

Reversible proton-coupled $\text{Re}^{\text{VII}}\text{-Re}^{\text{VI}}$ and $\text{Re}^{\text{VI}}\text{-Re}^{\text{V}}$ couples and crystal structure of $[\text{Re}^{\text{V}}\text{O}_2(\text{OH}_2)(\text{Me}_3\text{tacn})]\text{BPh}_4$ ($\text{Me}_3\text{tacn} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$)

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The electrochemistry of $[\text{Re}^{\text{VII}}\text{O}_3(\text{Me}_3\text{tacn})]\text{PF}_6$ ($\text{Me}_3\text{tacn} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$) in aqueous solution has been studied. At pH 1 it shows two quasi-reversible couples I at -0.14 and II at -0.36 V vs. saturated calomel electrode. Constant-potential coulometry at -0.50 V shows that the total number of electrons transferred for these two couples is two. The Pourbaix diagram over the range pH 0.9–12.2 shows that E_1 of couple I shifts cathodically by 60 mV per pH unit. For couple II there are two straight-line segments with slopes of -118 mV ($0.9 < \text{pH} < 4.1$) and -60 mV ($\text{pH} > 4.1$) per pH unit. The complex $[\text{Re}^{\text{V}}\text{O}_2(\text{OH}_2)(\text{Me}_3\text{tacn})]\text{BPh}_4$ was prepared and structurally characterized by X-ray crystal analysis: monoclinic, space group $P2_1/n$ (no. 14), $a = 10.387(9)$, $b = 21.176(4)$, $c = 15.452(2)$ Å, $\beta = 91.38(63)^\circ$, $Z = 4$. The Re-OH_2 distance is $2.10(2)$ Å and the Re=O distances are $1.78(1)$ and $1.82(1)$ Å. The two oxo groups are *cis* to each other with an angle of $106.7(5)^\circ$.

Proton-coupled electron-transfer reactions constitute an important area in the oxidation chemistry of high-valent oxometal complexes. Extensive studies on the electrochemistry of some $d^1\text{-}d^4$ oxo-metal complexes in aqueous solution have been reported. With a pyrolytic edge-plane graphite electrode, it has been possible to observe the reversible $\text{M=O} \rightarrow \text{M-OH}$ couple in aqueous solution.¹ The E° values of these couples provide useful information in understanding the reactivities of these oxometal complexes. Surprisingly, there are only few reports on the proton-coupled electron-transfer reactions of d^0 oxometal complexes² which exhibit promising oxidation chemistry.³ It would be interesting to determine the E° of $\text{Re}^{\text{VII}}\text{-O}$ complexes, which provides a quantitative measure of the oxidizing strength of this class of complexes. Our previous work revealed that macrocyclic amines are good ligand systems for investigating the redox chemistry of high-valent oxometal complexes in aqueous solution.⁴ Herein is described the electrochemistry of $[\text{Re}^{\text{VII}}\text{O}_3(\text{Me}_3\text{tacn})]\text{PF}_6$ ($\text{Me}_3\text{tacn} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$) and the crystal structure of $[\text{Re}^{\text{V}}\text{O}_2(\text{OH}_2)(\text{Me}_3\text{tacn})]\text{BPh}_4$. The latter is one of the few examples of a six-co-ordinate d^2 *cis*-dioxometal complexes to be structurally characterized.

Experimental

Materials

All preparations were performed using standard Schlenk techniques. The compound Re_2O_7 was obtained from Strem; 1,4,7-trimethyl-1,4,7-triazacyclononane⁵ and the complex $[\text{Re}^{\text{VII}}\text{O}_3(\text{Me}_3\text{tacn})][\text{ReO}_4]^-$ ⁶ were prepared by published procedures.

Physical measurements

Cyclic voltammetry was performed with a Princeton Applied Research model 273 A potentiostat. Rotating-disc voltammetry was performed with a Pine Instrument model AFMRX rotator. The working electrode used was edge-plane pyrolytic graphite (Union Carbide). The E_1 values were taken as the average of the anodic and cathodic peak potentials. All potentials are quoted with reference to the saturated calomel electrode (SCE). Constant-potential electrolysis was performed in a three-

compartment cell under a nitrogen atmosphere with a carbon cloth obtained from Sigr Carbon as working electrode. The UV/VIS absorption spectra were recorded on a Milton Roy 3000 spectrophotometer.

X-Ray crystallography

A pale blue crystal of complex **2** of dimensions $0.20 \times 0.05 \times 0.35$ mm was used for data collection at 25°C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) using ω - 2θ scans with ω -scan angle $(0.73 + 0.35 \tan \theta)^\circ$ at a scan speed of $16.0^\circ \text{min}^{-1}$ [up to four scans for reflection $I < 15\sigma(I)$]. Intensity data (in the range of $2\theta_{\text{max}} = 50^\circ$; h 0–11, k 0–23, l –17 to 17; three standard reflections measured after every 300, 3.67% decay), were corrected for decay and for Lorentz-polarization effects and empirical absorption corrections were applied based on the ψ scan of four strong reflections (minimum and maximum transmission factors 0.391 and 1.000). Upon averaging the 6401 reflections, 6054 of which were uniquely measured, 3225 with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure solved by direct methods (SIR 92⁷) and Fourier-difference syntheses and refined by full-matrix least squares using the software package TEXSAN⁸ on a Silicon Graphics Indy computer. All non-H atoms except the B atom were refined anisotropically. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. The two H atoms of the H_2O molecule were not included. Convergence for 366 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.026 F_o^2)^2]$ for 3225 reflections with $I > 3\sigma(I)$, was reached at $R = 0.053$ and $R' = 0.068$. The final Fourier-difference map was featureless. The ORTEP⁹ drawing of the complex cation shows thermal ellipsoids at the 50% probability level.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/513.

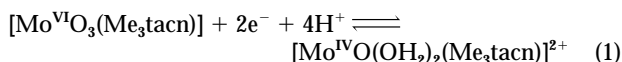
Syntheses

[Re^{VII}O₃(Me₃tacn)]X **1 (X = PF₆⁻ or BPh₄⁻).** The complex [Re^{VII}O₃(Me₃tacn)][ReO₄] (0.1 g) was dissolved in distilled water (30 cm³). The solution was filtered if necessary and addition of an excess of NH₄PF₆ or NaBPh₄ caused immediate precipitation of [Re^{VII}O₃(Me₃tacn)]PF₆ or [Re^{VII}O₃(Me₃tacn)]BPh₄. The product was filtered off and washed with water and diethyl ether. Yield 80%. ¹H NMR (CD₃CN) of [Re^{VII}O₃(Me₃tacn)]BPh₄: δ 7.29–7.20 (m, 8 H, H_{aryl}), 7.05–6.95 (m, 8 H, H_{aryl}), 6.87–6.82 (m, 4 H, H_{aryl}), 3.54–3.36 (m, 6 H, CH₂), 3.30 (s, 9 H, Me) and 3.3–3.14 (m, 6 H, CH₂).

[Re^VO₂(OH)₂(Me₃tacn)]BPh₄ **2.** A mixture of [Re^{VII}O₃(Me₃tacn)]BPh₄ (0.1 g) and an excess of zinc dust in aqueous MeOH (30 cm³, 95%) was refluxed for 4 d. The reaction mixture was filtered through Celite and the filtrate evaporated to dryness. The pale green residue was extracted with acetonitrile. Diffusion of diethyl ether into the acetonitrile extract gave pale green crystals; yield 5%. ¹H NMR (CD₃CN): δ 7.29–7.20 (m, 8 H, H_{aryl}), 7.05–6.95 (m, 8 H, H_{aryl}), 6.87–6.82 (m, 4 H, H_{aryl}), 3.88–3.52 (m, 2 H, CH₂), 3.45–3.32 (m, 2 H, CH₂), 3.41 (s, 3 H, Me), 3.16 (s, 6 H, Me), 3.14–3.04 (m, 3 H, CH₂) and 2.83–2.75 (m, 5 H, CH₂) [Found (Calc.): C, 54.1 (54.55); H, 6.20 (5.92); N, 5.40 (5.78)%].

Results and Discussion

d⁰ Oxometal complexes have long been known to be effective oxidative catalysts and one of the recent examples is methyltrioxorhenium(vii).³ However, no electrochemical study has been carried out on the Re^{VII}=O → Re^V-OH couple. The only analogous example is [MoO₃(Me₃tacn)],² which shows a quasi-reversible two-electron four-proton transfer couple at E^o = -0.075 V vs. the normal hydrogen electrode in 0.1 mol dm⁻³ MeSO₃H, equation (1).



In this work, the cyclic voltammograms of [Re^{VII}O₃(Me₃tacn)]PF₆ recorded at edge-plane pyrolytic graphite at various pH are shown in Fig. 1. Two quasi-reversible couples I and II are observed. At pH 1.0 the E_{1/2} values of I and II are -0.14 and -0.36 V vs. SCE respectively. Constant-potential coulometry at -0.50 V indicated that the total number of electrons transferred for these two couples is two. As shown in Fig. 2, the plateau currents for couples I and II from a rotating-disc voltammetric experiment are similar in magnitude; hence, it is reasonable to assign them to the Re^{VII}-Re^{VI} and Re^{VI}-Re^V couples respectively. The reversibility of these two couples and particularly that of II depends on pH. At pH < 7 the peak-to-peak separations for couples I and II are much larger than the 60 mV value expected for a reversible one-electron couple. For couple II and at low pH the reoxidation wave is usually broad. The two couples become more reversible at higher pH. With reference to previous electrochemical studies on Ru=O → Ru-OH₂ couples,¹⁰ the above finding is ascribed to the kinetic barrier associated with protonation/deprotonation electron-transfer reactions. The cyclic voltammetry data are listed in Table 1 and the Pourbaix diagram over the range pH 0.9–12.2 is shown in Fig. 3. At pH 0.9–12.2 the E_{1/2} of couple I shifts cathodically by 60 mV per pH unit. For couple II two straight-line segments with slopes of -118 (0.9 < pH < 4.1) and -60 mV per pH unit (pH > 4.1) are found. On the basis of these results, the electrode reactions are assigned as in equations (2)–(6). For couple II, the electrochemical data could not differentiate [Re^VO(OH)₂(OH)(Me₃tacn)]²⁺ from [Re^V(OH)₃(Me₃tacn)]²⁺ or [Re^VO₂(OH)₂(Me₃tacn)]⁺ from [Re^VO(OH)₂(OH)(Me₃tacn)]⁺. Attempts to isolate the reduced species of **1** by constant-potential electrolysis were unsuccessful but chem-

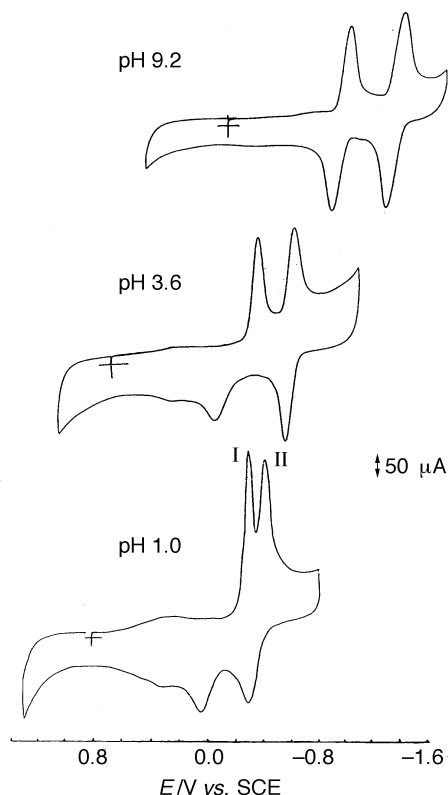


Fig. 1 Cyclic voltammogram of [Re^{VII}O₃(Me₃tacn)]⁺ at various pH; scan rate 100 mV s⁻¹

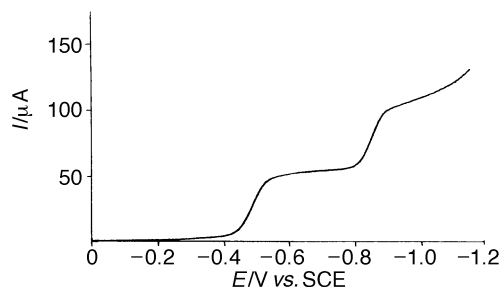
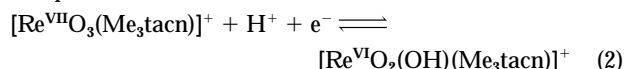


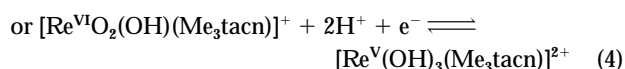
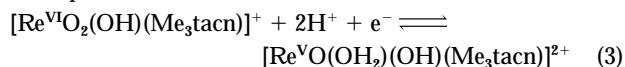
Fig. 2 Rotating-disc voltammetric studies of [Re^{VII}O₃(tmtacn)]⁺ at pH 5.9; scan rate 5 mV s⁻¹, disc rotation rate 400 revolutions min⁻¹

Couple I

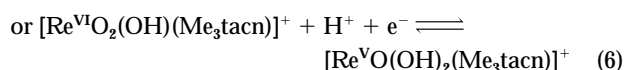
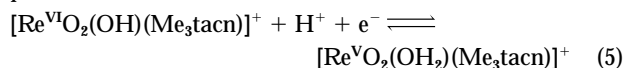


Couple II

0.9 < pH < 4.1



pH > 4.1



ical reduction of **1** by zinc powder in aqueous methanol (95%) afforded [Re^VO₂(OH)₂(Me₃tacn)]BPh₄ **2** which was isolated in low yield.

Table 1 Values of E_2^1 (V vs. SCE) for redox couples of $[\text{Re}^{\text{VII}}\text{O}_3(\text{Me}_3\text{tacn})]^+$ at different pH values

pH	Couple I	Couple II
0.9	-0.14	-0.36
1.8	-0.20	-0.51
2.6	-0.25	-0.54
3.6	-0.30	-0.68
4.7	-0.36	-0.76
5.9	-0.44	-0.86
7.0	-0.52	-0.91
8.0	-0.58	-0.99
9.2	-0.63	-1.03
9.9	-0.67	-1.07
11.4	-0.74	-1.12
12.2	-0.80	-1.19

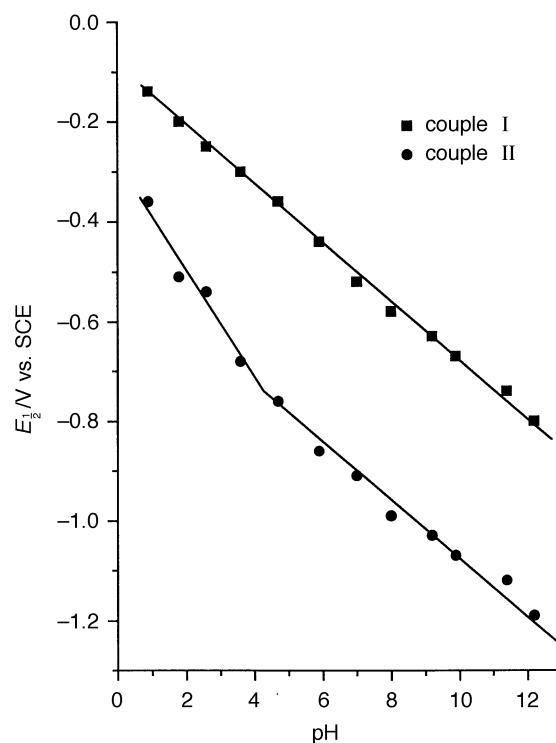
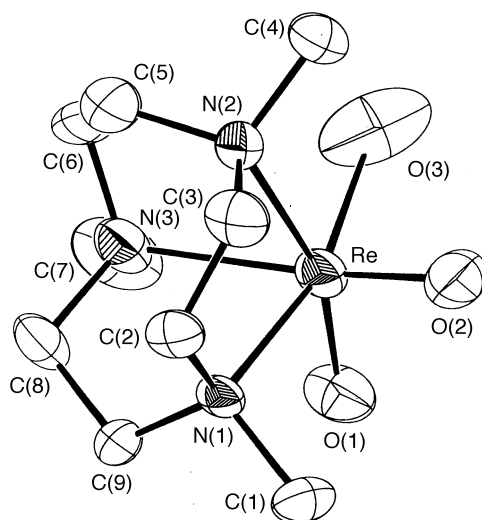
Table 2 Crystal data for complex **2**

Empirical formula	$\text{C}_{33}\text{H}_{43}\text{BN}_3\text{O}_3\text{Re}$
M	726.74
Crystal colour, habit	Blue, plate
Crystal dimensions/mm	$0.20 \times 0.05 \times 0.35$
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
$a/\text{\AA}$	10.387(9)
$b/\text{\AA}$	21.176(4)
$c/\text{\AA}$	15.452(2)
$\beta/^\circ$	91.38(3)
$U/\text{\AA}^3$	3397(2)
Z	4
$D_c/\text{g cm}^{-3}$	1.421
$F(000)$	1464
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	36.12
No. reflections measured	6401
No. unique reflections (R_{int})	6054 (0.034)
Function minimized	$\sum w(F_o - F_c)^2$
No. observations [$I > 3.00\sigma(I)$]	3225
No. variables	366
R, R'	0.053, 0.068
Goodness of fit	2.23
Maximum shift/error in final cycle	0.01
Maximum, minimum peaks in final difference map/ $e \text{\AA}^{-3}$	1.34, -1.01

Table 3 Selected bond lengths (\AA) and angles ($^\circ$) for complex **2**

Re-O(1)	1.78(1)	Re-O(2)	1.82(1)
Re-O(3)	2.10(2)	Re-N(1)	2.199(8)
Re-N(2)	2.26(1)	Re-N(3)	2.26(1)
O(1)-Re-O(2)	106.7(5)	O(1)-Re-O(3)	101.2(5)
O(1)-Re-N(1)	87.5(4)	O(1)-Re-N(2)	162.1(4)
O(1)-Re-N(3)	89.6(5)	O(2)-Re-O(3)	99.4(5)
O(2)-Re-N(1)	90.2(5)	O(2)-Re-N(2)	84.9(4)
O(2)-Re-N(3)	160.0(5)	O(3)-Re-N(1)	164.5(5)
O(3)-Re-N(2)	90.1(5)	O(3)-Re-N(3)	88.4(5)
N(1)-Re-N(2)	78.7(4)	N(1)-Re-N(3)	78.7(4)
N(2)-Re-N(3)	76.6(4)		

Fig. 4 shows the perspective view of $[\text{Re}^{\text{VO}_2}(\text{OH}_2)(\text{Me}_3\text{tacn})]^+$, crystallographic details are given in Table 2 and selected bond lengths and angles in Table 3. The co-ordination geometry of the rhenium atom is a highly distorted octahedron comprised of three nitrogen atoms from the macrocyclic tmtacn and three oxygen atoms from one aqua and two *cis* oxides. The Re-O(1) and Re-O(2) distances of 1.78(1) and 1.82(1) \AA are slightly longer than the average bond distance of 1.761 \AA for *trans*-dioxorhenium(v) complexes.¹¹ Interestingly, these distances are even 0.06 \AA longer than those in *cis*- $[\text{Re}^{\text{VO}_2}(\text{bipy})(\text{py})_2]^+$ (bipy = 2,2'-bipyridine, py = pyridine) average Re-O 1.74 \AA).¹² This may be correlated with the O=Re=O angle, which has a smaller value in **2** [106.7(5) $^\circ$] than in *cis*- $[\text{Re}^{\text{VO}_2}(\text{bipy})(\text{py})_2]^+$ [121.4(4) $^\circ$]. Indeed, the O=Re=O angle of **2** is comparable to the related values of 112.0(4) and 105.9(2) $^\circ$ in *cis*- $[\text{Ru}^{\text{VO}_2}\text{L}]^{2+}$ (L =

**Fig. 3** Pourbaix diagram of $[\text{Re}^{\text{VII}}\text{O}_3(\text{Me}_3\text{tacn})]^+$ over the range pH 0.9–12.2**Fig. 4** Perspective view of $[\text{Re}^{\text{VO}_2}(\text{OH}_2)(\text{Me}_3\text{tacn})]^+$

N,N,N,N-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine¹³ and $[\text{Mo}^{\text{VI}}\text{O}_2(\text{OME})(\text{Me}_3\text{tacn})]^+$ respectively.¹⁴ Interestingly, the Mo=O of 1.786 \AA in $[\text{Mo}^{\text{VI}}\text{O}_2(\text{OME})(\text{Me}_3\text{tacn})]^+$ is also larger than that in other oxomolybdenum complexes. The Re-O(3) distance in **2** of 2.10(2) \AA is indicative of a single bond and as expected longer than that of the Re-O (alkoxide) distance of 1.94 \AA in $[\text{Re}^{\text{VO}}(\text{O}_2\text{C}_2\text{H}_4)(\text{Me}_3\text{tacn})]^+$.¹⁵ On comparing with the complexes $[\text{Re}^{\text{VO}}\text{Cl}_2(\text{tu})_2(\text{H}_2\text{O})]^+$ and $[\text{Re}^{\text{VO}}\text{Cl}_3(\text{tu})(\text{H}_2\text{O})]$ (tu = thiourea) for which the Re-OH₂ distances are 2.231(10) and 2.291(20) \AA respectively,^{16,17} it is reasonable to assign O(3) to a co-ordinated aqua group. On the basis of the 18-electron rule, the Re=O bonds in **2** are double in character and exert a *trans* effect on the Re-N(2) and Re-N(3) bonds which are 0.06 \AA longer than Re-N(1), which is *trans* to O(3). Such a *trans* effect of the Re=O bonds is less important than that in the $[\text{Re}^{\text{VO}}(\text{O}_2\text{C}_2\text{H}_4)(\text{Me}_3\text{tacn})]^+$ complex. In the latter case, the O-Re^v bond is considered as triple in character [$\Delta(\text{Re-N}_{\text{trans to oxo}} - \text{Re-N}_{\text{cis to oxo}}) = 0.09 \text{\AA}$].

The UV/VIS spectrum of complex **2** is shown in Fig. 5. It

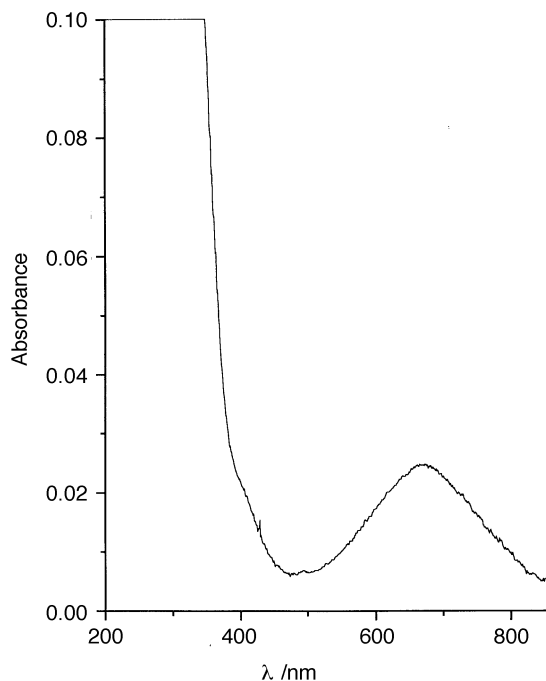


Fig. 5 Room-temperature absorption spectrum of complex **2** measured in acetonitrile solution (7.8×10^{-4} mol dm $^{-3}$)

shows similar low-energy d-d transition(s) to those of $[\text{ReO}(\text{O}_2\text{C}_2\text{H}_4)(\text{tacn})]^+$ and $[\text{ReO}(\text{OMe})_2(\text{tacn})]^+$ (tacn = 1,4,7-triazacyclononane).¹⁵ Based on these findings and the result from electrochemical studies, the electrode reactions of **1** can be assigned as (2) and (3) at $0.9 < \text{pH} < 4.1$, and (2) and (5) at $\text{pH} > 4.1$. The break point of the E_1 versus pH plot for couple II occurs at pH 4.1, which is assigned to the $\text{p}K_a$ value of $[\text{Re}^{\text{V}}\text{O}(\text{OH})(\text{OH}_2)(\text{Me}_3\text{tacn})]^{2+}$. There are relative few electrochemical studies on the $d^0 \text{M}=\text{O} \rightarrow d^2 \text{M}-\text{OH}_2$ couple. Compared to the E° of $[\text{MoO}_3(\text{Me}_3\text{tacn})]$ (-0.075 V vs. normal hydrogen electrode) at the same pH, **1** is less oxidizing.

Acknowledgements

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