3$)$_2$ ≡ TM-PAO[b]	3,9-dimethyl-4,8-diazaundecane-2,10-dione dioxime
	(CH$_3$)$_2$Pn(AO-CH$_3$)$_2$ ≡ HM-PAO[b]	3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime

[a] PnAO is the acronym used for this ligand in previously reported papers. For example, see ref 9. [b] This series of ligands are abbreviated as shown to illustrate the substitution of a hydrogen for a methyl group, or vice versa, on the AO or Pn portion of the backbone. The numbering system used hereafter for the ligand backbone is shown in Figure 1. The substitution of one hydrogen for a methyl group on carbon 3 gives Pn(AO)(AO-CH$_3$); two hydrogen atoms for two methyl groups on carbons 3 and 4 ives Pn(AO-CH$_3$)$_2$; and finally two methyl groups for two hydrogen atoms on carbon 13 and two hydrogen atoms for two methyl groups on carbons 3 and 4 gives (CH$_3$)$_2$Pn(AO-CH$_3$)$_2$. PM-PAO (pentamethyl propylene amine oxime), TM-PAO (tetramethyl propylene amine oxime), and HM-PAO (hexamethyl propylene amine oxime) are the acronyms used in the nuclear medicine literature. This last ligand, HM-PAO, has proven to be the most useful medically and is undoubtedly the abbreviation that will continue to be used in that field because of the importance of this ligand. We have chosen, however, to use the more detailed formulas here to explain more clearly the structure of each ligand. Both systems of acronyms are shown in this table.

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Table II. TLC Characterization

	R_f values			
	silica gel			reversed phase 75/25 (v/v) methanol/H_2O
complex	ether	acetone	methanol	
$TcOPn(AO)_2$	0.23	0.92	0.80	0.86
meso-$TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$	0.24	0.90	0.82	0.87
dl-$TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$	0.23	0.91	0.84	0.84
$TcOPn(AO)(AO\text{-}CH_3)$	0.15	0.82	0.76	0.80
$TcOPn(AO\text{-}CH_3)_2$	0.09	0.77	0.70	0.76

Table III. Crystal Data, Data Collection Parameters, and Refinement Parameters

	meso-$TcOPn(AO\text{-}CH_3)_2$	*dl*-$TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$	*meso*-$TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$	$TcOPn(AO)(AO\text{-}CH_3)$
formula	$TcO_3N_4C_{11}H_{21}$	$TcO_3N_4C_{13}H_{25}$	$TcO_3N_4C_{13}H_{25}$	$TcO_3N_4C_{12}H_{23}$
fw	355.3	383.4	383.4	369.3
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a, Å	8.607 (2)	6.948 (2)	11.231 (3)	13.048 (3)
b, Å	10.327 (2)	12.460 (3)	24.238 (7)	10.328 (2)
c, Å	16.345 (3)	19.299 (4)	12.645 (7)	12.984 (2)
α, deg	90	90	90	90
β, deg	90	90	93.90 (3)	116.68 (2)
γ, deg	90	90	90	90
V, Å^3	1453 (1)	1671 (1)	3434 (1)	1563 (1)
Z	4	4	8	4
D_{exptl}, g/cm^3	1.626 (3)	1.516 (3)	1.483 (3)	1.569 (3)
cryst size, mm	~0.20 × 0.30 × 0.30	~0.08 × 0.13 × 0.30	~0.10 × 0.20 × 0.23	~0.10 × 0.25 × 0.30
μ, cm^{-1}	9.77	8.54	8.315	9.10
abs cor range (empirical)	*a*	0.88–1.0	*a*	0.84–1.0
scan method	θ–2θ steps	θ–2θ steps	θ–2θ steps	θ–2θ steps
scan range	$0.70 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$	$0.50 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$
scan speed	*b*	*b*	*b*	*b*
no. of reflcns measd	2579	1455	4263	2277
no. of indep reflcns	2276	1352	3918	2029
no. of indep reflcns above 2σ used in refinement	2167	1191	2980	1608
no. of variables	256	190	387	273
$R(F)$	0.021	0.032	0.030	0.037
$R_w(F)$	0.029	0.039	0.041	0.045
max shift error on last cycle	0.29	0.025	0.04	0.22

[a] Not used (ψ scans indicated less than 2% range). [b] Variable to obtain 3% statistics up to a 90-s maximum.

National Laboratory, Oak Ridge, TN. Silica gel (NMFC No. 46050), silica gel 60 TLC plates (catalog no. 5538-7), and reversed-phase TLC plates (RPS-F) were obtained from J. T. Baker Chemical Co., MCB Reagents (Merck), and Analtech, respectively.

Oxo(tetradentate amine oxime)technetium(V) Complexes, TcOL (L = $Pn(AO)_2$, $Pn(AO)(AO\text{-}CH_3)$, $Pn(AO\text{-}CH_3)_2$, $(CH_3)_2Pn(AO\text{-}CH_3)_2$). A typical preparation is given for $TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$. 0.031 g (0.11 mmol) of $(CH_3)_2Pn(AO\text{-}CH_3)_2$ was dissolved in 5 mL of 0.9% saline and 1 drop of 5 M HCl. A 1.5-mL aliquot (0.055 mmol) of 3.64×10^{-2} M NH_4TcO_4, 2 mL of 1 M $NaHCO_3$ and 30 mL of diethyl ether were then added. A 0.033-g sample (0.12 mmol) of stannous tartrate, suspended in ca. 1.5 mL of 0.9% saline, was added dropwise, and the reaction was stirred at room temperature for ca. 10 min. The resultant mixture became bright yellow. The ether layer (containing the desired complex) was separated, and the aqueous layer was repeatedly extracted with ether until a yellow color was no longer observed in the ether. The ether extracts were combined, dried by gravity filtration through anhydrous sodium sulfate, and concentrated at <25 °C to ~1 mL with a rotary evaporator. Unreacted ligand was removed from the solution by sorbing the ether concentrate onto a column of silica gel in ether, washing with ca. 10 mL of ether, and displacing the yellow-orange $TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$ with methanol, leaving behind the ligand. The $TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]$ containing eluent was filtered, taken to dryness (<25 °C) on a rotary evaporator, dissolved in a minimum volume of ether (~1 mL), and allowed to crystallize at ca. −20 °C. The orange to rust-colored crystals were collected, washed quickly with cold ether, and air-dried.

The yields of these complexes were 70–90%, depending on the ligand. Their TLC behavior is shown in Table II.

Physical Measurements. Visible–UV spectra were recorded at ambient temperature on either a Perkin-Elmer 576 ST spectrophotometer or an LKB Ultraspec 4050 spectrophotometer interfaced to an Apple IIe computer. The infrared (IR) spectra were recorded as Nujol mulls on a Perkin-Elmer 180 grating infrared spectrometer. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 300-MHz Nicolet NT-300 spectrometer. The positive ion fast atom bombardment mass spectra (FABMS) were recorded in a glycerol matrix on a Kratus MS 25 mass spectrometer with a DS-55 data system.

Collection and Reduction of X-ray Data. Diffraction data collection, crystal parameters, and refinement information are summarized in Table III. For all compounds the data were collected at 22 (1) °C on a Enraf-Nonius CAD4 automated diffractometer using graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Lattice constants were obtained by least-squares fits of the setting angles of 25 carefully centered reflections for each compound. The intensities of three standard reflections measured after every 7200 s of X-ray exposure showed no significant variation. Orientation was checked after every 200 reflections

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Table IV. Visible–UV Spectrophotometric Results

complex	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	shoulder, nm
$\mathrm{TcOPn(AO)_2}$	methanol	295 (8080)	~360
$\mathrm{TcOPn(AO)(AO\text{-}CH_3)}$	methanol	292 (7700)	~350
$\mathrm{TcOPn(AO\text{-}CH_3)_2}$	methanol	291 (6500)	~345
meso-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$	methanol	291 (8100)	~360
dl-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$	methanol	292 (6960)	~350

Table V. Infrared Spectral Results[a]

complex	Tc=O stretch, cm^{-1}
$\mathrm{TcOPn(AO)_2}$	923
$\mathrm{TcOPn(AO)(AO\text{-}CH_3)}$	921
$\mathrm{TcOPn(AO\text{-}CH_3)_2}$	920
meso-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$	908
dl-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$	911

[a] IR spectra were obtained as Nujol mulls.

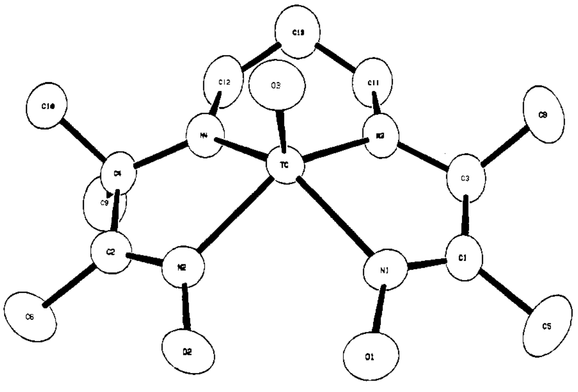

Figure 1. ORTEP representation of oxo(3,3,9-trimethyl-4,8-diazaundecane-2,10-dione dioximato(3–)-*N*,*N*′,*N*″,*N*‴)technetium(V), $\mathrm{TcOPn(AO)(AO\text{-}CH_3)}$.

with the use of three orientation standards. Recentering, using 25 reflections, was done if any of the orientation standards were found to be significantly off center.

Solution and Refinement of the Structure. All four structures were solved by conventional Patterson and Fourier methods. The full-matrix least-squares refinements minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma_{counting} + (0.05F_o^2)^2)/4F_o^2$. Atomic scattering factors were taken from ref 13 and included anomalous scattering contributions. The maximum electron densities on the final difference Fourier syntheses were less than 0.5 e/Å^3.

Results

The technetium(V) tetradentate amine oxime complexes were readily prepared by the reduction of pertechnetate with stannous ion in the presence of ligand. The neutral, lipophilic TcOL was then extracted into diethyl ether and isolated.

The chromatographic behaviors of these complexes on silica gel and reversed-phase TLC plates are presented in Table II. The visible–UV spectrophotometric data are given in Table IV. All the complexes exhibit a maximum absorbance at ca. 290 nm with a shoulder at ca. 350 nm. The infrared spectra all show the expected Tc=O stretch at ca. 920 cm^{-1} (Table V). The ^{1}H NMR spectral results are presented in Table VI and the ^{13}C NMR results in Table VII. The ^{1}H and ^{13}C NMR spectra are as expected for the amine oxime ligands coordinated to the technetium(V) center. The positive ion fast atom bombardment mass spectra of these complexes gave molecular ion peaks at $(M + 1)^+$.

The X-ray diffraction analyses of $\mathrm{TcO[Pn(AO)(AO\text{-}CH_3)]}$, *meso*-$\mathrm{TcO[Pn(AO\text{-}CH_3)_2]}$, *dl*-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$, and *meso*-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$ show all four complexes to be five-coordinate and to have square-pyramidal geometries with the oxo group occupying the apical position, as was found for the $\mathrm{TcOPn(AO)_2}$ structure.[9] The technetium atom lies about 0.68 Å above the plane defined by the four nitrogen atoms. On coordination to the technetium(V) center, the amine oxime ligands lose three protons (one oxime proton and two amine protons), as was the case in the $\mathrm{TcOPn(AO)_2}$ complex.[9] This results in a neutral complex and a strong intramolecular hydrogen bond between oxime oxygen atoms.

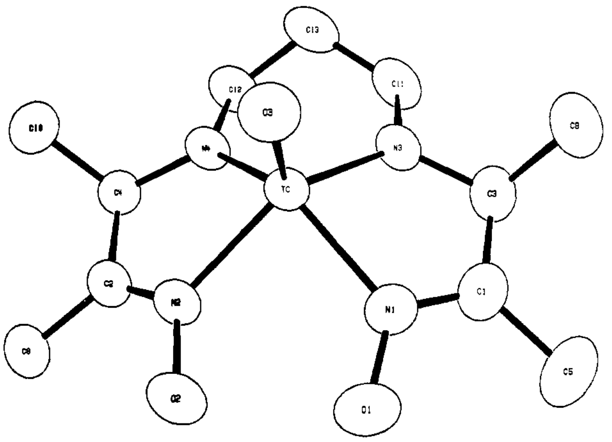

Figure 2. ORTEP representation of *meso*-oxo(3,9-dimethyl-4,8-diazaundecane-2,10-dione dioximato(3–)-*N*,*N*′,*N*″,*N*‴)technetium(V), *meso*-$\mathrm{TcOPn(AO\text{-}CH_3)_2}$.

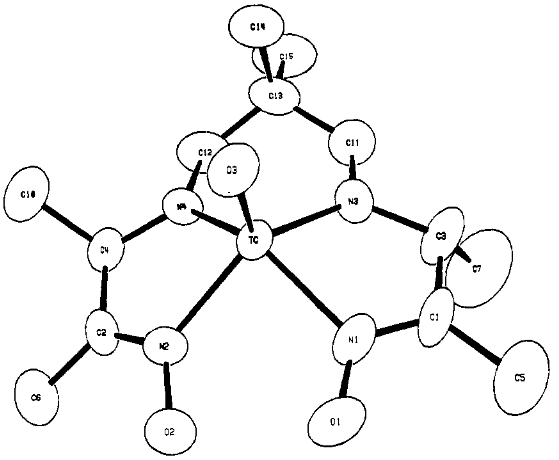

Figure 3. ORTEP representation of *dl*-oxo(3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(3–)*N*,*N*′,*N*″,*N*‴)technetium(V), *dl*-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$.

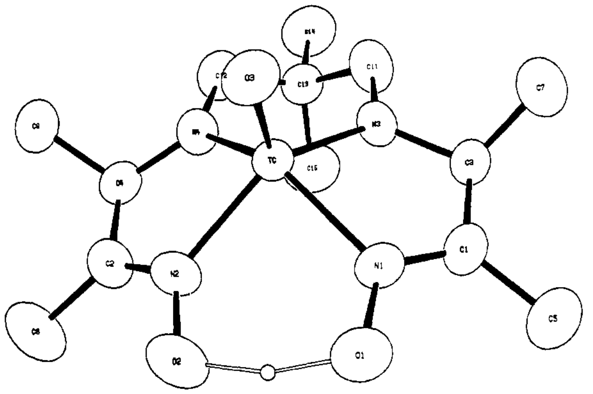

Figure 4. ORTEP representation of *meso*-oxo(3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(3–)-*N*,*N*′,*N*″,*N*‴)technetium(V), *meso*-$\mathrm{TcO[(CH_3)_2Pn(AO\text{-}CH_3)_2]}$.

Crystal data together with details of the determinations are summarized in Table III; atomic fractional coordinates and isotropic thermal parameters are listed in Table VIII. Selected bond lengths and angles are listed in Table IX and ORTEP representations

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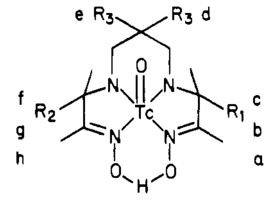
(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

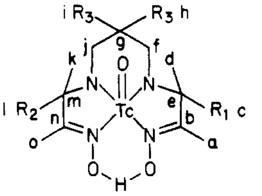
Table VI. ^{1}H NMR Spectral Results[a]



complex	R_1	R_2	R_3	protons	multiplicity	τ
TcOPn(AO)$_2$	CH_3	CH_3	H	a = h = CH_3	singlet	2.226
				b = g = CH_3	2 singlets	1.365, 1.406
				c = f = CH_3		
TcOPn(AO)(AO-CH_3)	CH_3	H	H	a, h = CH_3	2 singlets	2.280, 2.305
				b, c = CH_3	2 singlets	1.402, 1.470
				f = CH_3	doublet	1.498, 1.521
meso-TcOPn(AO-CH_3)$_2$	H	H	H	a = h = CH_3	singlet	2.281
				c = f = CH_3	doublet	1.489, 1.512
dl-TcOPn(AO-CH_3)$_2$	H	H	H	a, h = CH_3	2 singlets	2.281, 2.317
				c, f = CH_3	2 doublets	1.378, 1.401
						1.497, 1.519
meso-TcO[(CH_3)$_2$Pn(AO-CH_3)$_2$]	H	H	CH_3	a = h = CH_3	singlet	2.283
				c = f = CH_3	doublet	1.469, 1.492
				d, e = CH_3	2 singlets	0.914, 1.007
dl-TcO[(CH_3)$_2$Pn(AO-CH_3)$_2$]	H	H	CH_3	a, h = CH_3	2 singlets	2.289, 2.325
				c, f = CH_3	2 doublets	1.381, 1.405
						1.476, 1.498
				d, e = CH_3	2 singlets	1.009, 1.043

[a] Only methyl signals are included. The solvent was $CDCl_3/Me_4Si$. The meso and *dl* isomers of TcOPn(AO-CH_3)$_2$ were run as a mixture.

Table VII. ^{13}C NMR Spectral Results[a]



complex	R_1	R_2	R_3	τ				
				a, o, c, l, d, k, h, i[b]	b, n	e, m	f, j	g
TcOPn(AO)$_2$	CH_3	CH_3	H	12.760	174.425	79.142	49.650	33.149
				23.475				
				24.011				
TcOPn(AO)(AO-CH_3)	CH_3	H	H	12.363 23.352	171.388	e: under	49.339	32.819
				12.741 23.916	174.296	$CDCl_3$ or	53.382	
				17.966		not obsd		
						m: 79.649		
meso- and *dl*-TcOPn(AO-CH_3)$_2$	H	H	H	12.280 17.685	171.293	under $CDCl_3$	52.961	32.270
				12.388 18.047	171.610	or not	53.119	32.452
				13.070 18.363		obsd	53.582	
meso-TcO[(CH_3)$_2$Pn(AO-CH_3)$_2$]	H	H	CH_3	12.112	170.880	79.347	64.914	37.547
				17.568				
				24.587				
				26.196				
dl-TcO[(CH_3)$_2$Pn(AO-CH_3)$_2$]	H	H	CH_3	12.217 24.202	171.039	78.325	63.334	37.128
				13.224 27.745	171.191	78.554	65.147	
				17.708				
				18.415				

[a] Solvent: $CDCl_3/Me_4Si$. The *meso*- and *dl*-TcOPn(AO-CH_3)$_2$ isomers were run as a mixture. [b] Methyl carbons cannot be definitively assigned and are reported together.

are given in Figures 1–5. Parameters for the hydrogen atoms, thermal parameters, listings of observed and calculated structure factors, bond distances and angles not reported, and least-squares planes are available as supplementary material. All calculations were done on a PDP 11/34 computer with the Enraf Nonius SDP package. The hydrogen atoms were refined in the structures of TcO[Pn(AO)(AO-CH_3)] and *meso*-TcOPn(AO-CH_3)$_2$. In the remaining two structures the hydrogen atoms were held in fixed positions due to the limited data.

Discussion

The technetium(V) complexes were prepared by the reduction of pertechnetate in the presence of ligand. Attempts to synthesize these complexes by direct substitution from [$TcOCl_4^-$] proved unsuccessful (low to zero yields were obtained).

These neutral technetium(V) complexes are all quite lipophilic, as is indicated by their ability to be readily extracted into diethyl ether. On the basis of the number of methyl groups on the amine oxime backbone, the relative order of predicted lipophilicity of these TcOL complexes can be written as TcOPn(AO)$_2$ ~ TcO[(CH_3)$_2$Pn(AO-CH_3)$_2$] > TcOPn(AO)(AO-CH_3) > TcOPn(AO-CH_3)$_2$. This same ordering is observed in their TLC behavior, illustrated in Table II, which is consistent with a correlation between R_f values and lipophilicity. The more lipophilic the

Table VIII. Atomic Fractional Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms

atom	*x*	*y*	*z*	*B*, Å^2
TcOPn(AO)(AO-CH$_3$)				
Tc	−0.09260 (3)	0.08314 (4)	0.20651 (4)	2.594 (9)
O1	−0.0206 (4)	0.3626 (4)	0.1964 (4)	5.4 (1)
O2	0.1348 (3)	0.2049 (4)	0.2540 (4)	5.0 (1)
O3	−0.0862 (3)	0.0758 (4)	0.3778 (3)	3.8 (1)
N1	−0.1109 (4)	0.2764 (4)	0.1547 (4)	3.6 (1)
N2	0.0730 (4)	0.0931 (5)	0.2248 (4)	3.3 (1)
N3	−0.2483 (4)	0.0914 (5)	0.0901 (4)	3.4 (1)
N4	−0.0722 (4)	−0.0848 (5)	0.1560 (4)	3.3 (1)
C1	−0.2114 (5)	0.3169 (6)	0.0866 (5)	3.6 (1)
C2	0.1218 (5)	−0.0131 (6)	0.2186 (5)	3.7 (1)
C3	−0.3020 (5)	0.2172 (6)	0.0449 (5)	3.7 (1)
C4	0.0461 (5)	−0.1289 (6)	0.1836 (5)	3.4 (1)
C5	−0.2374 (7)	0.4555 (7)	0.0498 (7)	6.0 (2)
C6	0.2455 (5)	−0.0151 (8)	0.2452 (7)	6.4 (2)
C8	−0.3973 (5)	0.2488 (7)	0.0771 (6)	5.1 (2)
C9	0.0526 (6)	−0.1911 (7)	0.0806 (6)	5.5 (2)
C10	0.0892 (5)	−0.2235 (6)	0.2859 (5)	4.4 (2)
C11	−0.3219 (5)	−0.0191 (7)	0.0325 (5)	4.2 (2)
C12	−0.1621 (6)	−0.1787 (6)	0.0944 (6)	4.6 (2)
C13	−0.2731 (5)	−0.1424 (7)	0.0952 (6)	4.8 (2)
meso-TcOPn(AO-CH$_3$)$_2$				
Tc	−0.10942 (3)	0.09583 (2)	−0.12027 (1)	2.694 (4)
O1	−0.1481 (3)	−0.0762 (2)	0.0299 (1)	4.72 (6)
O2	−0.0586 (4)	0.1381 (3)	0.0625 (1)	5.12 (6)
O3	0.0701 (3)	0.0647 (2)	−0.1550 (2)	4.07 (5)
N1	−0.1881 (3)	−0.0584 (3)	−0.0498 (2)	3.40 (6)
N2	−0.0942 (3)	0.1967 (3)	−0.0096 (2)	3.45 (5)
N3	−0.2595 (3)	0.0176 (3)	−0.1909 (2)	3.33 (5)
N4	−0.1754 (3)	0.2661 (3)	−0.1502 (2)	3.27 (5)
C1	−0.2733 (4)	−0.1439 (3)	−0.0853 (3)	3.94 (7)
C2	−0.1127 (4)	0.3195 (3)	−0.0111 (2)	3.61 (6)
C3	−0.3146 (4)	−0.1129 (3)	−0.1713 (2)	3.93 (7)
C4	−0.1521 (4)	0.3736 (3)	−0.0930 (2)	3.45 (6)
C5	−0.3295 (7)	−0.2624 (4)	−0.0425 (3)	6.2 (1)
C6	−0.0924 (5)	0.4036 (4)	0.0625 (2)	4.81 (8)
C8	−0.2476 (5)	−0.2152 (4)	−0.2304 (3)	5.30 (9)
C10	−0.0233 (5)	0.4658 (4)	−0.1225 (3)	5.28 (9)
C11	−0.3379 (5)	0.0756 (4)	−0.2606 (2)	4.23 (7)
C12	−0.2686 (5)	0.3031 (4)	−0.2216 (2)	4.18 (7)
C13	−0.2632 (5)	0.2009 (4)	−0.2873 (2)	4.35 (8)
dl-TcO[(CH$_3$)$_2$Pn(AO-CH$_3$)$_2$]				
Tc	0.18898 (9)	0.01188 (4)	0.08966 (3)	2.46 (1)
O1	−0.0736 (8)	−0.0817 (5)	−0.0191 (3)	4.4 (1)
O2	0.1911 (9)	0.0234 (4)	−0.0680 (3)	4.4 (1)
O3	0.0522 (8)	0.1149 (4)	0.1170 (3)	3.6 (1)
N1	0.003 (1)	−0.0974 (5)	0.0438 (3)	3.6 (2)
N2	0.298 (1)	0.0386 (4)	−0.0085 (3)	3.0 (1)
N3	0.191 (1)	−0.1025 (5)	0.1556 (3)	3.6 (1)
N4	0.4546 (9)	0.0409 (5)	0.1070 (3)	2.9 (1)
C1	−0.056 (1)	−0.1736 (7)	0.0822 (5)	5.0 (2)
C2	0.468 (1)	0.0777 (6)	−0.0142 (4)	2.9 (2)
C3	0.047 (2)	−0.1870 (7)	0.1485 (5)	5.2 (2)
C4	0.569 (1)	0.0891 (6)	0.0526 (4)	3.3 (2)
C5	−0.215 (2)	−0.246 (1)	0.0590 (6)	8.6 (3)
C6	0.554 (1)	0.1048 (7)	−0.0812 (5)	4.8 (2)
C7	0.122 (2)	−0.2995 (9)	0.1515 (7)	9.8 (4)
C10	0.610 (1)	0.2088 (7)	0.0677 (5)	5.1 (2)
C11	0.323 (2)	−0.1179 (6)	0.2136 (4)	5.0 (2)
C12	0.567 (1)	0.0085 (8)	0.1664 (4)	4.5 (2)
C13	0.452 (1)	−0.0240 (7)	0.2302 (4)	4.3 (2)
C14	0.338 (2)	0.0714 (7)	0.2585 (4)	5.6 (2)
C15	0.594 (2)	−0.0602 (9)	0.2860 (5)	6.6 (3)
meso-TcO[(CH$_3$)$_2$Pn(AO-CH$_3$)$_2$]				
Tc	−0.03307 (4)	−0.27013 (2)	0.24445 (4)	2.75 (1)
Tc′	0.13045 (4)	−0.00163 (2)	0.26718 (4)	3.05 (1)
O1	−0.1340 (4)	−0.2130 (2)	0.0459 (4)	5.3 (1)
O1′	−0.0404 (4)	0.0810 (2)	0.3562 (4)	5.1 (1)
O2	0.0794 (4)	−0.2281 (2)	0.0487 (4)	5.4 (1)
O2′	−0.1326 (4)	0.0257 (2)	0.2120 (4)	5.3 (1)
O3	−0.0185 (4)	−0.2175 (2)	0.3304 (3)	4.1 (1)
O3′	0.2086 (4)	0.0376 (2)	0.1883 (3)	4.4 (1)
N1	−0.1596 (4)	−0.2482 (2)	0.1239 (4)	3.5 (1)
N1′	0.0574 (4)	0.0491 (2)	0.3786 (4)	3.8 (1)
N2	0.0914 (4)	−0.2643 (2)	0.1313 (4)	3.6 (1)
N2′	−0.0432 (4)	−0.0117 (2)	0.2019 (4)	3.6 (1)
N3	−0.1663 (4)	−0.3156 (2)	0.2729 (4)	3.4 (1)
N3′	0.2236 (4)	−0.0208 (2)	0.3947 (4)	3.6 (1)
N4	0.0779 (4)	−0.3277 (2)	0.2845 (4)	3.6 (1)
N4′	0.1315 (4)	−0.0761 (2)	0.2193 (4)	3.3 (1)
C1	−0.2661 (5)	−0.2662 (3)	0.1295 (5)	3.9 (1)
C1′	0.1114 (5)	0.0515 (2)	0.4721 (5)	3.6 (1)
C2	0.1877 (5)	−0.2932 (3)	0.1430 (5)	3.8 (1)
C2′	−0.0665 (5)	−0.0557 (3)	0.1480 (5)	3.9 (1)
C3	−0.2849 (5)	−0.3042 (3)	0.2189 (5)	4.1 (2)
C3′	0.2144 (5)	0.0129 (3)	0.4903 (5)	3.8 (1)
C4	0.1896 (5)	−0.3327 (3)	0.2321 (5)	3.7 (1)
C4′	0.0353 (5)	−0.0945 (3)	0.1428 (5)	3.6 (1)
C5	−0.3647 (6)	−0.2503 (4)	0.0523 (6)	6.4 (2)
C5′	0.0689 (6)	0.0877 (3)	0.5560 (5)	4.8 (2)
C6	0.2863 (6)	−0.2880 (4)	0.0731 (6)	6.7 (2)
C6′	−0.1856 (6)	−0.0671 (3)	0.0927 (6)	5.7 (2)
C7	−0.3685 (6)	−0.2782 (4)	0.2951 (6)	6.6 (2)
C7′	0.3299 (7)	0.0456 (3)	0.5176 (6)	5.5 (2)
C9	0.2983 (6)	−0.3235 (3)	0.3105 (6)	4.8 (2)
C9′	0.0776 (7)	−0.0954 (3)	0.0305 (6)	5.5 (2)
C11	−0.1643 (6)	−0.3622 (3)	0.3459 (6)	5.0 (2)
C11′	0.2901 (6)	−0.0713 (3)	0.4169 (6)	4.6 (2)
C12	0.0554 (6)	−0.3738 (3)	0.3555 (6)	4.6 (2)
C12′	0.2058 (5)	−0.1222 (3)	0.2592 (5)	4.1 (2)
C13	−0.0622 (5)	−0.4016 (3)	0.3363 (5)	3.7 (1)
C13′	0.3213 (5)	−0.1052 (3)	0.3209 (6)	4.2 (2)
C14	−0.0719 (7)	−0.4487 (3)	0.4137 (6)	6.1 (2)
C14′	0.4046 (6)	−0.0740 (3)	0.2510 (6)	5.4 (2)
C15	−0.0701 (7)	−0.4268 (3)	0.2226 (6)	6.2 (2)
C15′	0.3829 (7)	−0.1579 (3)	0.3630 (7)	6.3 (2)

complex, the greater is its mobility (R_f value) on silica with all solvents tested.

All of these complexes exhibit an intense absorbance at ca. 290 nm ($\epsilon \sim$ 6000–9000 M^{-1} cm^{-1}), with a shoulder tailing into the visible region (~350 nm) of the spectrum (Table IV), resulting in a yellow to orange-rust color. The intensity of the ca. 290-nm band suggests a charge-transfer transition, perhaps arising from a ligand to metal charge transfer from the π orbitals of the amide nitrogens to the empty d_{xz} and d_{yz} orbitals of the technetium.

The Pn(AO-CH$_3$)$_2$ ligand was obtained as a mixture of the *dl* and meso isomers. This resulted in the presence of a mixture of the isomers for the Tc(V) complex, as is evident in both the ^{1}H and ^{13}C NMR spectra (Tables VI and VII). Integration of the ^{1}H NMR spectrum of TcOPn(AO-CH$_3$)$_2$ shows close to a one to one mixture of the *dl* and meso isomers.

The infrared spectra of these TcOL complexes show the expected Tc=O stretch for a mono(oxo) species in the 908–923-cm^{-1} region (Table V). These are at the low-energy end of the range thus far observed for mono(oxo)technetium(V) complexes (910–1020 cm^{-1}).[14-19] This observation can be viewed as a

Table IX. Comparison of Selected Bond Distances (Å) and Angles (deg)

	meso-$TcOPn(AO\text{-}CH_3)_2$	TcOPn(AO)-(AO-CH_3)	*dl*-TcO[$(CH_3)_2$-Pn(AO-$CH_3)_2$]	*meso*-TcO[$(CH_3)_2$-Pn(AO-$CH_3)_2$]		$TcOPn(AO)_2$[9]
				meso	meso′	
Tc-O3	1.677 (2)	1.671 (3)	1.682 (5)	1.677 (3)	1.670 (4)	1.679 (3)
Tc–N1	2.079 (3)	2.085 (4)	2.073 (6)	2.082 (4)	2.080 (4)	2.093 (4)
Tc–N2	2.091 (3)	2.068 (4)	2.067 (6)	2.072 (4)	2.079 (4)	2.086 (3)
Tc–N3	1.912 (3)	1.914 (4)	1.911 (5)	1.912 (4)	1.918 (4)	1.908 (3)
Tc–N4	1.911 (3)	1.915 (4)	1.910 (6)	1.916 (4)	1.904 (4)	1.917 (3)
N1–O1	1.360 (4)	1.379 (5)	1.342 (8)	1.349 (6)	1.357 (5)	1.339 (4)
N2–O2	1.361 (4)	1.362 (5)	1.382 (7)	1.364 (5)	1.365 (6)	1.354 (4)
N3–C11	1.453 (5)	1.463 (7)	1.458 (10)	1.459 (7)	1.451 (7)	1.463 (5)
N4–C12	1.467 (5)	1.454 (7)	1.446 (8)	1.464 (7)	1.463 (7)	1.474 (5)
N3–C3	1.464 (5)	1.467 (6)	1.461 (11)	1.480 (6)	1.469 (7)	1.502 (5)
N4–C4	1.465 (4)	1.490 (6)	1.446 (9)	1.463 (7)	1.469 (6)	1.473 (5)
O3–Tc–N1	109.9 (1)	108.6 (2)	106.5 (3)	108.1 (2)	108.3 (2)	108.6 (1)
O3–Tc–N2	109.3 (1)	108.3 (2)	111.8 (2)	110.8 (2)	110.3 (2)	110.5 (1)
O3–Tc–N3	109.7 (1)	110.9 (2)	111.4 (2)	111.1 (2)	111.2 (2)	110.2 (2)
O3–Tc–N4	111.3 (1)	110.9 (2)	110.3 (3)	110.5 (2)	109.6 (2)	110.1 (1)
N1–Tc–N2	85.6 (1)	87.2 (2)	86.7 (3)	86.3 (2)	86.3 (2)	85.7 (1)
N1–Tc–N3	77.9 (1)	77.0 (2)	78.4 (3)	77.4 (2)	78.0 (2)	77.8 (2)
N1–Tc–N4	138.6 (1)	140.3 (2)	143.1 (3)	141.2 (2)	141.9 (2)	141.0 (1)
N2–Tc–N3	140.8 (1)	140.6 (2)	136.7 (2)	138.0 (2)	138.4 (2)	139.0 (1)
N2–Tc–N4	77.4 (1)	77.6 (2)	77.0 (2)	77.0 (2)	77.8 (2)	77.0 (1)
N3–Tc–N4	91.9 (1)	91.8 (2)	91.0 (3)	91.9 (2)	91.3 (2)	92.7 (2)

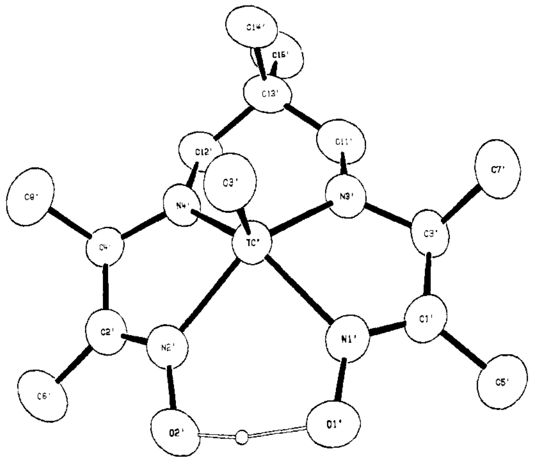


Figure 5. ORTEP representation of *meso′*-oxo(3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(3−)-*N*,*N′*,*N″*,*N‴*)technetium(V), *meso′*-TcO[$(CH_3)_2$Pn(AO-$CH_3)_2$].

weakening of the Tc═O bond by the multiple bond character of the two Tc–N amide bonds in the basal plane (vide infra). The average Tc═O bond distance for these complexes is at the long end of the range observed for mono(oxo)technetium(V) complexes (vide infra).

A mixture of the *dl* and meso isomers of $TcOPn(AO\text{-}CH_3)_2$ was obtained, as evidenced from the NMR studies, from a synthesis utilizing the *dl*/meso mixed-isomer ligand. However, the crystal selected for X-ray structural analysis contained only one isomer, the meso isomer.

Both the *dl* and the meso isomers of TcO[$(CH_3)_2$Pn(AO-$CH_3)_2$] were synthesized from the pure *dl* and meso isomers of the ligand. X-ray structures of both are presented. The crystal structure of *meso*-TcO[$(CH_3)_2$Pn(AO-$CH_3)_2$] has two independent molecules of the complex per unit cell, with one molecule having the central carbon atom of the propylene group directed up toward the oxo group and the second molecule having this carbon atom directed down and away from the oxo group (see Figures 4 and 5). The latter is the only example among the structures of the amine oximes with this conformation of the propylene group, which places the six-membered ring containing this propylene group into the chair conformation in contrast to the boat conformation in the remaining TcOL structures reported here and observed for other metal complexes of this ligand type.

These technetium(V) complexes, as well as the previously reported $TcOPn(AO)_2$,[9] are five-coordinate and exhibit square-pyramidal geometry with the yl oxygen situated at the apex. Two amine protons and an oxime proton are lost by the ligand on complex formation. The four nitrogen atoms define the basal plane, as evidenced by the least-squares planes (supplementary material), with the technetium atom located an average of 0.680 Å above this plane for the five structures. The six carbon atoms adjacent to the four nitrogen atoms can be considered as forming a rough plane below and parallel to that containing the four nitrogen atoms.

The average technetium–yl oxygen bond distance of 1.676 (8) Å found for these complexes is in the range expected for mono(oxo)technetium(V) complexes (1.610 (4)–1.672 (8) Å,[9,14–19] although it is at the long end of this range. This weakening of the Tc═O bond is not surprising when the multiple bond character of the two Tc–N amide bonds is taken into account (average 1.9 Å as compared to 2.1 Å for typical Tc—N single bonds).[15,20,21]

Complexes of other transition metals with tetradentate amine oxime ligands of the type reported here, namely $Pn(AO)_2$, are known. $[Pt^{II}(Pn(AO)_2)]^+$,[22] $[Pd^{II}(Pn(AO)_2)]^+$,[23] and $[Ni^{II}(Pn(AO)_2)]^+$[24] all exhibit the expected square-planar geometry, although the Ni(II) atom lies somewhat out of the ligand plane. $[Cu^{II}(Pn(AO)_2)(ReO_4)]$[25] and $[Cu^{II}(Pn(AO)_2(CN)]$[26] both show distorted square-pyramidal geometries. Intramoleculcar hydrogen

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bonding between the ReO_4^- and $Pn(AO)_2$ ligands causes the ReO_4^- group to lean in the direction of the hydrogen bonding in this case, and a strong Cu–CN bond results in a large displacement of the Cu(II) from the plane of the $Pn(AO)_2$. $[Rh^{III}(Pn(AO)_2Cl_2]$[27] and $[Co^{III}(Pn(AO)_2)(NO_2)_2]$[28] both form the expected octahedral complexes. However, steric interactions between one nitro group and the $Pn(AO)_2$ ligand cause the Co(III) to lie significantly out of the plane of the $Pn(AO)_2$ and result in unequal $Co–NO_2$ bond distances. In all of these examples, the tetradentate amine oxime ligand has lost an oxime proton, resulting in a strong intramolecular hydrogen bond. Several of these transition-metal complexes with $Pn(AO)_2$ show considerable distortion from ideal geometries, yet in no case were the two amine protons of the tetradentate amine oxime ligand lost on coordination to the metal as has been found here for the technetium(V) complexes.

These two deprotonated nitrogen atoms exhibit sp^2 character. The Tc–N amide bond distances are considerably shorter than those observed for Tc–N amine bonds. The average $Tc–N_{amide}$ bond distance for the complexes reported here is 1.913 (7) Å, while typical $Tc–N_{amine}$ bond distances are in the range 2.088 (3)–2.259 (4) Å.[15,20,21] The amide nitrogen, the technetium, and the two carbon atoms adjacent to this nitrogen are very close to coplanar (supplementary material), and the angles about the nitrogen are on the order of 120° rather than 109° as would be true if the nitrogen atoms were sp^3 hybridized.

Known technetium(V) complexes containing four-coordinated nitrogen atoms, such as the cyclam[21] or bis(ethylenediamine)[20] complex, retain their amine protons. These complexes, however, form the *trans*-dioxo core to reduce the high charge of the Tc(V) center.

The technetium(V) tetradentate amine oxime complexes contain the mono oxo core. Possibly, to avoid steric crowding of the bulky Tc═O group by the pendant methyl groups on the carbon atoms adjacent to the two amide nitrogens, the entire amine oxime ligand may be forced down and away from the oxo group on coordination. With the amine oxime ligand directed away from the oxo group, conditions would be sterically unfavorable for a second oxygen to be coordinated to the technetium in the position trans to the oxo group. This might then result in the deprotonation of the amine nitrogens to lower the charge on the Tc(V) center. Obviously the formation of two Tc–N multiple bonds through deprotonation and sp^2 hybridization adds more stabilization to the resultant Tc(V) complex than would be achieved by formation of the trans dioxo species, and additional stabilization is provided by the formation of the strong intramolecular O- - -O hydrogen bonds (2.403–2.448 (4) Å).

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Registry No. *meso*-$TcOPn(AO-CH_3)_2$, 99828-99-6; *dl*-$TcO[(CH_3)_2Pn(AO-CH_3)_2]$, 99944-78-2; *meso*-$TcO[(CH_3)_2Pn(AO-CH_3)_2]$, 99829-00-2; $TcOPn(AO)(AO-CH_3)$, 99829-01-3; $TcOPn(AO)_2$, 99829-02-4; NH_4TcO_4, 34035-97-7.

Supplementary Material Available: Tables reporting the observed and calculated structure factors, molecular geometry, least-squares planes, anisotropic thermal parameters, and hydrogen positional parameters for the four structures (71 pages). Ordering information is given on any current masthead page.

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Hydroquinone as a Proton Donor in Ambient-Temperature Chloroaluminate Ionic Liquids: Reaction with Chloride Ion

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The reaction of water and hydroquinone (H_2Q) as proton donors in either *N*-1-butylpyridinium chloride (BuPyCl)– or 1-methyl-3-ethylimidazolium chloride (ImCl)–aluminum chloride ambient-temperature ionic liquids has been investigated. Amperometric titrations of free chloride ion indicate that H_2Q reacts with 2 Cl^-, suggesting that HCl is undissociated in the molten salt. Comparison of the $D\eta/T$ values, where D, η, and T are the diffusion coefficient, viscosity, and temperature, respectively, suggest that both water and H_2Q give rise to two HCl molecules. Other observations regarding the interaction of water with the ambient-temperature molten salt are reported.

In the past several years low-temperature molten salt systems composed of aluminum chloride and either *N*-1-butylpyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (ImCl) have been found to be useful solvents for electrochemical and spectroscopic studies of both organic and inorganic species.[1-4] The reactions of water with $AlCl_3$–RCl melts, where $R^+ = BuPy^+$ or Im^+, are of particular importance since H_2O is one of the most common and obvious contaminants of the drybox atmosphere as well as of substrates used for preparation of these melts. The electrochemical behavior of water has been investigated in $AlCl_3$–BuPyCl melts,[5] and it was found that, throughout the entire range of melt composition, water undergoes chemical reaction(s) to generate HCl, which can be electrochemically reduced at a platinum electrode. However, the stoichiometry of these reactions remains unknown.

We described[6-8] a method of studying the stoichiometry of certain complex ions based on monitoring chloride and heptachloroaluminate ($Al_2Cl_7^-$) concentrations by observing changes in the diffusion-controlled chloride oxidation[7] and heptachloro-

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