Re(V) Complexes with an Open-Chain Quadridentate Ligand Containing Two Amine and Two Amido Donors. Synthesis, Characterization, and Solution Equilibria of Re_2O_3(dioxo-tetH_4)$_2$ and [ReO(H_2O)(dioxo-tetH_4)]Cl (dioxo-tetH_6 = 1,4,8,11-tetraazaundecane-5,7-dione)

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We are interested in identifying mononuclear cationic $[M(V)=O]^{3+}$ (M = Tc, Re) complexes for radiopharmaceutical applications. The open-chain ligand, 1,4,8,11-tetraazaundecane-5,7-dione (dioxo-tetH_6) with two amine and two amide donors, was selected for investigation since the literature led us to expect that a five-coordinate $[Re(V)=O$(dioxo-tetH_4)$]^+$ cation would dominate. Instead, the neutral μ-oxo bridged dinuclear complex, Re_2O_3-(dioxo-tetH_4)$_2$ (**1**), and a salt of the six-coordinate mononuclear cation, [ReO(H_2O)(dioxo-tetH_4)]$^+$ (**2**), were isolated; the structure of each was determined by X-ray crystallography. The cation (**2**) is unusual because it has a *trans*-oxo/aqua core. Such aqua compounds are rarely isolated, and the Re−OH_2 distance is relatively short (2.185 Å). The cation has two pK_a values, 4.1 and 8.7, determined with visible spectroscopy. Since the Re−OH_2 bond is short, the coordinated water is likely to be acidic. Thus the two pK_a's are assigned to the stepwise deprotonation of the water ligand to give a *trans*-oxo/hydroxo neutral form and a *trans*-dioxo anion. Although **1** was the first product isolated following ligand exchange of $ReOCl_3(Me_2S)(OPPh_3)$ with dioxo-tetH_6 under neutral conditions, it probably formed from the hydroxo mononuclear complex. Under concentrated conditions (∼300 mM) the dinuclear complex deposited from solution, but the ^{1}H NMR spectra of **2** (∼20 mM) were consistent with the presence of only monomeric forms in D_2O, pH 3−12. ^{1}H NMR experiments demonstrated that in DMSO-d_6 **2** converts to **1** upon addition of base, consistent with the proposal that two units of the hydroxo monomer condense to give the dinuclear form. In addition, all spectra of pure **1** dissolved in DMSO-d_6 included extra low intensity signals that were characteristic of the monomer. Thus, although **1** is favored over the neutral monomer in DMSO-d_6, the two complexes exist as a mixture of equilibrating forms. Our results do not support the previous findings for the Re(V) complex with a macrocyclic diamine−diamide ligand related to dioxo-tetH_6. The data indicate that the ability of an amido group to donate electron density to a Re(V) center is moderately greater than the donating ability of a neutral amine group.

Introduction

Rhenium(V) and technetium(V) complexes comprise a prominent class of compounds in radiopharmaceutical chemistry. Characteristically, these d^2 complexes have multiply bonded axial donor ligands. The donor p electrons interact strongly with the metal valence-shell d_{xz} and d_{yz} orbitals of π-symmetry, and the two metal d electrons reside in the nonbonding d_{xy} orbital.[1] Since M(V) (M = Re, Tc) radiopharmaceuticals are routinely prepared by reduction of $M(VII)O_4^-$ in aqueous solution, five-coordinate monoxo $[M(V)=O]^{3+}$ and six-coordinate *trans*-dioxo $[O=M(V)=O]^+$ agents are typically formed. The metal−axial ligand core that is obtained depends on the nature of the four equatorial donors. Softer/strong donors (thiolates, oximes) favor monoxo complexes.[2−5] Harder/less strong donors (amines, heterocyclic N-ligands) favor dioxo complexes.[6−10]

Since the monoxo and dioxo cores differ by a +2 charge, and the equatorial donor groups can be neutral or carry a −1 charge, the net charge of the complex can be varied. The net charge is important because it influences in vivo distribution. We are interested in cationic complexes because they may be

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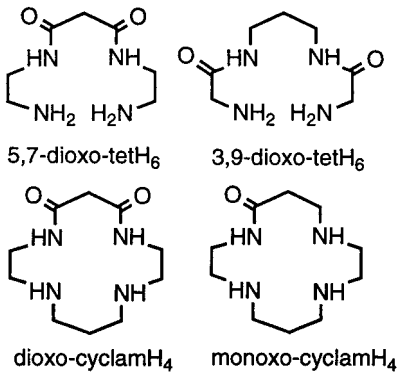
Chart 1



useful for renal imaging.[11−13] Cationic M(V) complexes are known but are limited essentially to *trans*-dioxo complexes with four equatorial donors that are all neutral amines[6−10,14] or all phosphines.[15,16] Some tetraamine complexes have been evaluated as renal imaging agents, but they were not suitable for clinical use.[11,12] Our aim is to identify additional cationic M(V) oxo complexes for renal imaging studies. A Re(V) complex with the macrocyclic diamine−diamide ligand (1,4,8,11-tetraazacyclotetradecane-5,7-dione, or dioxo-cyclamH_4, Chart 1)[17] and the open-chain diamine−diamide ligands (1,4,8,11-tetraazaundecane-5,7-dione, or 5,7-dioxo-tetH_6, and 1,4,8,11-tetraazaundecane-3,9-dione, or 3,9-dioxo-tetH_6), Chart 1)[18] were labeled at the tracer level with ^{99m}Tc. No complex was characterized in detail, but the Re complex was described as being cationic. Since some M(V) oxo complexes have structures that differ from those originally proposed,[19,20] we undertook a more detailed study. We selected the open-chain ligand 5,7-dioxo-tetH_6 (Chart 1) for complexation with Re(V) because the ^{99m}Tc derivative showed high renal specificity.[18] The geometric isomer, 3,9-dioxo-tetH_6 (Chart 1), was included since studies of isomeric complexes are important for understanding the influence of structure on renal clearance.

Experimental Section

5,7-Dioxo-tetH_6 was obtained by reaction of dimethyl malonate with an excess of ethylenediamine, followed by the removal of ethylenediamine under reduced pressure.[21] The ligand was not purified further. 3,9-Dioxo-tetH_6·2HCl was prepared from 1,3-diaminopropane and chloroacetyl chloride.[22] $ReOCl_3(Me_2S)(OPPh_3)$ was prepared by the literature method.[23] Unless specified otherwise, dioxo-tet refers to the 5,7-dione derivative. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. FTIR spectra were obtained in KBr pellets using a Nicolet 510M instrument.

Syntheses. Re_2O_3(dioxo-tetH_4)$_2$·4H_2O (1). $ReOCl_3(Me_2S)(OPPh_3)$ (400 mg, 0.6 mmol) was suspended in EtOH (15 mL). To the suspension were added triethylamine (0.5 mL) and 5,7-dioxo-tetH_6 (130 mg, 0.7 mmol) dissolved in H_2O (4 mL). The mixture was stirred at room temperature until complete dissolution of the starting complex (∼ 1 day). The resulting crimson solution was evaporated to near dryness by rotary evaporation; to the residue was added H_2O (15−20 mL), and an insoluble white solid was removed by filtration. The filtrate was concentrated to 6−8 mL, filtered, and extracted with $CHCl_3$. At this point, the aqueous solution was essentially neutral. The solution was then concentrated to 1−2 mL (∼300−600 mM), and allowed to stand at room temperature. The violet crystals that formed were collected and washed with water and EtOH. Yield: 97 mg (36%). Anal. Calcd for $C_{14}H_{36}N_8O_{11}Re_2$: C, 19.44; H, 4.20; N, 12.96. Found: C, 19.72; H, 4.05; N, 12.78. FTIR: $\nu_{Re=O}$ = 950, 956 cm^{-1}; $\nu_{Re-O-Re}$ = 658 cm^{-1}. ($\nu_{Re=O}$ = frequency of the Re=O stretching band.)

[ReO(H_2O)(dioxo-tetH_4)]Cl·H_2O (2). Complex **2** was obtained as described for **1** except for the final step. The aqueous solution was concentrated to 4 mL and then acidified by addition of concentrated HCl (0.1−0.2 mL). Addition of acid led to the immediate precipitation of lilac microcrystals, which were collected and washed with EtOH and diethyl ether. Yield: 110 mg (39%). Anal. Calcd for $C_7H_{18}ClN_4O_5Re$: C, 18.28; H, 3.95; Cl, 7.71; N, 12.19. Found: C, 18.70, H, 3.81; Cl, 7.60; N, 12.16. FTIR: $\nu_{Re=O}$ = 982 cm^{-1}; ν_{Re-O} = 569 cm^{-1}.[24,25]

Reaction of $ReOCl_3(Me_2S)OPPh_3$) with 3,9-Dioxo-tetH_6·2HCl. The reaction was carried out in the same manner as for **1** except that the aqueous solution of the ligand was neutralized by addition of 1 N NaOH before it was added to the reaction suspension. After 1 day, an insoluble black precipitate had formed (probably $Re(IV)O_2$). The black solid was removed by filtration. The filtrate, faintly crimson in color, became colorless on standing 2 days.

X-ray Crystallography. Single crystals of **1** were grown by slow evaporation of an aqueous solution of the complex at room temperature. For **2**, a concentrated aqueous solution of the complex (1.0−1.5 mL) was layered with acetonitrile (5 mL) and acidified with 2 drops of concentrated HCl. A violet crystal of **1** (0.36 × 0.28 × 0.26 mm^3) and a lilac crystal of **2** (0.24 × 0.16 × 0.16 mm^3) were used for data collection. Each crystal was mounted under Paratone-8277 on a glass fiber and immediately placed in a cold nitrogen stream at −80 °C on a standard Siemens SMART CCD area detector system equipped with a normal focus Mo-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). Data (1321 frames, 1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 10 s/frame for **1** (∼6 h) and 30 s/frame for **2** (∼12 h); the detector-to-crystal distance was 5.09 cm (maximum 2θ angle of 56.5°). Frames were integrated with the Siemens SAINT program giving 7402 reflections, of which 2851 were independent (R_{int} = 2.17%, R_{sig} = 2.59%) and 2733 were $>2\sigma(I)$ for **1**, and 6209 reflections, of which 2924 were independent (R_{int} = 2.05%, R_{sig} = 3.23%) and 2625 were $>2\sigma(I)$ for **2**. Laue symmetry revealed monoclinic crystal systems for both **1** and **2**. Final cell parameters were determined from least-squares refinement of the three-dimensional centroid of 7564 reflections for **1**, and 5995 reflections for **2**. Data were corrected for absorption with the SADABS program based on the method of Blessing.[26]

Heavy atom methods for **1** and direct methods for **2** were used for structure solution. Both structures were refined by full-matrix least-squares procedures on F^2 using SHELXL 93. All non-hydrogen atoms

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Table 1. Crystal Data and Structure Refinement for Re_2O_3(dioxo-tetH$_4$)$_2$·4H$_2$O (**1**) and [ReO(H$_2$O)(dioxo-tetH$_4$)]Cl·H$_2$O (**2**)

	1	**2**
chemical formula	$C_7H_{18}N_4O_{5.5}Re$	$C_7H_{18}ClN_4O_5Re$
fw	432.45	459.90
T (K)	193 (2)	183 (2)
λ (Å)	0.71073	0.71073
space group	C_2/c	$P2_1$/c
unit cell dimensions		
a (Å)	17.968 (3)	7.2400 (10)
b (Å)	8.583 (2)	26.536 (5)
c (Å)	16.309 (3)	7.1250 (10)
β (deg)	108.993 (11)	109.88 (3)
V (Å^3)	2378.2 (8)	1287.3 (4)
Z	8	4
ρ_{calc} (mg/m^3)	2.416	2.373
absorption coefficient (mm^{-1})	10.243	9.667
final *R* indices [$I > 4\sigma(I)$]	$R_1 = 0.0184$	$R_1 = 0.0261$
	$wR_2 = 0.0466$	$wR_2 = 0.0539$
R indices (all data)	$R_1 = 0.0197$	$R_1 = 0.0318$
	$wR_2 = 0.0471$	$wR_2 = 0.0558$

were refined anisotropically. The water and amine H atoms of **1** were located from a late-stage difference map and the positions refined. H atoms bound to carbon, as well as the amine H atoms of **2**, were generated at calculated positions (d(C−H) = 0.96 Å; d(N−H) = 0.90 Å). All H atoms were constrained using a riding model with isotropic thermal parameters 20% greater than the U(eq) of the bonded heavy atom. For **1** the halves of the complex are symmetry related ($-x,y,-z+1/2$), with the bridging oxo ligand O(2) occupying a special position (0, y, 0.25, occupancy $1/2$). Crystal data and refinement parameters for **1** and **2** are listed in Table 1.

UV−Visible Spectroscopy. UV−visible titrations of **2** were performed in 0.1 M $NaClO_4$ at 20 °C using a Specord M40 instrument. The solution of the complex was first acidified with $HClO_4$ to pH 1.61, and the pH was gradually raised with NaOH to a final pH of 11.18.

NMR Spectroscopy. ^{1}H NMR spectra were obtained with Varian Mercury 300 MHz and Varian Inova 400 MHz spectrometers. Chemical shifts (ppm) were referenced in D_2O to TSP (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt), and in DMSO-d_6 to the solvent peak (2.49 ppm); pH (uncorrected in D_2O) was adjusted by addition of NaOD (2.2 N).

Results

Syntheses. Ligand exchange of 5,7-dioxo-tetH$_6$ with $ReOCl_3(Me_2S)(OPPh_3)$ followed by workup produced a concentrated crimson-colored aqueous solution that yielded violet crystals of **1** upon standing. Elemental analysis of **1** is consistent with a Re_2O_3(dioxo-tetH$_4$)$_2$·4H$_2$O formula. These results suggest that a slow reaction converts a monomer to the dinuclear complex, **1**. The IR spectrum of **1** included a band with two maxima at 950 and 956 cm^{-1}, and a strong, broad band at 658 cm^{-1}. The frequencies of the bands are respectively similar to the symmetric Re═O stretch (969−973 cm^{-1}) and antisymmetric Re−O−Re stretch (670−686 cm^{-1}) observed for $Re_2O_3Cl_4$(R-py)$_4$ complexes (R-py = substituted pyridine).[27] Acidification with HCl of the crimson-colored solution from ligand exchange led to the immediate precipitation of lilac crystals of **2**. Elemental analysis for **2** was consistent with a [ReO(dioxo-tetH$_4$)]Cl·2H$_2$O formula. The IR spectrum of **2** included a strong band at 982 cm^{-1}, consistent with a Re═O stretching band.[28] Ligand exchange of 3,9-dioxo-tetH$_6$ and $ReOCl_3(Me_2S)(OPPh_3)$ was unsuccessful.

X-ray Crystallography. Perspective drawings of **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Table 2. Complex **1** is a neutral μ-oxo bridged dinuclear complex with terminal axial oxo ligands. The Re−O and Re═O bond distances are normal compared to those for other μ-oxo bridged Re(V) dinuclear species.[29−32] The O═Re−O−Re═O unit is not strictly linear (Figure 1), having Re−

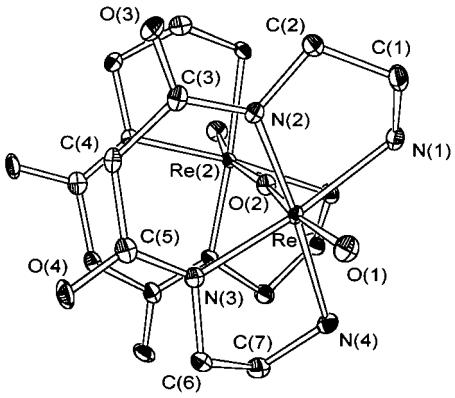

Figure 1. Perspective drawing of Re_2O_3(dioxo-tetH$_4$)$_2$ (**1**) with 50% probability for the thermal ellipsoids.

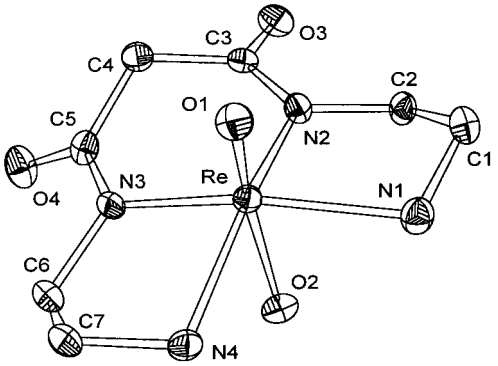

Figure 2. Perspective drawing of [ReO(H$_2$O)(dioxo-tetH$_4$)]$^+$ (cation of **2**) with 50% probability for the thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

1		**2**	
Re−O(1)	1.698(3)	Re−O(1)	1.677(3)
Re−O(2)	1.9342(4)	Re−O(2)	2.185(3)
Re−N(1)	2.192(3)	Re−N(1)	2.166(3)
Re−N(2)	2.024(3)	Re−N(2)	2.005(3)
Re−N(3)	2.030(3)	Re−N(3)	1.996(3)
Re−N(4)	2.195(3)	Re−N(4)	2.173(3)
O(2)−Re′	1.9343(4)		
O(1)−Re−O(2)	166.50(14)	O(1)−Re−O(2)	166.74(13)
O(1)−Re−N(1)	86.84(12)	O(1)−Re−N(1)	91.77(14)
O(1)−Re−N(2)	95.91(12)	O(1)−Re−N(2)	105.59(14)
O(1)−Re−N(3)	96.72(12)	O(1)−Re−N(3)	106.03(14)
O(1)−Re−N(4)	86.11(12)	O(1)−Re−N(4)	93.63(14)
O(2)−Re−N(1)	84.39(11)	N(1)−Re−O(2)	79.91(13)
O(2)−Re−N(2)	92.43(8)	N(2)−Re−O(2)	83.19(13)
O(2)−Re−N(3)	92.90(12)	N(3)−Re−O(2)	82.93(12)
O(2)−Re−N(4)	86.41(8)	N(4)−Re−O(2)	78.13(12)
N(1)−Re−N(4)	105.76(11)	N(1)−Re−N(4)	101.59(13)
N(2)−Re−N(1)	78.69(11)	N(2)−Re−N(1)	79.54(13)
N(2)−Re−N(3)	96.20(11)	N(3)−Re−N(2)	93.44(13)
N(2)−Re−N(4)	175.25(11)	N(2)−Re−N(4)	160.73(14)
N(3)−Re−N(1)	174.08(10)	N(3)−Re−N(1)	162.09(14)
N(3)−Re−N(4)	79.27(11)	N(3)−Re−N(4)	79.68(13)
Re−O(2)−Re′	173.4(2)		

[a] Symmetry transformations used to generate equivalent atoms: Re′ $-x,y,-z+1/2$.

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O−Re [173.4 (2)°] and O−Re−O [166.50 (14)°] bond angles that are, in general, more acute than those found in $Re_2O_3Cl_4(N)_4$ complexes (N = N-donor ligand). One smaller O−Re−O bond angle [165.5 (7)°] was found in $Re_2O_3Cl_4(py)_4$; all other angles were in the range 174.5 (9)−177.7 (4)° for Re−O−Re angles and 168.6 (3)−173.5 (3)° for O−Re−O angles.[29−32] The two quadridentate dioxo-tet ligands lie in the equatorial metal coordination planes. The Re−N bond distances are within the range expected for neutral amine, N(1) and N(4), and charged amido, N(2) and N(3), donor groups.[2,30] The interior portions of the ligands are nearly planar (mean deviation of the least-squares plane for C(2), N(2), C(3), C(4), C(5) N(3), C(6) is 0.0737 Å) and are stacked, but rotated by ∼45° with respect to each other so that the carbonyl groups and the flanking five-membered chelate rings are staggered. Stacking of the two nonterminal N-heterocyclic donor ligands (N) is a common feature in $Re_2O_3Cl_4(N)_4$ type complexes.[30,33,34] Stacking was also observed in $Re_2O_3(salpd)_2$ ($salpdH_2$ is *N*,*N*′-propane-1,3-disalicylideneamine). In this case the terminal salicylideneamine chelate rings are planar and the central propyl chelate ring is puckered. The salpd ligands are rotated 180° with respect to each other so that the salicylideneamine chelate rings are stacked and the propyl chelate rings are on opposite sides of the molecule.[35]

Complex **2** is a six-coordinate monomer, with the dioxo-tet ligand coordinating in the equatorial plane and with axial oxo and water ligands. The Re═O and Re−N bond distances are normal, but slightly shorter than the corresponding distances in **1**. Structural characterization of a Re−OH_2 grouping is rare, and the Re−O(2) bond (2.185 (3) Å) in **2** is relatively short (∼2 Å less than the sum of the van der Waals radii of Re(V) (2.60 Å)[2] and O (1.60 Å)).[36] In the three other examples of structurally characterized $[O{=}M(V){-}OH_2]^{3+}$ cores, $[^{99}TcO(H_2O)(N,N'$-ethylenebis(acetylacetone-thioimine))$]^+$, $[^{99}TcO(H_2O)(N,N'$-ethylenebis(acetylacetoneimine))$]^+$, and $[ReO(H_2O)Br_4]^-$, the M−OH_2 bond distances were 2.384 (3),[37] 2.3,[38] and 2.32 (4) Å,[39] respectively. Even in complexes with a CO_2^- group coordinated trans to the oxo ligand, the M−O bond distances [^{99}TcO(D-penH_2)(D-penH_3) (penH_3 is penicillamine) (2.214 (4) Å),[40] ReO(ethylenedi-L-cysteine) (2.252 (9) Å)][19] are longer than the Re−O(2) distance in **2**.

UV−Visible Spectroscopy. The visible spectrum of **2** in H_2O at pH ≤2.0 consists of a major band at 488 nm and a minor band at 633 nm. As the pH was raised, the spectrum changed in two distinct phases. Through the first phase (midpoint pH 4.14), there was an hypsochromic shift of the major band at 488−475 nm, accompanied by an increase in absorption intensity (ϵ increases from 35 to 75 M^{-1} cm^{-1}). The minor band at 633 nm remained almost unchanged. Through the second phase (midpoint pH 8.65) the bands at 475 and 633 nm declined in intensity and a single new band emerged at 443 nm (ϵ 145 M^{-1} cm^{-1}).

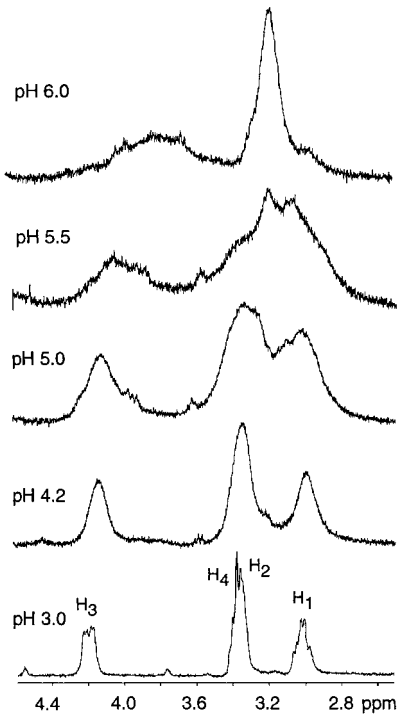

Figure 3. ^{1}H NMR spectra of $[ReO(H_2O)(dioxo\text{-}tetH_4)]Cl$ (**2**) in D_2O from pH 3.0 to 6.0.

These data indicate that **2** reacts stepwise with 2 equiv of hydroxide (pK_{a1} 4.1; pK_{a2} 8.7). Since **2** is a cation, consumption of the first equivalent of base results in a neutral form. Reaction of the neutral form with the second equivalent of base produces an anion.

In the UV region, pH-dependent changes were also observed. At pH 1.6 two bands were present at 283 (ϵ 6600 M^{-1} cm^{-1}) and 253 nm (ϵ 7400 M^{-1} cm^{-1}). As the pH was raised, the lower energy band progressively disappeared. The pH dependence of ϵ (at 283 nm) is consistent with the visible data.

NMR Spectroscopy. $[ReO(H_2O)(dioxo\text{-}tetH_4)]Cl{\cdot}H_2O$ (**2**) dissolves freely in water, giving an acidic solution. The ^{1}H NMR spectrum of such a solution (D_2O, pH 3.0, ∼20 mM) is shown at the bottom of Figure 3. Proton labeling is given in Chart 2. Signals for the malonyl protons (H5, H6) are not observed because of isotopic exchange. Assignments for the H1/H2 and H3/H4 signals (Chart 2) were based on assignments given for Ni(dioxo-tetH_4); the H3/H4 signals are downfield of the H1/H2 signals.[21] Signals for protons near (endo, H1/H3) and away (exo, H2/H4) from the oxo ligand were identified from the coupling patterns with the *trans*-H1/H4 pair having the largest vicinal coupling (10.4 Hz). Each of the four signals was somewhat broad at pH 3.0, and the line broadening became severe with increasing pH. Two relatively sharp signals were observed at high pH (Figure 4). From pH 8 to 10 the signals shifted, and there were no changes at pH values >10.

The observation of only two signals for the eight protons in the two five-membered chelate rings above pH 6 (Figure 4) indicates that only the monomeric form is present in detectable concentration. In addition, each proton belongs to one of two

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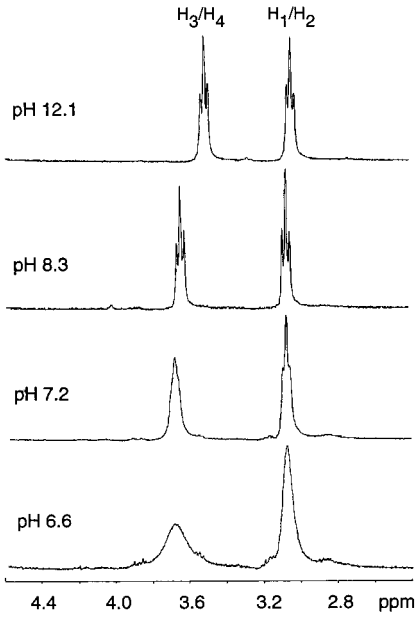
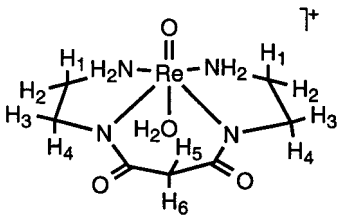
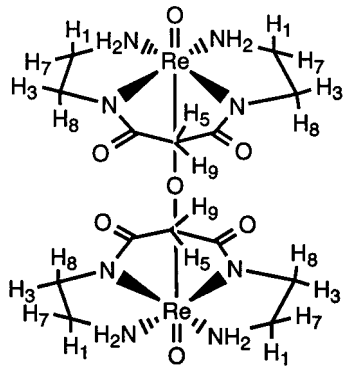


Figure 4. ^{1}H NMR spectra of [ReO(H_2O)(dioxo-tetH_4)]Cl (**2**) in D_2O from pH 6.6 to 12.1.

Chart 2



[ReO(H_2O)(dioxo-tetH_4)]$^+$



Re_2O_3(dioxo-tetH_4)$_2$

sets of magnetically equivalent protons; the equivalency must be the result of chemical exchange and/or high symmetry in the complex. Specifically, the halves of the dioxo-tet ligand and the members of each geminal pair of protons must be physically exchanging or be in identical environments. This result is discussed in more detail below. No evidence was found for the dinuclear complex in dilute solutions of **2** used in the NMR studies.

Although the dinuclear complex (**1**) crystallized from a concentrated aqueous solution (at least 300 mM), the resulting crystals had low solubility in D_2O. (This is evidence suggesting that **1** crystallizes as it forms from a monomer precursor.) Therefore, the ^{1}H NMR spectrum of **1** was recorded in DMSO-d_6 (Figure 5, top left). The spectrum of the aqua monomer (**2**) (Figure 5, bottom right) was obtained in DMSO-d_6 for comparison. The spectrum of **1** consisted of several broad CH signals of unequal intensity and two pairs of doublets. The intensity of one pair of doublets varied from sample to sample, but never surpassed that of the second pair.

Some signals in the spectrum of the dinuclear complex (**1**) (including the low-intensity pair of doublets) were similar to those observed for the aqua monomer (**2**). Contamination of **1** with **2** was ruled out because **2** is freely soluble in water, and a crystalline sample of **1** was first washed with D_2O and dried before it was dissolved in DMSO-d_6. However, partial decomposition of **1** to **2** was possible when pure **1** was dissolved in DMSO-d_6. A difficulty in interpreting the spectra was that decomposition of **1** should give a neutral hydroxo form of the monomer, and we did not know how the spectra of the aqua cation and the neutral monomer differed in DMSO-d_6. Therefore, we obtained spectra of **1** with DCl added (2.2 N, 2 and 4 μL) (Figure 5, middle and bottom left) and **2** with NaOD added (2.2 N 2 and 4 μL) (Figure 5, middle and top right). Addition of DCl (4 μL) to **1** resulted in a spectrum identical with that of **2**. Addition of NaOD (4 μL) to **2** gave a spectrum very similar to that of **1** (the minor differences are accounted for below). Our interpretation of the latter result is that base converts the aqua cation (**2**) to the neutral monomer; two units of the neutral monomer condense to give the neutral dinuclear complex (**1**). Since extra low intensity signals characteristic of the monomer were always present when pure **1** was dissolved in DMSO-d_6, we concluded that although **1** is favored in DMSO-d_6, the neutral mono- and dinuclear complexes exist in solution as a mixture of equilibrating forms.

For both complexes **1** and **2**, all protons lie to one side of the dioxo-tet ligand plane and are either close (endo) or away (exo) from a terminal oxo ligand (Chart 2). The endo protons are in similar environments, accounting for the presence of similar signals in the spectra of **1** and **2**; we give the endo protons the same numbers in each complex (H1, H2, H3). The exo protons are in dissimilar environments and have signals unique to the spectrum of each complex; we give the exo protons different numbers for each complex (H2, H4, H6 for the monomer and H7, H8, H9 for the dinuclear complex). Strong multiplets at 2.97 and 3.64 ppm and the strong downfield doublet at 3.77 ppm are assigned to H7, H8, and H9, respectively, since these signals are unique to the spectrum of **1**. The H5 doublets (just downfield of the water peak) of the mono- and dinuclear complexes are resolved but are overlapping; the more intense doublet is assigned to the dinuclear form. Signals at 2.72 and 4.13 ppm are assigned to H1 and H3, respectively, of both mono- and dinuclear complexes. The remaining weak signals are assigned to the exo protons of the monomer, H6 and H2/H4 (Figure 5). The presence of the monomer explains why the spectrum of **1** varied from sample to sample. The neutral monomer can be protonated by trace acid, deprotonated by trace base, and is fluxional (see below). Thus, the chemical shifts and line widths of the monomer signals, including those overlapping with signals from the dinuclear complex (H1 and H3), are sensitive to sample conditions and sometimes vary. Also, the concentration of monomer (and hence the intensity of the monomer signals) seems sensitive to sample conditions. In contrast, the exo signals (H7, H8, H9) of the dinuclear complex are always sharp and have the same shift and relative intensity from sample to sample.

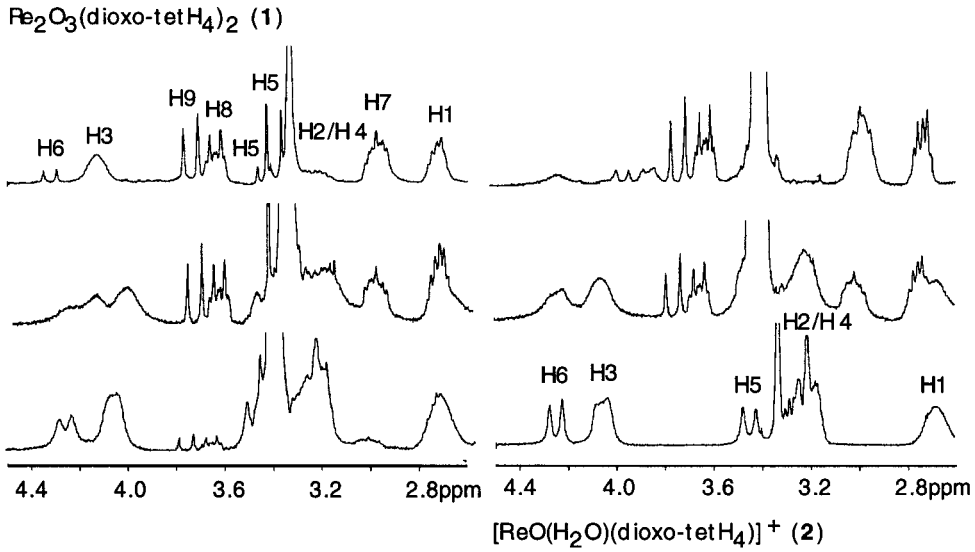


Figure 5. ^{1}H NMR spectra in DMSO-d_6 of Re_2O_3(dioxo-tetH_4)$_2$ (**1**) (top left) and [ReO(H_2O)(dioxo-tetH_4)]Cl (**2**) (bottom right). The middle left and bottom left spectra show conversion of **1** to **2** by addition of DCl. The middle right and top right spectra show conversion of **2** to **1** by addition of NaOD.

Discussion

Ligand exchange of $ReOCl_3(Me_2S)(OPPh_3)$ with 5,7-dioxo-tetH_6 proceeded cleanly to give **1** and **2** in ~40% yield. Examples of M(V) complexes with a *trans*-oxo/aqua core are known but uncommon. In one case, $[ReO(H_2O)(N)_4]^{3+}$ (N = 1-methylimidazole or 1,2-dimethylimidazole),[14] the oxo/aqua core was formed only under extreme acid conditions (pH −4); the resulting complex decomposed easily and could not be isolated.[14] In three other cases, identified by X-ray crystallography, the M−OH_2 distance is so great (2.3−2.4 Å) that the water is best described as an associated solvent molecule rather than as a coordinated ligand.[39] [ReO(H_2O)(dioxo-tetH_4)]Cl (**2**) is unusual because it has a *trans*-oxo/aqua core, and also because the complex is formed under moderately acidic conditions, is easily isolated, and the Re−O(water) distance is relatively short (2.185 Å).

In the solid, **2** (Figure 2) has mirror plane symmetry between the halves of the dioxo-tetH_4 ligand and the axial oxo and water ligands. In solution at pH 3.0, the ^{1}H NMR spectrum of **2** (Figure 3) has four signals for the eight CH protons of the dioxo-tet ligand, consistent with one set of signals for both halves of the ligand and different environments for the members of the two unique pairs of geminal protons. Thus, the NMR data for **2** at low pH indicate that this is very likely the aqua cation found in the solid state. In our discussion of the solution data, we shall assume that the most likely species present are six coordinate. Further arguments supporting this assumption are presented below.

Visible spectral changes for [ReO(H_2O)(dioxo-tetH_4)]Cl (**2**) as a function of pH in aqueous solution are interpreted to indicate the formation of a neutral form (pK_{a1} 4.1) and then an anion (pK_{a2} 8.7). This information was helpful in assessing the ^{1}H NMR data for **2** in D_2O above pH 3.0 (Figures 3 and 4).

At pH 3.0, the ^{1}H NMR signals of **2** were slightly broadened. Line broadening and merging of signals occurred over a broad pH range (pH 4.2−7). The four signals evident at low pH become two signals. Clear evidence of a shift change on increasing the pH above 3.0 is found in the slight upfield shift at pH 4.2 and 5.0 of the most upfield signal (labeled H_1 in Figure 3). The shift changes of other signals were masked to a large extent by the line broadening. From pH 5.5 to 7.2 the two broad signals gradually sharpened with little if any shifting by pH 7.2. The signals are too broad to estimate the shifts for *both* signals at pH 5.5. However, the average shift at pH 6.6 is about 0.1−0.2 ppm upfield of the average shift at pH 3.0, consistent with deprotonation of the complex. Since the midpoint of the pH range (3.0−5.5) for shifting corresponds to the pK_{a1} (4.1 in H_2O) of the complex, we attribute the shift changes to formation of the neutral form.

The shifts of the two signals at pH 6.6 are each near the average shift of two of the four low pH signals. The NMR characteristics indicate that an exchange process equilibrates the members of each geminal pair of protons, and also that the rate of exchange increases with increasing pH. This exchange is not due to a chemical exchange of the protons (otherwise they would exchange with D_2O). Evidence of exchange of the signals of each pair of geminal protons indicates that a magnetic equivalency results from a chemical exchange of the axial ligands as discussed in the next paragraph.

The rate of the axial ligand interconversion is intermediate on the NMR time scale below pH 6, but the rate of equilibration of the cationic and neutral forms is fast. The best explanation of the data invokes a neutral complex with hydroxo and oxo axial ligands. In Scheme 1, we show a mechanism based on previous work in which the evidence also suggested chemical exchange between axial ligands.[41] This mechanism for the exchange of the position of the oxo and (aqua/hydroxo) ligands proceeds mainly through the *trans*-oxo/hydroxo neutral complex, consistent with the observation that the rate increases with OH^- concentration. The aqua cation to hydroxo neutral complex exchange rate should be very fast. The process from top right to bottom right, in which the hydroxo and oxo ligands exchange places, is probably a concerted process that is the rate-determining step in Scheme 1. At pH 6 and below, the rate of the overall process is intermediate on the NMR time scale. At pH 6.6 and 7.2, the two signals become sharper. At these pH's, we believe the dioxo form may be involved in the exchange of the axial hydroxo and oxo ligands. Indeed, by pH 8.3, the signals are beginning to shift further upfield as the deprotonation of the hydroxo ligand in the neutral form becomes detectable. Since

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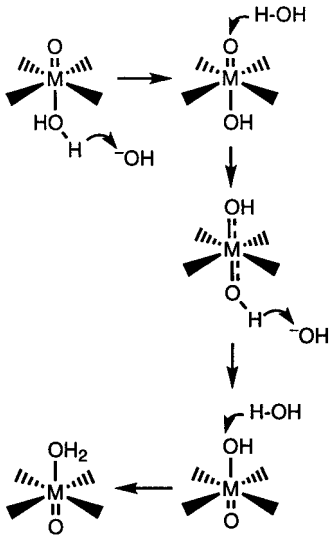
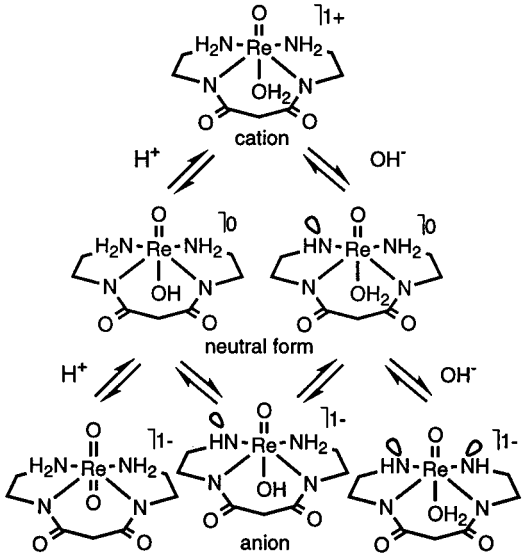
Scheme 1. Exchange of Oxo and Aqua Ligand Sites of **2** in One Direction



Scheme 2



the signals of geminal pairs of protons are equivalent in the dioxo anion and exchange between neutral and anion forms is fast, the time averaging is now fast. From pH 8.3 to 10 (not shown), the sharp signals shift, corresponding to conversion of the neutral form to the anion (pK_{a2} 8.7 in H_2O). The overall equilibria are shown on the left in Scheme 2 with down arrows for deprotonation by hydroxide and up arrows for protonation by H^+ (or possibly H_2O).

The *trans*-oxo/hydroxo form of **2** is not the only neutral form that must be considered. We exclude from further consideration a neutral form with a deprotonated malonyl CH_2 group because the CH_2 signals are clearly observed for the neutral monomer in DMSO-d_6 (Figure 5). Deprotonation of an amine would give a neutral *trans*-oxo/aqua complex having inequivalent amine donors (Scheme 2); one amine has two NH's, and one amine has an NH and a lone pair of electrons (NLp). Because the halves of the dioxo-tet ligand are now inequivalent, one might expect to observe two sets of CH NMR signals with slightly different shifts. We observed one set, apparently ruling out NH deprotonation. However, at a pH where enough of the deprotonated form is present, it is highly likely that the site of the NLp will exchange rapidly between the two amines. This exchange and interconversion of the axial ligands can account for the time averaging of the signals of geminal pairs leading to the observed simple spectrum. Thus we cannot rule out an NH-deprotonated neutral form, although we greatly favor the oxo/hydroxo formulation since the pK_a for amine deprotonation of Re(V) complexes is seldom <6.

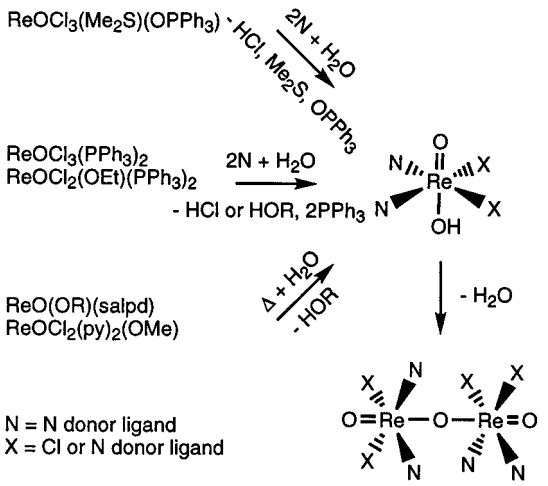
The anion has three possible forms (Scheme 2): *trans*-dioxo, *trans*-oxo/hydroxo with one N deprotonated, and *trans*-oxo/aqua with both N's deprotonated. The very simple ^{1}H NMR spectrum of the anion consists of two sharp signals. In the absence of fast chemical exchange, the *trans*-dioxo complex is the only form that will give only two signals. However, for the other two forms fast NH exchange and/or axial ligand exchange can explain the simple spectra.

The spectroscopic data do not distinguish between the possible forms for the neutral and anionic monomers. However, the factors that control formation of five-coordinate monoxo and six-coordinate *trans*-dioxo M(V) complexes lead us to favor the neutral form with a *trans*-oxo/hydroxo core and the anion with a *trans*-dioxo core (Scheme 2, left). Five-coordinate $[M(V)=O]^{3+}$ complexes exist when strong electron-donor groups are available. Basal coordination is preferred over axial coordination due to the trans influence of the oxo ligand. The complexes do not take up a sixth ligand because the five donor groups adequately meet the electronic requirements of the metal. Six-coordinate $[O=M(V)=O]^+$ complexes exist when weak basal donor ligands are present. Two strong oxo donors compensate for the weak basal donation. If a hypothetical five-coordinate $[M(V)=O]^{3+}$ complex had average basal donors, the electronic requirements of the metal would not be met. Although a deprotonated amide is a somewhat better donor than an amine, evidence suggests that "amido" groups are only slightly better donors than amines. Thus, if the basal ligand is a diamine−diamide chelate, we do not expect five-coordinate complexes to exist in water.

X-ray structural data are consistent with these expectations. Complexes with a *trans*-oxo/hydroxo core are seldom isolated in the solid state, but one such complex, [ReO(OH)(monoxo-cyclamH_3)][ReO_4] (monoxo-cyclamH_4 is 1,4,8,11-tetraazacyclotetradecane-5-one, Chart 1), has an M−OH bond distance (1.970 (8) Å)[17] $\sim$ 0.3 Å longer than a typical M=O bond distance. For the few cases in the solid in which a water molecule is trans to the oxo ligand,[37−39] the M−OH_2 distances are $\sim$0.3 Å longer than the M−OH distance in [ReO(OH)-(monoxo-cyclamH_3)][ReO_4]. The increase in the M−OH_n (n = 0−2) distances in the series *trans*-dioxo, *trans*-oxo/hydroxo, and *trans*-oxo/aqua suggests a relationship between M−O bond distance and the acidity of the axial ligand. In **2**, the Re−OH_2 distance (2.185 (3) Å) is significantly shorter than 2.3 Å, suggesting that the water ligand is acidic. The two pK_a values found for **2** are consistent with this expectation.

In contrast to our interpretation of the chemistry of the Re(V) complex of the open chain diamine−diamide dioxo-tetH_6 ligand (Chart 1), an interpretation supported by the X-ray structure of **2**, the macrocyclic diamine−diamide dioxo-cyclamH_4 ligand (Chart 1) was reported to form a five-coordinate monoxo cation, $[ReO(dioxo\text{-}cyclamH_2)]^+$.[17] This interpretation was based on IR data and elemental analysis. However, the reported $\nu_{Re=O}$ (912 cm^{-1}) for the latter cation is too low since in general $\nu_{Re=O}$ increases in order for *trans*-dioxo, *trans*-oxo/hydroxo, *trans*-oxo/aqua, and monoxo complexes. Also, the reported elemental analyses (Found: C, 29.69; H, 5.45; N, 13.66.) do not agree well with the calculated values (Calcd: C, 29.07; H, 4.69; N, 13.04.) for [ReO(dioxo-cyclamH_2)]Cl·DMF.

Scheme 3



It is possible that a neutral mono- or dinuclear complex of dioxo-cyclamH_4 was isolated since no acid was added to the reaction solution. The [ReO(OH)(dioxo-cyclamH_2)]·DMF and Re_2O_3(dioxo-cyclamH_2)$_2$·2DMF·2H_2O formulas agree better with the reported results. (Calcd for $C_{13}H_{26}N_5O_5Re$: C, 30.11; H, 5.05; N, 13.50. Calcd for $C_{26}H_{54}N_{10}O_{11}Re_2$: C, 29.60; H, 5.16; N, 13.27.)

Since we would not expect the $\nu_{Re=O}$ of Re_2O_3(dioxo-cyclamH_2)$_2$ and Re_2O_3(dioxo-tetH_4)$_2$ (950, 956 cm^{-1}) to differ by much, the 912 cm^{-1} $\nu_{Re=O}$ reported for the dioxo-cyclam complex suggests it may have a *trans*-oxo/hydroxo core. We expect $\nu_{Re=O}$ of [ReO(dioxo-cyclamH_2)]$^+$ to be higher than (or at least comparable to) that of **2** ($\nu_{Re=O}$ = 982 cm^{-1}). Of course, for Re(V) complexes with the same metal−axial ligand core, $\nu_{Re=O}$ decreases as the electron-donating ability of the equatorial donor set increases. The $\nu_{Re=O}$ values for [ReO(OH)(cysH_2)$_2$]$^{2-}$ and [ReO(OH)(penH_2)]$^{2-}$ (which have two strong thiolato donors) were 925 and 930 cm^{-1}, respectively.[41,42] The $\nu_{Re=O}$ of [ReO(OH)(monoxo-cyclamH_3)]$^+$ (one amido donor, Chart 1) (952 cm^{-1}) is lower than that of [ReO(OH)(cyclamH_4)]$^{2+}$ (no amido donors, Chart 1) (969 cm^{-1}). Thus, the amido donor can be considered to be a better donor than the amine donor. Dioxocyclam has two amido donors, and a value of 912 cm^{-1} for $\nu_{Re=O}$ is conceivable if the complex has a *trans*-oxo/hydroxo core. However, we think it is not possible for this second donor to decrease $\nu_{Re=O}$ to 912 cm^{-1} if the dioxocyclam complex has a monoxo core as suggested in the literature.[17] Thus, we suggest that the dioxocyclam complex has a *trans*-oxo/hydroxo core.

Finally, it is worth mentioning the possible role of *trans*-oxo/hydroxo complexes in the formation of dinuclear complexes. Dinuclear μ-oxo bridged M(V) complexes have been prepared by a variety of methods (Scheme 3). We have prepared $Re_2O_3Cl_4(L)_4$ complexes [L = 1,5,6-trimethylbenzimidazole, 3,5-lutidine, or pyridine (py)] from $ReOCl_3(Me_2S)(OPPh_3)$,[30,34] and *cis*,*cis*-$Re_2O_3Cl_4(py)_4$ has been prepared from $ReOCl_3(PPh_3)_2$, $ReOCl_2(OEt)(PPh_3)_2$, and $ReCl_5$.[43] Re_2O_3(salpd)$_2$ was prepared by recrystallization of ReO(OR)(salpd) from $CDCl_3$[35] and *trans*,*trans*-$Re_2O_3Cl_4(py)_4$ was obtained by heating $ReO(OMe)Cl_2(py)_2$ in toluene at reflux.[44] In each case the dinuclear complexes were thought to form by condensation of two units of a hydroxo intermediate (Scheme 3). The hydroxo intermediate is believed to form by coordination of H_2O trans to the oxo ligand, and loss of HCl or HOR. The hydroxo intermediates have not been isolated, but the corresponding alkoxo complexes are known.[43] The results from this work provide support for the existence of the hydroxo intermediate and for the proposed mechanism of formation of dinuclear μ-oxo bridged M(V) complexes.

Conclusion

The amido groups in dioxo-tet cannot be described as strong donors since the five-coordinate [Re(V)═O(dioxo-tetH_4)]$^+$ cation was not obtained; instead a rare *trans*-oxo/aqua complex (**2**) with an unusually short Re−OH_2 distance (2.185 Å) was isolated under mildly acidic conditions. However, related M(V) complexes with four equatorial amine donors have *trans*-dioxo cores, except under acidic conditions.[17,45] In contrast, the *trans*-dioxo anion, [ReO_2(dioxo-tetH_4)]$^-$, does not exist in solution below pH ∼8. Thus, the amido groups in the dioxo-tet ligand are clearly somewhat better donors than the amine groups. Previously we ranked the abilities of coordinated N centers to donate electron density to a [Re(V)═O]$^{3+}$ center in the following order: negatively charged amine ≫ amido ≥ neutral amine. This order was constructed by comparing the influence of these donors on the NH acidity of ReO(N_2S_2) complexes.[3] In this work, we show that this ranking applies also to ReO_2N_4 complexes. This information will be useful in designing radiopharmaceuticals. It seems clear that diamine−diamide N_4 type ligands bind as dinegative chelates favoring a *trans*-[MO(OH)]$^{2+}$ core. If the desired radiopharmaceutical is to bear charge, charged groups need to be incorporated on N_4 ligand side chains.

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Supporting Information Available: Crystallographic data for **1** and **2**, including tables of positional parameters, bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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