

coloration of these complexes, is thought to be due to an increased resonance interaction between the phenyl groups and the macrocyclic ring.²⁷ Further work on identifying the products of the reduction and the possible equilibria are in progress.

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Registry No. P(OH)₂, 87374-07-0; [P^V(OH)₂TPP]⁰, 92365-86-1; [P^V(OH)₂TPP²⁻]⁻, 92346-45-7; OH⁻, 14280-30-9; *O*-trimethylsilyl phosphorus porphyrin, 92365-87-2; *N*-(trimethylsilyl)imidazole, 18156-74-6; acetic acid, 64-19-7; tetraethylammonium hydroxide, 77-98-5.

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Synthesis, Spectra, and Structure of *af*-Dibromo-*b*-ethoxo-*d*-oxo-*ce*-bis(4-nitropyridine)technetium(V) and Related Complexes

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Compounds of the type [O(RO)X₂L₂Tc^V], where X = Cl or Br, L = 4-cyanopyridine or 4-nitropyridine, and RO = OCH₃ or OCH₂CH₃, have been synthesized by the direct combination of [*n*-Bu₄N][TcOX₄] with the appropriate pyridine ligand in the corresponding alcohol as solvent. A complete crystal and molecular structure determination was performed on [O(CH₃CH₂O)Br₂(4-nitropyridine)₂Tc^V], which crystallized in the triclinic space group, *P* $\bar{1}$, with cell constants *a* = 10.820 (1) Å, *b* = 11.146 (2) Å, *c* = 9.006 (1) Å, α = 102.82 (1)°, β = 108.11 (1)°, and γ = 64.53 (1)°. The unit cell volume is 927.1 (4) Å³ with *Z* = 2. The geometry of the molecule involves trans halides, trans pyridines, and trans alkoxy and oxo moieties. A high infrared stretching frequency (939 cm⁻¹) and short Tc-O bond length (1.684 Å) indicate a bond order of approximately 2.5 for the technetium(V)-oxo moiety. Similarly, the short Tc-OCH₂CH₃ bond length of 1.855 Å suggests a bond order of approximately 1.5 for the ethoxo bond. The average Tc-Br bond distance of 2.56 Å is the first reported for a Tc(V) complex, and the average Tc-N bond distance of 2.14 Å is now typical for Tc(V). Infrared and ¹H NMR spectra are reported with Tc-Cl and Tc-N stretching frequencies occurring at 309-344 and 220-270 cm⁻¹, respectively, and ring proton resonances being shifted somewhat downfield. All but the oxo ligands appear to be easily substituted in a variety of solvents.

Introduction

Complexes of Tc^V with π -donor ligands such as halides, thiolates, and alcoholates tend to form square-pyramidal complexes^{2,3} containing the technetyl group, [Tc=O]³⁺, while coordination with nitrogen ligands generally yields octahedral complexes⁴⁻⁶ containing *trans*-[O₂Tc]⁺. Davison has recently reported the synthesis of [O(EtO)Cl₂(bpy)Tc^V], which presumably contains the alcoholate *trans* to the oxo ligand with the halides in *cis* positions.⁷ On the other hand, analogous rhenium complexes with monodentate pyridine ligands exhibit a *trans* geometry with respect to both the pyridine and halide ligands, so that it appeared likely that the corresponding Tc^V complexes should adopt a similar geometry.⁸ We now report the synthesis, molecular structure, and spectroscopic characterization of a number of complexes of the type [O(RO)X₂L₂Tc^V], where L = 4-cyanopyridine (Cpy) or 4-nitropyridine (Npy), X = Cl or Br, and RO = methoxy or ethoxy.

Experimental Section

Synthesis. Compounds of the type [O(RO)X₂L₂Tc^V], where RO = MeO- or EtO-, X = Cl or Br, and L = 4-cyanopyridine or 4-

nitropyridine, were prepared by dissolving the pyridine ligand (1.6 mmol) together with [*n*-Bu₄N][TcOX₄] (0.2 mmol) at an 8/1 (ligand/metal) molar ratio in 35 mL of the appropriate alcohol. The solution was stirred for 2-3 min and then filtered (through filter paper) to obtain a green filtrate, which was loosely covered and allowed to stand. Green crystals usually began to precipitate within 1 h, and the product was normally collected by filtration after 24 h. Elemental analyses are summarized in Table I.

Caution! All syntheses were performed with ⁹⁹Tc, which is a β -emitting isotope with a half-life of 2.15 \times 10⁵ yr. Precautions for handling this material are described elsewhere.⁴

Compound Characterization. All elemental analyses (except for ⁹⁹Tc) were performed by the Stanford Microanalytical Laboratory, Stanford, CA (Table I). Technetium analyses were performed by dissolving a known quantity of the compound in 8 mL of acetone and adding approximately 2 mL of a 30% solution of H₂O₂ to oxidize the metal to TcO₄⁻. Calibration standards were similarly prepared by dissolving [NH₄][TcO₄], which had been recrystallized from 0.1 M ammonia with the addition of a few drops of H₂O₂ and then dried in a vacuum desiccator at 25 °C for 10 h. Aliquots of 25-125 μ L were then combined with 10 mL of Fischer Scintiverse scintillation cocktail and Tc determinations made on an LKB-1217 scintillation counter. Counting was done for 60 s over a ³H window (channels 8-110), with 10⁴-10⁵ counts usually being obtained for samples and standards. Unknown samples were determined from a linear least-squares fit to the standards. Infrared spectra were taken on a Perkin-Elmer Model 599B grating spectrophotometer in CsI pellets. UV-visible spectra were obtained on a Perkin-Elmer Model 575 equipped with a digital background corrector and a thermostated sample cell. ¹H NMR spectra were recorded on a Varian FT-80A Fourier transform spectrometer. All spectra were recorded at room temperature with a spectral width of 2000 Hz.

Structure Determination. Single crystals of [O(CH₃CH₂O)Br₂(Npy)₂Tc^V] were obtained on slow evaporation of the ethanol reaction

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Table I. Elemental Analyses for $[\text{O}(\text{RO})\text{X}_2\text{L}_2\text{Tc}^{\text{V}}]^{\text{a}}$

ligands			element	% calcd	% found
py	X	RO			
Cpy	Cl	MeO	C	36.73	35.35
			H	2.62	2.95
			N	13.18	12.53
			Tc	22.3	22.6
Cpy	Cl	EtO	C	38.30	38.02
			H	2.98	3.02
			N	12.76	12.35
			Tc	22.5	22.0
Cpy	Br	MeO	C	30.38	30.64
			H	2.16	2.06
			N	10.90	10.60
			Tc	31.09	27.59
Cpy	Br	EtO	C	31.85	31.66
			H	2.48	2.36
			N	10.61	10.45
			Tc	30.27	30.36
Npy	Cl	EtO	C	30.09	29.68
			H	2.74	2.69
			N	11.70	11.10
			Tc	14.8	14.7
Npy	Br	EtO	C	25.38	25.44
			H	2.31	2.23
			N	9.86	9.69
			Tc	28.14	28.05
bpy	Cl	EtO	C	37.23	37.13
			H	3.38	3.41
			N	7.24	7.24
			Tc	18.32	16.33
Me ₂ bpy	Cl	EtO	C	40.51	40.94
			H	4.13	4.32
			N	6.75	6.83
			Tc	17.08	17.87
			C	23.8	23.6

^a Cpy = 4-cyanopyridine; Npy = 4-nitropyridine; X = Br, Cl.

mixture. Intensity data were measured on a Syntex P₂ four-circle automated diffractometer using θ - 2θ scanning techniques. Conditions of data collection are summarized in Table II. The density was determined by flotation in aqueous thallium formate, with a darkening of the crystals occurring, possibly indicating hydration, which may account for the discrepancy between the observed and calculated densities. Background counts were collected at the extremes of the scan for half the time of the scan. Three standard reflections were measured every 50 reflections with no decrease in intensity during the course of the measurements.

The structure was solved by using direct methods (MULTAN78)¹⁰ to find the coordinates of the technetium atom, two bromines, and two rings. Fourier methods were used to find the locations of all other atoms. With $Z = 2$, one crystallographically unique molecule was found at a general position in the asymmetric unit. The structure was refined by full-matrix least-squares methods.¹¹ The final model used anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms set at 1.0 \AA^2 higher than the isotropic factor associated with the bonded carbon atoms. The coordinates for all hydrogen atoms were held constant at the positions found in the Fourier difference map. A final difference Fourier synthesis was judged to be essentially featureless. The final data/parameter ratio was 6.7.

Final values of atomic coordinates in the asymmetric unit of the structure are given in Table III. A listing of the hydrogen atom

Table II. Crystallographic Data for $[\text{O}(\text{CH}_3\text{CH}_2\text{O})\text{Br}_2(\text{Npy})_2\text{Tc}^{\text{V}}]$

formula	TcBr ₂ O ₆ N ₄ C ₁₂ H ₁₃
fw	568.07
cryst dimens	0.25 × 0.17 × 0.04 mm ³
color	emerald green
radiation source (Cu K α)	$\lambda = 1.5418 \text{ \AA}$
diffractometer	Syntex P ₂
space group	triclinic, $P\bar{1}$
cell consts: a, b, c	10.820 (1), 11.146 (2), 9.006 (1) \AA
α, β, γ	102.82 (1), 108.11 (1), 64.53 (1) ^o
V	927.1 (4) \AA^3
Z	2
$d(\text{calcd})$	2.03 g/cm ³
$d(\text{obsd})$	2.14 g/cm ³
total no. of observns	2023
obsd reflns ^a	1514
scan mode	θ - 2θ
2θ range	3-100 ^o
scan width above and below K α	0.5 ^o
scan rate	2-12 ^o /min
no. of variables in least squares	226
$R = \Sigma(F_o - F_c) / \Sigma F_o $	0.043
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{1/2}$	0.045
goodness-of-fit = $[\Sigma w(F_o - F_c)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$	2.71

^a Reflections with $F_o > 3\sigma(F_o)$ were retained as observed and used in the solution and refinement of the structure.

Table III. Atomic Coordinates in the Unit Cell of $[\text{O}(\text{CH}_3\text{CH}_2\text{O})\text{Br}_2(\text{Npy})_2\text{Tc}^{\text{V}}]^{\text{a}}$

atom	x	y	z
Tc	0.3901 (1)	0.3621 (1)	0.1019 (1)
Br1	0.2254 (1)	0.5137 (1)	0.2805 (2)
Br2	0.5394 (1)	0.1973 (1)	-0.0806 (1)
O1	0.2642 (7)	0.2778 (7)	0.0279 (8)
O2	0.4877 (7)	0.4553 (7)	0.1748 (8)
O3	0.7449 (12)	-0.1162 (12)	0.6387 (14)
O4	0.8324 (10)	0.0381 (12)	0.7664 (13)
O5	-0.0393 (12)	0.7177 (11)	-0.5486 (14)
O6	0.0646 (14)	0.8553 (13)	-0.4160 (16)
N1	0.5134 (9)	0.2342 (9)	0.2864 (11)
N2	0.2676 (9)	0.4934 (10)	-0.0784 (11)
N3	0.7569 (13)	-0.0096 (14)	0.6529 (16)
N4	0.0457 (15)	0.7551 (16)	-0.4289 (16)
C1	0.5775 (14)	0.2836 (13)	0.4243 (15)
C2	0.6583 (14)	0.2072 (15)	0.5465 (15)
C3	0.6700 (13)	0.0786 (14)	0.5238 (16)
C4	0.6071 (14)	0.0244 (12)	0.3866 (15)
C5	0.5276 (13)	0.1074 (13)	0.2700 (15)
C6	0.2403 (13)	0.6256 (13)	-0.0472 (13)
C7	0.1686 (13)	0.7142 (12)	-0.1598 (16)
C8	0.1251 (12)	0.6598 (14)	-0.3084 (15)
C9	0.1489 (14)	0.5260 (15)	-0.3465 (15)
C10	0.2211 (13)	0.4465 (12)	-0.2274 (16)
C11	0.1334 (13)	0.2690 (14)	0.0051 (16)
C12	0.1272 (16)	0.1458 (15)	-0.0894 (15)

^a The numbers in parentheses are the estimated standard deviations.

positions (Table Is), temperature factors for non-hydrogen atoms (Table IIs), bond distances (Table IIIs), bond angles (Table IVs), and the final and observed structure amplitudes ($\times 10$) (Table Vs) are available as supplementary material.

Results

Structure Description. Figure 1 is a computer-drawn model of $[\text{O}(\text{CH}_3\text{CH}_2\text{O})\text{Br}_2(\text{Npy})_2\text{Tc}^{\text{V}}]$ as it exists in the crystal.¹² Bond distances and angles in the coordination sphere and ethoxo ligand are summarized in Table IV. The geometry

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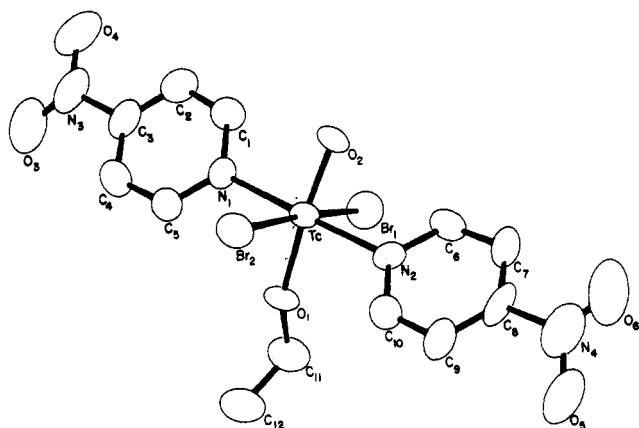


Figure 1. ORTEP diagram of $[\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{Br}_2(\text{Npy})_2\text{Tc}^{\text{V}}]$. Atom contours are shown at 50% probability.

Table IV. Bond Distances and Angles^a in the Coordination Sphere and Ethoxo Ligand for $[\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{Br}_2(\text{Npy})_2\text{Tc}^{\text{V}}]$

Distance, Å			
Tc-O1	1.855 (6)	Tc-Br1	2.570 (4)
Tc-O2	1.684 (6)	Tc-Br2	2.538 (4)
Tc-N1	2.147 (8)	O1-C11	1.41 (1)
Tc-N2	2.141 (8)	C11-C12	1.46 (2)
Angle, deg			
O1-Tc-N1	92.5 (3)	N1-Tc-Br1	89.1 (2)
O1-Tc-N2	88.5 (3)	N1-Tc-Br2	90.0 (2)
O1-Tc-Br1	85.3 (2)	N2-Tc-Br1	90.1 (2)
O1-Tc-Br2	89.2 (2)	N2-Tc-Br2	90.9 (2)
O2-Tc-O1	172.9 (3)	N2-Tc-N1	178.7 (3)
O2-Tc-N1	90.4 (3)	Br1-Tc-Br2	174.3 (1)
O2-Tc-N2	88.5 (3)	Tc-O1-C11	154.0 (7)
O2-Tc-Br1	88.4 (3)	O1-C11-C12	112.3 (10)
O2-Tc-Br2	97.2 (3)		

^a The numbers in parentheses are the estimated standard deviations in the last significant figure.

around the technetium atom is approximately octahedral. The bromine atoms are at an average distance of 2.55 (2) Å with a Br1-Tc-Br2 bond angle of 174.3 (1)°. At the present time there are no Tc^V-Br bond lengths available for comparison.^{3,5} The Tc-O2 bond distance of 1.684 (6) Å is between the Tc=O bond distances seen in octahedral complexes containing *trans*-[O₂Tc]⁺ (for example, 1.75 Å in [TcO₂(en)₂]⁺⁴ and 1.748 Å [TcO₂(*t*-Bupy)₄]⁺)¹³ and the shorter Tc-O distances seen in square-pyramidal Tc^V complexes. The latter range between 1.62 and 1.65 Å and are generally represented as Tc=O double bonds.^{3,5,6}

The longer Tc-O1 bond distance of 1.855 (6) Å reflects a lower bond order assignment to the ethoxo ligand. However, since an average Tc^V-O single-bond distance is taken to be 2.02 Å,³ it is apparent that this bond is intermediate between a single and double bond. In *trans*-dioxotechnetium complexes the O-Tc-O bond angle is essentially linear, whereas in this oxo-ethoxo compound the O1-Tc-O2 bond angle is 172.9 (3)°. The ethoxo ligand itself is quite normal, with the O1-C11-C12 bond angle of 112 (1)° being nearly the expected tetrahedral angle. The O1-C11 bond distance is in the range expected for a single bond, but the C11-C12 bond distance is shorter than a typical paraffinic single bond by 0.1 Å, which is attributed to thermal motion of the methyl group.

The average Tc-N distance of 2.14 (1) Å is similar to the Tc-N bond distances found in *trans*-[O₂(en)₂Tc]⁺ (2.15 Å)⁴ and in the analogous complexes with 4-*tert*-butylpyridine¹³ (2.146 Å) and imidazole⁵ (2.12–2.17 Å). The N1-Tc-N2

Table V. Infrared Stretching Frequencies of $[\text{O}(\text{RO})\text{X}_2\text{L}_2\text{Tc}^{\text{V}}]$

ligands	str freq, cm ⁻¹					
	L	X	RO	Tc-N	Tc=O	Tc-X
Cpy	Cl	Et		276, 242	940 (913)	344
Cpy	Cl	Me		230	938	338
Cpy	Br	Et		203	940 (918)	
Cpy	Br	Me		204	939 (900)	
Npy	Cl	Et		291, 250	938 (920)	344
Npy	Br	Et		220	938 (920)	
bpy	Cl	Et		255	938 (917)	319
Me ₂ bpy	Cl	Et		210	935 (915)	309

bond angle is 178.7 (3)°, and the technetium atom is not substantially displaced from the mean plane defined by any set of four roughly coplanar atoms coordinated to it.

The aromatic ring in each pyridine ligand is planar within ±0.005 Å. However, the nitro groups are not within that plane but are twisted out of the plane of the pyridine ring. The dihedral angle between the planes of the rings and their respective nitro groups are 11.0 and 25.7° for the pyridines associated with N1 and N2, respectively. Intermolecular nonbonded contacts between the nitro groups are O3-O5 (3.01 Å), O3-N4 (3.13 Å), and O4-O6 (3.13 Å) between molecules at *x*, *y*, *z* and 1 + *x*, 1 - *y*, 1 + *z*. The planes of these two nitro groups form an angle of 3.1° with one another.

The pyridine rings are twisted 59° (N1 ring) and 49° (N2 ring) from a plane defined by the two nitrogens and the two bromines, 90 and 87° from that of the two bromines and two oxygens and 30 and 40° from that of the two oxygens and two nitrogens. The ethoxo ligand forms angles of 88, 13, and 77° with these same three defining planes.

Spectra. Pertinent bands in the infrared spectra of the various complexes are summarized in Table V. The Tc=O stretching bands, which occur around 939 cm⁻¹, are at the low end of the range seen for monooxo square-pyramidal Tc^V complexes (930–1020 cm⁻¹)⁵ and are lower than that observed in [O(OH)(py)₂Br₂Re] at 975 cm⁻¹,¹⁴ while being somewhat higher than those exhibited by complexes containing *trans*-[O₂Tc]⁺ (820–880 cm⁻¹)⁴. The Tc-C1 symmetric stretch frequencies fall into the range expected for this vibrational mode.¹⁵ However, the Tc-Br vibrational frequencies fell below the range of the available instrumentation. The Tc-N frequencies are similar to those observed in other Tc^V complexes with nitrogen ligands.¹⁶

All of the prepared compounds rapidly decomposed when dissolution in water was attempted. While these compounds were readily soluble in a variety of organic solvents including Me₂SO, CHCl₃, CH₂Cl₂, and DMF, they invariably underwent substitution of at least the ethoxo ligand as evidenced by the appearance of free ethanol peaks in their ¹H NMR spectra and shifts in the other proton resonances. Only in Me₂SO did the complexes persist sufficiently long to obtain reasonable ¹H NMR spectra (see Table VI). In general, coordination of the technetyl ion shifted the pyridine proton resonances somewhat downfield and the alkoxo protons upfield. The methyl protons of the ethoxo ligands, especially in the bipyridine complexes, exhibited the greatest upfield shifts. While none of the solvent-modified species were investigated, they appeared to be stable in their respective solvents.

Syntheses performed with pyridine derivatives not containing strongly electron-withdrawing substituents yielded only complexes of the type *trans*-[O₂(py)₄Tc]⁺. Placing complexes of the type [O(RO)X₂L₂Tc^V] in neat pyridine solvents also resulted in *trans*-[O₂(py)₄Tc]⁺. Continued heating in the neat

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Table VI. ¹H NMR Data for [O(RO)X₂L₂Tc^V] in Me₂SO-d₆^a

L	X	RO	assignt	δ ^a	no. of protons	no. of peaks in mult	³ J _{H-H} , Hz
Cpy			ring H	7.91	2	2	5.8
			ring H	6.93	2	2	5.9
Npy			ring H	7.60	2	2	7.6
			ring H	7.38	2	2	7.4
Cpy	Cl	MeO	ring H	8.21	2	2	6.4
			ring H	7.42	2	2	6.4
			CH ₃	2.64	2	1	
Cpy	Cl	EtO	ring H	9.14	2	2	6.3
			ring H	8.29	2	2	6.4
			CH ₂	3.78	2	4	6.9
			CH ₃	0.94	3	3	7.0
Cpy	Br	MeO	ring H	8.02	2	2	6.3
			ring H	7.18	2	2	6.4
			CH ₃	2.41	3		
Cpy	Br	EtO	ring H	9.56	2	2	6.3
			ring H	8.71	2	2	6.5
			CH ₂	4.20	2	4	6.8
			CH ₃	1.35	3	3	6.9
Npy	Cl	EtO	ring H	8.23	2	2	6.4
			ring H	7.49	2	2	6.7
			CH ₂	2.80	2	4	6.7
			CH ₃	0.01	3	3	6.8
Npy	Br	EtO	ring H	8.47	2	2	5.9
			ring H	7.67	2	2	5.5
			CH ₂	3.02	2	4	7.0
			CH ₃	0.21	3	3	6.8
bpy	Cl	EtO	H(3,3')	7.02	2	3	6.6
			H(4,4')	7.52	2	3	7.7
			H(5,5')	7.92	2	2	7.7
			H(6,6')	8.62	2	2	5.8
			CH ₂	1.75	2	4	6.8
			CH ₃	-0.71	3	3	6.9
Me ₂ bpy	Cl	EtO	H(3,3')	8.00	2	1	
			H(5,5')	7.07	2	3	5.9
			H(6,6')	8.64	2	2	5.5
			C(4,4')H ₃	1.81	6	1	
			CH ₂	1.98	2	4	5.6
			CH ₃	-0.47	3	3	7.0

^a Positions are given relative to tetramethylsilane at 37 °C.

pyridine ligands with added halide produced compounds of the general category [pyX₄Tc-O-Tc(py)₄X].¹⁷

Owing to the instability of these complexes in all solvents attempted, quantitative electronic spectra could not be determined. However, a listing of λ_{max} values for the various complexes in ethanol is given in Table VI in the supplementary material. All complexes exhibited a fairly intense (ε ≈ 10³-10⁴ M⁻¹ cm⁻¹) charge-transfer transition around 640 nm with 4-cyanopyridine and 625 nm with 4-nitropyridine. The cyanopyridine complexes also showed a second band around 358-370 nm. This feature was obscured with the nitropyridine complexes owing to strong absorption of the pyridine ligand in this region. The bands in the visible region are tentatively assigned as pyridine to technetium charge-transfer transitions.

Discussion

Synthesis and Stability. While direct combination of pyridine or pyridine derivatives with electron-donor substituents in the para position generally yield *trans,trans*-[O₂(py)₄Tc]⁺, the para nitro and para nitrile derivatives yield [O(RO)X₂L₂Tc^V]. The addition of only two pyridines is consistent with decreased donor ability of the ring nitrogen due to the electron-withdrawing substituents and consequent lower affinity for metal cations. It has been suggested that solvent

substitution in the open position opposite the *trans* labilizing oxo ligand followed by metal ion induced deprotonation results in alkoxo complexes similar to those reported here.¹⁸ If this precedes pyridine attack, the pyridine addition in *trans* positions suggests that the pyridine *trans* effect in these complexes is greater than that of the halides; however, it is also possible that initial attack by the pyridine ligands occurs at the open position in the square-pyramidal starting material and that rearrangement to the *trans* configuration takes place on steric grounds. This would then be followed by alcohol addition and deprotonation opposite the oxo. The recent report of *cis*-[OCl(quin)₂Tc], where quin = 2-methyl-8-quinolinolato, is consistent with initial ligand attack at the labile site opposite the oxygen.¹⁹ Deprotonation following oxygen ligand addition in the position *trans* to the multiply bonded oxygen is supported by the structure of *trans*-[O(OH₂)(*acac*)₂en]Tc⁺, where (*acac*)₂en = *N,N'*-ethylenebis(acetylacetonate imine),²⁰ and the observation that the quinolinolato complex undergoes solvolysis in methanol to yield a methoxo species.¹⁹

Somewhat surprisingly, attempts to form the analogous products with longer chain alcohols were unsuccessful as were reactions involving 4-nitropyridine in methanol. The latter yielded only discrete crystals of the pyridine ligand and [*n*-Bu₄N][TcO₄], which were separated and characterized by their infrared spectra. It is unknown whether the oxidant for the technetium was nitropyridine or atmospheric oxygen.

The solution instability of these compounds attests to the ease with which the ligands are substituted. The NMR results in Me₂SO solution indicate that ethoxo substitution is complete within 30 min to yield a fairly stable form of a Me₂SO-solvated technetium ion or possibly a species containing *trans*-[O₂Tc]⁺. The similar, but more rapid, behavior noted in CHCl₃, CH₂Cl₂, and ethanol for both the *cis* and *trans* complexes reported in this work, together with the facile substitution of the equatorial ligands in neat pyridine, suggests that this family of easily prepared compounds may be synthetically useful in the preparation of other Tc^V complexes.

Since addition of these complexes to neat pyridine quickly resulted in *trans*-[O₂(py)₄Tc]⁺, it is likely that the formation of the latter type of complexes generally proceeds through *trans*-dihalo-*trans*-bis(pyridine) species as intermediates. The complex *trans*-[O₂(py)₄Tc]⁺ has been shown to be an intermediate in the formation of [pyX₄Tc-O-Tc(py)₄X] on heating a variety of technetium starting materials in pyridine.¹⁷

Structure and Bonding. The structure of [O(CH₃CH₂O)-Br₂(Npy)₂Tc^V] is essentially identical to that of [O-(CH₃CH₂O)Cl₂(py)₂Re], in which short Re=O and Re-OR bond distances are also observed.⁸ Owing to the very short Tc=O distances evident in the square-pyramidal, monooxo technetium(V) complexes, it is reasonable that the oxo moiety is actually triply, rather than doubly, bonded in these complexes. Since there are four metal orbitals available for σ and π bonding along the RO-Tc-O (*z*) axis and the presence of the coordinated halide ions should enhance the donor ability of the metal ion, the oxo ligand may bind to the metal through accepting the two d electrons available on the metal ion and donating two pairs of π electrons to form a Tc=O triple bond. Such π bonding also occurs in the *trans*-dioxotechnetium(V) complexes to form the O=Tc=O moiety, with both oxygens doubly bonded to the metal ion. In the present case, the shortness of the Tc-O bond and its relatively high infrared stretching frequency suggest a bond order intermediate between 2 and 3.²¹ Similarly, the short Tc-OR bond distance

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suggests significant π bonding to this moiety as well,²¹ which would alter the hybridization state of the bonded oxygen. This bond is substantially shorter than the 2.28-Å distance to the water molecule in *trans*-[O(OH₂)(*acac*)₂en]Tc⁺ and the more typical 2.02-Å Tc(V)-O single-bond distances evident in the equatorial oxygens in this structure.²⁰ While the abnormally large Tc-O-C11 bond angle of 154° must largely result from steric repulsion between the methylene hydrogens of the ethoxo group and the adjacent Br1, expansion of this angle should also be facilitated by a change in hybridization on the oxygen from approximately sp³ in free ethanol to substantially sp², when involved in π bonding to the technetium.

The downfield ¹H NMR shifts of the ring protons, which is attenuated by distance, and the upfield shifts of the alkoxo protons, which is larger for the methyl protons on the ethoxo relative to the methoxo ligands, are understandable on the basis of an anisotropic magnetic field generated by the circulation of electrons around the Tc=O bond. Reference to Figure 1 shows that the appreciable upfield shift for the methyl protons on the ethoxo ligands results from their being closer to the dipolar (Tc=O) axis than the methylene protons.²⁴

While the electronic, infrared, and NMR spectra of these complexes are similar to their *cis* analogues with bipyridine ligands, steric requirements imposed by the bulky halide ions generally cause the pyridines to adopt a *trans* arrangement in similar transition-metal complexes.⁸ In doing so the pyridines are allowed some degree of rotational flexibility around their Tc-N bonds, and packing forces result in their being

canted at 30 and 40° from the plane of the two oxygens and two nitrogens. The twisting of the nitro groups out of planarity with the pyridine rings is not particularly unusual. While this group is strictly coplanar with the aromatic ring in crystalline nitrobenzene,²⁵ in other aromatic rings containing the nitro substituent steric factors twist this group out of planarity. For example, the dihedral angle between the aromatic ring and the nitro group is 3.0° in *p*-nitrotoluene²⁶ and 9.5° in *p*-dinitrobenzene.²⁷ Steric factors also cause the nitro group to be twisted by 64° in 9,10-dinitroanthracene and even to 85° in 9-nitroanthracene.²⁵ The steric interaction between the nitro groups on translationally related molecules in the unit cell appears to cause the distinct twists out of planarity with the pyridine rings in the structure of [O(CH₃CH₂O)Br₂(Npy)₂Tc^V].

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Registry No. [O(MeO)Cl₂(Cpy)₂Tc], 92622-14-5; [O(EtO)Cl₂(Cpy)₂Tc], 92622-15-6; [O(MeO)Br₂(Cpy)₂Tc], 92622-16-7; [O(EtO)Br₂(Cpy)₂Tc], 92622-17-8; [O(EtO)Cl₂(Npy)₂Tc], 92622-18-9; [O(EtO)Br₂(Npy)₂Tc], 92622-19-0; [O(EtO)Cl₂(bpy)Tc], 92622-20-3; [O(EtO)Cl₂(Me₂bpy)Tc], 92622-21-4; [*n*-Bu₄N][⁹⁹TcOBr₄], 92622-23-6; [*n*-Bu₄N][⁹⁹TcOCl₄], 92622-25-8.

Supplementary Material Available: Listings of hydrogen atom positions (Table Is), temperature factors for non-hydrogen atoms (Table IIs), bond distances and angles for complete structures (Tables IIIs and IVs), calculated and observed structure factor amplitudes for [O(CH₃CH₂O)Br₂(Npy)₂Tc^V] (Table Vs), and electronic spectra for [O(RO)X₂L₂Tc^V] (Table VIs) (14 pages). Ordering information given on any current masthead page.

- (21) From a modification of Pauling's bond order relation²² with standard average Tc-O bond lengths^{3,13,23} taken to be Tc-O = 1.98 Å, Tc=O = 1.74 Å, and Tc=O = 1.65 Å yields a Tc-O bond order of 2.54 and a Tc-OR bond order of 1.45.
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Kinetic and Mechanistic Study of the Succinic Anhydride Reductive-Elimination Reaction from the Six-Coordinate

Ir(H)[σ -CHCH₂C(O)OC(O)](σ -carb)(CO)(PhCN)(PPh₃) Complex

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The hydridoalkyliridium(III) complex Ir(H)[σ -CHCH₂C(O)OC(O)](σ -carb)(CO)(PhCN)(PPh₃), where carb = 7-C₆H₅-1,7-C₂B₁₀H₁₀, undergoes reductive-elimination reaction of succinic anhydride under mild conditions. This reaction, which represents a crucial step in the homogeneous hydrogenation of maleic anhydride catalyzed by the four-coordinate iridium(I) complex Ir(σ -carb)(CO)(PhCN)(PPh₃) at *T* = 50 °C (*P*_{H₂} = 1 atm), has been kinetically investigated in 1,2-dichloroethane solution by IR spectroscopy between 35 and 45 °C. The elimination reaction implies preliminary PhCN dissociation to give a five-coordinate intermediate that then undergoes intramolecular reductive elimination of succinic anhydride. The obtained activation parameters indicate that the reductive elimination of succinic anhydride from the five-coordinate hydridoalkyliridium(III) intermediate is a highly concerted process whose driving force is the incipient formation of the strong C-H bond of the product.

Introduction

We have previously reported that iridium(I) complexes of the type Ir(σ -carb)(CO)(RCN)(PPh₃), where carb = 7-

C₆H₅-1,7-C₂B₁₀H₁₀ and R = CH₃ or C₆H₅, are efficient hydrogenation catalysts for a series of terminal alkenes and of alkynes.¹ The hydrogenation reaction occurs at room temperature with unactivated olefins, whereas higher temperatures

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