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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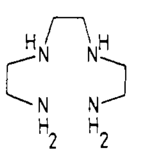
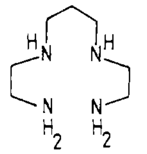
reported dioxorhenium(V) complexes, however, are susceptible to ligand dissociation reactions and are typically unstable in solution at low pH.[3] The choice of a suitable coordinating ligand is critical in stabilizing ReO_2^+ ions in solution.

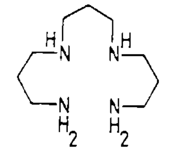
The synthesis of $[LReO_2]X$ = ($X = Cl^-, CH_3CO_2^-, PF_6^-$) from *trans*-$ReOCl_3(PPh_3)_2$ and the free tetraamine ligands L^1–L^3 is described. For L^2 and L^3, the isolated complexes are resistant not only to ligand dissociation but also to high acid concentrations: they are stable in the pH range 0 → 13. The free tetraamine ligands react almost instantaneously with $ReOCl_3(PPh_3)_2$ in chloroform to form $[LReO_2]Cl$. Previous methods[3] used to generate $[L_nReO_2]^+$ complexes (e.g. L = en, py) either involved long reaction times and multistep operations or required the use of a large excess of the free ligand.



L^1



L^2



L^3

Experimental Section

$KReO_4$ and the ligands 1,4,7,10-tetraazadecane, 1,4,8,11-tetraazaundecane, and 1,5,9,13-tetraazatridecane were purchased from Aldrich Chemical Co. Amberlite CG-50 (Carboxylic Type, H^+ form) was purchased from Sigma, and all analytical grade solvents were further purified by standard methods.[4] *trans*-$ReOCl_3(PPh_3)_2$ and $[Re(en)_2O_2]Cl$ were prepared according to published procedures.[3] All other chemicals were of reagent grade and were used without further purification, unless otherwise stated. Infrared spectra were obtained as KBr disks by using a Perkin-Elmer 587 spectrophotometer, and electronic spectra were measured on a Pye-Unicam PU 8720 UV–vis scanning spectrophotometer. Conductance values were measured on a Jenway 4010 conductivity meter for a ca. 10^{-3} M aqueous solution of the respective compound. Proton and carbon-13 NMR spectra were recorded on a Bruker AC-250 spectrometer, and chemical shifts are reported in ppm to higher frequency of Me_4Si or relative to HOD at δ 4.63 (external TMS). Fast atom bombardment mass spectra were recorded on a VG 7070E instrument, using an aqueous glycerol of *m*-nitrobenzyl alcohol matrix and fast xenon atoms (8 keV).

Preparation of Complexes. The isolated complexes were prepared in similar manners, and a representative procedure is described: To a stirred solution of the acyclic tetraamine (0.5 mmol) in dry chloroform (20 cm^3) was added *trans*-$ReOCl_3(PPh_3)_2$ (0.20 g, 0.24 mmol), and stirring was continued at room temperature for 10 min. A yellow solid precipitated and was filtered out, washed with cold chloroform (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), and dried over P_2O_5, in vacuo.

1. $[L^1ReO_2]Cl$. For this complex the yield was 0.05 g (52%). IR ν_{max} (cm^{-1}, KBr disk): 800 (vs, b), 810 (sh) (ν_{ReO_2}). *m/z* (FABMS, H_2O–glycerol): 347, 345 ($C_6H_{18}N_4ReO_2 - H_2O^+$); 330, 328 ($C_6H_{16}N_4Re^+$). $\delta_C(D_2O)$: 57.0, 55.8, 54.8, 50.2, 47.2, 46.2, 38.9, 37.9 (cf. L^1 in D_2O δ_C 53.2, 50.1, 42.3). Anal. Calcd for $C_6H_{18}N_4ReO_2Cl$: C, 18.0; H, 4.5; N, 14.1. Found: C, 20.5; H, 6.36; N, 14.9. $\lambda_{max}(H_2O)$: 470, 350, 260 nm. In aqueous solution, the FABMS data and electronic spectra suggest that the complex exists as a monooxo species, although in the solid state the IR data clearly indicate that the complex is a dioxo compound (see Results and Discussion). Further purification of the extremely hygroscopic complex by precipitating it from an aqueous solution with a bulky anion, e.g. BPh_4^-, PF_6^-, or ClO_4^-, or by using cation-exchange chromatography (Amberlite CG-50) could not be accomplished because of the instability of the complex in aqueous solution. The absence of any ReO_4^- impurity in its aqueous solution was confirmed by TLC (SiO_2, Me_2CO) and negative ion FABMS.

2. $[L^2ReO_2]X$ (X = Cl, PF_6). The chloro complex precipitated as a yellow-orange microcrystalline solid, 0.05 g (50%). Anal. Calcd for $C_7H_{20}N_4ClO_2Re$: C, 20.3; H, 4.9; N, 13.5. Found: C, 20.6; H, 5.4; N, 12.9. IR (cm^{-1}): 790 (vs), 810 (s) (split band) (ν_{ReO_2}). $\delta_C(D_2O)$: 58.6, 56.3, 50.0, 45.6, 45.0, 36.8, 30.5, 25.1 (cf. L^2 in D_2O δ_C 50.5, 46.3, 39.6, 28.3). Bright yellow needle-shaped crystals of the hexafluorophosphate salt were obtained by adding excess aqueous $NaPF_6$ to a saturated solution of the chloride salt. Anal. Calcd for $C_7H_{20}N_4F_6O_2PRe$: C, 16.0; H, 3.85; N, 10.7. Found: C, 15.7; H, 4.20; N, 10.5. IR (cm^{-1}): 790 (vs), 810 (s) (split band) (ν_{ReO_2}); 850 (s) 560 (s) (ν_{PF}). *m/z* (FABMS, glycerol): 379, 377 ($C_7H_{20}N_4ReO_2^+$); 361, 359 ($C_7H_{20}N_4ReO_2 - H_2O^+$); 344, 342. $\lambda_{max}(H_2O)$: 560 (sh), 435 nm (ϵ 35 dm^3 mol^{-1} cm^{-1}). $\Lambda(H_2O)$: 125 mhos cm^2 mol^{-1} (Cl^- salt). $\delta_C(D_2O)$: 58.6, 56.3, 50.0, 30.5.

3. $[L^3ReO_2]Cl$. The complex is extremely hygroscopic. Yield: 0.04 g (34%). Anal. Calcd for $C_9H_{24}N_4ClO_2Re$: C, 24.4; H, 5.47; N, 12.7. Found: C, 24.7; H, 6.0; N, 12.6. IR (cm^{-1}): 790 (vs), 805 (sh) (ν_{ReO_2}). $\delta_C(D_2O)$: 59.4, 57.9, 46.4, 45.8, 45.3, 37.4, 28.1, 25.5. The complex was purified by cation-exchange chromatography (Amberlite CG-50, H^+ form), eluting with an aqueous acetonitrile/acetic acid solvent (80:10:10). Anal. Calcd for $C_{11}H_{27}N_4O_4Re \cdot CH_3CO_2H$: C, 29.6; H, 5.90; N, 10.6. Found: C, 29.0, H, 6.09; N, 10.2. IR (cm^{-1}): 790 (vs), 805 (sh) (ν_{ReO_2}), 1010, 750 (ν_{CH_3}, δ_{OCO}). *m/z* (FABMS, *m*-nitrobenzyl alcohol): 407, 405 ($C_9H_{24}N_4O_2Re^+$), 389, 387 ($C_9H_{24}N_4O_2Re - H_2O^+$); 370, 368. $\lambda_{max}(H_2O)$: 550 (sh), 440 nm (ϵ 20). $\Lambda_M(H_2O)$: 130 mhos cm^2 mol^{-1} (Cl^- salt). $\delta_C(D_2O)$: 164.0 ($OCOCH_3$), 59.5, 58.0, 46.5, 45.0, 44.8, 36.8, 28.1 ($OCOCH_3$), 24.1, 23.3 (cf. L^3 in D_2O δ_C 46.5, 46.0, 38.4, 31.4, 28.3).

Results and Discussion

Previous routes for the synthesis of $[ReO_2(amine)_n]^+$ complexes have required very forcing conditions: Wilkinson et al. reported the reaction of $ReOCl_3(PPh_3)_2$ with pyridine or ethylenediamine (in boiling ethanol),[3] while Murmann et al. devised an improved method in which K_2ReCl_6 was treated for several hours with a large excess of pyridine or ethylenediamine under oxygen.[3] A simple route has been devised in which $ReOCl_3(PPh_3)_2$ reacts with the acyclic tetraamine in chloroform (10 min, room temperature) to yield the desired dioxo complex $[L^nReO_2]Cl$ as a yellow precipitate. Indeed, an authentic sample of $[ReO_2(en)_2]^+$ was prepared within 10 min at room temperature by reacting ethylenediamine with $ReOCl_3(PPh_3)_2$ in chloroform. The source of oxygen in these reactions is probably adventitious water: the tetraamine ligands are very hygroscopic, and the reaction was performed under aerobic conditions. The enhanced reactivity of $ReOCl_3(PPh_3)_2$ in chloroform with respect to ethanol may be related to a differential solubility effect for this heterogeneous reaction. Both $ReOCl_3(PPh_3)_2$ and $[L^nReO_2]Cl$ are insoluble in chloroform, whereas PPh_3 is soluble and so is effectively removed into solution. The chloride complexes are soluble in water but insoluble in common organic solvents. In aqueous solution, $[(L^1)ReO_2]^+$ seems to lose a molecule of water and apparently forms a monooxo species—as deduced from its FABMS and electronic spectra. The solid-state IR spectrum of $[L^1ReO_2]Cl$ is comparable to that of $[L^2ReO_2]Cl$ and $[L^3ReO_2]Cl$ (see Experimental Section), indicating the presence of a dioxo core. Attempts to isolate this putative monooxo species have proved unsuccessful so far. In aqueous solution, the complexes $[L^nReO_2]Cl$ (n = 2,3) retain their dioxo constitution for an indefinite period in the absence of free ligand and in the pH range 1–13. In this pH regime, protonation of yl oxygens was not observed spectrophotometrically nor could any change in their ^1H NMR spectra be discerned.

Infrared Spectra. All three complexes in the solid state (KBr disk) exhibited double absorption at ca. 800 cm^{-1}, which can be assigned to an asymmetric stretching frequency (A_{2u}) of the *trans*-ReO_2^+ moiety.[5] In addition, the expected[6] N–H and antisymmetric NH_2 bending and chelate ring CH_2 bending vibrations were observed at 3300–2900, 1600, and 1450 cm^{-1}, respectively. All reported *trans*-dioxorhenium(V) complexes[3] exhibit IR absorptions in the 810-cm^{-1} region. In the complexes described herein, the local symmetry of the $[ReO_2(NH)_2(NH_2)_2]$ chromophore with a *trans*-ReO_2 core is C_{2v}. The appearance of two absorptions for all complexes may be attributed either to the lower symmetry (C_{2v}) of the complexes compared to other known dioxo

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Scheme I

$$\begin{array}{lccc} & \underset{\text{yellow}}{[L^nReO_2]^+} \quad \underset{\text{base}}{\overset{\text{concd HCl}}{\rightleftharpoons}} & \underset{\text{purple}}{[L^nReO(OH)]^{2+}} \quad \xrightarrow{\text{concd } H_2SO_4} & \underset{\text{blue-violet}}{[L^nReO(OH_2)]^{3+}} \\ n = 2.\ \lambda_{max}: & 560\ (sh),\ 435\ (35) & 616\ (7),\ 490\ (20) & 710\ (sh),\ 550\ (26) \\ n = 3.\ \lambda_{max}: & 550\ (sh),\ 440\ (20) & 650\ (sh),\ 485\ (15) & 720\ (sh),\ 564\ (20) \end{array}$$

Table I. Electronic Spectral Data and Conductance Values

complex	λ_{max}, nm[a] (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)	Λ_M, mhos $cm^2\ mol^{-1}$ [a]
$[L^1ReO_2]Cl$	470, 350, 268	
$[L^2ReO_2](Cl\ or\ PF_6)$	560 (sh), 435 (35)	125 (Cl salt); 90 (PF_6 salt)
$[L^3ReO_2](Cl\ or\ OAc)$	550 (sh), 440 (20)	130 (Cl salt); 75 (OAc salt)

[a] In H_2O.

complexes (C_{4v}) or to a solid-state effect, i.e. unit-cell coupling.[7] This parallels the observation of two metal-oxygen stretches in some *trans*-OsO_2[8] and *trans*-$[UO_2]$[9] complexes; e.g., in $K_2[OsO_2(OH)_2(NO_2)_2]$, ν_{MO_2} = 840, 883 cm^{-1}; in $[UO_2(py)_2(NO_3)_2]$, ν = 911, 921 cm^{-1}; and in $[UO_2(Ph_3PO)_2(NO_3)_2]$, ν = 920, 932 cm^{-1}. The compounds are soluble only in water, and attempts to record their FT IR spectra in H_2O (AgCl cell) were unsuccessful.

Electronic Spectra and Conductance. The UV-visible spectra and molar conductances of the isolated complexes are given in Table I. The electronic spectra of $[L^2ReO_2]$ and $[L^3ReO_2]^+$ are very similar above 400 nm, with a single band at 440 nm accompanied by a much less intense shoulder to lower energy. They are similar to previously reported spectra of *trans*-dioxorhenium(V) complexes,[3] although the intensity of the 440-nm band assigned to a singlet-singlet d-d transition[10] is somewhat weaker than in the reported cyanato, ethylenediamine, or pyridine complexes. The spectrum of $[L^1ReO_2]Cl$ is markedly different and suggests that, in solution, a dioxo core is not retained (see mass spectroscopic data).

Protonation of the oxo ligands occurs in strongly acidic solution, and reaction of $[L^2ReO_2]^+$ and $[L^3ReO_2]^+$ with 6 M HCl and 18 M H_2SO_4 produced $[LReO(OH)]^{2+}$ and $[LReO(OH_2)]^{3+}$, respectively, as depicted in Scheme I and illustrated in Figure 1. In 6 M HCl, protonation occurs, *reversibly*, to yield the monooxo dication with λ_{max} of 485 nm (for L^3) and 490 nm (for L^2). In concentrated H_2SO_4, a second irreversible protonation occurs, with the main band shifting to 564 nm (L^3) and 550 nm (L^2). It has previously been argued by Murmann and co-workers that protonation of the oxo ligands in rhenium dioxo amino complexes should reduce the CFSE and shift the d-d transition to lower energy.[3] The addition of the second proton in the present case could only be achieved by using concentrated H_2SO_4 (not concentrated HCl). In acidic solution (6 M HCl) the complex $[L^1ReO_2]Cl$ irreversibly decomposes, producing a colorless solution containing free ligand and perrhenate.

The conductance values measured were as expected for a 1:1 electrolyte (Table I), and the complexes gave similar retention times on cation-exchange HPLC, consistent with that expected for a unipositive cationic complex.

FAB Mass Spectra. A summary of the observed molecular ions and fragmentation patterns observed is given in Scheme II. With the complex $[L^1ReO_2]^+$, the positive ion FABMS spectrum (8-keV Xe atoms in an aqueous glycerol matrix) revealed a parent ion peak at m/z 347/345, with a daughter ion at *m/z* 330/328 following loss of hydroxyl. A daughter-parent scan confirmed that the *m/z* 347/345 peak was not a daughter ion of the unobserved *m/z* 365/363 peaks. This behavior is consistent with formation of a monooxo species in aqueous solution by elimination of water from the unstable dioxo species observed in the solid state by IR spectroscopy. The complexes $[L^2ReO_2]^+$ and $[L^3ReO_2]^+$ gave well-defined parent ion peaks corresponding to a dioxo cation and gave a daughter ion at ($M^+ - 18$) following loss of water. Subsequent fragmentation proceeded with loss of hydroxyl. Similar behavior was observed with authentic $[Re(en)_2O_2]^+$, which gave two daughter ions following consecutive loss of mass 18 and 17. All of these assignments were confirmed with the aid of separate parent-daughter scans, and the observed and calculated isotope patterns showed excellent agreement.

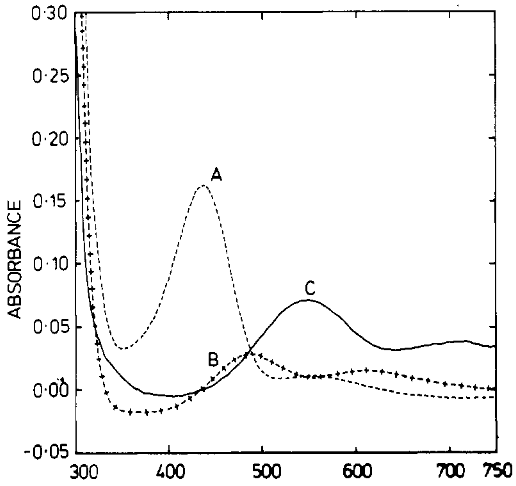

Figure 1. Spectral changes accompanying protonation of $[L^2ReO_2]^+$: (A) at pH 7; (B) in 6 M HCl; (c) in 18 M H_2SO_4.

Scheme II[a]

$$\begin{array}{l} [L^1ReO_2]^{+}:^{a} \ldots \xrightarrow{H_2O} \underset{347/345}{(C_6H_{16}N_4ReO)^+} \xrightarrow[(-17)]{-OH} \underset{330/328}{(C_6H_{15}N_4Re)^+} \\ [L^2ReO_2]^{+}: \underset{379/377}{(C_7H_{20}N_4ReO_2)^+} \xrightarrow[(-18)]{-H_2O} \underset{361/359}{(C_7H_{18}N_4ReO)^+} \xrightarrow[(-17)]{-OH} \underset{344/342}{(C_7H_{17}N_4Re)^+} \\ [L^3ReO_2]^{+}: \underset{407/405}{(C_9H_{24}N_4ReO_2)^+} \xrightarrow[(-18)]{-H_2O} \underset{389/387}{(C_9H_{22}N_4ReO)^+} \xrightarrow[(-19)]{-OH,-2H} \underset{370/368}{(C_9H_{19}N_4Re)^+} \\ [Re(en)_2O_2]^{+}: \underset{339/337}{(C_4H_{16}N_4ReO_2)^+} \xrightarrow[(-18)]{-H_2O} \underset{321/319}{(C_4H_{14}N_4ReO)^+} \xrightarrow[(-17)]{-OH} \underset{304/302}{(C_4H_{13}N_4Re)^+} \end{array}$$

[a] Separate daughter-parent scans indicated that in aqueous glycerol (1:4) this dioxorhenium cation does not exist, as peaks at *m/z* 365/363 could neither be discerned nor traced.

Stereochemistry and NMR Spectra. Of the possible stereoisomers of an $[LMO_2]^+$ species with a flexible tetradentate ligand,[11] only structures with a *trans*-MO_2 core spanned in the equatorial plane by four nitrogens are consistent with the IR and electronic spectral data. Accordingly, there are three possible diastereoisomers depending upon the configuration at the secondary nitrogens: an enantiomeric *RR* and *SS* pair and the *RS* diastereoisomer.[12]

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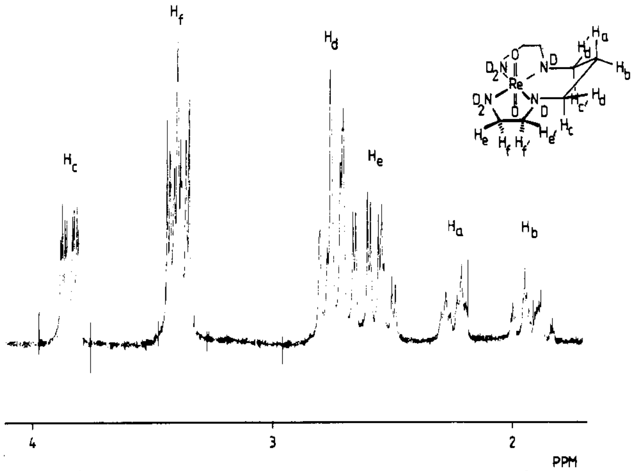

Figure 2. ^{1}H NMR spectrum (298 K, D_2O, 250 MHz) of $[L^2ReO_2]PF_6$. Proton assignments were made with the aid of selective decoupling experiments and a 2D COSY spectrum.

For the complexes $[L^2ReO_2]Cl$ and $[L^3ReO_2]X$ (X = Cl, OAc), a mixture of the trans-racemic and trans-meso diastereoisomers was obtained as deduced most clearly from the ^{13}C NMR data.[12] With $[L^2ReO_2]Cl$, for example, eight resonances were observed: four each of the C_2-symmetric racemic and the σ-symmetric meso diastereoisomers. When the hexafluorophosphate salt was crystallized, only one diastereoisomer was isolated. It was stable in aqueous solution for up to 1 week (in the presence and absence of free ligand), in the pH regime 5–8, and its proton NMR spectrum is shown in Figure 2, which highlights that the methylene protons are all diastereotopic. At this stage it is not possible to assign the configuration of the pure diastereoisomer isolated: a crystallographic analysis or an attempted resolution is required. For the corresponding complexes with L^3, both diastereoisomers were observed by ^{13}C NMR spectroscopy. Each diastereoisomer should give rise to five distinct resonances, but only eight were observed due to the anisochrony of two pairs of peaks. Fractional crystallization, with different anions, from water failed to separate the diastereoisomers.

Conclusion

Reaction of $ReOCl_3(PPh_3)_2$ with the acyclic tetraamine ligands L^1–L^3 affords a quick and convenient synthesis of the *trans*-$[L^nReO_2]$ cationic complexes. With L^2 and L^3, the resultant dioxorhenium(V) complexes are stable in aqueous solution over a wide range of pH, reversibly protonate in 6 M HCl, and do not undergo ligand-exchange reactions. The ^{1}H and ^{13}C NMR spectra reveal that a single diastereoisomer of $[L^2ReO_2]^+$ may be easily separated as its hexafluorophosphate salt, while the diastereoisomers of the acetate and chloro salts of $[L^3ReO_2]^+$ were not separable by fractional crystallization.

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Registry No. $[L^1ReO_2]Cl$, 116784-22-6; $[L^2ReO_2]PF_6$, 116839-34-0; *trans-rac*-$[L^2ReO_2]Cl$, 116784-23-7; *trans-meso*-$[L^2ReO_2]Cl$, 116839-36-2; *trans-rac*-$[Cl^3ReO_2]Cl$, 116784-24-8; *trans-meso*-$[L^3ReO_2]Cl$, 116839-35-1; *trans-rac*-$[L^3ReO_2]PF$, 116784-30-6; *trans-meso*-$[L^3ReO_2]PF_6$, 116839-38-4; $[L^2ReO(OH)]^{2+}$, 116784-25-9; $[L^3RO(OH)]^{2+}$, 116784-26-0; $[L^2ReO(OH_2)]^{3+}$, 116784-27-1; $[L^3RO(OH_2)]^{3+}$, 116784-28-2; $[Re(en)_2O_2]^+$, 14405-69-7; *trans*-$ReOCl_3(PPh_3)_2$, 34248-12-9.

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Formation and Decomposition of Transient Complexes with a Copper–Carbon σ-Bond in the Reaction of Copper(I) Phenanthroline with Aliphatic Free Radicals. A Pulse Radiolysis Study

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The oxidation of copper(I) phenanthroline by $^\bullet CH_2CH_2OH$ and $^\bullet CH_2C(CH_3)_2OH$ free radicals yields ethylene and 2-methylpropene, respectively. During this process transients with a copper–carbon σ-bond have been observed with an absorbance similar to that of copper(I) phenanthroline in the visible region. Rate constants for the formation of these transients are estimated to be larger than 10^{10} M^{-1} s^{-1}. These intermediates decompose via a β-hydroxyl elimination reaction with specific rate constants of $(1.7 \pm 0.4) \times 10^3$ and $(1.1 \pm 0.3) \times 10^4$ s^{-1} for $^\bullet CH_2C(CH_3)_2OH$ and $^\bullet CH_2CH_2OH$ in the pH range 4–10, respectively. The mechanism of the decomposition is discussed, and a stability constant for the ligation of $^\bullet CH_2C(CH_3)_2OH$ and $^\bullet CH_2CH_2OH$ to the cuprous complex is estimated to be larger than 6×10^6 M^{-1}.

Introduction

Reactions between copper ions and aliphatic free radicals occur in metal-catalyzed oxidations of organic compounds as well as in many biochemical processes.[1-4] Mechanistic studies indicate that aliphatic free radicals ($R^\bullet$) react with cupric and cuprous ions via a mechanism that involves the formation of short-lived intermediates having a copper–carbon σ-bond:

$$Cu_{aq}^{2+} + R^\bullet \rightarrow Cu^{III}\text{–}R \qquad (1)$$

$$Cu_{aq}^{+} + R^\bullet \rightarrow Cu^{II}\text{–}R \qquad (2)$$

With use of the pulse radiolysis technique, the chemical properties of several short-lived intermediates formed in reactions 1 and 2 have been studied. It was found that Cu_{aq}^+ reacts faster than Cu_{aq}^{2+} with aliphatic free radicals to yield transients with a copper–carbon σ-bond with specific rate constants approaching

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