Preparation, Characterization, and ^{17}O NMR Kinetic Studies of Analogous Technetium(V) and Rhenium(V) Complexes Which Contain a Seven-Membered Chelate Ring. Single-Crystal Structure Analyses of $[Ph_4P][TcO(DBDS)]$ and $[Ph_4As][ReO(DBDS)]$, Where DBDS Is *N,N'*-Bis(mercaptoacetyl)butane-1,4-diamine

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The preparation and characterization of monooxotechnetium(V) and -rhenium(V) complexes with *N,N'*-bis(mercaptoacetyl)butane-1,4-diamine (DBDS) and its phenyl-substituted derivative (RDBDS) are described. These ligands are designed to provide complexes with 7-membered chelate rings, the backbone of which can be readily modified to incorporate functional groups. $[Ph_4P][TcO(DBDS)]\cdot{}^1/_4CH_3OH$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.398$ (4) Å, $b = 13.942$ (3) Å, $c = 23.749$ (8) Å, $\beta = 98.54$ (3)°, $V = 3077$ (2) Å^3, and $Z = 4$. The isostructural $[Ph_4As][ReO(DBDS)]\cdot{}^1/_4CH_3OH$ has $a = 9.4539$ (8) Å, $b = 14.011$ (3) Å, $c = 23.841$ (7) Å, $\beta = 98.92$ (2)°, and $V = 3119.7$ Å^3. In both structurally characterized complexes the metal ion is in a square pyramidal, five-coordinate environment. The Tc and Re atoms lie 0.67 and 0.66 Å, respectively, above the basal N_2S_2 plane toward the multiply bound oxygen atom. A preliminary kinetic study of the exchange of oxygen between water and the complexes $[ReO(DBDS)]^-$, $[TcO(DBDS)]^-$, and the 5,5,5-chelate analog $[ReO(DADS)]^-$ indicates operation of an associative exchange mechanism; observed rate constants at 25 °C are 7.5×10^{-3} M^{-1} s^{-1}, 7.1×10^{-4} M^{-1} s^{-1} and 1.6×10^{-5} M^{-1} s^{-1} for the $[ReO(DBDS)]^-$, $[TcO(DBDS)]^-$, and $[ReO(DADS)]^-$ complexes, respectively. Associative activation accounts for the relative rates of oxygen atom exchange of the $ReO(DBDS)^-$ and $ReO(DADS)^-$ complexes since the butylenediamine moiety of DBDS provides more flexibility and less steric constraint than does the ethylenediamine backbone of DADS. Associative activation for these five-coordinate complexes also accounts for the fact that k^{Tc}/k^{Re} is 0.1, while k^{Tc}/k^{Re} is $\approx 10^3$ for six-coordinate complexes which undergo dissociative activation.

Introduction

Research into the preparation and chemistry of analogous technetium and rhenium complexes arises both from the utility of technetium and rhenium isotopes in nuclear medicine and also from the periodic relationship between technetium and rhenium. Therapeutic ^{186}Re and ^{188}Re radiopharmaceuticals can be designed by analogy to existing ^{99m}Tc diagnostic radiopharmaceuticals, and rhenium analogs of existing ^{99m}Tc radiopharmaceuticals can be used to obtain information about the biological mechanism of action of the ^{99m}Tc agents.[4]

A dominant feature of Tc(V) and Re(V) chemistry is the existence of a large number of stable, diamagnetic complexes in which the metal center forms multiple bonds to oxo ligands. These complexes usually exhibit an octahedral or square pyramidal arrangement of ligand atoms about the metal center. Many Tc(V) and Re(V) complexes are important intermediates in the preparation of lower oxidation state complexes, while other Tc(V) or Re(V) complexes display remarkable bioactivity on their own.[4-9] In 1979 Davison and co-workers[10,11] introduced a new class of tetradentate chelating agents for Tc; these ligands contain two amido nitrogen donor atoms plus two thiolato sulfur donor atoms, and members of this class of ligands are generally referred to as N_2S_2 ligands. The prototypical complex of this series, the oxo(*N,N'*-bis(mercaptoacetyl)ethylenediaminato)technetate(V) (Tc(V)–DADS) anion, demonstrates rapid renal excretion in animals.[12] Tc–DADS complexes are anionic because all four ligating atoms are ionized and the monooxo Tc(V) core carries a formal 3+ charge, $[Tc^VO]^{3+}$.[13] Clinical evaluation of $[^{99m}Tc^VO(DADS)]^-$ in renal-transplant patients indicates that its biological behavior in people with good renal function correlates well with the animal biodistribution data.[14]

There is considerable interest in the design of new ligands within the DADS ligand series. A variety of substituted ^{99m}Tc–DADS complexes[15-17] based on ethanediamine have been synthesized and their biodistributions evaluated. These studies clearly show that the biological behavior of the compounds is dependent on the nature and position of substituents attached to the N_2S_2 ligand. In the N_2S_2 ligands discussed herein (Figure 1), the diamine portion of the ligand is expanded from ethanediamine to butanediamine, thus producing novel Tc and Re

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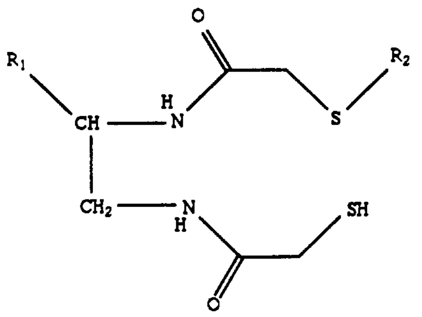
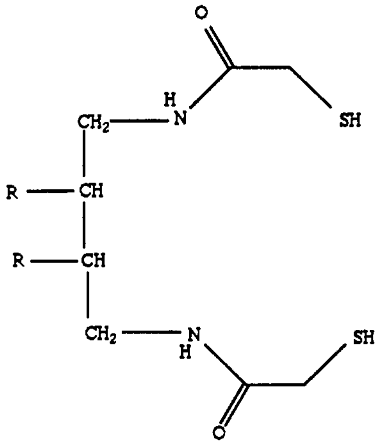


DADS: $R_1 = H$, $R_2 = H$

map: $R_1 = COOH$, $R_2 = H$

ema(morph): $R_1 = H$, R_2 = ethylmorpholine



DBDS: R = H

RDBDS: $R = C_6H_5$

Figure 1. Abbreviations used in this paper.

complexes which contain seven-membered rings. These seven-membered rings provide synthetic flexibility for the attachment of different side-chain substituents which can be used to vary the biodistributions of the complexes.

In this work, prototypical $Tc–N_2S_2$ and $Re–N_2S_2$ complexes based on butanediamine are synthesized, structurally characterized, and subject to preliminary kinetic studies. Quantitative delineation of the rates of substitution of ligands bound to Re and Tc complexes is fundamental to the characterization of their reactivity and is a prerequisite to their subsequent use in the systematic study of redox reactions. Our current knowledge in this area is almost nil. Even within the relatively large class of characterized Tc(V) and Re(V) complexes, there have been only very limited quantitative kinetic studies reported to date. The only existing comparative Tc/Re bimolecular rate data are those that our group has collected on six-coordinate complexes: pyridine exchange on *trans*-$[MO_2(py)_4]^+$ and thiocyanate displacement of water on *trans*-$[MO(H_2O)(CN)_4]^-$ (M = Tc(V) and Re(V)).[18-20] Fritzberg and co-workers have reported on the unimolecular racemization of technetium(V) and rhenium(V) penicillamine complexes.[21]

Thus, we report herein the synthesis and characterization of new $Tc–N_2S_2$ and $Re–N_2S_2$ complexes which contain a seven-membered chelate ring; the N_2S_2 ligands are *N,N'*-bis(mercaptoacetyl)butane-1,4-diamine (DBDS) and its phenyl-substituted derivative (RDBDS). We also present single-crystal structure analyses of the anionic complexes $[MO(DBDS)]^-$ (M = Tc(V) and Re(V)) and delineate the rate and mechanism of oxygen atom transfer between water and the complexes $[ReO(DBDS)]^-$, $[TcO(DBDS)]^-$, and $[ReO(DADS)]^-$.

Acronyms and Abbreviations. The following acronyms and abbreviations are used in this article: DADS = *N,N'*-bis(mercaptoacetyl)ethane-1,2-diamine; DBDS = *N,N'*-bis(mercaptoacetyl)butane-1,4-diamine; epa = ethylenebis(2-phenoxyacetamide); FAB = fast atom bombardment; LTMCT = ligand to metal charge transfer; Me = methyl; Ph = phenyl; RDBDS = *N,N'*-bis(mercaptoacetyl)-2,3-diphenylbutane-1,4-diamine.

Experimental Section

General Data. Syntheses of technetium complexes were performed with technetium-99, a low-energy (0.292 MeV) β-emitter with a half-life of 2.12×10^5 year. When handled in milligram quantities, ^{99}Tc does not present a serious health hazard. Bremsstrahlung is not a significant problem due the low-energy β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. In this work all manipulations were carried out in a Vacuum Atmospheres drybox in a radiation laboratory. ^{99}Tc was purchased in the form of NH_4TcO_4 from Oak Ridge National Laboratory and purified by adding excess 30% H_2O_2 to oxidize the small amount of TcO_2 impurity.[22] $KTcO_4$ was obtained by simple metathesis with KOH in aqueous media. All common laboratory chemicals were of reagent grade. *S*-benzoyl-DBDS and *S*-benzoyl-RDBDS were prepared as previously described.[23] $[ReO_2py_4]Cl·2H_2O$ was prepared by a literature method.[24]

Synthesis of $[Ph_4X][TcO(DBDS)]$ (X = As, P). The synthesis of this compound is similar to the preparation of $[Ph_4As][TcO(DADS)]$ reported by Davison et al.[10] The resulting brown precipitate was recrystallized from methanol/water by slow evaporation at room temperature. Yield = 90%, based on Tc. Anal. Calcd for $C_{32}H_{32}N_2S_2O_3PTc·{}^1/_4CH_3OH$: C, 55.76; H, 4.76; N, 4.03; S, 9.22. Found: C, 55.39; H, 4.79; N, 3.95; S, 9.50. UV-vis (CH_3CN): 356 nm (3.64×10^3 M^{-1} cm^{-1}); 433 nm (4.01×10^3 M^{-1} cm^{-1}). ^1H NMR (CD_3NO_2): 3.8 ppm (s), 4 H for $-SCH_2-$; 3.9–3.4 ppm (m), 4 H for $-NCH_2-$; 2.1–1.7 ppm (m), 4 H for $-NCH_2CH_2-$. FT-IR: 954 (s), 903 cm^{-1} (m). FAB MS (*m/e*) (negative mode): M^-(obs) = 347; MW(theory) = 347.

Synthesis of $[Ph_4X][TcO(RDBDS)]$ (X = As, P). This compound was prepared in a manner similar to that used for the preparation of $[Ph_4X][TcO(DBDS)]$. The crude product was dissolved in 5 mL of methanol, and the solution was filtered to remove a small amount of white precipitate; ether was added to the resulting filtrate to form a brown precipitate, which was collected by filtration and washed with methanol/water and then ether. The product was recrystallized twice from dichloromethane/hexane mixtures. The resulting dark brown microcrystalline solid was collected by filtration and washed with dichloromethane/hexane and ether and then dried in vacuum. The yield of the dark brown precipitate is 55–60% based on Tc. Anal. Calcd for $C_{44}H_{40}N_2S_2O_3AsTc$: C, 59.86; H, 4.54; N, 3.17; S, 7.26. Found: C, 59.70; H, 4.62; N, 3.09; S, 7.12; UV-vis (CH_3CN): 353 nm (3.51×10^3 M^{-1} cm^{-1}); 430 nm (2.90×10^3 M^{-1} cm^{-1}). FT-IR: 994 (s), 944 (s), 898 cm^{-1} (m). FAB MS *m/e* (negative mode): M^-(obs) = 499; MW(theory) = 499.

Synthesis of $[Ph_4As][ReO(DBDS)]$. A suspension of 450 mg (0.55 mmol) of benzoyl-protected DBDS was made in a solution of 120 mL of methanol and 6 mL of 1.0 N sodium hydroxide. This was heated to 80–85 °C for 5–10 min to dissolve the ligand. To the resulting clear solution was added a suspension of 300 mg (0.50 mmol) of $[ReO_2py_4]Cl·2H_2O$ in 20 mL of methanol. The reaction mixture was stirred at 80 °C for 45 min before being rotaevaporated to reduce the volume to about 10 mL. After the deep brown solution was cooled to ambient temperature and filtered, an aqueous solution of tetraphenylarsonium chloride monohydrate (1.0 g, 2.3 mmol) was added to yield a fine brown precipitate. This was separated by filtration, and the crude product was washed with

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50–60 mL of water. The resulting solid was recrystallized twice from a methanol/water mixture by slow evaporation at room temperature. The yield is up to 65% (ca. 260 mg) based on Re. The product is soluble in methanol, ethanol, acetone, acetonitrile, and chloroform to yield brown solutions; it is insoluble in water and ether. Anal. Calcd for $C_{32}H_{32}N_2S_2O_3AsRe\cdot{}^1/_4CH_3OH$: C, 46.90; H, 4.00; N, 3.39; S, 7.76. Found: C, 46.52; H, 4.00; N, 3.36; S, 7.81. UV–vis (CH_3CN) [λ, nm (ε, M^{-1} cm^{-1})]: 292 (4094), 353 (3893), 533 (48). IR (cm^{-1}): 994 (m), 969 (s), 937 (m), 904 (m). FAB MS (*m*/*e*) (negative mode): M^-(obs) = 435, 433; MW(theory) = 435, 433. ^1H NMR (d_6-DMSO) (ppm): 7.9–7.7 (m), 20 H for $-(C_6H_5)_4$; 3.9 (d) and 3.6 (d), 4 H for $-SCH_2-$; 4.0–3.9 (m) and 3.3–3.2 (m), 4 H for $-NCH_2-$; 3.3 (s), H_2O in d_6-DMSO; 2.5 (m), trace $-CH_3$ in d_6-DMSO; 2.1–2.0 (m) and 1.8–1.7 (m), 4 H for $-NCH_2\mathit{CH}_2-$.

Synthesis of [Ph_4As][ReO(RDBDS)]. This complex was prepared in a manner which is similar to that used in the preparation of [Ph_4As][ReO(DBDS)]. The crude product was dissolved in 10 mL of methanol and filtered to remove a small amount of white, insoluble impurities. The resulting clear brown solution was rotaevaporated to dryness. The precipitate was removed to a small vial and dissolved in 4–5 mL of methanol. The open vial was then placed in a larger bottle which contained 20–30 mL of ether; the larger vial was then sealed. Two days later, the dark brown microcrystalline solid was collected by filtration, washed with 5 mL of 1:5 methanol/ether and ether, and then dried in vacuum. The yield is up to 45% (ca. 43 mg) based on Re. The product is soluble in methanol, ethanol, acetone, acetonitrile, chloroform, and dichloromethane, yielding brown solutions. It is insoluble in water and ether. Anal. Calcd for $C_{44}H_{40}N_2S_2O_3AsRe$: C, 54.46; H, 4.16; N, 2.89; S, 6.61. Found: C, 54.32; H, 4.35; N, 3.17; S, 7.04. UV–vis (CH_3CN) [λ, nm (ε, M^{-1} cm^{-1})]: 296 (3741), 356 (4339), 526 (55). IR (cm^{-1}): 997 (s), 958 (s), 907 (s). FAB MS (*m*/*e*) (negative mode): M^-(obs) = 587, 585; MW(theory) = 587, 585. ^1H NMR (d_6-DMSO) (ppm): 7.9–7.8 (m), 20 H for $-(C_6H_5)_4$; 7.0–6.7 (m), 10 phenyl H for $C_6H_5CH-CHC_6H_5$; 3.7 (d) and 3.2 (d), 4 H for $-SCH_2-$; 4.1 (t), 2 H for $-CH_2-Ph\mathit{CH}-\mathit{CH}Ph-CH_2$; 4.0–3.7 (m), 4 H for $-NCH_2-$; 3.3 (s), H_2O in DMSO; 2.5 (m), trace $-CH_3$ in DMSO.

Measurements. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer in KBr pellets. UV–vis absorption spectra were obtained using a Cary 210 spectrophotometer (Varian) at room temperature. The mass spectral analyses were conducted on a VG 30-250 quadrupole mass spectrometer (VG Instruments Inc.) fitted with a FAB source. Xenon was used as the primary gas, and the ion gun was operated at 7 KeV and 1 mA. ^1H NMR spectra were obtained on a Bruker AC 250 spectrometer. HPLC chromatograms were obtained on a Perkin-Elmer 400 LC system with a Beckman Model 153 UV detector operating at 254 nm. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

NMR Measurements. The rate of water exchange on [ReO(DADS)]$^-$, [ReO(DBDS)]$^-$, and [TcO(DBDS)]$^-$ in d_6-DMSO was measured as a function of time by recording a series of ^{17}O-NMR spectra on a Bruker AC-250 spectrometer (5.9-T wide bore magnet, 5-mm ϕ broad-band probe with ^1H decoupling coil) working at 33.908 MHz. The data collection sequences were programmed and executed automatically.

A series of spectra were measured at fixed time intervals and stored on disk. The 16K data points were acquired using a frequency range of 8000 Hz and a pulse length of 15 μs. A total of 1000–5000 transients were summed. The temperature was controlled to within ±0.1 °C by a Bruker B-VT 1000 temperature controller.

To measure the rates of exchange of the oxo ligands of the rhenium and technetium complexes with $^{17}OH_2$, the complexes were dissolved in DMSO, the resulting solution of complex was mixed with 10% ^{17}O-enriched water (the total water concentration in the reaction system is between 1.0% and 20%), and then 10–40 μL of methanolic solution (4.37 or 0.437 M) of sodium methoxide was added. This reaction mixture was then placed in a tube and transferred into the NMR magnet. An ^{17}O-labeled Na_2SO_4 solution was sealed in a capillary tube, which was placed in the center of the NMR tube and used as an external standard.

Crystallography. Single-crystal X-ray diffraction experiments were performed on a Nicolet P2$_1$ automated diffractometer (with Mo Kα radiation (λ = 0.710 73 Å) for the technetium complex and Cu Kα radiation (λ = 1.541 78 Å) for the rhenium compound) and a graphite monochromator at ambient temperature. Relevant data are summarized in Table I. All non-hydrogen atoms were refined anisotropically except for those of the methanol solvent which were described isotropically. Phenyl rings in the cations are defined as rigid bodies (C–C = 1.395 Å and C–C–C = 120°). Hydrogen atoms were placed in calculated or observed positions. No hydrogen atoms were placed in the solvent. Both structures were refined in full matrices with the programs of SHELX-76.[25] Neutral-atom scattering factors and corrections for anomalous dispension were from ref 26.

Table I. Crystallographic Data

	[Ph_4P][TcO(DBDS)]$\cdot{}^1/_4CH_3OH$	[Ph_4As][ReO(DBDS)]$\cdot{}^1/_4CH_3OH$
formula	$C_{32.25}H_{33}S_2N_2O_{3.25}PTc$	$C_{32.25}H_{33}S_2N_2O_{3.25}AsRe$
weight	694.64	825.88
T, °C	20	20
λ, Å	0.710 73	1.541 78
space group	$P2_1/n$ (No. 14, nonstandard)	$P2_1/n$ (No. 14, nonstandard)
a, Å	9.398 (4)	9.4539 (8)
b, Å	13.942 (3)	14.011 (3)
c, Å	23.749 (8)	23.841 (7)
β, deg	98.54 (3)	98.92 (2)
V, Å^3	3077 (2)	3120 (1)
Z	4	4
ρ(calc), g cm^{-3}	1.499	1.758
μ, cm^{-1}	6.73	100.41
transm coeff	0.706–0.639	0.252–0.157
R[a]	0.037	0.034
R_w[a]	0.038	0.038

[a] $R = (\Sigma|\Delta F|)/\Sigma|F_o|$; $R_w = [(\Sigma w|\Delta F|^2)/\Sigma wF_o^2]^{1/2}$.

Results

Syntheses. Pertechnetate is a good starting material for preparation of the metal(V) complexes, while perrhenate is not. The desired Re(V) complexes can be obtained by ligand substitution onto commonly used rhenium(V) starting materials such as [$ReOCl_2(EtO)(Ph_3P)_2$], [$ReOI_2(EtO)(Ph_3P)_2$], [$ReOCl_3(Ph_3P)_2$], and [$ReO_2(py)_4$]Cl; the latter material provides the cleanest reaction and product. A large counterion such as Ph_4As^+ (or Ph_4P^+) facilitates formation of crystalline salts of the [MOL]$^-$ anions (M = Tc(V) or Re(V), L = DBDS or RDBDS); these salts can be easily purified through recrystallization from methanol/water, acetone/water, or dichloromethane/hexane mixtures. No pure tetrabutylammonium or tetraethylammonium salts of [ReO(DBDS)]$^-$ could be isolated. The Na[ReO(DBDS)] salt is very soluble in water and other organic solvents.

Properties. The elemental analyses of all four complexes yield results which are in acceptable agreement with the proposed formulations. However composition assignments are more reliably made by negative-ion FAB mass spectrometry, because the interpretation of high mass ion fragments is not complicated by the possible presence of coprecipitated salts. Negative-ion FAB MS analyses show parent peaks at *m*/*z* = 347 for [TcO(DBDS)]$^-$ and at *m*/*z* = 499 for [TcO(RDBDS)]$^-$, consistent with the formulation of these anions. For [TcO(RDBDS)]$^-$, the formulation is further verified by a small *m*/*z* = 501 peak in the positive-ion FAB MS spectrum, which can be assigned as $M^- + 2H^+$. Negative-ion FAB MS reveals pairs of intense parent peaks at *m*/*z* (433, 435) and (585, 587) for [ReO(DBDS)]$^-$ and [ReO(RDBDS)]$^-$, respectively. The intensity ratio of the peaks within each pair is about 0.5, which is close to the isotopic ratio for $^{185}Re/^{187}Re$ ($^{185}Re/^{187}Re$ = $^{37}/_{63}$ = 0.59).

The UV–vis spectra of [TcO(DBDS)]$^-$ and [TcO(RDBDS)]$^-$ are very similar with two prominent absorption bands. For the rhenium analogs, three bands can be observed (Table II).

When compared to the spectra of the DBDS and RDBDS ligands, the infrared spectra of the title complexes exhibit extra strong M═O stretching vibrations at 954 cm^{-1} for [TcO(DBDS)]$^-$, 948 cm^{-1} for [TcO(RDBDS)]$^-$, 969 cm^{-1} for [ReO(DBDS)]$^-$,

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Table II. UV–Visible Data in Acetonitrile [ν(max)/10^3 cm^{-1} (ϵ/10^3 M^{-1} cm^{-1})]

[TcO(DBDS)]$^-$	28.09 (3.64)	23.10 (4.01)	
[TcO(RDBDS)]$^-$	28.33 (3.51)	23.26 (2.90)	
[ReO(DBDS)]$^-$	34.25 (4.09)	28.33 (3.89)	18.76 (0.048)
[ReO(RDBDS)]$^-$	33.78 (3.74)	28.09 (4.34)	19.01 (0.055)

Table III. Atomic Positional Parameters for $[Ph_4P][TcO(DBDS)]\cdot{}^1/_4CH_3OH$

atom	*x*	*y*	*z*
Tc(1)	0.11234 (3)	0.18672 (2)	0.09953 (1)
S(1)	0.3584 (1)	0.17015 (8)	0.10546 (5)
S(2)	0.1557 (1)	0.15502 (9)	0.19411 (5)
O(1)	0.0453 (3)	0.0923 (2)	0.0623 (1)
O(2)	0.2893 (4)	0.3768 (3)	−0.0053 (2)
O(3)	−0.2182 (4)	0.2805 (3)	0.1861 (2)
N(1)	0.1496 (4)	0.3022 (2)	0.0523 (2)
N(2)	−0.0698 (4)	0.2507 (2)	0.1205 (2)
C(1)	0.3890 (5)	0.2412 (4)	0.0450 (2)
C(2)	0.2707 (5)	0.3124 (4)	0.0284 (2)
C(3)	0.0461 (6)	0.3823 (3)	0.0412 (3)
C(4)	−0.0823 (6)	0.3554 (4)	−0.0026 (3)
C(5)	−0.1680 (5)	0.2764 (4)	0.0168 (2)
C(6)	−0.1941 (5)	0.2847 (3)	0.0783 (3)
C(7)	−0.1041 (5)	0.2483 (4)	0.1735 (2)
C(8)	−0.0019 (5)	0.2020 (4)	0.2187 (2)
P(1)	0.4706 (1)	0.33041 (7)	0.32158 (4)
C(9)	0.5951 (3)	0.4071 (2)	0.3646 (1)
C(10)	0.6163 (3)	0.3971 (2)	0.4237 (1)
C(11)	0.7164 (3)	0.4548 (2)	0.4572 (1)
C(12)	0.7954 (3)	0.5226 (2)	0.4317 (1)
C(13)	0.7742 (3)	0.5327 (2)	0.3726 (1)
C(14)	0.6741 (3)	0.4749 (2)	0.3390 (1)
C(15)	0.3130 (2)	0.3181 (2)	0.3547 (1)
C(16)	0.2566 (2)	0.3989 (2)	0.3781 (1)
C(17)	0.1244 (2)	0.3933 (2)	0.3979 (1)
C(18)	0.0484 (2)	0.3070 (2)	0.3943 (1)
C(19)	0.1048 (2)	0.2263 (2)	0.3708 (1)
C(20)	0.2370 (2)	0.2318 (2)	0.3510 (1)
C(21)	0.4189 (3)	0.3803 (2)	0.25241 (9)
C(22)	0.2836 (3)	0.4218 (2)	0.23724 (9)
C(23)	0.2462 (3)	0.4621 (2)	0.18331 (9)
C(24)	0.3441 (3)	0.4609 (2)	0.14454 (9)
C(25)	0.4794 (3)	0.4194 (2)	0.15971 (9)
C(26)	0.5168 (3)	0.3791 (2)	0.21364 (9)
C(27)	0.5499 (3)	0.2150 (1)	0.3151 (1)
C(28)	0.6370 (3)	0.1745 (1)	0.3617 (1)
C(29)	0.6891 (3)	0.0814 (1)	0.3583 (1)
C(30)	0.6542 (3)	0.0287 (1)	0.3082 (1)
C(31)	0.5672 (3)	0.0691 (1)	0.2616 (1)
C(32)	0.5150 (3)	0.1623 (1)	0.2650 (1)
O(4)	0.036 (2)	0.036 (1)	0.4724 (6)
C(33)	−0.062 (2)	−0.034 (2)	0.483 (1)

and 958 cm^{-1} for [ReO(RDBDS)]$^-$; these values are consistent with other values reported for monooxo Tc(V) and Re(V) species.[27-29]

^{1}H NMR spectra of the [TcO(DBDS)]$^-$ and [ReO(DBDS)]$^-$ complexes show three sets of signals in the ratio 1:1:1. The $-NCH_2-$ protons give two multiplets at ca. 3.9 and 3.4 ppm for the technetium complex and at ca. 3.95 and 3.25 ppm for the rhenium complex; the observation of $-NCH_2-$ multiplets indicates that the environments of these two protons on the butylenediamine backbone are not equivalent. This phenomenon is also observed in the ^{1}H NMR spectrum of the five-membered ring derivative [TcO(DADS)]$^-$;[10] multiplets at 3.98–3.48 ppm are assigned to $-NCH_2-$ protons in the ethylenediamine backbone of the DADS ligand. The $-NCH_2\mathit{CH_2}-$ protons appear at ca. 2.1–1.7 ppm for [TcO(DBDS)]$^-$ and at ca. 2.1 and 1.8 ppm for [ReO(DBDS)]$^-$.

Table IV. Atomic Positional Parameters for $[Ph_4As][ReO(DBDS)]\cdot{}^1/_4CH_3OH$

atom	*x*	*y*	*z*
Re(1)	0.11273 (3)	0.18880 (2)	0.10127 (1)
S(1)	0.3580 (2)	0.1740 (2)	0.10652 (9)
S(2)	0.1528 (2)	0.1605 (2)	0.19631 (9)
N(1)	0.1460 (6)	0.3034 (4)	0.0532 (3)
N(2)	−0.0730 (6)	0.2514 (4)	0.1195 (3)
O(1)	0.0477 (5)	0.0918 (3)	0.0645 (2)
O(2)	0.2835 (8)	0.3767 (6)	−0.0057 (3)
O(3)	−0.2254 (7)	0.2791 (5)	0.1833 (3)
C(1)	0.3872 (9)	0.2446 (7)	0.0458 (3)
C(2)	0.268 (1)	0.3133 (6)	0.0288 (3)
C(3)	0.042 (1)	0.3821 (6)	0.0408 (4)
C(4)	−0.085 (1)	0.3558 (7)	−0.0035 (4)
C(5)	−0.1712 (9)	0.2727 (6)	0.0154 (4)
C(6)	−0.1945 (9)	0.2821 (6)	0.0773 (4)
C(7)	−0.110 (1)	0.2482 (6)	0.1728 (4)
C(8)	−0.0084 (9)	0.2070 (7)	0.2191 (4)
As(1)	0.46611 (8)	0.33106 (5)	0.32094 (3)
C(9)	0.2991 (4)	0.3196 (3)	0.3554 (2)
C(10)	0.2221 (4)	0.2343 (3)	0.3521 (2)
C(11)	0.0906 (4)	0.2303 (3)	0.3716 (2)
C(12)	0.0360 (4)	0.3115 (3)	0.3945 (2)
C(13)	0.1130 (4)	0.3968 (3)	0.3978 (2)
C(14)	0.2446 (4)	0.4008 (3)	0.3782 (2)
C(15)	0.4139 (5)	0.3853 (3)	0.2478 (2)
C(16)	0.2802 (5)	0.4281 (3)	0.2331 (2)
C(17)	0.2430 (5)	0.4696 (3)	0.1796 (2)
C(18)	0.3396 (5)	0.4682 (3)	0.1409 (2)
C(19)	0.4734 (5)	0.4253 (3)	0.1557 (2)
C(20)	0.5105 (5)	0.3838 (3)	0.2092 (2)
C(21)	0.5999 (4)	0.4104 (3)	0.3670 (2)
C(22)	0.6214 (4)	0.4002 (3)	0.4260 (2)
C(23)	0.7203 (4)	0.4581 (3)	0.4597 (2)
C(24)	0.7976 (4)	0.5263 (3)	0.4345 (2)
C(25)	0.7762 (4)	0.5366 (3)	0.3755 (2)
C(26)	0.6773 (4)	0.4786 (3)	0.3418 (2)
C(27)	0.5480 (5)	0.2082 (3)	0.3143 (2)
C(28)	0.6295 (5)	0.1663 (3)	0.3617 (2)
C(29)	0.6816 (5)	0.0737 (3)	0.3583 (2)
C(30)	0.6523 (5)	0.0230 (3)	0.3074 (2)
C(31)	0.5709 (5)	0.0649 (3)	0.2600 (2)
C(32)	0.5188 (5)	0.1576 (3)	0.2634 (2)
C(33)/O(33)	0.047 (3)	0.040 (2)	0.490 (1)

Table V. Selected Bond Lengths (Å) and Angles (deg)

	[TcO(DBDS)]$^-$	[ReO(DBDS)]$^-$
M–S(1)	2.308 (1)	2.312 (2)
M–S(2)	2.266 (1)	2.273 (2)
M–O(1)	1.657 (3)	1.681 (5)
M–N(1)	2.021 (3)	2.024 (6)
M–N(2)	2.056 (3)	2.068 (6)
S(1)–C(1)	1.803 (5)	1.809 (8)
S(2)–C(8)	1.794 (5)	1.816 (9)
M–S(1)–C(1)	100.0 (2)	100.6 (3)
M–S(2)–C(8)	102.4 (2)	102.6 (3)
M–N(1)–C(2)	122.8 (3)	122.3 (5)
M–N(1)–C(3)	122.5 (3)	123.4 (5)
M–N(2)–C(6)	124.7 (3)	125.4 (4)
M–N(2)–C(7)	122.7 (3)	122.0 (5)
S(1)–M–S(2)	83.62 (4)	85.40 (7)
S(1)–M–O(1)	104.6 (1)	103.8 (2)
S(1)–M–N(1)	81.9 (1)	81.9 (2)
S(1)–M–N(2)	153.1 (1)	154.7 (2)
S(1)–C(1)–C(2)	111.9 (3)	111.5 (5)
S(2)–M–O(1)	111.83 (9)	111.7 (2)
S(2)–M–N(1)	133.2 (1)	133.3 (2)
S(2)–M–N(2)	82.98 (9)	83.1 (2)
S(2)–C(8)–C(7)	113.8 (3)	113.6 (6)
O(1)–M–N(1)	114.9 (1)	115.0 (2)
O(1)–M–N(2)	102.1 (1)	101.5 (2)
N1–M–N(2)	90.5 (1)	89.7 (2)

The multiplets arising from the butylenediamine or ethylenediamine protons strongly suggest a twisted conformation of the M(NCCCCN) seven-membered ring and M(NCCN) five-membered ring (M = Tc(V) or Re(V)).

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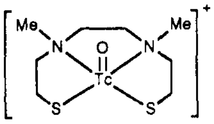
Table VI. Comparison of Selected Structural Parameters (Å, deg) in Monooxo M(V) Complexes with N_2S_2 Ligands[a,b]

M=O	M–S	M–N	S–M–N bite	N–M–N bite	S–M–S	M dist to basal plane	ref
			$[TcO(DBDS)]^-$				
1.66	2.29 (thiol)	2.04 (amide)	82.4	90.5	83.6	0.67	*c*
			$[ReO(DBDS)]^-$				
1.68	2.29 (thiol)	2.05 (amide)	82.5	89.7	85.4	0.66	*c*
			$[TcO(map)]^-$ [d]				
1.65	2.28 (thiol)	1.98 (amide)	82.6	77.7	89.0	0.75	39
			$[ReO(map)]^-$				
1.66	2.28 (thiol)	1.98 (amide)	82.9	77.1	88.4	0.75	39
			[TcO(ema(morph))]				
1.66	2.26 (thiol) 2.39 (thioether)	1.98 (amide)	82.3	78.9	91.1	0.74	17
							
1.65	2.25 (thiol)	2.16 (amide)	83.4	80.1	85.9	0.77	50

[a] The crystallographic estimates of precision errors, often given as esd's, are generally quite low (<0.01 Å or 0.2°) but not necessarily indicative of accuracy. Distances are in Å; angles in deg. [b] The structure of $[Tc^VO(DADS)]^-$ has been reported in an abstract,[51] but no coordinates are available. [c] This work. [d] Both syn and anti isomers were examined.

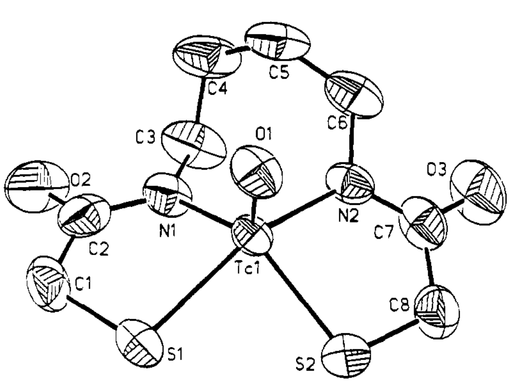


Figure 2. Perspective view of $[TcO(DBDS)]^-$. Ellipsoids here and in Figure 3 represent 50% probability.

HPLC analysis, with UV detection, of methanolic solutions of $[ReO(RDBDS)]^-$ and $[TcO(RDBDS)]^-$ reveals two peaks at 4.8 and 5.2 min. This implies the presence of two diastereoisomers which stem from the two chiral carbon atoms of the phenyl-substituted butylene backbone. These same HPLC peaks (but with radiometric detection) were observed after labeling RDBDS with ^{99m}Tc.[23]

Crystal Structure. In each structure, the asymmetric unit consists of an independent cation and anion plus $^1/_4$ equiv of methanol. The solvent lies near an inversion center, and so it is disordered with respect to that symmetry element. Atomic positional parameters are given in Tables III and IV. The atom-labeling scheme and geometry within $[TcO(DBDS)]^-$ are shown in Figure 2. $[ReO(DBDS)]^-$ is altogether similar in geometry, and the corresponding atoms are identically labeled. Selected bond lengths and angles are listed in Table II. The central metal is surrounded by an approximately square pyramidal arrangement of five ligating atoms. The multiply bound oxygen (O(1)) atom is located at the apex of the pyramid. M=O is 1.66 Å for Tc and 1.68 Å for Re, typical distances for monooxo M(V) complexes. The N_2S_2 base of the square pyramid is distorted in a ruffled manner: S(1) and N(2) are displaced from the mean N_2S_2 plane toward O(1), while S(2) and N(1) are displaced toward the opposite side (mean RMSD for the N_2S_2 atoms is ±0.17 Å for M = Tc and ±0.18 Å for M = Re). The M=O vector is tilted 2° from perpendicularity with respect to this mean basal plane. O=M–N,S angles range over 102–105°; the spread is due to the ruffling effect. The metal ions lie 0.67 Å (Tc) and 0.66 Å (Re) out of the mean N_2S_2 basal plane. The DBDS ligand is asymmetrically wrapped around the metal ion. The 5-membered ring consisting of S(1), C(1), C(2), N(1), and M is in a distorted half-chair conformation with an approximate 2-fold rotation axis passing through the atom C(2) (ΔC_2 = 3.3° for M = Tc and 1.9° for M = Re).[30,31] The absolute value of the torsion angles in this ring range from 9 to 22°. The opposite 5-membered ring, consisting of M, N(2), C(7), C(8), and S(2) is in an approximate envelope conformation with $\Delta C_s \approx 1.0°$. This ring is more planar than the previous one, with maximum intra-ring torsion angles of ±4° for Tc and ±6° for Re. Chelate bite angles for the mercaptoacetamido rings are 82° for S(1)–M–N(1) and 83° for S(2)–M–N(2). The 7-membered butanediamine ring is in a distorted twist-boat conformation with an approximate C_2 axis passing through the C(4) atom, ΔC_2 = 12.1° (Tc) and 10.4° (Re). The four carbon atoms of this ring all lie above the N(1), M, and N(2) plane (toward O(1)). The bite angle N(1)–M–N(2) is ≈ 90°.

In the DBDS ligand, the S–M–N axis that is puckered toward O(1) shows slightly longer bond lengths to the metal (by 0.04 Å) than those puckered away from O(1). The average M–thiol distance is 2.29 (2) Å for both Tc and Re. The noncyclic S(1)–M–S(2) angle is 83.6° for Tc and 85.4° for Re. The nonbonding S···S distance is 3.05 Å for Tc and 3.11 Å for Re. The M–N(amide) lengths average 2.04 (2) Å for Tc and 2.05 (3) Å for Re. The absence of hydrogen atoms on these nitrogen atoms is established by ^{1}H NMR but is also confirmed by the crystallographic analysis, which shows no room for placement of a hydrogen atom at these sites. The angles about N range over 111–125°.

The cations in both structures are ordinary. P–C averages 1.787 (3) Å, and As–C averages 1.899 (4) Å.

Kinetics. Selected observed rate constants governing the oxygen-exchange reactions of $[ReO(DADS)]^-$, $[ReO(DBDS)]^-$, and $[TcO(DBDS)]^-$ with $^*OH_2$ are listed in Table VII. The rate constants (k_{298}) and the associated activation parameters obtained from nonlinear least-square analyses are listed in Table VIII.

Discussion

Synthesis. The thiol functionalities in the noncoordinated DBDS and RDBDS ligands are protected by benzoyl ester groups

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(30) Asymmetry parameters (DC2 and DCs) are discussed in: Ladd, M. F. C.; Palmer, R. A. *Structure Determination by x-ray Crystallography*, 2nd ed.; Plenum Press: New York, 1985; pp 352–355.

(31) Ring conformations through torsion angle analyses are discussed in: Toromanoff, E. *Tetrahedron* **1980**, *36*, 2809.

Table VII. Selected Rate Data for the ReO(DADS)–H_2O^*, ReO(DBDS)–H_2O^*, and TcO(DBDS)–H_2O^* Oxygen Atom Exchange Reactions

$[H_2O]$ (M)	[M=O] (M)	T (K)	$[CH_3O]$ (M)	$10^{-4}k'$ (s^{-1})
		$[ReO(DADS)]^-$		
5.26	0.059	323	0.208	1.73 (8)
5.39	0.058	323	0.107	0.69 (2)
5.04	0.056	323	0.406	4.39 (20)
2.63	0.058	323	0.208	1.69 (9)
10.52	0.058	323	0.208	1.60 (12)
2.63	0.044	323	0.156	1.20 (14)
2.63	0.090	323	0.156	1.38 (8)
2.63	0.049	323	0.312	2.92 (7)
		$[ReO(DBDS)]^-$		
1.18	0.033	298	0.0186	0.35 (2)
1.18	0.033	298	0.0279	1.08 (17)
2.36	0.033	298	0.0186	0.36 (1)
1.18	0.033	298	0.0232	0.71 (2)
1.18	0.034	298	0.0372	1.76 (12)
1.18	0.034	298	0.0325	1.40 (9)
0.59	0.034	298	0.0186	0.27 (2)
1.18	0.061	298	0.0186	0.35 (2)
2.36	0.036	298	0.0184	0.32 (1)
4.73	0.030	298	0.0184	0.32 (2)
0.35	0.030	298	0.0184	0.29 (2)
		$[TcO(DBDS)]^-$		
2.32	0.036	298	0.397	2.14 (21)
2.42	0.037	298	0.570	3.88 (24)
4.84	0.037	298	0.570	4.04 (22)
2.42	0.036	298	0.199	1.23 (16)

Table VIII. Rate Constants and Activation Parameters for Oxygen Atom Exchange Reactions onto $[(L)MO]^-$ (M = Re, Tc; L = DADS, DBDS)

	$[ReO(DADS)]^-$	$[ReO(DBDS)]^-$	$[TcO(DBDS)]^-$
k_{298} (M^{-1} s^{-1})	$(1.6 \pm 1.1) \times 10^{-5}$	$(7.6 \pm 0.1) \times 10^{-3}$	$(7.1 \pm 1.2) \times 10^{-4}$
ΔH^* (kJ mol^{-1})	123 ± 8^a	37 ± 3	
ΔS^* (J mol^{-1} K^{-1})	78 ± 10	53 ± 4	

[a] Errors are one standard deviation.

to prevent oxidation of these functionalities. These protecting benzoyl groups can be easily removed in warm alkaline solutions.[10–23] In the presence of an excess amount of the deprotected ligand, dithionite reduction of pertechnetate affords good yields of the oxotechnetate(V) DBDS and RDBDS complexes. However, no oxorhenate(V) complexes could be isolated through analogous treatment of perrhenate with dithionite. This presumably results from the fact that perrhenate is more difficult to reduce than is pertechnetate.[4,32] The desired $[ReO(DBDS)]^-$ and $[ReO(RDBDS)]^-$ complexes can be easily prepared by ligand-substitution reactions on $[ReO_2(py)_4]Cl$.

Both $[TcO(DBDS)]^-$ and $[ReO(DBDS)]^-$ are very stable in methanol or mixed methanol/water solvents, but their phenyl-substituted derivatives $[TcO(RDBDS)]^-$ and $[ReO(RDBDS)]^-$ decompose to form a white precipitate within 12 h after dissolution in methanol/water. The lower stability of the RDBDS compounds may result from steric constraints engendered by the two phenyl substituents on the butanediamine backbone. This could also account for the lower preparative yields of the RDBDS complexes relative to the DBDS analogs (55–60% for $[TcO(RDBDS)]^-$ vs 90% for $[TcO(DBDS)]^-$; 45% for $[ReO(RDBDS)]^-$ vs 65% for $[ReO(DBDS)]^-$).

Both the $[TcO(DBDS)]^-$ and $[ReO(DBDS)]^-$ complexes are very stable toward ligand substitution. All efforts to add small molecules such as CH_3SH, C_5H_5N, C_6H_5ONa, or $(C_2H_5)_3P$ to the vacant coordination position situated trans to M=O failed. The complexes do not appear to be able to accept a small entering group to form a six-coordinated species, possibly for steric reasons. The steric crowding about the 5-coordinate Tc and Re environments is readily observed in the structures of the complexes (Figures 2 and 3).

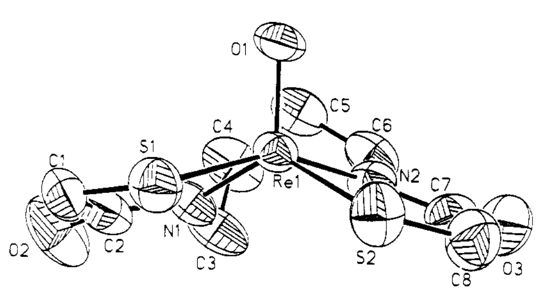

Figure 3. Perspective view of $[ReO(DBDS)]^-$ viewed perpendicular to the Re=O axis.

Properties. The UV–vis spectra of the title complexes all exhibit two strong absorption bands. The molar extinction coefficients of these peaks are all greater than 1000, and thus the absorptions presumably arise from charge-transfer transitions. These CT bands can be tentatively assigned as ligand-to-metal charge-transfer (LTMCT) transitions on the basis of the high formal charge on the Tc(V) and Re(V) centers. This assignment is supported by the fact that the transitions of the rhenium complexes occur at higher energies than do those of the technetium analogs; Re complexes are thermodynamically more stable in their higher oxidation states,[4,32] and thus LTMCT bands occur at higher energy for rhenium complexes than for their technetium analogs. The absorption bands for $[TcO(DADS)]^-$ (5,5,5-chelate system) occur at higher energies than those of $[TcO(DBDS)]^-$ (5,7,5-chelate system).[10] This might be attributable to poorer overlap between the d orbitals of the technetium atom and the p orbitals of the DADS ligand, resulting from the more severe geometric restraints of the 5,5,5-chelate system of the $[TcO(DADS)]^-$ complex. The Re–N_2S_2 complexes also exhibit a low-intensity transition which occurs at 18.8 × 10^3 cm^{-1} (48 M^{-1} cm^{-1}) and 19.0 × 10^3 cm^{-1} (55 M^{-1} cm^{-1}) for $[ReO(DBDS)]^-$ and $[ReO(RDBDS)]^-$, respectively; these are tentatively assigned as d–d transitions on the basis of their small molar extinction coefficients. No corresponding d–d transitions could be observed for the three Tc–N_2S_2 analogs, presumably due to overlap with the strong charge-transfer bands which occur at 440–430 nm in the Tc–N_2S_2 complexes.

Crystal Structures of $[Ph_4X][MO(DBDS)]$ (X = P, As; M = Tc(V), Re(V)). The extensive similarities in the structures of $[TcO(DBDS)]^-$ and $[ReO(DBDS)]^-$ reinforce the strong pattern of structurally interchangeable Tc/Re complex pairs that has been emerging in the literature.[33–41] The near identical structural parameters of analogous Tc and Re complexes make such pairs useful probes in biological systems which recognize only the peripheral aspects (e.g. overall size, shape, dipole moment, etc.) of the complexes.[4,32,35,36,41]

The vacant sixth coordination site in $[Tc/ReO(DBDS)]^-$ is effectively blocked by the folding of the tetradentate ligand. Figure 3 shows a view of the anion perpendicular to the M=O vector. Note especially that the N_1–M–S_2 angle is only 133°; the vacant

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coordination site bisects this angle, and thus addition of a sixth ligand to the complex would require significant reorganization of the DBDS conformation and introduction of considerable strain into the complex.

A handful of other 5-coordinate Tc(V) and Re(V) complexes with N_2S_2 ligands have been structurally characterized, and these are summarized in Table VI. All M=O bonds are 1.65–1.66 Å in length, except for that in $[ReO(DBDS)]^-$, which is slightly longer at 1.68 Å. The M–thiol lengths range over 2.25–2.29 Å. $[Tc^VO(SCH_2CH_2S)_2]^-$ and $[Re^VO(SCH_2CH_2S)_2]^-$ show similar M–S distances of 2.30–2.31 Å.[42,43] Six-coordinate Tc(III) complexes characteristically exhibit Tc–thiol distances of 2.29–2.30 Å,[33] which leads to the inference that the $Tc^V{=}O^{3+}$ core exhibits to a thiolato ligand approximately the same electron density as does a Tc^{3+} core. The single M–thioether bond length in Table VI shows that it is at least 0.10 Å longer than a M–thiolato bond, in accord with the expectation that a thioether is a poorer σ-donor than is a thiolato ligand. M–N lengths are 1.98 Å for amides involved in 5-membered chelate rings, 2.04 and 2.05 Å for the amides involved in the less strained 5,7,5-membered chelate rings, and 2.16 Å for the Tc–ammine bonds. The negatively charged amide nitrogen atoms are more effective σ-donors than are the neutral ammines. These M–N and M–S distances are in agreement with several other similar Tc(V) and Re(V) monooxo complexes.[37,44,45] The S–M–N chelate bite angles in Table VI are all constant at 82–83° and are normal for 5-membered rings. However the N–M–N angles for the DBDS complexes are much larger due to the constraints of the 7-membered ring. Because DBDS is able to expand to a greater extent than ligands with only 5-membered rings, the metal is able to reside nearer the basal plane (0.67 vs 0.76 Å,[46] and concomitantly the average O–M–(N,S) angle is smaller in these $[MO(DBDS)]^-$ complexes (108°) compared to that of the others in Table VI (111°). For comparison, the $[TcO(epa)]^-$ complex contains a 6,5,6-chelate ring system in its tetradentate ligand and shows Tc to be 0.65 Å displaced from the N_2O_2 basal plane,[45] indicating that the larger chelate rings produce less distorted complexes in this series.

Kinetics. Isotopic oxygen exchange between oxo ions and water can proceed through a first-order process provided only small quantities of ^{17}O-labeled reactants are introduced into the equilibrium solutions.[47] The kinetic rate law which describes the exchange reaction is commonly referred to as the McKay equation.[48,49] For the reaction

$$(L)M{=}O + H_2O^* \rightarrow (L)M{=}O^* + H_2O \qquad (1)$$

the McKay equation is

$$Rt = [ab/(a + b)][\ln(1 - F)] \qquad (2)$$

where R is the overall rate of the oxygen transfer between the oxo ion and water, t is time, a and b are the concentrations of metal complex and water, and F is the fraction of exchange completed. Since $[H_2O] \gg [(L)M{=}O]$ in our studies, eq 2 reduces to

$$-\ln(1 - F) = Rt/[(L)M{=}O] = k't \qquad (3)$$

where k' is the rate constant governing oxygen exchange between (L)M=O and free water.

The kinetics of isotope exchange were studied in DMSO media because (1) the complexes have high solubility in DMSO, (2) DMSO solutions of the title complexes are very stable (no decomposition could be found 5 days after heating the solution at 50 °C), and (3) there is no observable reaction between DMSO and H_2O^*.

The oxygen-exchange reactions of $[ReO(DBDS)]^-$, $[TcO(DBDS)]^-$, and $[ReO(DADS)]^-$ are base catalyzed; no exchange could be detected without the addition of base. In alkaline solutions, additional ^{17}O signals are observed at 647, 716, and 850 ppm for $[ReO(DADS)]^-$, $[ReO(DBDS)]^-$, and $[TcO(DBDS)]^-$, respectively (relative to the free water signal at 0 ppm). In order to avoid introducing extra ^{16}O water to the reaction mixture, sodium methoxide was used as a catalyst. The relatively slow oxygen exchanges on $[TcO(DBDS)]^-$ and $[ReO(DADS)]^-$ require higher concentrations of base in order to proceed at reasonable rates. These reactions were performed at $[CH_3O^-] = 0.20–0.57$ M for $[TcO(DBDS)]^-$ and $[CH_3O^-] = 0.11–0.41$ M for $[ReO(DADS)]^-$. The more facile oxygen exchange on $[ReO(DBDS)]^-$ requires a lower concentration of base to proceed at a reasonable rate, and the data were collected at $[CH_3O^-] = 0.019–0.037$ M.

The $[(L)MO]^-–[H_2O^*]$ oxygen atom exchange reactions summarized in Table VII show that the reaction is independent of $[H_2O^*]$ and first-order in $[CH_3O^-]$ for the three systems studied; L = DADS with M = Re, L = DBDS with M = Re, and L = DBDS with M = Tc. The k'–$[CH_3O^-]$ plots for all the three complexes are linear with small, statistically insignificant, negative intercepts. The rate law for oxo oxygen atom exchange on $[ReO(DADS)]^-$, $[ReO(DBDS)]^-$, and $[TcO(DBDS)]^-$ can thus be expressed as

$$R = k[(L)MO^-][CH_3O^-]$$

This rate law, and the associated positive ΔS^* values, are consistent with an associative mode of activation in which base attack on the metal center leads to expansion of the coordination number of M from 5 to 6. Such an associative activation explains the relative rates of oxygen atom exchange of the ReO(DBDS) and ReO(DADS) complexes, since the butylenediamine moiety of DBDS provides more flexibility and less steric constraint than does the ethylenediamine backbone of DADS. This presumably lowers the activation energy required to convert the Re(V) center to a 6-coordinated transition state and accounts for the faster reaction rate of the ReO(DBDS) complex.

The results of Table VII show that $TcO(DBDS)^-$ undergoes oxygen atom exchange more slowly than does $ReO(DBDS)^-$ ($k^{Tc}/k^{Re} = 0.1$). This is consistent with the X-ray crystallographic data for $[TcO(DBDS)]^-$ and $[ReO(DBDS)]^-$ complexes listed in Table V, which show that Tc=O is significantly shorter than Re=O (1.657 (3) Å vs 1.681 (5) Å). The shorter, stronger Tc=O bond generates larger structural and kinetic trans effects and makes associative attack by CH_3O^- less favorable. In addition, X-ray crystallographic data also show that Tc sits a bit further above the basal plane formed by the two nitrogen and two sulfur atoms of the DBDS than does Re (0.6726 (3) Å for Tc and 0.6616 (3) Å for Re). This also contributes to the greater activation energy required to attain 6-coordination for the Tc complex.

The only existing comparative Tc/Re bimolecular rate data are those that our group have collected on six-coordinate com-

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plexes; pyridine exchange on *trans*-$[MO_2(py)_4]^+$ [18,20] and thiocyanate displacement of water on *trans*-$[MO(OH_2)(CN)_4]^-$ [19,20] (M = Tc(V) and Re(V)). In marked contrast to the five-coordinate complexes studied herein, these six-coordinate complexes react by a dissociative mode of activation, and the Tc complexes react very much more rapidly than do their Re analogs (k^{Tc}/k^{Re} ca. 10^3). The different modes of activation for six-coordinate and five-coordinate complexes, and the resulting inversion in relative rates (six-coordinate, dissociative, Tc > Re; five-coordinate, associative, Re > Tc) are readily understood on the basis of classical steric arguments. Only one set of comparative Tc/Re unimolecular rate date are known to us: the racemization of six-coordinate M(V) penicillamine complexes.[21] In this reaction k^{Tc}/k^{Re} is about 57 at room temperature, which, in the context of the above discussion, implies that racemization proceeds primarily through a dissociative mode of activation.

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Supplementary Material Available: Tables A–F, listing additional crystallographic data, bond lengths and angles, and thermal and hydrogen atomic parameters for $[Ph_4P][TcO(DBDS)]$ and $[Ph_4P][TcO(DBDS)]$, and Figures A–E, showing plots of k' versus $[CH_3O^-]$ for $[ReO(DADS)]^-$, $[ReO(DBDS)]^-$, and $[TcO(DBDS)]^-$ and Eyring plots for $[ReO(DADS)]^-$ and $[ReO(DBDS)]^-$ (12 pages). Ordering information is given on any current masthead page.