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Supplementary Material Available: Tables A–E, listing thermal parameters for **1**, hydrogen parameters for **1**, thermal parameters for **2**, hydrogen parameters for **2**, and least-squares planes (5 pages); tables of calculated and observed structure factors for **1** and for **2** (54 pages). Ordering information is given on any current masthead page.

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Electrochemistry of Oxo–Technetium(V) Complexes Containing Schiff Base and 8-Quinolinol Ligands

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The electrochemistry of six-coordinate, monooxo technetium(V) complexes containing Schiff base ligands has been studied in acetonitrile and *N,N'*-dimethylformamide solutions. The complexes have the general formula $TcOCl(L_B)_2$ or $TcO(L_T)(L_B)$, where L_B represents a bidentate-N,O Schiff base ligand or a bidentate-N,O 8-quinolinol ligand and L_T represents a tridentate-O,N,O Schiff base ligand. Cyclic voltammetry at a platinum-disk electrode, controlled-potential coulometry, and thin-layer spectroelectrochemistry were used to probe both the oxidation and the reduction of these complexes. The results of these studies, and previously reported results on the analogous Re(V) complexes, can be understood within a single general reaction scheme. The salient features of this scheme are (i) one-electron reduction of Tc(V) to Tc(IV), (ii) subsequent loss of a ligand situated cis to the Tc=O linkage, and (iii) subsequent isomerization of this unstable Tc(IV) product to a more stable complex in which the site trans to the Tc=O linkage is vacant. The Tc(IV) complexes can also be reduced to analogous Tc(III) species, which appear to undergo the same ligand loss and isomerization reactions. The technetium complexes are 400–500 mV easier to reduce than are their rhenium analogues. The 8-quinolinol ligands, and especially the 5-nitro derivative, both thermodynamically and kinetically stabilize the Tc(IV) and Tc(III) oxidation states. These electrogenerated species are unusual in that they constitute the bulk of the known examples of monomeric Tc(IV) and Tc(III) complexes containing only N- and O-donating ligands.

Introduction

In the past several years considerable effort[4–14] has been focused on the electrochemistry of technetium complexes containing this element in oxidation states ranging from +1 to +3. This focus stems partly from the importance of low-valent technetium-99 complexes, and their associated in vivo redox chemistry, in nuclear medicine.[15–19] These electrochemical studies have been facilitated by the fact that the π-acid ligands used to stabilize low oxidation states of technetium also tend to promote facile, electrochemically reversible, electron-transfer reactions.[20,21]

Technetium(V) complexes containing the monooxo TcO^{3+} or dioxo *trans*-TcO_2^+ cores are also of great importance in nuclear medicine,[16,17,19] and there have been recent indications that these species may also undergo in vivo redox reactions that affect their biodistributions.[22] However, only a few electrochemical investigations of oxo–technetium(V) complexes have been reported, primarily because these species do not generally undergo electrochemically reversible redox processes.[23,24] We have recently observed[25,26] that oxo–rhenium(V) complexes containing Schiff base ligands exhibit reversible electrochemical reactions and thus thought that a study of the analogous oxo–technetium(V) com-

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(1) CNR.
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(4) Mazzocchin, G. A.; Seeber, R.; Mazzi, U.; Roncari, E. *Inorg. Chim. Acta* **1977**, *29*, 5.
(5) Mazzi, U.; Roncari, E.; Seeber, R.; Mazzocchin, G. A. *Inorg. Chim. Acta* **1980**, *41*, 95.
(6) Seeber, R.; Mazzocchin, G. A.; Roncari, E.; Mazzi, U. *Transition Met. Chem.* (*London*) **1981**, *6*, 123.
(7) Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 3298.
(8) Roncari, E.; Mazzi, U.; Seeber, R.; Zanello, P. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *132*, 221.
(9) Seeber, R.; Mazzocchin, G. A.; Mazzi, U.; Roncari, E.; Refosco, F. *Transition Met. Chem.* (*London*) **1984**, *9*, 315.
(10) Ichimura, A.; Heineman, W. R.; Vanderheyden, J.-L.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 1272.
(11) Bandoli, G.; Mazzi, U.; Ichimura, A.; Libson, K.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2898.
(12) Jurisson, S. S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743.
(13) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134.
(14) Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1987**, *26*, 3108.
(15) Vanderheyden, J.-L.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1666.
(16) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75.
(17) Deutsch, E.; Libson, K. *Comments Inorg. Chem.* **1984**, *3*, 83.
(18) Deutsch, E.; Libson K.; Vanderheyden, J.-L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465.
(19) Clarke, M. J.; Podbielski, L. *Coord. Chem. Rev.* **1987**, *78*, 253.
(20) Doyle, M. N.; Libson, K.; Woods, M.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1986**, *25*, 3367.
(21) Libson, K.; Doyle, M. N.; Thomas, R. W.; Nelesnik, T.; Woods, M.; Sullivan, J. C.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3614.
(22) Neirinckx, R. D.; Harrison, R. C.; Forster, A. M.; Burke, J. F.; Anderson, A. R.; Lassen, N. A. *J. Nucl. Med.* **1987**, *28*, 559.
(23) Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227.
(24) Vanderheyden, J.-L; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, L. R.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184.
(25) Seeber, R.; Mazzocchin, G. A.; Mazzi, U.; Refosco, F.; Tisato, F. *Polyhedron* **1986**, *5*, 1975.
(26) Seeber, R.; Mazzocchin, G. A.; Refosco, F.; Mazzi, U.; Tisato, F. *Polyhedron* **1987**, *6*, 1647.

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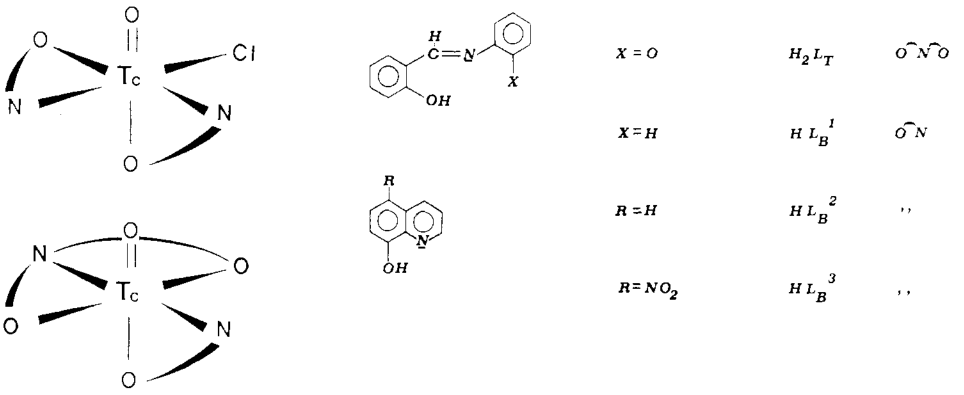
Chart I



plexes might provide useful information about the redox chemistry of these species. In this paper we report on the results of these electrochemical studies and compare these results to those obtained for the analogous oxo–rhenium(V) systems.

Experimental Section

Technetium. All experiments were conducted with the isotope ^{99}Tc and thus all references to the element technetium are to this specific isotope. *Caution!* Technetium-99 emits a low-energy (0.292-MeV) β particle with a half-life of 2.1×10^5 years. When this material is handled in milligram amounts, it 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 and inadvertent ingestion or inhalation of this isotope.

Technetium-99 of >99% radiochemical purity was purchased in the form of ammonium pertechnetate from Oak Ridge National Laboratory, Oak Ridge, TN. Quantitative determinations of ^{99}Tc were performed by liquid scintillation β counting on a Rackbeta II (Model 1215) instrument using premixed Insta-gel scintillation cocktail (Packard Instruments, Inc., Zurich).

Materials. Both *N*,*N*-dimethylformamide (DMF) and acetonitrile (ACN) were Aldrich Gold Label quality (packaged under nitrogen, <0.005% water) and were used without purification. Tetraethylammonium perchlorate (TEAP, Fluka) was dried at 50 °C under vacuum for 2 days and used without purification. No significant electroactive impurities were detected in either the solvents or the supporting electrolyte.

The complexes $TcOCl(L_{B^1})_2$, $TcOCl(L_{B^2})_2$, $TcOCl(L_{B^3})_2$, $TcO(L_T)(L_{B^1})$, and $TcO(L_T)(L_{B^2})$ were prepared as previously described[27-29] and exhibited visible–UV and IR spectrophotometric properties identical with those previously reported. Structural formulas of the complexes and ligands are given in Chart I; L_{B^1} represents the monoanion of *N*-phenylsalicylideneamine, L_{B^2} represents the monoanion of quinolin-8-ol, L_{B^3} represents the monoanion of 5-nitroquinolin-8-ol, and L_T represents the dianion of *N*-(2-oxidophenyl)salicylideneamine.

(5-Nitroquinolin-8-olato-*O*,*N*)(*N*-(2-oxidophenyl)salicylideneaminato-*O*,*N*,*O*)oxotechnetium(V), $TcO(L_T)(L_{B^3})$. This new complex was synthesized in 85% yield by the procedure used to prepare its homologues[29] and was characterized by comparison of its properties with those of previously characterized homologues. Anal. Calcd for $C_{22}H_{14}N_3O_6Tc$: C, 51.28; H, 2.73; N, 8.16; Tc, 19.19. Found: C, 51.13; H, 2.70; N, 8.12; Tc, 19.00. Main IR bands (cm^{-1}): 1603 (C=N); 954 (Tc=O); 1293, 1503 (N—O). Vis-UV (DMF); λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 350 (21 000); 465 (26 000); 600 (sh). This green complex is soluble in DMF, dichloromethane, and acetone, is slightly soluble in ethanol, methanol, and diethyl ether, and is insoluble in hydrocarbons.

Methods. In general, electrochemical experiments were conducted as previously described.[7,10,13,30] Solutions in either DMF or ACN were prepared and maintained under an inert atmosphere; the concentration of complex was about 0.001 M, and the concentration of TEAP was either 0.10 or 0.50 M. Some complexes are only slightly soluble in ACN; in these systems, ACN was used only for determination of formal potentials. Low-temperature measurements were made in dry ice/ACN slurries when ACN was used as solvent and in dry ice/ethanol slurries when DMF was used as solvent.

Cyclic voltammetric data were used to calculate $E^r_{1/2}$, the average of the anodic and cathodic peak potentials obtained under conditions where the ratio of peak currents was approximately 1. The superscript "r" indicates that this potential refers to a reversible electrochemical process. Values of $E^r_{1/2}$ are experimental approximations of the standard potential of the redox couple; they were measured with ferrocene as internal standard and are reported vs the ferrocenium/ferrocene couple.[31,32] Hence, they are directly comparable to identically referenced potentials measured in a previous study of analogous rhenium(V) complexes.[25] To allow comparisons to potentials measured versus other references, we note that under our experimental conditions $E^r_{1/2}$ for the ferrocenium/ferrocene couple is +0.38 V vs the aqueous saturated calomel electrode.

Instrumentation. Voltammetric data were obtained with a BAS (Bioanalytical Systems, Inc.) CV-1B or CV-27 cyclic voltammograph, connected to a Hewlett-Packard 7045A X/Y recorder, and the following three electrodes supported in a BAS VC-2 voltammetry cell: 1.6 mm diameter platinum-disk working electrode (PDE), saturated calomel reference electrode isolated by a salt bridge containing solvent and supporting electrolyte, and a platinum-spiral-wire auxiliary electrode.

Controlled-potential coulometry was performed with an Amel Model 552 potentiostat, connected to an Amel Model 721 integrator, and the following electrodes: platinum-spiral-wire working electrode (area about 3.3 cm^2), a platinum-foil auxiliary electrode, which was isolated inside a salt bridge by a medium glass frit, and a saturated calomel reference electrode.

Spectroelectrochemical measurements were made with an optically transparent thin-layer electrode (OTTLE)[33] with a 100 wires/in. gold minigrid working electrode, a platinum auxiliary electrode, and an aqueous Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems RE-1), which was isolated from the solution by a porous Vycor plug. In the spectropotentiostatic experiments, 7 min elapsed between the time at which the potential was applied and the time at which the spectrum was recorded.

Visible–UV spectrophotometric measurements were obtained with a Cary 14 instrument. The cell compartment of this spectrophotometer was fitted with the appropriate electrical and inert-gas line connections necessary for spectroelectrochemistry.[33]

Results and Discussion

Electrochemistry of $TcOCl(L_B)_2$ Complexes. All of the cyclic voltammetric and coulometric results observed for the three $TcOCl(L_B)_2$ complexes, and the two analogous $ReOCl(L_B)_2$ complexes investigated previously,[25] can be rationalized within Scheme I. A central feature of this scheme is irreversible loss of the chloride ligand following reduction from M(V) to M(IV). This chloride loss has been definitively established for the rhenium system by isolation of the $Re^{IV}O(L_{B^1})_2$ species[25] and in the technetium system is supported by the detection of free chloride ion after $TcOCl(L_{B^1})_2$ has been completely reduced to Tc(IV) (vide infra). Chloride loss from M(IV) leads to a five-coordinate species that is relatively unstable since the chloride originates from a site

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(27) Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 2455.

(28) Wilcox, B. E.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2962.

(29) Mazzi, U.; Refosco, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1623.

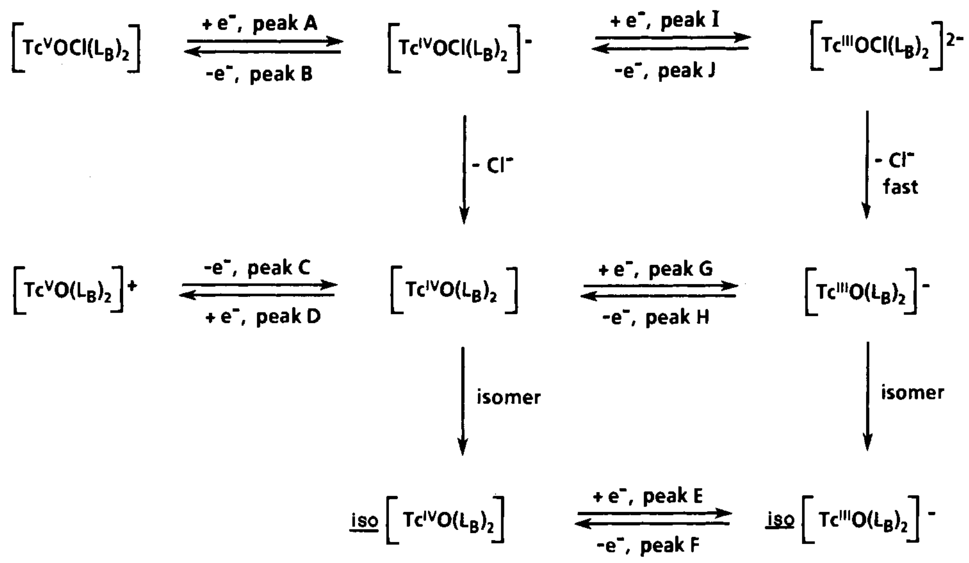
(30) Rohrbach, D. F.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 2536.

(31) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(32) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(33) DeAngelis, T. P.; Heineman, W. R. *J. Chem. Educ.* **1976**, *53*, 594.

Scheme I



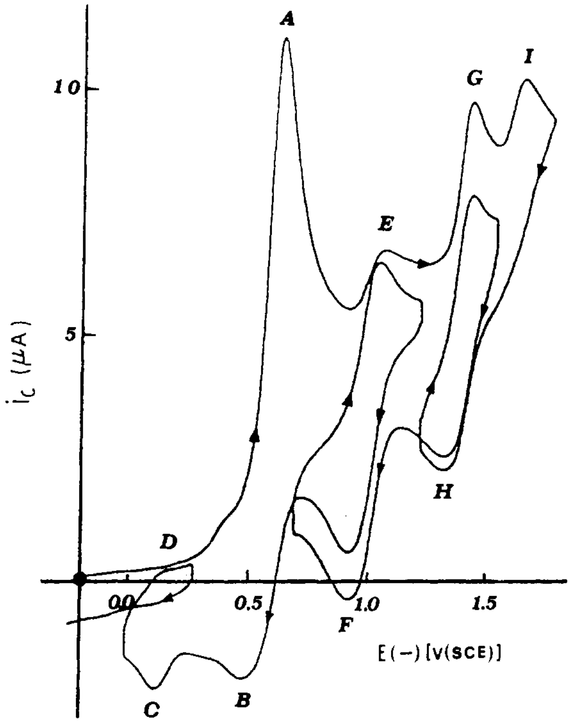


Figure 1. Cyclic voltammogram of 2.6 mM $TcOCl(L_{B'})_2$ in bulk solution at a PDE. Conditions: 0.10 M TEAP/ACN, scan rate 0.2 V/s, room temperature. ● designates the starting potential; this designation is used in all figures.

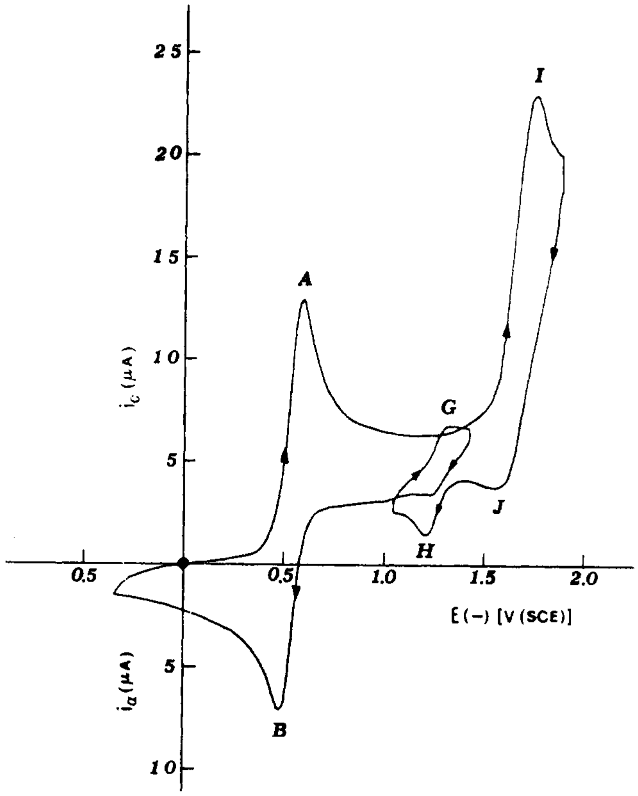


Figure 2. Cyclic voltammogram of 2.6 mM $TcOCl(L_{B'})_2$ in bulk solution at a PDE. Conditions are the same as in Figure 1 except $t = -35$ °C.

cis to the M=O linkage; in the rhenium system this species appears to isomerize into a relatively stable square-pyramidal configuration in which the site trans to the M=O linkage is vacant.[25] The Tc system has been studied in both ACN and DMF (the Re system was studied only in ACN), and similar cyclic voltammograms are observed in the two solvents. This observation implies that the isomerization is not sensitive to the nature of the solvent and supports its assignment as an intramolecular process.[25]

(i)$TcOCl(L_{B'})_2$. A typical bulk-solution cyclic voltammogram of $TcOCl(L_{B'})_2$ in 0.10 M TEAP/ACN at a PDE is shown in Figure 1. A negative potential scan yields an initial reduction at peak A, with which the anodic peak B is associated. At room temperature the ratio of peak currents for B/A is significantly less than 1 for all scan rates investigated (0.02–0.5 V/s). However, this ratio tends toward unity at low temperatures (−40 °C), consistent with an irreversible chemical reaction following the initial reduction. At room temperature, two additional reversible or quasi-reversible reductions (peaks E and G) and the final cathodic peak I (which has no associated anodic peak) are observed. As the scan rate is increased, the height of peak G increases while that of peak E decreases. At temperatures below 0 °C the pairs of peaks C/D (which are only observed in the reverse scan) and E/F disappear, while a new, small anodic peak J (which is directly associated with I) appears. Furthermore, at low temperatures (−35 °C) peaks G/H are only present in a second cycle; i.e., if the potential scan is reversed after traversing peak I, peak H is recorded in the positive scan and peak G appears in the following negative scan. This behavior is shown in the cyclic voltammogram of Figure 2.

Exhaustive coulometric reduction at peak A ($E_{app} = -0.70$ V; $t = 20$ °C) shows a one-electron process ($n = 0.99$ e/mol). A voltammogram recorded on this reduced solution shows that only peaks E/F remain (Figure 3). However, a large anodic current attributable to the oxidation of free chloride ions is observed to commence at about +0.8 V.

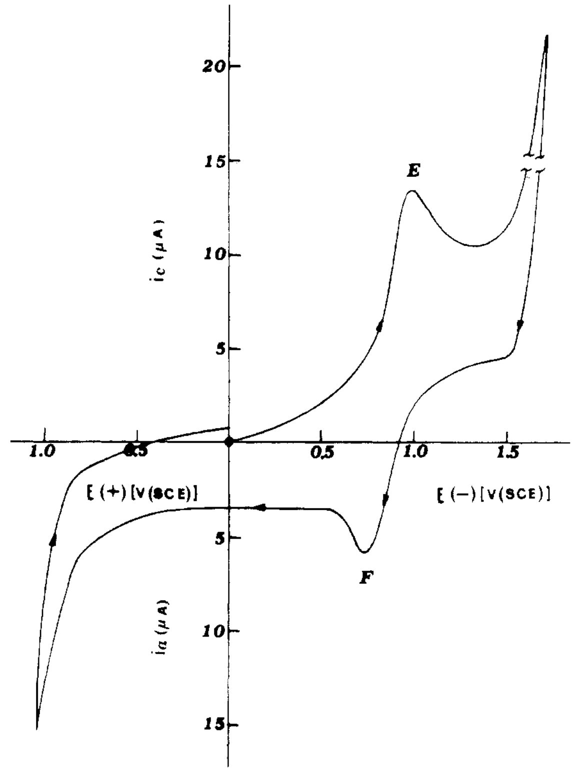


Figure 3. Cyclic voltammogram of 2.6 mM $\mathrm{TcOCl(L_{B^1})_2}$ that had previously been exhaustively reduced at −0.70 V. Conditions are the same as in Figure 1.

At room temperature, all three of the Tc(IV) species shown in Scheme I can be observed in a cyclic voltammogram run at 0.2 V/s. Under conditions designed to render ineffective the chemical reaction leading to chloride loss from $\mathrm{[Tc^{IV}OCl(L_{B^1})_2]^-}$ (high scan rate or low temperature), reduction of this species to the analogous Tc(III) complex occurs with reasonable efficiency. This Tc(III) product can then undergo chloride loss and isomerization processes analogous to those proposed for Tc(IV).

(ii) $\mathrm{TcOCl(L_{B^2})_2}$. A typical bulk-solution cyclic voltammogram of $\mathrm{TcOCl(L_{B^2})_2}$ in 0.10 M TEAP/DMF at a PDE is shown in Figure 4. This voltammogram is very similar to that observed for the analogous $\mathrm{L_{B^1}}$ complex (Figure 1), the primary differences arising from the different stabilities of the various intermediates: (i) the first reduction (peak A) and its associated oxidation (peak B) exhibit peak current ratios of unity for all scan rates investigated (0.05–0.5 V/s); (ii) peak E and its associated anodic peak F exhibit the behavior described above for the $\mathrm{L_{B^1}}$ complex, but at room temperature and a scan rate of 0.2 V/s these peak heights are smaller than those observed for the $\mathrm{L_{B^1}}$ system; (iii) adsorption of the electrogenerated product leads to peaks I and I′;[34] (iv) at temperatures below 0 °C, coupled peaks G and H are recorded *after* scanning through peak I (Figure 5).

Exhaustive coulometric reduction at peak A ($E_{\text{app}} = -0.50$ V; $t = 20$ °C) shows a one-electron process ($n = 0.98$ e/mol). A voltammogram recorded on this reduced solution shows that only peaks E/F remain.

These voltammetric and coulometric results observed for $\mathrm{TcOCl(L_{B^2})_2}$ are readily explicable within Scheme I. The initially electrogenerated Tc(IV) complex $\mathrm{[TcOCl(L_{B^2})_2]^-}$ is more stable than the $\mathrm{L_{B^1}}$ analogue, and thus this is the only species present in a significant concentration at the electrode after traversing peak A. This Tc(IV) intermediate is further reduced at peak I, but the resulting Tc(III) complex is very unstable and rapidly loses chloride ion; oxidation of this dehalogenated Tc(III) species at peak H generates the Tc(IV) complex that is responsible for peak G. Peak G is only detectable at low temperature; at higher temperatures the dehalogenated Tc(III) species isomerizes, and oxidation of this isomerized product occurs as peak F (Figure 4). These observations justify the inclusion in Scheme I of the isomerization process for Tc(III) and indicate that the $\mathrm{L_{B^2}}$–Tc(III) species isomerizes more rapidly than does the $\mathrm{L_{B^1}}$–Tc(IV) species.

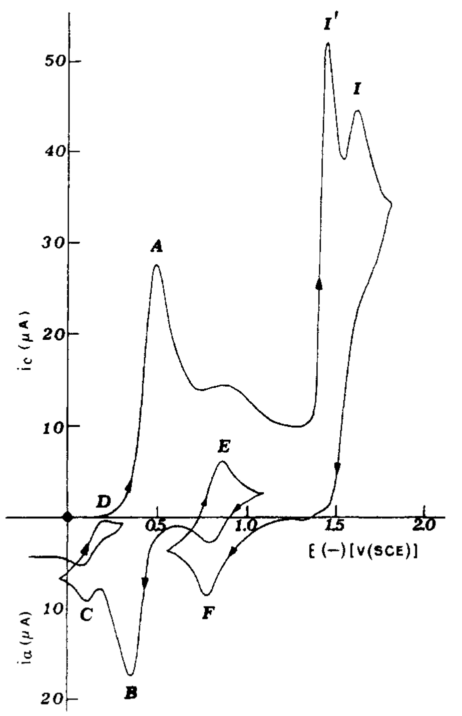


Figure 4. Cyclic voltammogram of 3.7 mM $\mathrm{TcOCl(L_{B^2})_2}$ in bulk solution at a PDE. Conditions: 0.10 M TEAP/DMF, scan rate 0.2 V/s, room temperature.

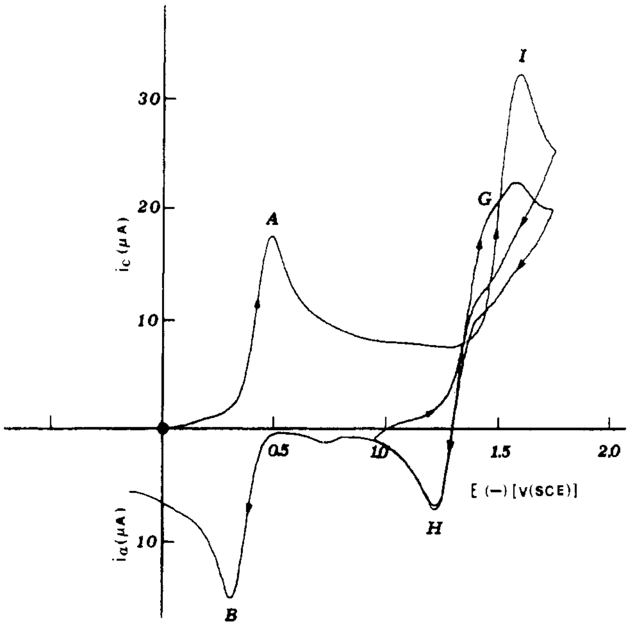


Figure 5. Cyclic voltammogram of 3.7 mM $\mathrm{TcOCl(L_{B^2})_2}$ in bulk solution at a PDE. Conditions are the same as in Figure 4 except $t = -50$ °C.

(iii) $\mathrm{TcOCl(L_{B^3})_2}$. The electrochemical behavior of this complex is considerably simpler than that of the $\mathrm{L_{B^1}}$ and $\mathrm{L_{B^2}}$ analogues in that the initially generated Tc(IV) complex $\mathrm{[TcOCl(L_{B^3})_2]^-}$ is very stable. The ratio of anodic and cathodic peak currents for this Tc(V)/Tc(IV) process is unity over all temperatures (25–40 °C) and scan rates (0.02–0.50 V/s) investigated. Moreover, after exhaustive coulometry ($E_{\text{app}} = -0.25$ V) the Tc(IV) complex is the only species that can be detected by cyclic voltammetry, and the Tc(V) starting material can be regenerated from it by anodic reoxidation.

The enhanced stability of the $\mathrm{L_{B^3}}$–Tc(IV) electrogenerated product is undoubtedly due to the electron-withdrawing properties

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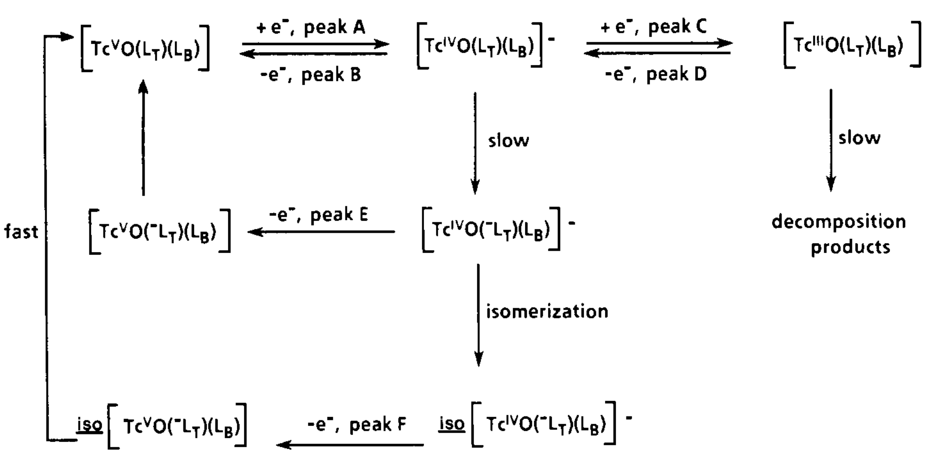
[34] Wopshall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

Scheme II



$^{-}L_T$ = ligand with a non-coordinated phenolate group

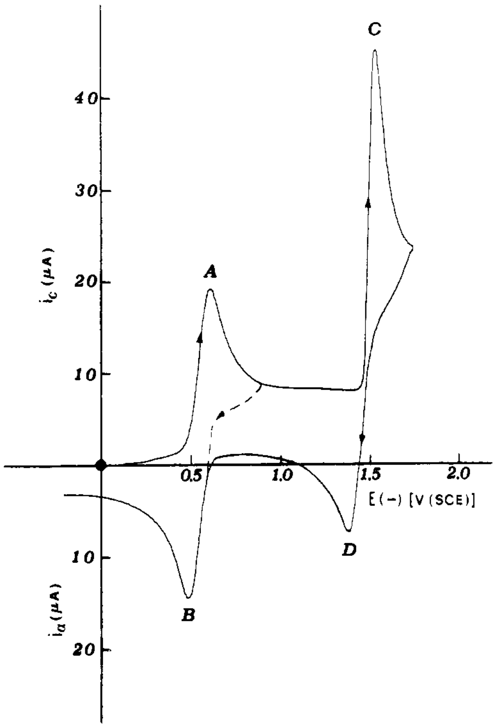


Figure 6. Cyclic voltammogram of 2.1 mM $TcO(L_T)(L_{B^1})$ in bulk solution at a PDE. Conditions: 0.10 M TEAP/ACN, scan rate 0.2 V/s, room temperature.

of the nitro substituent on L_{B^3}. For the L_{B^1} and L_{B^2} systems, reduction of Tc(V) to Tc(IV) sufficiently increases the electron density on the metal center to labilize the Tc–Cl linkage; further reduction to Tc(III) causes even more rapid Tc–Cl bond fission. However, for the L_{B^3} system it appears that the electron added upon reducing Tc(V) to Tc(IV) is delocalized onto the nitro group to such an extent that the Tc–Cl bond is not appreciably labilized.

Unfortunately, the presence of the nitro group on L_{B^3} precludes investigation of the electrochemistry of $TcOCl(L_{B^3})_2$ at more negative potentials. At potentials more negative than that of the initial Tc(V)/Tc(IV) reduction, adsorption and poisoning phenomena lead to irreproducible voltammetric responses.

Electrochemistry of $TcO(L_T)(L_B)$ Complexes. All of the cyclic voltammetric and coulometric results observed for the three $TcO(L_T)(L_B)$ complexes, and the two analogous $ReO(L_T)(L_B)$ complexes investigated previously,[25] can be rationalized within Scheme II. This scheme is closely related to Scheme I in that its central feature is irreversible Tc(IV)–ligand bond fission subsequent to the initial electrochemical reduction. For the $TcOCl(L_B)^2$ complexes in Scheme I, it is the Tc–Cl bond that undergoes fission; for the $TcO(L_T)(L_B)$ complexes in Scheme II, it is the comparable Tc–phenolate bond within the L_T ligand that is hypothesized[25] to undergo fission. This bond fission converts the tridentate L_T ligand into a bidentate ligand, which in Scheme II is designated as $^{-}L_T$. Loss of the phenolate group leads to a five-coordinate species that is relatively unstable since this group was originally located cis to the M=O linkage. Scheme II includes isomerization of this unstable five-coordinate Tc(IV) complex into a relatively stable square-pyramidal configuration wherein the site trans to the M=O linkage is vacant.

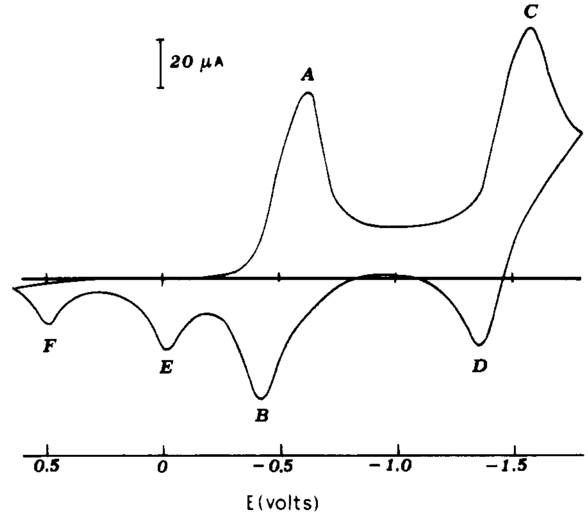


Figure 7. Thin-layer cyclic voltammogram of 2.3 mM $TcO(L_T)(L_{B^1})$ at a gold OTTLE. Conditions: 0.50 M TEAP/DMF, scan rate 0.002 V/s, initial open circuit potential 0.0 V, cathodic scan. Potentials are vs Ag/AgCl (3 M NaCl).

(i) **$TcO(L_T)(L_{B^1})$.** A typical bulk-solution voltammogram of $TcO(L_T)(L_{B^1})$ in 0.10 M TEAP/ACN at a PDE is shown in Figure 6. A negative potential scan yields two reversible reductions (coupled peaks A/B and C/D); the sharpness of the latter reduction (peak C) indicates that it is affected by electrode adsorption phenomena. In contrast to the complicated $TcOCl(L_B)_2$ cyclic voltammograms (Figures 1 and 4), the cyclic voltammograms obtained for $TcO(L_T)(L_{B^1})$ are remarkably simple and exhibit no evidence for coupled chemical reactions at any of the scan rates investigated (0.05–0.50 V/s). The only observed scan-rate dependence appears to result from electrode adsorption; i.e., the ratio of the peak current (for peak C) to the square root of the scan rate increases as the scan rate increases, and the ratio $(i_p)_B/(i_p)_A$ is significantly greater than 1.

The relatively high stability of the $TcO(L_T)(L_{B^1})$ reduction product observed in bulk-solution cyclic voltammograms provides the impetus for an OTTLE study. An OTTLE cyclic voltam-

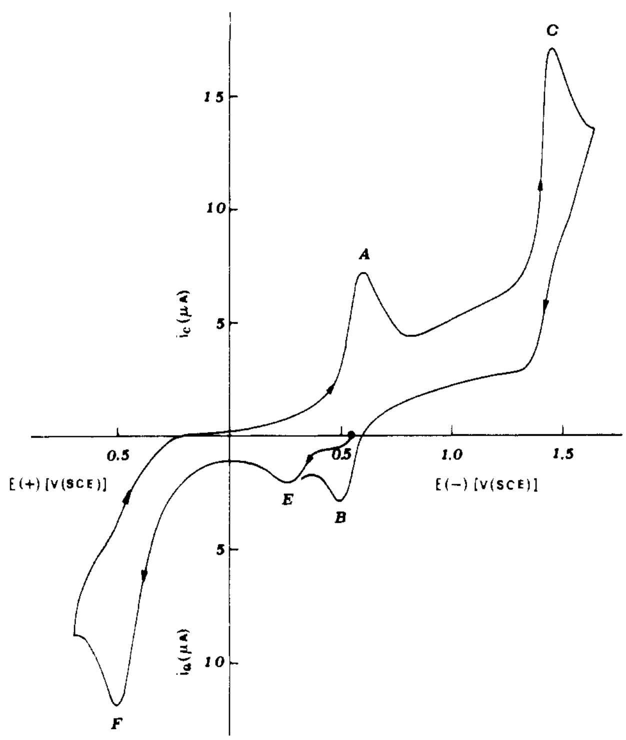


Figure 8. Cyclic voltammogram of 2.1 mM $TcO(L_T)(L_{B^1})$ that had previously been exhaustively reduced at −0.625 V. Conditions are the same as in Figure 6.

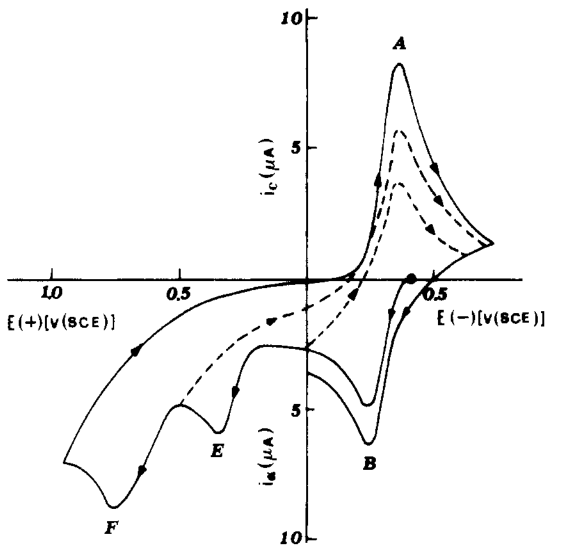


Figure 9. Cyclic voltammogram of 2.5 mM $TcO(L_T)(L_{B^3})$ that had previously been exhaustively reduced at −0.40 V. Conditions are the same as in Figure 6.

mogram recorded at 0.002 V/s in 0.50 M TEAP/DMF is shown in Figure 7. In addition to the coupled peaks A/B and C/D observed in bulk solution, the OTTLE study shows two anodic peaks (E and F) that are not associated with any cathodic peaks; peaks E and F can also be detected by reversing the scan direction immediately after traversing peak A. These observations establish that irreversible chemical reactions are occurring on the very slow time scale of the OTTLE experiment. Specifically, it appears as though the Tc(IV) complex $[Tc^{IV}O(L_T)(L_{B^1})]^-$ initially formed at peak A converts slowly into two other species. In Scheme II these new species are assigned to be the Tc(IV) complex in which the Tc–phenolate bond has broken and the more stable isomeric form of this intermediate.

The operation of irreversible chemical reactions over the period defined by the OTTLE scan rate is supported by visible–UV spectra recorded during the OTTLE experiment. For a truly reversible system, the initial and final spectra would be identical; the fact that they are not and the fact that the final spectrum lies under the initial spectrum are wholly consistent with chemical instability of the electrogenerated Tc(IV) complex. The observation of intense absorption at about 660 nm in the spectrum recorded at −1.70 V implies that in this system at least one of the Tc(III) products absorbs strongly in this region of the spectrum. A less definitive peak at about 420 nm is present for the Tc(IV) product(s).

Exhaustive coulometric reduction in bulk solution at peak A (E_{app} = −0.625 V) shows a one-electron process (n = 0.96 e/mol). A bulk-solution cyclic voltammogram recorded on this completely electrolyzed solution is shown in Figure 8. This voltammogram shows that the species responsible for peak B, i.e., the initial reduction product $[Tc^{IV}O(L_T)(L_{B^1})]^-$, has disappeared to form a stable product that is oxidized at peak F. Moreover, oxidation of this stable product leads to an almost quantitative regeneration of the starting Tc(V) complex (as established by the recording of peaks A/B and C/D on the return scan). In Scheme II this stable product is the stable Tc(IV) isomer; since oxidation of this species directly yields the original Tc(V) complex, isomerization of the Tc(V) system must occur quickly on the time scale of this voltammogram (0.2 V/s).

The Tc(III) product(s) in this system appear to have moderate stability, even on the time scale of the OTTLE experiment (Figure 7). However, exhaustive coulometric reduction in bulk solution at peak C (E_{app} = −1.60 V; n = 2.14 e/mol) leads to solutions that exhibit ill-defined, irreproducible cyclic voltammograms. Accordingly, reoxidation of these exhaustively reduced solutions does not lead to any of the complexes that appear in Scheme II. This suggests that the Tc(III) product(s) formed at peak C undergoes irreversible decomposition on the time scale of minutes.

(ii) $TcO(L_T)(L_{B^2})$. The electrochemical behavior of this L_{B^2} complex is qualitatively similar to that of the analogous L_{B^1} complex. As observed in the $TcOCl(L_B)_2$ system, the L_{B^2}–Tc(IV) intermediate is more stable than the corresponding L_{B^1}–Tc(IV) intermediate. For both the $TcOCl(L_B)_2$ and $TcO(L_T)(L_B)$ systems, this trend presumably results from the more rigid structure of L_{B^2} (relative to that of L_{B^1}), which retards the rate of Tc–ligand bond fission.

Exhaustive coulometric reduction in bulk solution at peak A (E_{app} = −0.50 V) shows a one-electron process (n = 0.98 e/mol). A cyclic voltammogram recorded on this solution immediately after electrolysis shows the presence of peaks E and F, as well as of peak B. At increasing times after the electrolysis, the height of peak F increases while that of peak B decreases; at about 30 min after electrolysis, peak F is the only anodic peak detectable in the direct scan (i.e., from peak A toward positive potentials). Again, within Scheme II peak F corresponds to oxidation of the stable isomeric form of the Tc(IV) product. Reoxidation at peak F almost quantitatively regenerates the starting Tc(V) complex, again implying that the Tc(V) system isomerizes rapidly on the time scale of this experiment.

OTTLE experiments conducted with this L_{B^2} system yield results comparable to those obtained with the L_{B^1} system. Important features of visible–UV spectra obtained during the OTTLE experiment are (i) incomplete regeneration of the initial spectrum after the OTTLE voltammographic cycle, (ii) the intense absorption at about 420 nm resulting from the Tc(IV) product(s), and (iii) the intense absorption at about 660 nm resulting from the Tc(III) product(s).

(iii) $TcO(L_T)(L_{B^3})$. This new complex was prepared with the aim of stabilizing the electrogenerated Tc(IV) complexes. Reduced complexes of the $TcO(L_T)(L_B)$ system are more stable than those of the $TcOCl(L_B)_2$ system, and within the $TcOCl(L_B)_2$ system the L_{B^3} ligand affords the greatest stability to reduced oxidation states because of the electron-withdrawing character of its nitro substituent (vide supra). Thus, for the ligands investigated in this work, the $TcO(L_T)(L_{B^3})$ complex should generate maximum stability for the Tc(IV) products.

Cyclic voltammograms recorded in DMF solutions of this L_{B^3} complex are not significantly different from those recorded for the analogous L_{B^1} and L_{B^2} complexes, except that the potentials

Table I. Comparison of $E^r_{1/2}$ Values for the M(V/IV) Couple (M = Tc, Re)[a]

M(V) complex[b]	$E^r_{1/2}$ Tc	$E^r_{1/2}$ Re	$E^r_{1/2}$(Tc) − $E^r_{1/2}$(Re)
$MOCl(L_B{}^1)_2$	−0.91[c]	−1.43[d]	0.52
$MOCl(L_B{}^2)_2$	−0.87		
$MOCl(L_B{}^3)_2$	−0.54		
$MO(L_T)(L_B{}^1)$	−0.92	−1.38[d]	0.46
$MO(L_T)(L_B{}^2)$	−0.88		
$MO(L_T)(L_B{}^3)$	−0.73		

[a] $E^r_{1/2}$ values are measured in acetonitrile versus the ferrocenium/ferrocene couple by cyclic voltammetry at 0.2 V/s. [b] Ligand definitions are given in the text. [c] Measured at −35 °C. [d] Data taken from ref 25; corrected from the reported −1.33 V at 20 V/s.

for the redox couples are shifted in the positive direction (vide infra). Exhaustive coulometric reduction at peak A (E_{app} = −0.40 V) shows a one-electron process (n = 0.97 e/mol). Figure 9 shows cyclic voltammograms recorded on this electrolyzed solution. All three anodic peaks B, E, and F are recorded on the first positive scan initiated at the electrolysis potential. Moreover, Figure 9 shows that all three oxidation processes defined by these peaks lead to regeneration of the starting Tc(V) complex; i.e., the height of peak A increases upon reversing the potential scan after traversing (i) just B, (ii) B and E, and finally (iii) B, E, and F. Within Scheme II, these processes correspond to oxidation of the three forms of Tc(IV), each oxidation directly yielding the initial Tc(V) complex via relatively rapid isomerization of the Tc(V) system. One hour after exhaustive electrolysis, peak F is the only anodic peak detectable in the positive scan, and its height is noticeably increased over that in the voltammogram obtained immediately after electrolysis. Within Scheme II, peak F corresponds to oxidation of the most stable isomeric form of Tc(IV). Oxidation of the reduced solution at the potential of peak F quantitatively regenerates the starting Tc(V) complex.

Exhaustive coulometric reductions at peak C (E_{app} = −1.25 V) yield an irreproducible number of electrons consumed per mole of complex; this strongly implies that both the technetium center and the nitro group of L_{B^3} are being reduced under these conditions.

In sum, of the six complexes investigated in this work, the $TcO(L_T)(L_{B^3})$ complex does indeed afford the most stable Tc(IV) product. However, even in this system the initially electrogenerated Tc(IV) product undergoes slow Tc–phenolate bond fission and subsequent isomerization. The presence of these three moderately stable Tc(IV) species, and their reoxidation to the Tc(V) starting material, are nicely illustrated in the cyclic voltammogram of Figure 9.

Comparisons of $E^{\circ\prime}$ Values. Electrochemical studies on a variety of technetium and rhenium systems have shown that the Re complexes are consistently more difficult to reduce than their Tc analogues.[14,18] The majority of such Tc/Re systems studied to date involve low-valent metal centers, and for these systems the difference in reduction potentials is usually about 200–300 mV.[14,18] The data of Table I show that for the two comparisons made available by this study [$MOCl(L_{B^1})_2$ and $MO(L_T)(L_{B^1})$], the Re complex is indeed more difficult to reduce than the Tc analogue, but the difference in M(V/IV) reduction potentials is in the range of 400–500 mV. Whether these larger potential differences of Table I result from the high metal oxidation states involved in the couples, and the concomitant involvement of the M=O linkage, or from some systematic error(s) inherent in determining these potential differences, will have to be determined by further studies.

Within each of the $TcOCl(L_B)_2$ and $TcO(L_T)(L_B)$ series of complexes, the L_{B^1} complex is more difficult to reduce than the L_{B^2} analogue, which in turn is more difficult to reduce than the L_{B^3} analogue. This trend in Tc(V/IV) reduction potentials (Table I) is also followed in the Tc(IV/III) reduction potentials of the $TcO(L_T)(L_B)$ series: L_{B^1}, −1.82 V; L_{B^2}, −1.79 V; L_{B^3}, −1.46 V. These results, combined with the above-noted observations on relative kinetic stabilities of the reduced complexes, lead to two generalizations about the effect of ligand structure: (i) replacing the L_{B^1} Schiff base ligand by the L_{B^2} 8-quinolinol ligand both thermodynamically and kinetically stabilizes the lower oxidation states; (ii) adding a nitro group to the 8-quinolinol ligand (to generate L_{B^3}) also thermodynamically and kinetically stabilizes the lower oxidation state complexes.

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Synthesis and Characterization of Stable Rhenium(V) Dioxo Complexes with Acyclic Tetraamine Ligands, $[LReO_2]^+$

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A single-step synthesis of complexes of the type $[L^nRe^VO_2]^+$ from *trans*-$ReOCl_3(PPh_3)_2$ and the tetraamine ligands 1,4,7,10-tetraazadecane (L^1), 1,4,8,11-tetraazaundecane (L^2), and 1,5,9,13-tetraazatridecane (L^3) is reported. Successive protonation of the oxo ligands has been monitored spectrophotometrically: the first protonation occurs reversibly in 6 M HCl; the second (18 M H_2SO_4) is irreversible. With $[L^2ReO_2]^+$, one diastereoisomer may be isolated by crystallization of the hexafluorophosphate salt, as deduced by ^1H and ^{13}C NMR spectroscopy.

Introduction

The chemistry of oxotechnetium(V) complexes with various tetraamine and amine–oxime ligands is well documented primarily because of the usage of these complexes in diagnostic nuclear medicine.[1] Oxo complexes of the metastable isotope ^{99m}Tc (γ = 140 keV, $t_{1/2}$ = 6.02 h) are widely used clinically as scanning agents for certain vital organs. More recently, radioisotopes of the β-emitting nuclides ^{186}Re (β^- = 1.07 MeV, $t_{1/2}$ = 90 h) and ^{188}Re (2.12 MeV, $t_{1/2}$ = 17 h) have been proposed as suitable candidates for therapeutic applications.[2] An investigation of the structure, solution behavior, and pH sensitivity of the related oxorhenium complexes is therefore of considerable interest. As a result of the inherent instability and high charge requirement of the rhenium(V) ion, the most effective way of stabilizing this oxidation state in aqueous solution is as its dioxo complex. The

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(1) Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 875. Brenner, D.; Davison, A.; Lister-James, J.; Jones, A. G. *Inorg. Chem.* **1984**, *23*, 3793. Jurisson, S.; Schlemper, E. O.; Troutner, D. E.; Canning, L. R.; Nowotnik, D. P.; Neirinckx, R. D. *Inorg. Chem.* **1986**, *25*, 543.

(2) Deutsch, E.; Libsow, K.; Vanderheyden, J. L.; Ketring, A. L.; Marxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465.