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Rhenium(V)-Oxo Complexes of Neutral and Monoanionic Tetraazamacrocycles. X-ray Structures of *trans*-Oxohydroxo(1,4,8,11-tetraazacyclotetradecan-2-one)rhenium(V) Perrhenate and *trans*-Oxohydroxo(1,4,8,11-tetraazacyclotetradecane)rhenium(V) Bis(perchlorate)

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The complexes of ReO_2^+ and $ReO(OH)^{2+}$ with 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,8,11-tetraazacyclotetradecan-2-one (O_1cyclam) have been synthesized and characterized. The complexes were prepared by ligand exchange reactions of the macrocycles with a variety of starting compounds including $ReOCl_3(PPh_3)_2$ and $ReO_2(en)_2Cl$. The $ReO(OH)^{2+}$ complexes have been structurally characterized. $ReO(OH)(H_{-1}O_1cyclam)ReO_4$ crystallizes in the monoclinic $P2_1/n$ space group with a = 10.308(3) Å, b = 9.527(2) Å, c = 17.808(3) Å, and β = 106.57(2)°. $ReO(OH)(cyclam)(ClO_4)_2$ crystallizes in the monoclinic $C2/c$ space group with a = 9.734(4) Å, b = 16.999(5) Å, c = 12.187(5) Å, and β = 106.36°. The complex $ReO(OH)(H_{-1}O_1cyclam)ReO_4$ has a distorted octahedral structure with one short ReO(oxo) bond and one long ReO(hydroxo) bond (1.685(8) vs 1.970(8) Å). The deprotonated amide ReN(sp^2) bond is shorter than the other three ReN(sp^3) bond lengths (1.98(1) vs 2.13(3) Å (average)). The structure of the $ReO(OH)(cyclam)(ClO_4)_2$ complex shows no distinction between the lengths of the two ReO(oxo and hydroxo) bonds (1.766(5) Å) due to disorder of the oxo and hydroxo groups. Spectroscopic evidence is reported to confirm the presence of both oxo and hydroxo groups coordinated to rhenium.

Introduction

While research on Tc(V) macrocyclic complexes has been pursued because of the potential development of useful radiopharmaceuticals, the work on similar Re complexes has been somewhat neglected. However, some Re isotopes have been suggested for the development of diagnostic and therapeutic radiopharmaceuticals.[1-3] Most rhenium studies have concentrated on complexes with multidentate open-chain ligands, primarily simple bidentate ligands.[4] The syntheses of complexes of technetium with tetraaza macrocycles such as cyclam and its derivatives and biodistributions of some of these complexes have been reported in the literature.[5-8] Structural studies of both $ReO_2(cyclam)^+$ and $TcO_2(cyclam)^+$ have been published.[9,10] Other examples of macrocyclic complexes on which structural studies have been reported include the TcO_2^+ complex with 14-ane-N_2S_2 containing two thioether donor groups in place of two amino groups and the (octaethylporphyrinato)oxorhenium(V) and technetium(V) complexes.[11-13]

In most cases, with Re and Tc in the oxidation state +5, the macrocycle forms a stable and readily characterized complex with the $M-O_2^+$ core (M = Tc, Re). However, adding negatively charged donor groups can remove the need for two multiply bound oxo groups as in the case of monooxo square pyramidal complexes such as $ReO(ethanedithiolato)_2^-$.[14] The present study was undertaken to synthesize and characterize Re(V) complexes with cyclam and the cyclam derivatives shown in Figure 1. The additional thermodynamic stability provided by macrocyclic ligands over open-chain ligands warrants the development of efficient ways of synthesizing these types of complexes. In this study, we report the syntheses by ligand exchange reactions and characterizations of the $ReO_2(cyclam)^+$, $ReO(OH)(cyclam)^{2+}$, $ReO_2(H_{-1}O_1cyclam)$, $ReO(OH)(H_{-1}O_1cyclam)^+$, and $ReO(H_{-2}O_2cyclam)Cl$, and structural determinations of the two oxo-hydroxo complexes.

Experimental Section

Materials. $KReO_4$ was purchased from Strem Chemical Co. $ReO_2(en)_2Cl$, $ReOCl_3(PPh_3)_2$, $ReO_2I(PPh_3)_2$, and $ReOCl_4N(n\text{-}Bu_4)$ were synthesized by the use of literature methods.[15-18] 1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Aldrich Chemical Co. 1,4,8,11-Tetrazacyclotetradecan-2-one (O_1cyclam) and 1,4,8,11-tetraazacyclotetradecane-2,4-dione (O_2cyclam) were synthesized by modifications of known methods.[19,20]

Methods. IR spectra were measured with an IBM FTIR 40S spectrophotometer in KBr pellets. UV-vis spectra were measured with a Perkin-Elmer fast scan UV-vis spectrophotometer with 1.000 ± 0.001 cm matched quartz cells. All ^1H-NMR spectra were measured with an XL200 NMR spectrometer. Mass spectra were obtained by fast atom bombardment on a VG Analytical 70S high-resolution double-focusing magnetic sector spectrometer attached to a VG Analytical 11/250J data system, with nitrobenzyl alcohol as the matrix solvent, by Tom Sharp at the Mass Spectrometry Applications Laboratory, Center for Chemical Characterization and Analysis, Texas A&M University.

$ReO_2(cyclam)ClO_4 \cdot H_2O$. Method 1. To a solution of 0.16 g of cyclam (0.79 mmol) in 2 mL of H_2O and 2 mL of MeOH was added a solution of 0.10 g of $ReO_2(en)_2Cl$ (0.262 mmol). The solution color immediately

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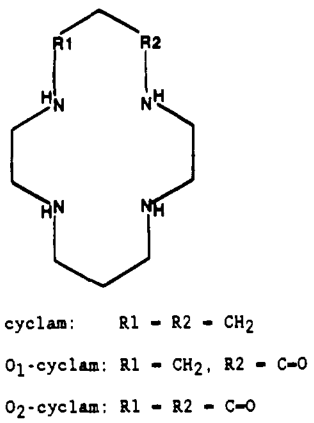

Figure 1. Macrocyclic ligands to be studied.

became golden yellow. The reaction mixture was refluxed for 6 h. After the solution was cooled, it was extracted with three 5-mL portions of $CHCl_3$ to remove excess ligand. The volume of the aqueous layer was reduced by half and excess $NaClO_4$ was added. The solvent was allowed to slowly evaporate on standing, yielding orange-yellow crystals of the product. The crystals were washed with cold EtOH (30%). In the absence of $NaClO_4$, the chloride salt was isolated in a 60% yield; mp 195–197 °C. Anal. Calcd for $ReO_2(cyclam)ClO_4{\cdot}H_2O$: C, 22.41; H, 4.89; N, 10.45. Found: C, 22.30; H, 4.97; N, 10.30. FAB$^+$ MS: m/z 419 $[ReO_2(cyclam)^+]$ and m/z 403 $[ReO(cyclam)^{2+} - e^-]$. FTIR (KBr pellet): 772 cm^{-1} ν_{as}(ReO). Caution! Precaution must be used when working with perchlorate compounds as explosions have been known to occur.

Method 2. A 0.15-g sample of n-$Bu_4NReOCl_4$ (0.26 mmol) and 0.16 g of citric acid monohydrate (0.79 mmol) were dissolved in 5 mL of MeOH. To this solution was added 0.16 g of cyclam (0.79 mmol) in 1 mL of MeOH. The solution color changed from blue to yellow upon adjustment of the pH to 11 with 1 M NaOH. The MeOH was removed by evaporation and the aqueous solution was extracted with three 5-mL portions of $CHCl_3$. Excess $NaClO_4$ was added to the aqueous layer. Orange-yellow plates of product were isolated and washed with cold EtOH (40%). FAB$^+$ MS: m/z 419 $[ReO_2(cyclam)^+]$. FTIR (KBr pellet): 772 cm^{-1} ν_{as}(ReO).

ReO(OH)(cyclam)ClO$_4$PF$_6$. A 100-mg sample of $ReO_2(cyclam)PF_6$ was dissolved in a minimal amount of 2 M $HClO_4$, and the lavender product was precipitated out with acetone. UV-vis ($HClO_4$): 646, 482, 210, 195 nm. FTIR (KBr pellet): 969 cm^{-1} ν_{as}(ReO). Anal. Calcd for $ReC_{10}H_{25}N_4O_6ClPF_6$: C, 18.09; H, 3.79; Re, 28.04. Found: C, 18.03; H, 3.76; Re, 29.77

Crystals suitable for X-ray structure analysis were grown from a solution of the lavender precipitate in 2 M $HClO_4$ over 1 week and formulated as the diperchlorate salt (structure I).

ReO(OH)(H$_{-1}$O$_1$cyclam)$^+$. Method 1. A 0.26-g sample of $ReOCl_3(PPh_3)_2$ (0.31 mmol) was suspended in 17 mL of dry CH_2Cl_2, and the solution was purged with N_2. To this suspension were added 0.13 g of O_1cyclam (0.62 mmol) and 100 μL of triethylamine in 3 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 8 h, the solvent was then removed, and the brown residue was taken up in 5 mL of H_2O. The insoluble PPh_3 was removed by filtration and the aqueous solution was extracted with $CHCl_3$ to remove excess ligand. The solution was set aside for slow evaporation, and after several days violet microcrystals of the Cl salt were formed (57%). Anal. Calcd for $ReO_3C_{10}H_{24}N_4Cl$ $(ReO(OH)(H_{-1}O_1cyclam)Cl)$: C, 25.67; H, 4.74; N, 11.97; Cl, 7.57. Found: C, 25.52; H, 4.85; N, 11.92; Cl, 7.29. Diamagnetism was determined with the Evan's NMR method[21] in D_2O with CH_3CN as the reference. FTIR (KBr pellet): 952 cm^{-1} ν_{as}(ReO). FAB$^+$M S: m/z 415.

Method 2. A 0.12-g sample of $ReO_2I(PPh_3)_2$ (0.14 mmol) was suspended in 2 mL of MeOH. A solution of 0.07 g of O_1cyclam (0.33 mmol) and 46 μL of triethylamine (0.33 mmol) in 3 mL of CH_2Cl_2 was added to the suspension. The reaction mixture was refluxed for 1 h, and the orange-brown solution was set aside for evaporation, yielding a violet microcrystalline solid of the I$^-$ salt. FAB$^+$ MS: m/z 415. FTIR (KBr pellet): 952 cm^{-1} ν_{as}(ReO).

Table I. Crystal Data, Data Collection, and Solution Refinement Parameters

	ReO(OH)(cyclam)-(ClO$_4$)$_2$ (I)	ReO(OH)(H$_{-1}$-oxocyclam)ReO$_4$ (II)
empirical formula	$C_{10}H_{25}N_4O_{10}Cl_2Re$	$C_{10}H_{21}N_4O_7Re_2$
color and habit	violet parallelepiped	red sphere
cryst size	0.3 mm × 0.5 mm × 0.6 mm	0.05 mm
space group	monoclinic, $C2/c$ (No. 15)	monoclinic, $P2_1/n$ (No. 14)
unit cell dimens	$a = 9.734(4)$ Å $b = 16.999(5)$ Å $c = 12.187(5)$ Å $\beta = 106.36(3)°$	$a = 10.303(4)$ Å $b = 9.533(3)$ Å $c = 17.813(7)$ Å $\beta = 106.44(2)°$
volume	1935.1(13) Å^3	1678(1) Å^3
formula units/cell	4	4
fw	618.4 amu	682.7 amu
density (calcd)	2.123 g/cm^3	2.702 g/cm^3
abs coeff	67.0 cm^{-1}	147 cm^{-1}
F(000)	1208 e$^-$	1264 e$^-$
temp	193 K	296 K
scan mode	ω (Wyckoff)	$\theta/2\theta$
2θ range	4.0–50.0	4.0–50.0
index ranges	$-11 < h < 11, -20 < k < 0, -14 < l < 0$	$-12 < h < 12, -11 < k < 0, 21 < l < 6$
no. of reflcns collcd	1859	3206
no. of unique reflcns	1712	2951
no. of obsd reflcns	1631 $|\geq 1.0\sigma(I)$	2951
abs cor	semiempirical	semiempirical
T_{max}–T_{min}	0.999–0.666	0.965–0.806
extinction cor[22]	$\chi = 0.00013(2)$ where $F^* = F_c/[1 + 0.002\chi F_c^2/(\sin 2\theta)]^{0.25}$	$\chi = 0.00003(2)$ where $F^* = F_c/[1 + 0.002\chi F_c^2/(\sin 2\theta)]^{0.25}$
final residuals[a]	$R = 0.066$; $R_w = 0.073$	$R = 0.067$; $R_w = 0.063$
goodness of fit[a]	$S = 6.85$	$S = 1.07$
largest, mean d/s	0.044, 0.009	0.05, 0.003
data-to-param ratio	11.6:1	14:1

[a] Residuals: $R = \sum||F_o| - |F_c||/\sum F_o$; $R_w = ([\sum w(|F_o| - |F_c|)^2]/[\sum w(F_o)^2])^{1/2}$; $S = ([\sum w(|F_o|-|F_c|)^2]/[N_{data} - N_{parms}])^{1/2}$. Quantity minimized: $\sum w(|F_o|-|F_c|)^2$; $w^{-1} = \sigma^2 F + gF^2$ ($g = 0.00010$ for II; 0.00001 for I).

Crystals suitable for X-ray structure analysis were grown from an aqueous solution of the violet solid over several weeks and were formulated as the perrhenate salt (structure II).

ReO$_2$(H$_{-1}$O$_1$cyclam). A 1.1-g sample of $ReO_2(en)_2Cl$ (0.47 mmol) was dissolved in 2 mL of H_2O. To this solution was added 0.20 g of O_1cyclam (0.93 mmol) in 1 mL of 1 M NaOH. The reaction solution was refluxed for 2 h, and the hot solution was extracted with $CHCl_3$ to remove the excess ligand. The solvent was removed from the aqueous layer, and the remaining yellow residue was extracted with CH_3CN. Upon removal of the solvent, an orange-yellow solid remained. FTIR (KBr pellet): 771 cm^{-1} n$_{as}$(ReO). FAB$^+$ MS: cluster of peaks at m/z 431 corresponding to $[ReO_2(H_{-1}O_1\text{-}cyclam)^{-e}]^+$.

ReO(H$_{-2}$O$_2$cyclam)Cl·DMF. Method 1. To a degassed solution of 0.10 g of $ReOCL_3(PPh_3)_2$ (0.120 mmol) in 10 mL of CH_2Cl_2 was added 30 mg of O_2cyclam in 1 mL of EtOH. The solution was stirred under argon for 24 h. Immediately upon addition of the ligand solution, the green solution of the starting compound turned dark brown. A light gray precipitate was filtered off and washed with EtOH, reprecipitated in DMF/EtOH, and dried in vacuo; yield 83%. FTIR (KBr pellet): 912 ν_{as}(ReO); 1540, 1644 ν(CO); 3245 ν(NH). Anal. Calcd. for $ReC_{13}H_{25}H_5O_4Cl$: C, 29.07; H, 4.69; N, 13.04. Found: C, 29.69; H, 5.45; N, 13.66.

Crystal Data Collection, Solution, and Refinement. The crystal data and details of data collection and refinement are summarized for both crystal structures in Table I, while the X-ray experimental methods are described below. For both crystals, preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (Mo Kα, λ = 0.710 73 Å radiation, with oriented graphite monchromator). The solution and refinement of the structures were performed with SHELXTL PLUS (MicroVax II).[22] Background measurement by stationary crystal and counter technique was done at the beginning and end of each scan for half of the total scan time. Three control reflections, collected every 97 reflections, showed no significant trends. A semiem-

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pirical absorption correction[22] was applied to the data for structures I and II. Neutral atom scattering factors and anomalous scattering correction terms were taken from refs 23,24. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. For structures I and II the extinction coefficient χ was refined to 0.00013(2) and 0.00021(5), respectively.[25]

The largest peaks in the final Fourier difference map were 1.47 and 1.69 e Å^{-3} for structures I and II, respectively. Both peaks were near a rhenium atom, indicating possible errors in the absorption correction methods for both structures.

Structure I was seen to crystallize in the space group *C*2/*c* or *Cc*. The structure of I was solved in both space groups; however, attempts to anisotropically refine I in the space group *Cc* failed, presumably due to high correlation of the parameters of atoms related by a pseudoinversion center. The space group *C*2/*c* was eventually chosen for further structural refinement. For structure I only half of the [ReO(OH)(cyclam)]$^{2+}$ was contained in the asymmetric unit, with the rhenium atom located on the crystallographic inversion center. The remaining half of the molecule can be generated by the inherent symmetry.

The anisotropic parameters measured for the rhenium atom in structure I were unusual. It is unclear whether these parameters are due to problems in the overall absorption correction or due to disorder of the rhenium atom. It has been suggested that coordination of the rhenium atom to both an oxo and hydroxy ligand would draw the rhenium atom out of the plane of the four ligating nitrogen atoms. For this structure such a displacement would result in an apparent disorder of the rhenium atom.

Two choices of counter ions (PF_6 and ClO_4) were possible for structure I, based upon the synthetic pathway. Initial bond distances between the central atom of the counter ion fragment and the terminal atoms (1.33–1.38 Å) were judged too short for P–F bond lengths (1.55–1.60 Å), and thus the choice of counter ion was perchlorate. Both perchlorate anions were found to sit on the crystallographic 2-fold axis. One of the two anions was found to be disordered. The disordered anion was modeled by positioning the chlorine atom on the crystallographic axis and locating the oxygen atoms on general positions, with their site occupation factors fixed at 50%. Bond distance restraints were imposed on the chlorine–oxygen and oxygen–oxygen distances. The chlorine atom of the second perchlorate anion was positioned on the crystallographic 2-fold axis, and two oxygen atoms were located on general positions, in such a way as to utilize the apparent 2-fold axis in the perchlorate tetrahedron. The resulting model was refined anisotropically. The anisotropic thermal parameters for the anion were very large, indicating possible disorder. An attempt to model the disorder failed. It is unclear whether the large anisotropic parameters are a result of disorder or thermal motion of the terminal atoms. The anisotropic model was finally chosen, and the structure was refined to convergence.

Solution Studies. The ligand dissociation constant, K$_a$, was determined by titration of an 8.03 × 10^{-3} M solution of ReO_2(cyclam)Cl, adjusted to an ionic strength of 0.100 M with KCl, with a standard 0.0975 M HCl solution delivered with a Metrohm piston buret, in a jacketed cell to maintain a constant temperature of 25.0 ± 0.1 °C sealed under purified N_2 as described by Martell and Motekaitis.[26] The –log [H$^+$] measurements were taken with a Model 150 Corning p[H] meter using a Corning glass electrode and saturated calomel reference electrode filled with saturated KCl, after calibration of the electrodes using standard aqueous HCl and NaOH solutions at μ = 0.100 M to read –log [H$^+$] directly. The method of Martell and Motekaitis (program BEST)[26] was utilized to compute the value of K_a for the equilibrium:

Table II. UV–Visible and Infrared Spectral Results

complex	UV–vis, nm (ϵ, M^{-1} cm^{-1})	IR[a] ν_{as}(ReO), cm^{-1}
ReO_2(cyclam)$^+$	440 (16), 284 (1049), 258 (466)	772
ReO(OH)(cyclam)$^{2+}$	646 (12), 482 (16)	969
ReO_2(O_1cyclam)	446 (17)	771
ReO(OH)(O_1cyclam)$^+$	648 (12), 490 (37), 280 (1060)	952, 908[b]
ReO(O_2cyclam)Cl	not measured	912

[a] KBr pellets. [b] ν_{as}(ReO) for ReO_4^-.

$$ReO_2L^+ + H^+ \overset{K_a}{\rightleftharpoons} ReO(OH)L^{2+}$$

Results

Synthesis and Characterization of Metal Complexes. The *trans*-ReO^{2+} and *trans*-ReO(OH)$^+$ macrocyclic complexes are readily prepared by ligand displacement reactions between the appropriate macrocycle and the starting complexes $ReO_2(en)_2Cl$, $ReOCl_3(PPh_3)_2$, $ReO_2I(PPh_3)_2$, and "Re(V)–citrate". "Re(V)–citrate" is formed in situ by addition of citric acid to a methanolic solution of [$ReOCl_4^-$][*n*-Bu_4N^+] and neutralization to pH 7. This intermediate is commonly used for formation of amine complexes of Re(V) or Tc(V), where the disproportionation of the $ReOCl_4^-$ to ReO_{4-} and ReO_2 would otherwise occur.[27] ReO_2(cyclam)ClO_4 was prepared in aqueous solution from the reaction of $ReO_2(en)_2Cl$ (en = ethylenediamine) with excess cyclam under basic conditions, isolated in 58% yield as the chloride salt and recrystallized in the presence of $NaClO_4$ to give orange-yellow crystals of the perchlorate salt. ReO_2(cyclam)Cl was isolated in slightly better yield when the preparation involved the reaction of cyclam with an alkaline aqueous solution of "Re(V)–citrate". Without prior coordination of citrate to the metal, $ReOCl_4^-$ completely disproportionates to ReO_2 and ReO_4^- before ligand exchange with cyclam occurs. The use of citrate or other polyhydric ligands has been used extensively to stabilize both Tc(V) and Re(V) in the preparation of complexes where the ligand is slow to coordinate to the metal.[28]

The protonation of one of the oxo groups on ReO_2(cyclam)Cl was achieved by dissolving the dioxo complex in 2 M perchloric acid and precipitating out a lavender solid with acetone, yielding ReO(OH)(cyclam)$(ClO_4)_2$. The *trans*-dioxo complex shows a ν_{as}(ReO) stretching frequency at 780 cm^{-1}, within the observed range for *trans*-MO_2^+ (M = Re, Tc) (750–850 cm^{-1}).27 The ν_{as}(ReO) stretch for the oxo–hydroxo complex is dramatically higher, at 969 cm^{-1}, indicating one strongly bound oxo ligand and one weakly bound hydroxy ligand. The visible spectrum also changes, with shifts to lower energy wavelengths for the protonated complex (Table II).

The neutral ReO_2(H_{-1}oxo) complex was formed by the same method as that used for the preparation of the *trans*-dioxo cyclam complex and was characterized by IR, FAB-MS, and UV–vis spectroscopy. The ν_{as}(ReO) stretch at 771 cm^{-1} and visible maximum at 438 nm is consistent with the ReO_2($H_{-1}O_1$cyclam) formulation.

In the reaction of $ReOCl_3(PPh_3)_2$ with O_1cyclam, the only product isolated is the lavender ReO(OH)($H_{-1}O_1$cyclam)Cl in about a 60% yield. It is also the major product in the reactions of excess O_1cyclam with $ReO(OEt)Cl_2(PPh_3)_2$. The iodide salt is formed when *cis*-$ReO_2I(PPh_3)_2$ is used as the starting compound. The ν_{as}(ReO) stretch of 950 cm^{-1} in the IR spectrum falls within the range for an ReO^{3+} complex (900–1000 cm^{-1})[27] consistent

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(22) All crystallographic calculations were performed with SHELXTL-PLUS Rev 3.4, 1988 (G. M. Sheldrick, Institut fur Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Gottingen, FRG) supplied by Nicolet Analytical X-ray Instruments, Madison, WI, on a μVaxII minicomputer.

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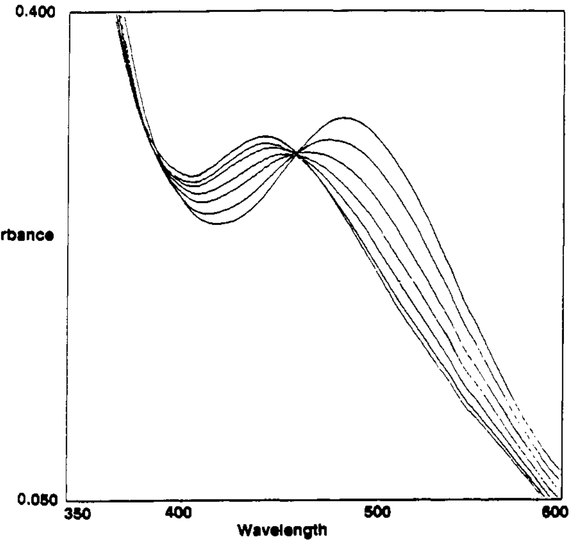

Figure 2. Visible spectra of a 1.0 × 10^{-2} M solution of ReO(OH)(O_1cyclam)Cl in H_2O after six additions of 0.14 equiv of neat pyridine. Growth of the peak at 450 nm indicates the formation of the ReO(py)(O_1cyclam)$^{2+}$ complex.

with the presence of a coordinated hydroxo ligand trans to the oxo group. The visible spectrum is very similar to that of the protonated cyclam complex with electronic spectral maxima at 648 and 490 nm (see Table II). The possibility that a chloro ligand is trans to the oxo group is ruled out by the observation of the same spectropic characteristics of the product isolated when $ReO_2I(PPh_3)_2$ is used as the starting material, where no chlorine is present.

The visible spectrum of an aqueous solution of the compound changes upon addition of pyridine, a coordinating base. The visible maximum of the compound decreases with concomitant increase in a new peak at higher energy (see Figure 2). The presence of an isosbestic point indicates displacement of the trans-hydroxyl ligand by a pyridyl ligand to form a new species, ReO(py)($H_{-1}O_1$cyclam)$^{2+}$. Addition of diethylamine or NaOH in place of pyridine, to a solution of ReO(OH)($H_{-1}O_1$cyclam)$^+$, results in a decrease in the 490-nm peak and growth of a new peak at 438 nm, the same position as the visible maximum for the *trans*-dioxo complex. However, an isosbestic point was not found, and the peak at 438 nm starts to decrease before complete addition of 1 equiv of either base, indicating that, upon deprotonation, disproportionation of the complex is probably occurring.

In the reaction of $ReOCl_3(PPh_3)_2$ with O_2cyclam in CH_2Cl_2/EtOH solvent, a gray powder precipitates out during the course of the reaction and is formulated as ReO($H_{-2}O_2$cyclam)Cl·DMF on the basis of IR and elemental analysis. The strong band in the FTIR spectrum at 912 cm^{-1} is assigned to the ν_{as}(ReO) stretch, within the range for an ReO^{3+} compound. The low value of the ν_{as}(ReO) stretch for this diamide complex as compared to the monoamide complex indicates much greater charge neutralization of the metal center and consequent weakening of the ReO bond. The FTIR data are summarized in Table II for all of the above compounds, and the values of n_{as} frequencies show the expected trend to lower energies as the positive charge on the complex is reduced, either with deprotonation of the hydroxyl ligands trans to the oxo group or coordination of additional deprotonated amide groups.

The log K_a acid association constant for ReO_2(cyclam)Cl was determined by the method of Motekaitis and Martell,[26] and compared with the corresponding value for $ReO_2(en)_2Cl$ determined by Murmann.[29] The titration of the $ReO_2(en)_2Cl$ complex with acid was repeated for comparison and the titration curves for both complexes are shown in Figure 3. The hydroxo group on the cyclam complex is a stronger acid than the hydroxyl of the en complex with log K_a's of 2.95 ± 0.05 at μ = 0.100 M and 25.0 °C compared with 3.29 ± 0.02 at μ = 0.50 M and 25.3 °C, respectively. While the addition of a second proton at high acidity was reported for $ReO(OH)(en)_2^{2+}$,[30] attempts to achieve this second protonation for ReO(OH)(cyclam)$^{2+}$ were unsuccessful due to the rapid disproportionation of the complex. Disproportionation also occurs rapidly for the ReO(OH)($H_{-1}O_1$cyclam)$^+$ complex in dilute acid.

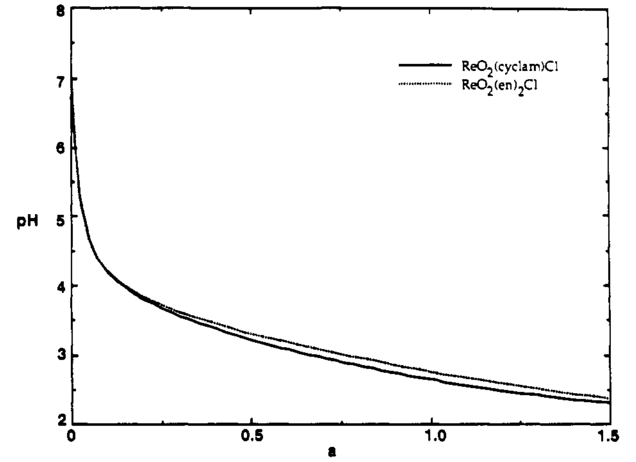

Figure 3. Potentiometric equilibrium curves for the protonatin of oxo ligands on ReO_2(cyclam)Cl and $ReO_2(en)_2Cl$. Metal complex initial concentrations were 8.10 × 10^{-3} and 7.68 × 10^{-3} M, respectively; t = 25.0 °C; μ = 0.100 M (KCl); a is the moles of metal complex present per mole of standard HCl added.

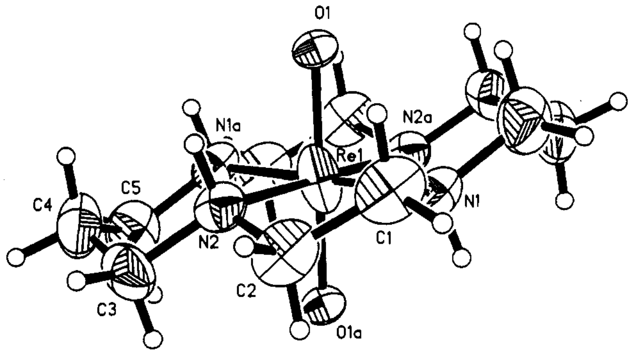

Figure 4. Thermal ellispoid plot (50% probability) diagram of the dication [ReO(OH)(cyclam)$^{2+}$].

Magnetic susceptibility measurements by Evan's NMR method on crystals of compounds I and II show both complexes to be diamagnetic, consistent with assignment of both as Re(V) d^2 complexes.

Results of Structural Analyses. The X-ray diffraction studies of both *trans*-oxo–hydroxo complexes, ReO(OH)(cyclam)$(ClO_4)_2$ and ReO(OH)(O_1cyclam)ReO_4, show both Re(V) metal ions to be six-coordinate in a distorted octahedral geometry with four nitrogen atoms occupying the equatorial plane and two oxygen atoms in the axial positions (Figures 4 and 5). Two perchlorate anions are associated with each Re(V) dication in structure I, and one perrhenate anion is associated with each Re(V) cation in structure II. Crystal data and details of the determinations are given in Table I. Atomic coordinates and isotropic displacement parameters for all non-hydrogen atoms are given in Table III. Selected bond lengths and angles are given in Tables IV and V. Hydrogen atom and thermal parameters, are available as supplementary material.

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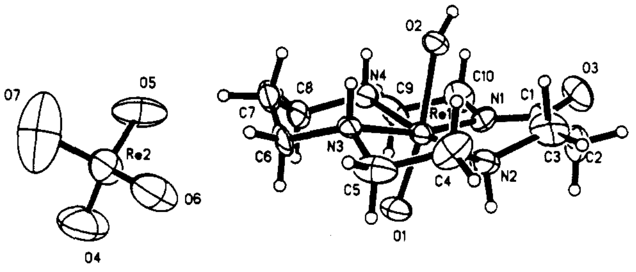


Figure 5. Thermal ellipsoid plot (50% probability) diagram of the cation [ReO(OH)($H_{-1}O_1$cyclam)$^+$] and the perrhenate anion.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (A^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a,b]
		ReO(OH)(cyclam) $(ClO_4)_2$ (I)		
Re1	5000	5000	5000	52(1)
Cl1	5000	7542(2)	7500	45(1)
Cl2	0	3963(3)	2500	50(1)
O1	4297(7)	5048(3)	3499(5)	31(2)
O2	4961(30)	7812(11)	8551(11)	77(10)
O3	6027(28)	7932(13)	7152(25)	139(20)
O4	5305(26)	6746(5)	7577(22)	82(12)
O5	3693(20)	7649(12)	6718(21)	126(12)
O6	−159(24)	3730(15)	1388(11)	207(13)
O7	1126(31)	4471(20)	2800(14)	328(22)
N1	4070(9)	6093(5)	5123(7)	44(3)
N2	3053(9)	4565(5)	5151(7)	41(3)
C1	2510(12)	5963(7)	4968(11)	57(4)
C2	2288(12)	5235(8)	5565(11)	56(4)
C3	3181(13)	3824(7)	5837(10)	57(4)
C4	3962(15)	3195(7)	5397(12)	63(5)
C5	5587(15)	3274(7)	5614(12)	65(5)
		ReO(OH)(O_1cyclam)ReO_4 (II)		
Re1	1775(1)	6954(1)	1225(1)	26(1)
O1	2755(9)	6730(10)	2150(5)	38(3)
O2	576(9)	6721(9)	154(5)	30(3)
O3	847(11)	11104(10)	696(6)	51(4)
N1	1872(11)	8993(12)	1037(6)	34(4)
C1	858(14)	9914(14)	997(8)	38(5)
C2	−255(17)	9506(16)	1346(10)	55(7)
C3	−950(15)	8041(16)	1188(9)	52(6)
N2	−25(12)	6923(11)	1567(6)	35(4)
C4	−639(16)	5495(15)	1440(9)	51(7)
C5	509(16)	4425(16)	1655(8)	47(6)
N3	1427(10)	4720(10)	1167(5)	24(3)
C6	2685(14)	3906(13)	1319(8)	39(5)
C7	3507(14)	4346(15)	778(9)	44(5)
C8	4328(13)	5708(15)	976(8)	40(5)
N4	3416(11)	6948(12)	732(6)	37(4)
C9	4071(13)	8312(15)	913(9)	43(5)
C10	3018(14)	9470(15)	722(9)	44(6)
Re2	6849(1)	2036(1)	1657(1)	58(1)
O4	8280(15)	2092(19)	2394(8)	113(8)
O5	6949(16)	3195(17)	951(7)	97(7)
O6	5472(13)	2352(18)	1962(8)	93(7)
O7	6667(16)	385(18)	1230(14)	154(12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Estimated standard deviations are given in parentheses.

Both compounds form weak hydrogen bonds between the axial hydroxo ligands and oxygen atoms of adjacent molecules. For structure I a very long interaction is seen between the disordered axial hydroxo ligand on one cation and the disordered oxo ligand on the adjacent cation [O1···O1 = 3.11(3) Å]. The cations stack along the crystallographic *c* axis in such a way as to form one-dimensional chains. The close interaction of the axial oxygen atoms of adjacent cations indicates the possibility of a hydrogen bond (Figure 6). The cations are in turn hydrogen bound, through a nitrogen hydrogen, to an oxygen atom of the nearby perchlorate anion [N1···O4 = 2.95(3) Å and N2···O7 = 2.95(9) Å] (Figure 6).

Table IV. Selected Bond Angles (deg) and Bond Lengths (Å) for ReO(OH)(cyclam)$(ClO_4)_2$ (I) with Esds in Parentheses

		Bond Angles	
O1–Re1–N1	89.1(3)	O1–Re1–N2	90.6(3)
N1–Re1–N2	83.5(3)	O1–Re1–O1A	180.0(1)
N1–Re1–O1A	90.9(3)	N2–Re1–O1A	89.4(3)
N2–Re1–N1A	96.5(3)	N1–Re1–N1A	180.0(1)
O2–C11–O4	109(1)	O2–C11–O3	110(2)
O2–C11–O5	110(1)	O3–C11–O4	110(1)
O4–C11–O5	109(1)	O3–C11–O5	110(1)
O6–C12–O6A	147(2)	O6–C12–O7	108(1)
Re1–N1–C1	107.7(6)	O7–C12–O6A	93(1)
C1–N1–C5A	114.9(9)	Re1–N1–C5A	114.9(8)
Re1–N2–C3	114.3(7)	Re1–N2–C2	107.7(6)
N1–C1–C2	110.2(9)	C2–N2–C3	114.6(9)
N2–C3–C4	112(1)	N2–C2–C1	108(1)
C4–C5–N1A	110.7(9)	C3–C4–C5	119(1)
		Bond Lengths	
Re1–O1	1.766(5)	Re1–N1	2.091(9)
Re1–N2	2.091(9)	C11–O3	1.36(3)
C11–O2	1.37(2)	C11–O5	1.37(2)
C11–O4	1.38(1)	C12–O7	1.36(3)
C12–O6	1.38(1)	C12–O7A	1.36(3)
C12–O6A	1.38(1)	N1–C5A	1.50(2)
N1–C1	1.49(1)	N2–C3	1.50(1)
N2–C2	1.52(2)	C3–C4	1.50(2)
C1–C2	1.48(2)		
C4–C5	1.53(2)		

Table V. Selected Bond Angles (deg) and Bond Lengths (Å) for ReO(OH)(O_1cyclam)ReO_4 (II) with Esds in Parentheses

		Bond Angles	
O1–Re1–O2	166.1(4)	O1–Re1–N1	104.2(4)
O2–Re1–N1	89.7(4)	O1–Re1–N2	92.7(4)
O2–Re1–N2	85.2(4)	N1–Re1–N2	98.8(5)
O1–Re1–N3	88.1(4)	O2–Re1–N3	78.0(3)
N1–Re1–N3	167.6(4)	N2–Re1–N3	81.5(4)
O1–Re1–N4	94.5(4)	O2–Re1–N4	87.4(4)
N1–Re1–N4	81.2(5)	N2–Re1–N4	172.6(4)
N3–Re1–N4	96.9(4)	Re1–N1–C1	125(1)
Re1–N1–C10	116.1(9)	C1–N1–C10	117(1)
O3–C1–N1	122(1)	O3–C1–C2	120(1)
N1–C1–C2	119(1)	C1–C2–C3	122(1)
C2–C3–N2	111(1)	Re1–N2–C3	111.6(9)
Re1–N2–C4	110(1)	C3–N2–C4	114(1)
N2–C4–C5	108(1)	C4–C5–N3	108(1)
Re1–N3–C5	106.5(8)	Re1–N3–C6	112.7(7)
C5–N3–C6	118(1)	N3–C6–C7	111(1)
C6–C7–C8	117(1)	C7–C8–N4	110(1)
Re1–N4–C8	113.1(9)	Re1–N4–C9	106.3(9)
C8–N4–C9	115(1)	N4–C9–C10	110(1)
N1–C10–C9	106(1)	O4–Re2–O5	109.6(8)
O4–Re2–O6	112.1(7)	O5–Re2–O6	110.8(8)
O4–Re2–O7	109.5(8)	O5–Re2–O7	107(1)
O6–Re2–O7	107.9(9)		
		Bond Lengths	
Re1–O1	1.685(8)	Re1–O2	1.970(8)
Re1–N1	1.98(1)	Re1–N2	2.11(1)
Re1–N3	2.16(1)	Re1–N4	2.11(1)
O3–C1	1.25(2)	N1–C1	1.35(2)
N1–C10	1.51(2)	C1–C2	1.50(2)
C2–C3	1.56(2)	C3–N2	1.46(2)
N2–C4	1.49(2)	C4–C5	1.53(2)
C5–N3	1.48(2)	N3–C6	1.47(2)
C6–C7	1.51(2)	C7–C8	1.54(2)
C8–N4	1.50(2)	N4–C9	1.46(2)
C9–C10	1.52(2)	Re2–O4	1.67(1)
Re2–O5	1.70(1)	Re2–O6	1.68(1)
Re2–O7	1.74(2)		

The hydrogen bonding interactions for structure II are not similar to those seen for structure I. The hydroxo hydrogen from the cation is seen to be in close contact with the carbonyl oxygen of a nearby cation [O2···O3 = 2.74(2) Å] and not the oxo ligand. In fact no close contacts are seen for the oxo ligand suggesting the absence of a hydrogen bond to the oxo ligand (Figure 7). A

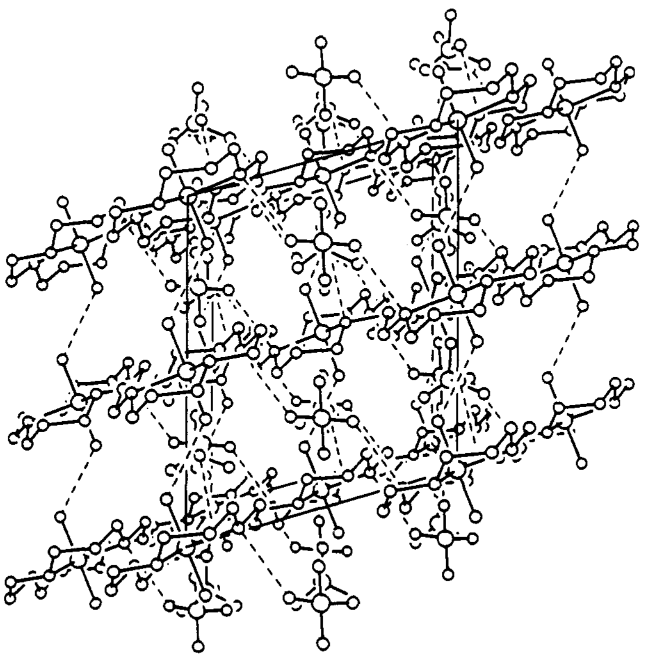


Figure 6. View of the crystal packing for structure I showing the separation of cationic molecules by perchlorate anions. The view is down the *b* axis, with *a* axis top and *c* axis across.

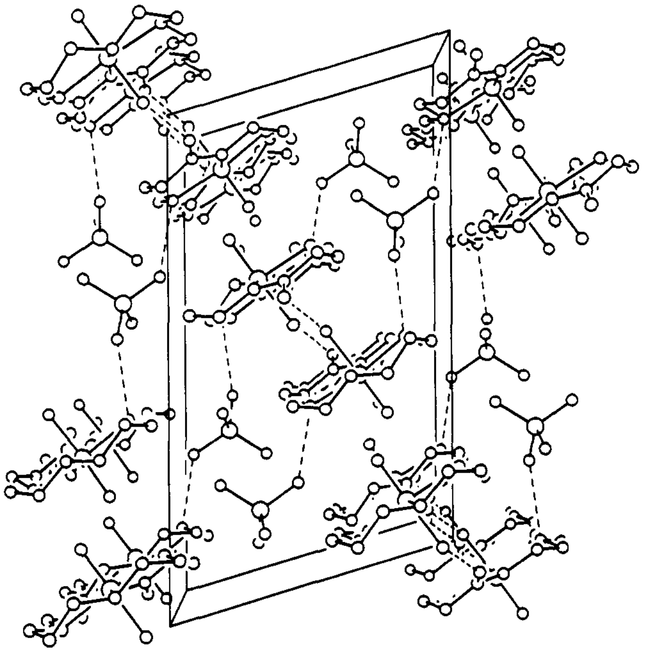
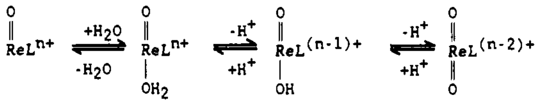


Figure 7. View of the crystal packing for structure II showing the separation of cationic molecules by perhenate. The view is down the *b* axis, with *a* axis top and *c* axis across..

second shorter interaction is seen between a nitrogen hydrogen of the cation and an oxygen of the ReO_4 anion [N4··O5 = 2.92(2) Å and N2··O6 = 2.82(2) Å]. The interactions themselves link the adjacent cations and anions in a sheetlike pattern which propagates along the crystallographic *b* axis.

Discussion

The Re(V) macrocyclic complexes were synthesized in good yields by ligand displacement reactions with a variety of monooxo and *trans*-dioxo starting complexes containing ligands displaced under mild reaction conditions. The ReO_2(cyclam)Cl complex was synthesized in a greater yield than previously reported for Re and the analogous Tc complex.[9,10] Starting with the metal already in the desired oxidation state increases the yield because no reduction of the metal center is required and the possibility of side products with the metal in different oxidation states is avoided. Starting with a compound containing the same number of oxo ligands as desired for the product is not necessary, because in the presence of water, addition or loss of an oxo ligand is possible according to the following scheme:



$$\overset{O}{\overset{\|}{ReL^{n+}}} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \overset{O}{\overset{\|}{\underset{OH_2}{\underset{|}{ReL^{n+}}}}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \overset{O}{\overset{\|}{\underset{OH}{\underset{|}{ReL^{(n-1)+}}}}} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \overset{O}{\overset{\|}{\underset{O}{\underset{\|}{ReL^{(n-2)+}}}}}$$

Transformations of this type have been previously suggested[28] and should occur readily in those complexes where the high cationic charge on the metal is not satisfied by the coordinating ligands for a monooxo complex or where the ligands provide too much electron density to stabilize a dioxo complex. Cotton and Lippard reported the preparation of $ReO_2(py)_4Br$ from the reaction of $[ReOBr_4^-][n\text{-}Bu_4N^+]$ with pyridine and a small amount of water.[18] Previous workers describe the preparation of an unstable $ReO(cyclam)^{3+}$ complex from the reaction of $ReOCl_3(PPh_3)_2$ and cyclam, with subsequent hydrolysis in solution to the $ReO_2(cyclam)^+$ complex.[10] The monooxo complex ReO(mercaptoacetyltriglycine)$^-Ph_4As^+$ was prepared from a dioxo starting compound, $ReO_2(en)_2Cl$,[30] where protonation and displacement of one of the oxo groups occurs.

Neutralization of high charge on the metal ion, either negative or positive, drives the above equilibria. In this work the oxo-hydroxo complex is the most stable species for the Re(V) complex with the uninegative oxocyclam ligand, and while spectroscopic evidence suggests that deprotonation of the hydroxyl group can be achieved, the *trans*-dioxo complex is not exclusively formed when base is added to a solution of the complex. A coordinating base such as pyridine displaces the hydroxo ligand easily, but a sterically hindered base such as diethylamine deprotonates the hydroxo group, and possibly a ligand amino nitrogen as well. Deprotonation of two amine nitrogens of a tetradentate amine oxime ligand by TcO^{3+} has been reported.[31]

From this evidence, one concludes that the H_{-1}oxocyclam ligand, upon coordination to the metal center, does not sufficiently neutralize the cationic charge on the metal center to promote the formation of a stable monooxo species. A weak σ-donor ligand trans to the oxo is necessary, but another strong σ or π-donor is not required.

In contrast to the weakly basic oxo ligand on the $ReO_2(H_{-1}O_1cyclam)^+$ complex, the oxo ligand on $ReO_2(cyclam)^+$ is much less basic, with a pK_a of 2.95 ± 0.05. The neutral cyclam ligand upon coordination does not contribute a negative charge to the metal center as does the deprotonated oxocyclam, and stronger Re–O(oxo) and ReN(amino) bonding results. The IR ν_{as}(ReO) stretching frequencies for the two cyclam complexes in Table II are higher than those for the two oxocyclam complexes, reflecting the stronger Re–oxo bonding in the cyclam complexes. The shorter ReN(amine) bond lengths for the cyclam complexes (Table VI) as compared to the oxocyclam complex, reflects the stronger Re–N(amino) bonding.

The X-ray structural analyses of the ReO(OH)(cyclam)$(ClO_4)_2$ shows that the Re atom sits on an inversion center with the oxo and hydroxo oxygens disordered, resulting in the observation of average ReO bond lengths of 1.766(5) Å. Several pieces of evidence preclude assignment of this structure as the *trans*-dioxo–Re(VI)–cyclam complex. The diamagnetism found for this complex is inconsistent with known Re(VI) complexes which generally exhibit paramagnetism with magnetic moments between 1.2 and 1.7 μ_B.[32] The only two analogous Re(V) and Re(VI) compounds structurally characterized, $[ReOCl_4^-][Ph_4As^+]$

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Table VI. Selected Bond Distances (Å) for ReV/TcV Macrocyclic Complexes

complex	M–O-(oxo)	M–N-(amine)	M–N-(amide)	ref
$ReO_2(cyclam)Cl(BPh_3)\cdot H_2O$	1.756(3)	2.132 (av)		10
$ReO(OH)(cyclam)_2(ClO_4)_2$	1.766(5)[a]	2.100 (av)		this work
$ReO(OH)(O_1cyclam)ReO_4$	1.704(10)	2.151 (av)	1.981	this work
$TcO_2(cyclam)ClO_4$	1.749(3)	2.124 (av)		8
$TcN(O_2cyclam)H_2O$	1.612(4)	2.127 (av)	2.051	9
$[ReO(OH)(CN)_4][PPh_4]_2$	1.69			37
$[TcO(OH)(diphos)2][CF_3SO_3]_2$[b]	1.79			38

[a] Average distance of ReO(oxo) and ReO(hydroxyl) bond lengths. [b] Average distance of TcO(oxo) and TcO hydroxyl.

and $ReOCl_4$, respectively, have identical ReO(oxo) bond lengths of 1.63 Å and similar ReO stretching frequencies.[33,34] Therefore, detection of a strong absorption in the ReO^{3+} stretching frequency region precludes a *trans*-dioxo formulation. The nitrogens of the cyclam adopt a trans III configuration to minimize ring strain[35] as in the $ReO_2(cyclam)^+$ structure previously reported.[10]

From the presence of perrhenate as counter ion for the crystal grown from an aqueous solution of $ReO(OH)(H_{-1}O_1cyclam)Cl$, one can assume that some of the complex was hydrolyzed in solution over the several weeks needed to grow the crystals followed by oxidation of the metal center. The perrhenate anion was detected by the presence of a large $\nu_{as}(ReO)$ stretching frequency at 907 cm^{-1} in the IR spectrum of the crystals, which otherwise was identical to that of the original complex. Examples of oxidation of *trans*-ReO_{2+} complexes have been reported. One such example involves the $ReO_2(en)_{2+}$ cation where spectrophotometric analysis of an aqueous solution of the chloride complex showed a decrease in the amount of the complex and formation of ReO_4^-.[36] No other new species were formed. ^{18}O tracer studies of the oxidation of $ReO_2(en)_2^+$ to ReO_4^- showed that 50% of the oxygen atoms on the perrhenate came from the original complex, 40% were derived from H_2O, and only 10% came from the oxidant, O_3.[36] Similarly, in an aqueous solution of $ReO(OH)(H_{-1}O_1cyclam)^+$, about 50% hydrolysis of the compound occurs over two weeks time producing ReO_4^- anions, free ligand, and H^+.

The Re1 atom in $ReO(OH)(H_{-1}O_1cyclam)ReO_4$ is displaced from the basal plane towards the oxo oxygen by about 0.14 Å, typical for metal monooxo complexes. Due to Coulombic repulsion the O1–Re1–O2 bond angle is bent away from the negatively charged nitrogen by 13°. The O1–Re1–N1 and O2–Re–N1 bond angles of 104.3 and 89.1°, respectively, indicate that only the oxo and not the hydroxyl group is repelled away from the negatively charged amide group and that the proximity of the perrhenate anion to the oxo group may also cause distortion. The negative charge and consequent greater ligand field strength of the deprotonated amide nitrogen results in the shorter ReN1 bond length as compared to those of the other three Re–N (amine) bonds. The ReO(hydroxo) bond length is quite long due to the ground-state trans-labilization effect of the strongly σ- and π-bound oxo ligand.

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Supplementary Material Available: Tables of anisotropic displacement parameters and hydrogen atom parameters (4 pages). Ordering information is given on any current masthead page.

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