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Spectroscopy, Molecular Structure, and Electrochemistry of Rhenium(V) Oxo and Imido Complexes of 1,4,8,11-Tetraazacyclotetradecane (cyclam)

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trans-[ReO$_2$(cyclam)]ReO$_4$·$^1/_2$H$_2$O, *trans*-[ReO(OEt)(cyclam)](ClO$_4$)$_2$, and *trans*-[Re(NPh)(OH)(cyclam)](ClO$_4$)$_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) were prepared and structurally characterized by X-ray crystallography. The structure of *trans*-[ReO$_2$(cyclam)]ReO$_4$·$^1/_2$H$_2$O is quite similar to that of the previously reported *trans*-[ReO$_2$(cyclam)]Cl and *trans*-[ReO$_2$(cyclam)]PF$_6$. Crystal data: *trans*-[ReO$_2$(C$_{10}$H$_{24}$N$_4$)]ReO$_4$·$^1/_2$H$_2$O, $M = 676.74$, orthorhombic, space group *Pnma*, $a = 17.717(5)$ Å, $b = 17.073(4)$ Å, $c = 5.466(2)$ Å, $V = 1653.4(9)$ Å^3, $Z = 4$, $d_{\text{calcd}} = 2.719$ g cm^{-3}, μ(Mo Kα) = 14.86 mm^{-1}; *trans*-[ReO(OEt)(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)$_2$, $M = 646.49$, orthorhombic, space group $P2_12_12_1$, $a = 8.869(4)$ Å, $b = 13.850(3)$ Å, $c = 17.681(3)$ Å, $V = 2172(1)$ Å^3, $Z = 4$, $d_{\text{calcd}} = 1.977$ g cm^{-3}, μ(Mo Kα) = 5.97 mm^{-1}; *trans*-[Re(NPh)(OH)(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)$_2$, $M = 693.55$, orthorhombic, space group *Pnma*, $a = 17.651(6)$ Å, $b = 15.702(5)$ Å, $c = 8.695(2)$ Å, $V = 2410(1)$ Å^3, $Z = 4$, $d_{\text{calcd}} = 1.912$ g cm^{-3}, μ(Mo Kα) = 5.50 mm^{-1}. The rhenium–oxo bond distances in *trans*-[ReO$_2$(cyclam)]$^+$ and *trans*-[ReO(OEt)(cyclam)]$^{2+}$ are 1.775(9) and 1.643(9) Å, respectively. The UV–vis spectrum of *trans*-[ReO$_2$(cyclam)]$^+$ shows two ligand field transitions at 423 and 530 nm. For *trans*-[ReO(OEt)(cyclam)]$^{2+}$, the corresponding ligand field bands red shift to 481 and 625 nm. *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$ is stable in aqueous medium. The measured Re≡NPh distance of 1.731(9) Å and Re≡N—Ph bond angle of 176.2(8)° are consistent with the metal–imido formulation. The cyclic voltammogram of *trans*-[ReO$_2$(cyclam)]$^+$ in aqueous medium shows a quasi-reversible 2H$^+$–2e$^-$ couple corresponding to the reduction of Re(V) to Re(III). Both *trans*-[ReO(OEt)(cyclam)]$^{2+}$ and *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$ show a 1e$^-$ reduction wave in acetonitrile at potentials of −1.0 and −1.4 V vs SCE, respectively. $E°$ of the *trans*-[Re$^{\text{v}}$(NPh)(OH)(cyclam)]$^{2+}$/*trans*-[Re$^{\text{IV}}$(NPh)(OH)(cyclam)]$^{2+}$ couple is smaller than that of *trans*-[Re$^{\text{V}}$O(OEt)(cyclam)]$^{2+}$/*trans*-[Re$^{\text{IV}}$O(OEt)(cyclam)]$^+$.

Introduction

High-valent rhenium complexes with metal–ligand multiple bonds have received current attention for their intriguing photochemical[1,2] and electrochemical[3,4] properties. Most of the cationic Re$^{\text{V}}$≡O, Re$^{\text{V}}$≡N, and Re$^{\text{V}}$≡NR complexes have diphosphines,[5] diamines,[2a] pyridine,[1–4,6] or α-diimines[1b] as auxilary ligands. To our knowledge, studies on rhenium macrocyclic complexes are sparse, apart from the structural work on rhenium oxo complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam)[7,8] and 1,4,7-triazacyclononane and its N-methylated derivatives.[9,10] Our previous work indicated that macrocyclic amines are good ligand systems for investigating the redox chemistry of high-valent metal oxo complexes.[11] Herein is described the structure and electrochemistry of oxo– and imido–rhenium(V) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam). *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$ is an intriguing metal–imido complex in that it is stable in aqueous medium.

Experimental Section

KReO$_4$ was obtained from Janssen Chimica Co. The ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) and the metal complexes ReOCl$_3$(Ph$_3$)$_2$,[12] ReO$_2$I(PPh$_3$)$_2$,[13] and Re(NPh)Cl$_3$(PPh$_3$)$_2$[14] were prepared by literature methods.

Synthesis. *trans*-[ReO$_2$(cyclam)]ClO$_4$. A mixture of ReO$_2$I(PPh$_3$)$_2$ (0.2 g) and cyclam (0.05 g) in 1:1 CH$_3$OH/CH$_3$CN (20 mL) was stirred for 1 h under nitrogen. The product *trans*-[ReO$_2$(cyclam)]ClO$_4$ was precipitated by addition of LiClO$_4$ followed by excess diethyl ether (yield 50%). The crude product was recrystallized by diffusion of diethyl ether into a CH$_3$OH/CH$_3$CN mixture (1:1) to yield pale yellow crystals. Anal. Calcd for ReO$_2$(C$_{10}$H$_{24}$N$_4$)ClO$_4$·$^1/_2$H$_2$O: C, 22.5; H, 4.7; N, 10.5.

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Table I. Summary of Crystallographic Data for *trans*-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_2H_2O$, *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$, and *trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$

	trans-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_2H_2O$	*trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$	*trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$
molecular formula	$C_{10}H_{24}N_4O_6Re_2 0.5H_2O$	$C_{12}H_{29}N_4O_{10}Cl_2Re$	$C_{16}H_{30}N_5O_9Cl_2Re$
M	676.74	646.49	693.55
cryst system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnma*	$P2_12_12_1$	*Pnma*
a/Å	17.717(5)	8.869(4)	17.651(6)
b/Å	17.073(4)	13.850(3)	15.702(5)
c/Å	5.466(2)	17.681(3)	8.695(2)
V/Å^3	1653.4(9)	2172(1)	2410(1)
Z	4	4	4
ρ_{calcd}/g cm^{-3}	2.719	1.977	1.912
μ/mm^{-1}	14.86	5.97	5.50
radiation (λ/Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)
R^a	0.037	0.039	0.044
$R_w{}^b$	0.036	0.035	0.035

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_w = (\sum w(|F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Found: C, 22.6; H, 4.5; N, 10.4. IR: 788 cm^{-1} ($\nu_{Re=O}$). UV–vis [λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1})]: 259 (980), 283 (540 sh), 315 (230 sh), 423 (27), 530 (9).

***trans*-[ReO(OEt)(cyclam)](ClO₄)₂.** A mixture of $ReOCl_3(PPh_3)_2$ (0.4 g) and cyclam (0.2 g) in dry CH_2Cl_2 (100 mL) was stirred for 1 h. The solvent was removed under vacuum, and the residue was dissolved in absolute ethanol. $N_2H_4 \cdot 2HCl$ (0.1 g) and PPh_3 (0.2 g) were added, and the resulting mixture was heated to 60 °C for 5 min. The product was precipitated upon addition of $LiClO_4$ (yield 35%). The crude product was recrystallized by diffusion of diethyl ether into a CH_3CN solution to give brown crystals. Anal. Calcd for $[ReO(OC_2H_5)(C_{10}H_{24}N_4)](ClO_4)_2$: C, 22.3; H, 4.5; N, 8.7. Found: C, 22.5; H, 4.1; N, 8.7. IR: 958 cm^{-1} ($\nu_{Re=O}$). ^1H NMR (270 MHz) in CD_3CN: 1.17 (t, 3H), 3.68 (q, 2H), 5.98 (s, 2H), 5.15 (s, 2H). UV–vis [λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1})]: 270 (720 sh), 481 (28), 623 (5).

***trans*-[Re(NPh)(OH)(cyclam)](ClO₄)₂.** A mixture of $Re(NPh)Cl_3(PPh_3)_2$ (0.2 g) and cyclam (0.1 g) was stirred in dry CH_2Cl_2 (100 mL) for 24 h to give a pale green solution. The mixture was evaporated to dryness under vacuum. The residue was dissolved in absolute ethanol. Upon addition of $LiClO_4$, blue microcrystalline solid precipitated. The solid was recrystallized by diffusion of diethyl ether to an acetonitrile solution. ^1H NMR (270 MHz) in CD_3CN: 5.51 (s, 2H), 5.10 (s, 2H), 7.71 (tt, 1H), 7.41 (q, 2H), 7.45 (dd, 2H). IR: 1033 cm^{-1} ($\nu_{Re=NPh}$). UV–vis [λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1})]: 308 (10 970), 648 (53), 760 (56).

Physical Measurements. UV–visible absorption spectra were recorded on a Milton Roy Spectronic 3000 diode array spectrophotometer. Infrared spectra were obtained as Nujol mulls on a Nicolet 20FXC FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Jeol 270-MHz NMR spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 175 universal programmer and a Model 173 potentiostat. Glassy carbon (Tokai) or pyrolytic graphite (Union Carbide) was used as the working electrode. A conventional two-compartment cell was used. All potentials were quoted with respect to a saturated calomel electrode (SCE). A PAR Model 179 digital coulometer was used in conjunction with the potentiostat for constant-potential coulometry experiments. All experiments were performed at room temperature (25 ± 2 °C).

X-ray Structure Determination. Intensity data were obtained at 297 K on a Nonius CAD4 diffractometer with graphite-monochromatised Mo Kα radiation (λ = 0.709 30 Å) using the $\theta/2\theta$ scan mode with $2\theta_{max}$ = 50°. A summary of crystal and data parameters is given in Table I. Intensity data were corrected for Lorentz and polarization effects and empirical absorption. For *trans*-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_2H_2O$, 1505 independent reflections were measured of which 1184 reflections with $I_0 > 2.0\sigma(I_0)$ were used in the structure analysis. For *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$, 2187 independent reflections were measured of which 1892 reflections with $I_0 > 2.0\sigma(I_0)$ were used. For *trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$, 2205 unique reflections were taken and 1721 reflections with $I_0 > 2.0\sigma(I_0)$ were used in the structure analysis. The structure were solved by the Patterson method and refined by least squares. All data reduction and structure refinement were performed using the NRCC–SDP–VAX packages. The weighting scheme $w^{-1} = \sigma^2(F)$ was used for *trans*-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_2H_2O$ and *trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$, and $w^{-1} = \sigma(F) + 0.00002F^2$ was used for *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$. The non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included at idealized positions with a fixed contribution. Fractional atomic coordinates are given in Tables II–IV. Selected bond distances and angles are given in Tables V–VII.

Table II. Fractional Atomic Coordinates and B Values (Å^2) of *trans*-$[ReO_2(cyclam)]ReO_4 \cdot {}^1/_4H_2O$

	x	y	z	$B_{iso}{}^a$
Re(1)	0	$^1/_2$	$^1/_2$	1.26(3)
N(1)	−0.0160(5)	0.4038(6)	0.2554(21)	1.8(4)
N(2)	0.1159(5)	0.4654(7)	0.4768(19)	1.9(5)
C(3)	0.1221(7)	0.4134(9)	0.257(3)	2.1(6)
C(4)	0.0557(7)	0.3567(8)	0.267(3)	2.2(6)
C(5)	−0.0842(7)	0.3582(8)	0.312(3)	2.5(7)
C(6)	−0.1544(7)	0.4103(9)	0.307(3)	2.9(7)
C(7)	0.1674(6)	0.5355(9)	0.475(3)	2.4([illegible])
Re(2)	0.23124(5)	$^1/_4$	0.6739(2)	2.37(4)
O(1)	0.1865(6)	0.3330(7)	0.764(2)	4.3(6)
O(2)	0.3207(8)	$^1/_4$	0.785(4)	6.1(11)
O(3)	0.2283(9)	$^1/_4$	0.361(3)	4.4(8)
O(4)	0.0138(5)	0.5639(5)	0.2477(16)	1.9(4)
O	0.015(4)	$^3/_4$	0.254(17)	19.2(27)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Results and Discussion

Two research groups previously reported the synthesis and X-ray structure of *trans*-$[ReO_2(cyclam)]^+$, which was isolated as the PF_6^- salt by Duatti and co-workers[7a] and the Cl^- salt by Schroder and co-workers.[8] Recently, the synthesis and crystal structure of $[ReO(OH)(cyclam)](ClO_4)_2$ has also been reported by Tsang et al.[7b] When we attempted to prepare *trans*-$[ReO_2(cyclam)]^+$ by following literature procedures,[7a,8] a white product identified by X-ray crystallography and IR spectroscopy as $[cyclamH]ReO_4$ was always obtained if the reaction was carried out in the presence of air. By performance of the synthesis under a nitrogen atmosphere, the desired product isolated as a perchlorate salt was obtained in high yield. *trans*-$[ReO_2(cyclam)]ClO_4$ is a diamagnetic, air-stable solid. However, upon prolonged standing of it in acetonitrile/methanol, pale yellow crystals of *trans*-$[ReO_2(cyclam)]ReO_4$, identified by X-ray crystallography, were obtained. The IR spectrum of *trans*-$[ReO_2(cyclam)]ClO_4$ shows an intense absorption band at 788 cm^{-1} assignable to the $\nu_{as}(ReO_2)$ stretch and intense absorptions at 1100–1000 cm^{-1} due to the ClO_4^- ion. However, two intense ν(N–H) stretches at ca. 3100 cm^{-1} are also found. This is not typical of *trans*-dichloro(cyclam)metal complexes, which show only one ν(N–H) stretch in normal cases.[15] For this reason, an X-ray analysis was undertaken. Figure 1a shows a perspective view of the *trans*-$[ReO_2(cyclam)]^+$ cation. The structure is identical to Duatti's and Schroder's[7a,8] structures. The measured Re=O distance of 1.775(9) Å in this work is comparable to that of 1.756(3) Å[8] and

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[15] Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1336.

Table III. Fractional Atomic Coordinates and *B* Values (Å^2) of *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$

	x	y	z	B_{iso}[a]
Re	0.54932(6)	0.03069(4)	0.42857(3)	3.282(21)
N(1)	0.4202(12)	0.1479(9)	0.3846(6)	5.2(6)
N(2)	0.6731(12)	0.0510(10)	0.3283(6)	6.2(7)
N(3)	0.6601(15)	−0.0884(9)	0.4679(6)	6.1(7)
N(4)	0.4179(10)	0.0053(8)	0.5272(5)	4.3(5)
C(1)	0.5093(17)	0.1933(12)	0.3238(9)	7.6(10)
C(2)	0.5867(18)	0.1131(16)	0.2761(7)	8.9(11)
C(3)	0.7305(19)	−0.0399(16)	0.2951(9)	9.4(12)
C(4)	0.8086(20)	−0.1013(15)	0.3524(10)	9.0(12)
C(5)	0.7238(20)	−0.1536(13)	0.4121(12)	9.1(12)
C(6)	0.5669(21)	−0.1381(12)	0.5275(9)	7.9(10)
C(7)	0.5017(14)	−0.0609(10)	0.5759(8)	5.9(8)
C(8)	0.3675(17)	0.0976(12)	0.5627(8)	6.8(9)
C(9)	0.2833(19)	0.1630(12)	0.5079(10)	7.2(10)
C(10)	0.3698(18)	0.2138(11)	0.4479(10)	7.1(10)
C(11)	0.2964(23)	−0.1150(18)	0.3515(10)	11.9(15)
C(12)	0.273(3)	−0.103(3)	0.2805(15)	18.6(24)
O(1)	0.4224(11)	−0.0535(7)	0.3781(4)	5.2(5)
O(2)	0.6566(10)	0.1069(6)	0.4752(5)	4.6(5)
O(3)	0.5794(12)	0.1499(10)	0.0815(7)	10.2(8)
O(4)	0.3817(18)	0.0907(13)	0.0056(7)	15.5(12)
O(5)	0.3731(14)	0.0760(16)	0.1285(7)	16.9(15)
O(6)	0.5384(19)	−0.0041(10)	0.0685(14)	23.3(19)
O(7)	−0.0577(17)	0.1744(11)	0.2347(6)	12.6(11)
O(8)	−0.0651(18)	0.1810(12)	0.3586(7)	14.6(12)
O(9)	0.1160(18)	0.2733(10)	0.3085(8)	11.7(10)
O(10)	0.1242(19)	0.1076(12)	0.3077(11)	17.3(13)
C1(1)	0.4704(4)	0.0768(3)	0.0723(2)	6.80(22)
C1(2)	0.0311(5)	0.1854(3)	0.2984(2)	5.82(21)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Fractional Atomic Coordinates and *B* Values of *trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$

	x	y	z	B_{iso}[a]
Re	0.34577(3)	$^3/_4$	0.22627(6)	3.259(22)
O(1)	0.4233(5)	$^3/_4$	0.0722(12)	5.9(5)
N(1)	0.4094(4)	0.6479(5)	0.3207(8)	5.2(4)
N(2)	0.2973(4)	0.6486(5)	0.0946(8)	5.1(4)
N(3)	0.2712(5)	$^3/_4$	0.3556(11)	3.4(5)
C(1)	0.3952(6)	0.5691(5)	0.2266(12)	6.9(6)
C(2)	0.3135(6)	0.5687(5)	0.1785(11)	6.8(6)
C(3)	0.2195(6)	0.6656(7)	0.0471(11)	6.9(6)
C(4)	0.2134(8)	$^3/_4$	−0.434(15)	6.8(9)
C(5)	0.4896(6)	0.6667(7)	0.3493(11)	7.0(6)
C(6)	0.5024(9)	$^3/_4$	0.4382(20)	8.8(11)
C(7)	0.2074(7)	$^3/_4$	0.4524(13)	3.6(6)
C(8)	0.1743(5)	0.8249(5)	0.4964(11)	5.4(5)
C(9)	0.1089(5)	0.8228(6)	0.5835(12)	6.0(5)
C(10)	0.0764(7)	$^3/_4$	0.6266(14)	5.0(7)
Cl(1)	0.6139(1)	0.4333(1)	0.2735(3)	5.51(13)
O(2)	0.6363(7)	0.4866(6)	0.1664(9)	20.4(11)
O(3)	0.6260(7)	0.3545(5)	0.2435(16)	21.1(11)
O(4)	0.6432(7)	0.4568(7)	0.4080(10)	19.5(10)
O(5)	0.5402(6)	0.4325(7)	0.2982(20)	23.7(14)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-$[ReO_2(cyclam)]ReO_4\cdot{}^1/_4H_2O$

Re(1)–N(1)	2.136(11)	Re(1)–O(4)	1.775(9)
Re(1)–N(2)	2.141(9)		
N(1)–Re(1)–N(1)[a]	180.0	O(4)–Re(1)–O(4)[a]	180.0
N(1)–Re(1)–N(2)	83.0(4)	Re(1)–N(1)–C(4)	105.8(8)
N(1)–Re(1)–O(4)	90.2(4)	Re(1)–N(1)–C(5)	112.6(8)
N(2)–Re(1)–O(4)	89.5(4)	Re(1)–N(2)–C(3)	106.3(7)
N(2)a–Re(1)–O(4)	90.5(4)	Re(1)–N(2)–C(7)	111.2(8)

[a] Center of inversion.

1.78(1) Å[7a] reported previously. As reported by Duatti and coworkers,[7a] there exists intramolecular hydrogen bonding between the N–H hydrogen on the cyclam ligand and the ReO_2 unit. This may explain the observed splitting pattern of the ν(N–H) stretch in the infrared spectrum.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$

Re–N(1)	2.133(11)	Re–O(1)	1.850(8)
Re–N(2)	2.104(10)	Re–O(2)	1.643(9)
Re–N(3)	2.041(13)	C(11)–O(1)	1.48(2)
Re–N(4)	2.126(10)		
N(1)–Re–N(2)	82.6(5)	N(3)–Re–N(4)	81.4(4)
N(1)–Re–N(3)	175.6(4)	N(3)–Re–O(1)	87.0(4)
N(1)–Re–N(4)	97.5(4)	N(3)–Re–O(2)	94.0(4)
N(1)–Re–O(1)	88.7(4)	N(4)–Re–O(1)	87.5(4)
N(1)–Re–O(2)	90.3(4)	N(4)–Re–O(2)	90.7(4)
N(2)–Re–N(3)	98.3(5)	O(1)–Re–O(2)	177.9(4)
N(2)–Re–N(4)	177.3(4)	C(5)–N(3)–C(6)	114(1)
N(2)–Re–O(1)	89.8(4)	Re–O(1)–C(11)	167(1)
N(2)–Re–O(2)	92.0(4)		

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-$[Re(NPh)(OH)(cyclam)](ClO_4)_2$

Re–O(1)	1.915(9)	Re–N(3)	1.731(9)
Re–N(1)	2.123(7)	N(3)–C(7)	1.406(15)
Re–N(2)	2.140(7)		
O(1)–Re–N(1)	83.8(3)	N(1)–Re–N(2)	81.7(3)
O(1)–Re–N(2)	84.9(3)	N(1)–Re–N(2)	98.7(3)
O(1)–Re–N(3)	176.1(4)	N(2)–Re–N(3)	92.5(3)
N(1)–Re–N(1)[a]	98.1(3)	Re–N(3)–C(7)	176.2(8)

[a] Mirror.

Previous studies by Schroder and co-workers[8] suggested that $ReO(cyclam)Cl_3$ was formed when $[ReOCl_3(PPh_3)_2]$ was allowed to react with cyclam in dry dichloromethane. However, a pure sample of this species had not been obtained by these workers. In this work, *trans*-$[ReO(OEt)(cyclam)]^{2+}$ was accidentally isolated when we tried to convert *trans*-$[ReO_2(cyclam)]^+$ to a Re≡N species through its reaction with $N_2H_4\cdot2HCl$ and PPh_3. *trans*-$[ReO(OEt)(cyclam)](ClO_4)_2$ is an air-stable solid and can easily be converted to *trans*-$[ReO_2(cyclam)]^+$ upon dissolution in H_2O. Its infrared spectrum shows an intense absorption band at ~958 cm^{-1}, which is typical for the ν(Re≡O) stretch of monooxorhenium(V) complexes.[7b,16] A perspective view of the *trans*-$[ReO(OEt)(cyclam)]^{2+}$ cation is shown in Figure 1b. The measured rhenium–oxo bond distance of 1.643(9) Å is consistent with a metal–oxo triple bond and is comparable to related values found in other monooxorhenium(V) complexes such as 1.684(7) Å in $ReO(OEt)Cl_2py_2$ (py = pyridine)[17] and 1.666(4) Å in $[ReO(L)(OMe)_2]ClO_4$[6] (L = 2,2′:6′,2″:6″,2‴ quaterpyridine). The Re–OEt distance of 1.850(8) Å indicates that there is a significant metal–ligand π-bonding interaction.

The *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ complex was easily prepared by the reaction of $Re(NPh)Cl_3(PPh_3)_2$ with cyclam under a dry nitrogen atmosphere. The product yield was found to be significantly reduced by the presence of water during the reaction. Unlike most other metal–imido complexes which are easily hydrolyzed by moisture, *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ is stable enough in water to allow both ^1H NMR and cyclic voltammetric measurements to be done. Figure 1c shows a perspective view of the *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ cation. The measured Re≡NPh distance of 1.731(9) Å is similar to that of 1.726(6) Å in $Re(NPh)Cl_3(PPh_3)_2$[18] and 1.740(6) Å in $[Re(NPh)(bpy)_2(OEt)]^{2+}$.[1b] In accordance with the metal–imido formulation, the Re≡N—Ph angle of 176.2(8)° is virtually linear. The Re–OH distance of 1.915(9) Å suggests the presence of a significant Re–OH π-bonding interaction. For all the three complexes, the coordinated cyclam ligand in each case shows a *RRSS* conformation with two amine protons lying above and two amine protons below the ReN_4 plane.

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(17) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333.

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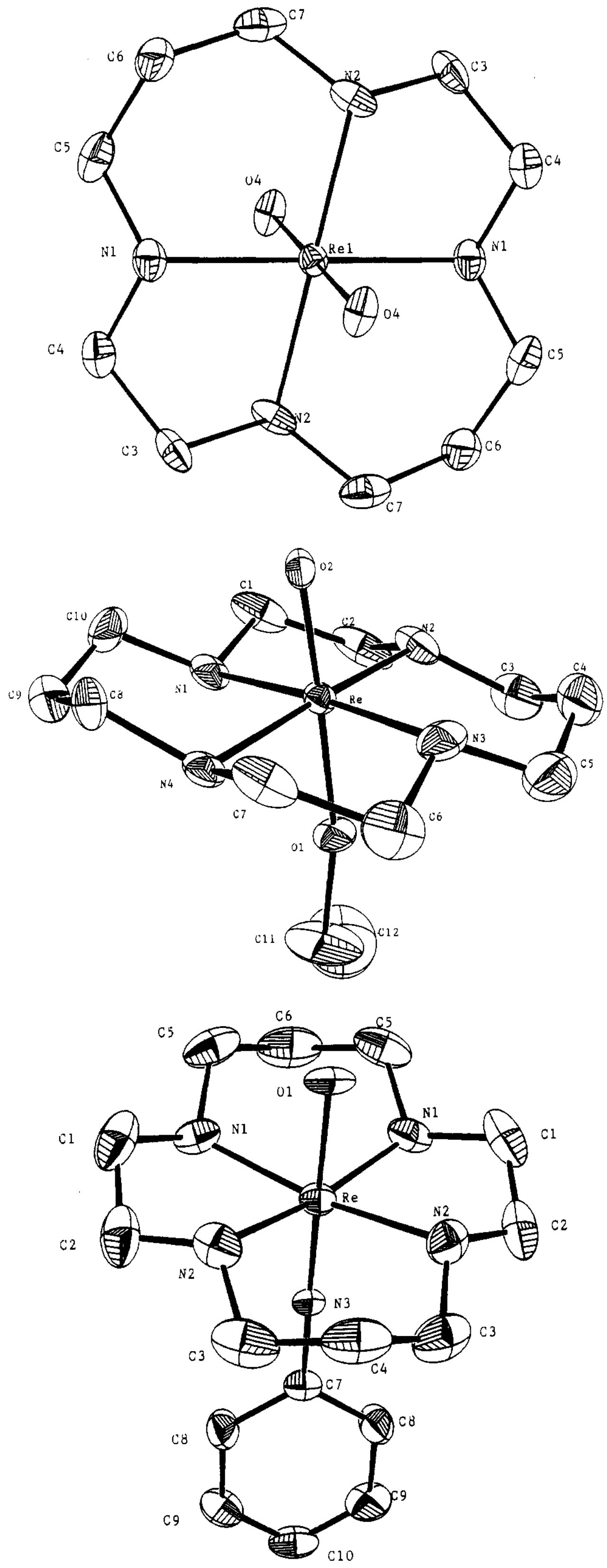

Figure 1. Perspective view of (a, top) *trans*-[ReO$_2$(cyclam)]$^+$, (b, middle) *trans*-[ReO(OEt)(cyclam)]$^{2+}$, and (c, bottom) *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$.

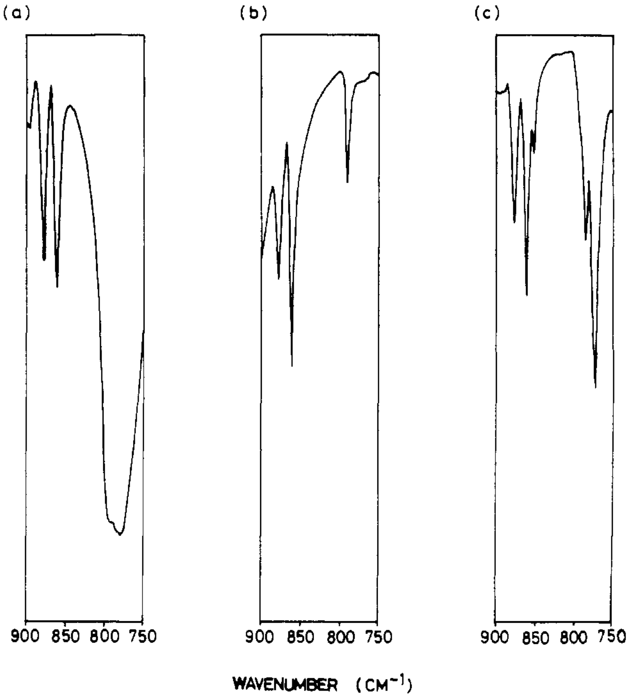

Figure 2. Infrared spectra in the region 750–900 cm^{-1} of (a) *trans*-[ReO$_2$(cyclam)]$^+$, (b) *trans*-[ReO(OEt)(cyclam)]$^{2+}$, and (c) *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$.

Poon and co-workers[15] reported that metal complexes of cyclam in the trans configuration would have three IR absorption bands at 750–950 cm^{-1} which are due to the secondary amine and methylene vibrations. Figure 2 compares the IR spectra of these complexes in this region. For *trans*-[ReO$_2$(cyclam)]ClO$_4$, two sharp bands appear at 860 and 880 cm^{-1}. The methylene vibration near 800 cm^{-1} is probably obscured by the intense ν_{as}(ReO$_2$) stretch. For *trans*-[ReO(OEt)(cyclam)](ClO$_4$)$_2$ and *trans*-[Re(NPh)(OH)(cyclam)](ClO$_4$)$_2$, the three characteristic bands appear at 788, 860, 880 cm^{-1} and 790, 860, 880 cm^{-1}, respectively.

Figure 3 shows the UV–vis absorption spectra of *trans*-[ReO$_2$(cyclam)]$^+$, *trans*-[ReO(OEt)(cyclam)]$^{2+}$, and *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$ in acetonitrile. The spectrum of *trans*-[ReO$_2$(cyclam)]$^+$ is characterized by two moderate intense absorption peaks at 259 and 283 nm, the latter one appears as a shoulder. Judging from the ϵ_{max} values, these two bands may be d–d transitions which gain intensity through coupling with the [p$_\pi$(O) → d$_\pi$*(Re)] charge-transfer transition.[2a] There are also some weak absorption bands at 423 and 530 nm. With reference to previous studies by Winkler and Gray on the related dioxorhenium(V) systems,[2a] these two bands are tentatively assigned to originate from the $d_{xy} \rightarrow (d_{xz},d_{yz})$ transitions.

For *trans*-[ReO(OEt)(cyclam)]$^{2+}$, the spectrum in the UV region is featureless. There are, however, two weak absorptions at 481 and 625 nm, which may have the same electronic origin as the 422- and 530-nm bands of *trans*-[ReO$_2$(cyclam)]$^+$. The red shift of the $d_{xy} \rightarrow (d_{xz},d_{yz})$ transition from *trans*-[ReO$_2$(cyclam)]$^+$ to *trans*-[ReO(OEt)(cyclam)]$^{2+}$ is not unreasonable given the stronger ligand field strength of O^{2-} than OEt$^-$.

The UV–vis absorption spectrum of *trans*-[Re(NPh)(OH)(cyclam)]$^{2+}$ in acetonitrile is featured by an intense absorption band at 300 nm, which is absent in *trans*-[ReO$_2$(cyclam)]$^+$ or *trans*-[ReO(OEt)(cyclam)]$^{2+}$. This has to be due to a dipole-allowed transition because of its large ϵ_{max} values. Either intraligand transition of the phenylimido moiety or PhN^{2-} → Re(V) charge-transfer transition is possible. Assignment of this band to the latter is less likely since the p$_\pi$(O) → Re(V) transition of *trans*-[ReO(OEt)(cyclam)]$^{2+}$, if present, would occur at $\lambda_{max} \leq 260$ nm.

Electrochemistry. The cyclic voltammogram of *trans*-[ReO$_2$(cyclam)]$^+$ in 0.1 M CF$_3$CO$_2$H is shown in Figure 4. A quasi-reversible couple (I) is observed at –0.66 V upon reduction of the complex. $E_{1/2}$ of couple I shifts cathodically by about 60 mV per unit pH as the pH of the medium is raised from 1 to 11. (pH, $E_{1/2}$: 1, –0.66; 2, –0.71; 3, –0.83; 5, –0.91; 7, –1.07; 9, –1.19; 11, –1.30 V vs SCE.) Constant-potential coulometry at

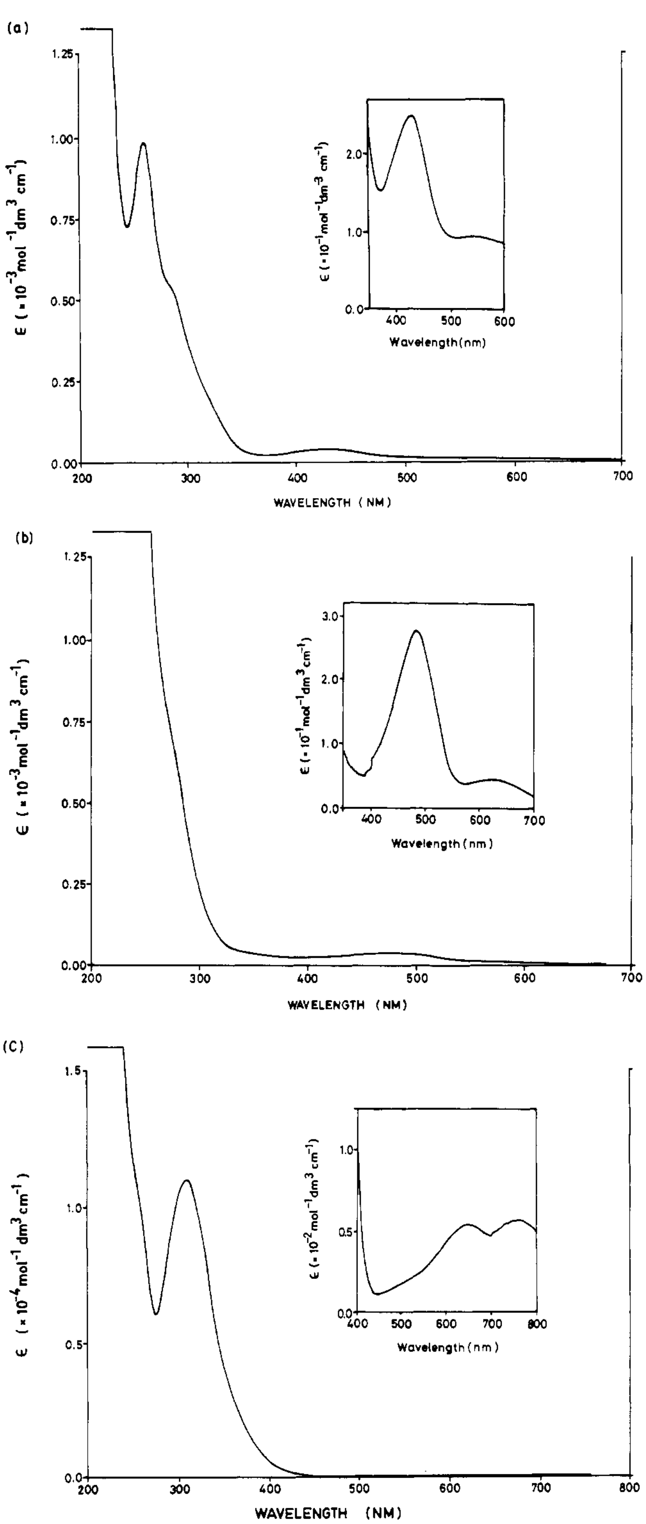

Figure 3. UV–vis absorption spectra of (a) *trans*-$[ReO_2(cyclam)]^+$, (b) *trans*-$[ReO(OEt)(cyclam)]^{2+}$, and (c) *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$. Solvents: (a) CH_3CN–CH_3OH (1:1); (b, c) CH_3CN.

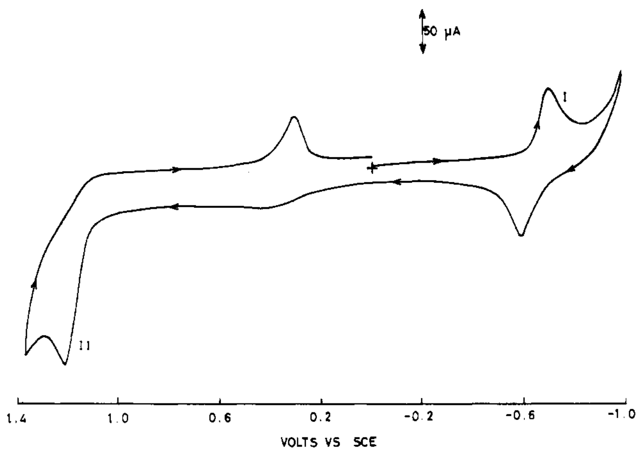

Figure 4. Cyclic voltammogram of *trans*-$[ReO_2(cyclam)]^+$ in 0.1 M CF_3CO_2H. Working electrode: edge plane pyrolytic graphite. Scan rate: 50 mV s^{-1}.

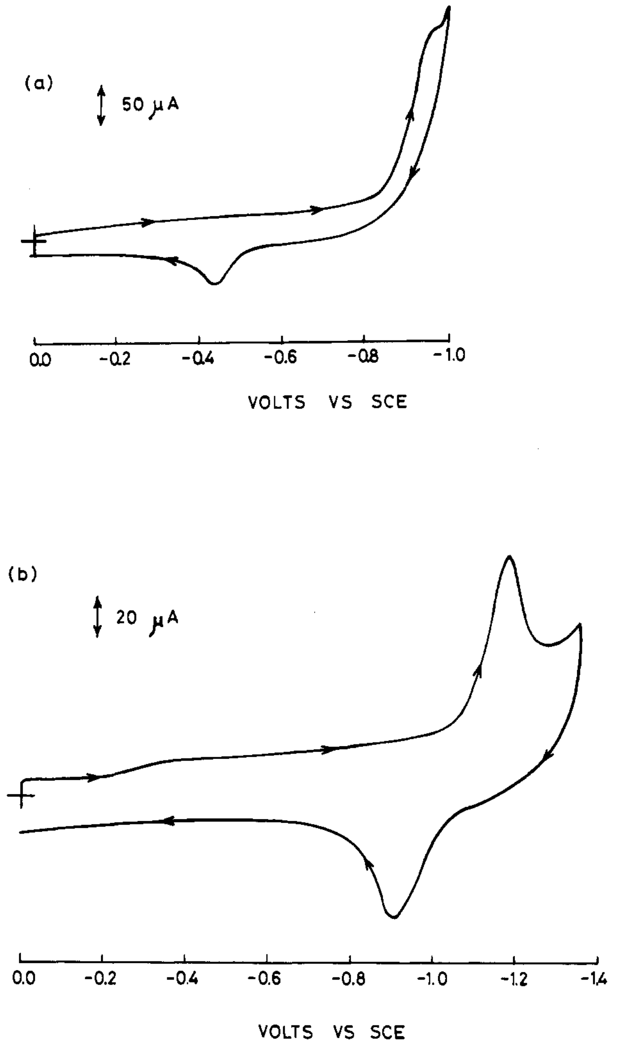

Figure 5. Cyclic voltammograms of *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ in (a) 0.1 M CF_3CO_2H and (b) pH 7.0 phosphate buffer. Working electrode: edge plane pyrolytic graphite. Scan rate: 50 mV s^{-1}.

–0.7 V indicated that this is a two-electron reduction couple ($n = 2.0 \pm 0.4$). Hence couple I is assigned to either of the following two possible electrode reactions:

$$trans\text{-}[ReO_2(cyclam)]^+ + 2H^+ + 2e^- \rightleftharpoons trans\text{-}[ReO(OH_2)(cyclam)]^+$$

$$trans\text{-}[ReO_2(cyclam)]^+ + 2H^+ + 2e^- \rightleftharpoons trans\text{-}[Re(OH)_2(cyclam)]^+$$

The reaction product could either be *trans*-$[ReO(OH_2)(cyclam)]^+$ or *trans*-$[Re(OH)_2(cyclam)]^+$.[3,4] A similar proton-coupled two-electron reduction has been observed at –0.42 V for *trans*-$[ReO_2(py)_4]^+$ in 0.1 M acid.[4] $E_{1/2}$ of the Re(V)/Re(III) couple for *trans*-$[ReO_2(cyclam)]^+$ is more cathodic than that of *trans*-$[ReO_2(py)_4]^+$ by 240 mV. This is not unexpected since previous studies on the isoelectronic *trans*-dioxoruthenium(VI) species[11] also showed that replacement of the saturated amine ligands by those having pyridyl groups would lead to an increase in the $E°$ values. The Re(III)/Re(II) couple of *trans*-$[ReO_2(cyclam)]^+$, which probably occurs at a potential beyond the solvent decomposition limit, has not been observed. Upon oxidation, *trans*-$[ReO_2(cyclam)]^+$ displays an irrevesible wave at 1.21 V (labeled II), the peak potential of which is independent of pH. The size of wave II indicates it is multi-electron in nature. Meyer and co-workers[4] previously reported a one-electron oxidation of *trans*-$[ReO_2(py)_4]^+$ to *trans*-$[ReO_2(py)_4]^{2+}$ in aqueous medium. For *trans*-$[ReO_2(cyclam)]^+$, oxidation to the highly oxidizing Re(VI) state may lead to oxidative dehydrogenation of the cyclam ligand, thus accounting for the irreversible multi-electron oxidative wave II.

trans-$[ReO(OEt)(cyclam)]^{2+}$ shows a quasi-reversible reduction wave (E_p = 175 mV, $i_{pa}/i_{pc} = 0.8$ measured at 200 mV s^{-1}) at −1.0 V vs SCE in acetonitrile. Constant-potential coulometry indicated $n = 1.0 \pm 0.1$. Thus the electrode reaction can be assigned as

$$[ReO(OEt)(cyclam)]^{2+} + e^- \rightleftharpoons [ReO(OEt)(cyclam)]^+$$

The cyclic voltammogram of *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ in 0.1 M CF_3CO_2H displays a reduction wave at −0.98 V vs SCE as shown in Figure 5a. The corresponding oxidation wave appears at −0.37 V. The potential of the waves shifts cathodically as the pH of the medium increases. The electrode reaction could be either of the following proton-coupled reduction processes:

$$trans\text{-}[Re^V(NPh)(OH)(cyclam)]^{2+} + H^+ + e^- \rightleftharpoons trans\text{-}[Re^{IV}(NHPh)(OH)(cyclam)]^+ \quad \text{or}$$

$$trans\text{-}[Re^V(NPh)(OH)(cyclam)]^{2+} + H^+ + e^- \rightleftharpoons trans\text{-}[Re^{IV}(NPh)(OH_2)(cyclam)]^{2+}$$

As the pH of the medium reaches ~7 and above, the couple becomes more reversible, and the peak to peak separation of the oxidation and reduction waves decreases (Figure 5b). It is possible to estimate the $E_{1/2}$ values from pH 7 to 10, and $E_{1/2}$ was found to shift cathodically by 60 mV/pH. Attempts to estimate the n value by constant-potential coulometry were unsuccessful because the reduced species was found to catalyze the reduction of water to hydrogen, and gas bubbles were observed on the electrode surface. In acetonitrile, the complex showed an irreversible reduction wave at −1.40 V and an irreversible oxidation wave at 1.3 V vs SCE. Constant-potential coulometry at −1.45 V established $n = 1.0 \pm 0.1$, suggesting that the electrode reaction is

$$[Re(NPh)(OH)(cyclam)]^{2+} + e^- \rightarrow [Re(NPh)(OH)(cyclam)]^+$$

Compared to $[Re(NPh)(OEt)(bpy)_2]^{2+}$ ($E°_{Re(V)/(IV)} = -1.0$ V vs SCE),[1b] the reduction of *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ occurs at more negative potential, and once again this is attributed to the different σ-donating strength between cyclam and bipyridine.

Anodic scan in the cyclic voltammogram of *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ in 0.1 M CF_3CO_2H shows an irreversible wave at 1.0 V vs SCE. The peak potential of the irreversible wave was found to shift cathodically by approximately 60 mV per pH unit as the pH of the medium was raised. The oxidation appears to be multi-electron in nature judging from the size of the wave, which is more than twice that of the reduction wave at −0.98 V. Rhenium(V) phenylimido complex is known to undergo irreversible oxidation to rhenium(VI).[1b] However, since the oxidation involves more than one electron, this suggests that the electrogenerated Re(VI) may oxidize the cyclam ligand. We suggest the electrode is

$$trans\text{-}[Re^{VI}(NPh)(O)(cyclam)]^{2+} + H^+ + e^- \rightleftharpoons trans\text{-}[Re^V(NPh)(OH)(cyclam)]^{2+}$$

This is a $1H^+$–$1e^-$ couple which is consistent with the pH dependence of the oxidation reaction.

General Comments. A series of isoelectronic Re(V)–cyclam complexes with oxo, dioxo, and phenylimido moiety have been prepared. Because cyclam does not have any absorption in the normal UV–vis region, these complexes can serve as models for understanding the electronic transitions associated with a Re(V)–heteroatom multiple bond. Judging from the electrochemical data, PhN^{2-} is concluded to be a better π-donor than O^{2-}. The fact that Re(V)–phenylimido complex is stable in water is important in the context of investigating redox reactions of (organoimido)metal complexes in aqueous media.

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Supplementary Material Available: Tables giving crystal data and details of structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (9 pages). Ordering information is given on any current masthead page.