

ments on colloidal CdS particles in acetonitrile. They associated the three observed lifetimes to "initial weak trapping, electron reemission to the conduction band and radiative recombination from the conduction band after traps are filled". However, many decay curves and, as shown in Figure 8, any series of phase/modulation data could be described fairly well with three components. Additionally, the CdS particles investigated here fall in the polymolecular quantum-size regime (BEL position at 460 nm) while CdS particles in acetonitrile have rather macrocrystalline properties (BEL position at 515 nm). Additional work is needed to prove the significance of the three-component ϕ/m decay data.

In summary, this paper provides the first description of the sol-gel based preparation of a compact quantum semiconductor

membrane. In this preliminary work we have only attempted to give a general overview of their spectroscopic properties. Additionally, the preliminary results presented here have demonstrated the usefulness of the multiple-frequency phase/modulation approach and shown that this approach is at least comparable to picosecond time-domain techniques. These results also demonstrate that the technique of MHFT spectroscopy might be extended to dynamic semiconductor surface investigations.

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A Novel Monooxoruthenium(V) Complex Containing a Polydentate Pyridyl Amine Ligand. Syntheses, Reactivities, and X-ray Crystal Structure of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$

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Abstract: The syntheses and characterization of $\text{cis-}[\text{Ru}^{\text{III}}(\text{tepa})\text{Cl}_2]^+$, $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$, and $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complexes are described [tepa = tris(2-(2-pyridyl)ethyl)amine, N_4OH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine]. The molar magnetic susceptibilities for $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ and $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complexes are 1.79 and 2.2 μ_{B} , respectively. The X-ray structure of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ has been determined: $[\text{Ru}^{\text{III}}(\text{C}_{21}\text{H}_{23}\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$, $M = 666.43$, monoclinic, space group $P2_1/c$ (no. 13), $a = 11.644$ (1) Å, $b = 11.937$ (3) Å, $c = 18.856$ (6) Å, $\beta = 105.39$ (2)°, $V = 2527$ (1) Å³, $Z = 4$, $D_x = 1.753$, $D_c = 1.752$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 8.82$ cm⁻¹. The Ru-O(OH₂) and Ru-O(N₄O) distances are 2.115 (3) and 1.961 (4) Å, respectively. The $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex shows an intense Ru=O stretch at 872 cm⁻¹ which is absent in the $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ complex. The Ru(V) state in $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ has also been confirmed by spectrophotometric redox titration in 0.1 M HClO₄ by using $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{bpy})]^{2+}$ (bpy = 2,2'-bipyridine) as the redox titrant. A stoichiometry of 1:3 has been obtained. The cyclic voltammograms of both $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ and $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complexes show two couples at 0.35 and 1.02 V vs SCE in aqueous medium at pH = 1, assignable to a Ru(III/II) and a Ru(V/III) couple, respectively. At 5.5 > pH > 3.5, the wave for the Ru(V/III) couple splits into two waves, a pH-independent one-electron wave for the Ru(V/IV) couple and a two-proton-one-electron wave with a slope of -117 mV/pH unit for the Ru(IV/III) couple. The Ru(IV) state is found to be thermodynamically unstable with respect to disproportionation into Ru(III) and Ru(V) at pH < 3.5. The $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex is found to be an active oxidant, capable of oxidizing both activated C-H bonds and the C-H bond of cyclohexane. Studies on the reactions of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ with organic substrates indicated that the Ru(V)=O has a higher affinity for hydrogen atom/hydride abstraction than oxo-transfer reaction to C=C double bond.

High-valent oxo complexes of ruthenium have long been known to be active oxidants for a variety of substrate oxidation reactions.² The interest in studying these complexes stems its origin from the postulation that high-valent oxoiron species is involved in the enzymatic reactions of cytochrome P-450, which is the hemo-protein known to catalyze hydroxylation of unactivated C-H bonds under mild conditions. Ruthenium, being in the same group as iron, is particularly interesting to study owing to the wide applicability of its oxides such as RuO₄ in synthetic organic chemistry. Despite the recent progress in successful isolation and characterization of monooxoruthenium(IV) and dioxo-ruthenium(VI) complexes,^{2,3} there are few studies on oxo-ruthenium(V) species^{4,5} which are suggested to be the reactive intermediates in the oxidation of water to oxygen.⁶ The monooxoruthenium(V) complexes should deserve special attention since they could provide an insight into the mechanism played by the Ru(V)=O moiety in these reactions. Although a large number of catalytic systems using ruthenium(III) complexes and an oxygen atom donor such as PhIO⁷ or NaOCl⁸ are known to activate

epoxidation of olefins via a postulated "Ru(V)=O" intermediate, attempts to isolate this class of compounds have been unsuccessful.

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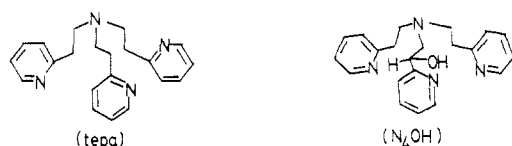


Figure 1. Tris(2-(2-pyridyl)ethyl)amine (tepa) and bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine (N_4OH).

To our knowledge, monooxoruthenium(V) complexes have not yet been isolated. The ligand tris(2-(2-pyridyl)ethyl)amine, abbreviated as *tepa* (Figure 1), was initially employed to generate a stable *cis*-dioxoruthenium(VI) complex owing to the tripodal nature of the ligand. In the course of our studies, we have found that the aliphatic C–H bond adjacent to one of the pyridine rings is easily oxidized to a C–OH group. Deprotonation of the hydroxyl group produces a monoanionic, pentadentate N_4O^- ligand⁹ (Figure 1). The anionic chelating nature of the N_4O^- ligand, which is also oxidation resistant, should render the stabilization of a high oxidation state and formation of strongly oxidizing complexes possible. In this contribution, we report the synthesis, characterization, electrochemistry, and reactivities of a novel ruthenium(V)-oxo complex and the X-ray structure of its precursor $[Ru^{III}(N_4O)(H_2O)]^{2+}$ species.

Experimental Section

$K_2[RuCl_5(H_2O)]$ was purchased from Johnson Matthey Chemical Ltd. *cis*- $[Ru^{II}(NH_3)_4(bpy)](PF_6)_2$ (*bpy* = 2,2'-bipyridine) was prepared according to the literature method.¹⁰ Acetonitrile (Mallinckrodt, ChromAR, HPLC grade) was twice distilled over CaH_2 and $KMnO_4$. All other reagents and solvents used in syntheses and physical measurements were of analytical grade.

Ligand Synthesis. The tripodal tris(2-(2-pyridyl)ethyl)amine (*tepa*) ligand was synthesized according to Karlin's method¹¹ by reaction of excess 2-vinylpyridine with ammonium acetate in methanol. After removal of methanol by rotary evaporation, the reaction mixture was cooled to ca. 5 °C in an ice bath. Sodium hydroxide solution (20%) was slowly added to the solution with stirring until the mixture became alkaline. The solution was then extracted with CH_2Cl_2 (4 × 100 mL). The CH_2Cl_2 extracts were combined, dried over anhydrous $MgSO_4$, filtered, and rotary-evaporated to give an oily residue. This was column-chromatographed on silica gel with methanol as the eluent. Collection of different fractions was continuously monitored by thin-layer chromatography on silica gel with methanol as the mobile phase. The first fraction collected was unreacted 2-vinylpyridine, which was followed by a second fraction of the *tepa* ligand: ¹H NMR in $CDCl_3$ δ in ppm 2.9 (s, 12 H), 7.2 (m, 9 H), 8.4 (d, 3 H).

Caution: The following three compounds are isolated as perchlorate salts, which are potentially explosive and should be handled in small quantities.

Syntheses of Ruthenium Complexes. *cis*- $[Ru^{III}(tepa)Cl_2]Y$ ($Y = Cl, ClO_4$). An ethanolic solution of the ligand *tepa* (0.5 g in 200 mL) was added dropwise to a refluxing and vigorously stirred ethanolic suspension of $K_2[RuCl_5(H_2O)]$ (0.5 g in 200 mL). The addition process took about 3 h to complete, and the mixture was further refluxed for 1 day. This was filtered, and the filtrate, with a few drops of hydrochloric acid (12 M) added, was evaporated to dryness. A reddish brown solid was obtained, which was recrystallized in hot HCl (2 M) to give reddish brown crystals of *cis*- $[Ru^{III}(tepa)Cl_2]Cl$ (yield ≈ 46%). The perchlorate salt of *cis*- $[Ru^{III}(tepa)Cl_2]^+$ was obtained as a reddish brown solid by metathesis reaction with $NaClO_4$ in an HCl (2 M) solution: UV-vis in HCl (1 M), λ_{max}/nm ($\epsilon_{max}/mol^{-1} dm^3 cm^{-1}$) 380 (1520), 267 (12170), 215 (17030). Anal. Calcd for $[Ru^{III}(tepa)Cl_2]Cl$: C, 46.7; H, 4.5; N, 10.4; Cl, 19.7. Found: C, 46.6; H, 4.6; N, 10.0; Cl, 19.5.

$[Ru^{III}(N_4O)(H_2O)](ClO_4)_2$. Treatment of *cis*- $[Ru^{III}(tepa)Cl_2]Cl$ (0.3 g) with silver(I) *p*-toluenesulfonate (0.6 g) in deionized water (20 mL) at ca. 80 °C for 0.5 h gave a yellowish green solution which was then filtered to remove the insoluble $AgCl$. H_2O_2 (30%, 3 mL) was slowly added to the filtrate, while the solution was kept at 60 °C for 5 min. The solution was then cooled in an ice bath. Upon addition of $NaClO_4$, golden brown crystals of $[Ru^{III}(N_4O)(H_2O)](ClO_4)_2$ which could be recrystallized from hot $HClO_4$ (0.1 M, 60 °C) deposited (yield, 52%). Sometimes if the reaction mixture was overheated in the chloro-removal step, the solution became dark blue-green in color, and upon addition of $NaClO_4$, a dark blue-green solid was deposited together with the golden brown $[Ru^{III}(N_4O)(H_2O)](ClO_4)_2$ crystal. This dark solid could be removed by either washing the mixture of solids with acetonitrile or by warming in perchloric acid (0.1 M, 60 °C) for ca. 15 min. Anal. Calcd for $[Ru^{III}(N_4O)(H_2O)](ClO_4)_2 \cdot H_2O$: C, 36.7; H, 3.9; N, 8.1; Cl, 10.4. Found: C, 37.0; H, 3.8; N, 7.6; Cl, 10.1. UV-vis in H_2O , λ_{max}/nm ($\epsilon_{max}/mol^{-1} dm^3 cm^{-1}$) 405 sh (920), 290 (6990), 267 (7930), 228 (7370), 200 (14620); IR ν (OH), 3290 cm^{-1} ; Λ_M in H_2O 253 $\Omega^{-1} mol^{-1} cm^2$ at 297 K; μ_{eff} (solid sample, Gouy method) 1.79 μ_B at 300 K.

$[Ru^V(N_4O)O](ClO_4)_2$. $[Ru^{III}(N_4O)(H_2O)](ClO_4)_2$ (0.2 g) was dissolved in minimum amount of deionized water with slight warming. To an ice-cooled, vigorously stirred solution of excess $(NH_4)_2[Ce(NO_3)_6]$ was slowly added the saturated solution of $[Ru^{III}(N_4O)(H_2O)](ClO_4)_2$, with subsequent darkening of the reaction mixture, to give a dark brown solution. This was followed by subsequent precipitation of $[Ru^V(N_4O)O](ClO_4)_2$ with $NaClO_4$. The $[Ru^V(N_4O)O](ClO_4)_2$ complex was obtained as a brownish green microcrystalline solid (yield, 50%). UV-vis in H_2O , λ_{max}/nm ($\epsilon_{max}/mol^{-1} dm^3 cm^{-1}$) 300 sh (2490), 260 (8180), 210 (14260); IR ν ($Ru=O$), 872 cm^{-1} ; Λ_M in H_2O , 302 $\Omega^{-1} mol^{-1} cm^2$ at 297 K. μ_{eff} (solid sample, Gouy method) 2.29 μ_B at 300 K. Anal. Calcd for $[Ru^V(N_4O)O](ClO_4)_2$: C, 37.8; H, 3.5; N, 8.4; Cl, 10.7. Found: C, 37.4; H, 3.4; N, 8.0; Cl, 10.6.

Instrumentation and Techniques. UV-vis spectra were obtained on a Shimadzu UV-240 spectrophotometer. NMR spectra were run on a Jeol Model FX90Q (90 MHz) spectrometer. Magnetic susceptibility was determined by using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. Redox titration of $[Ru^V(N_4O)O](ClO_4)_2$ was performed on the Shimadzu UV-240 spectrophotometer by using *cis*- $[Ru^{II}(NH_3)_4(bpy)](PF_6)_2$ as the redox titrant and by monitoring the drop in intensity of the $[Ru^{II}(NH_3)_4(bpy)](PF_6)_2$ absorption band at 522 nm in 0.1 M $HClO_4$ + 0.1 M $NaClO_4$ with addition of $[Ru^V(N_4O)O](ClO_4)_2$ in steps of 20 μL using a micropipette. The pK_a value measurements were performed by using the spectrophotometric method. Data were taken at two independent wavelengths (240 and 340 nm), and the results obtained are in good agreement to each other.

Cyclic voltammetry and controlled potential coulometry were performed by using a Princeton Applied Research (PAR) Model 175 universal programmer, Model 173 potentiostat, and Model 179 digital coulometer. The working electrode used was an edge plane pyrolytic graphite (EPG, Union Carbide) electrode. The electrode surfaces were pretreated by procedures as previously described.¹² Rotating disc voltammetry was performed by using a Pine Instrument Model RDE4 bi-potentiostat with an ASR-2 analytical rotator and an EPG (0.32 cm^2) electrode. Treatments of electrodes were done in the same way as in cyclic voltammetry.

Stoichiometric oxidation of organic substrates by $[Ru^V(N_4O)O](ClO_4)_2$ (20 mg) was performed by suspending the ruthenium complex in acetonitrile (1 mL) containing the dissolved substrates (solid, 50–100 mg; liquid, 0.2 mL). The reaction mixture was degassed, filled with argon, and stirred for 20–30 min with a magnetic stirrer, and the temperature was maintained at room temperature in a water bath. A control experiment in the absence of the ruthenium complex was performed for each reaction. The products were analyzed by GC, ¹H NMR, and UV-vis spectroscopy. Gas chromatographic analyses were conducted by using a Varian Model 940 gas chromatograph with a flame ionization detector. Gas chromatographic columns used included a 10% w/w Carbowax 20M on chromosorb W (80–100 mesh), a 10% w/w SE-30 on chromosorb W (80–100 mesh), and a 10% TCEPE on chromosorb P (80–100 mesh), with nitrogen as the carrier gas. Component identification was established by comparing the retention time with an authentic sample or by gas chromatographic-mass spectral analysis (GC-MS). *cis*- and *trans*-Stilbene oxides were quantified by ¹H NMR spectroscopy by using deoxybenzoin as the internal standard. The reaction mixture was rotary evaporated and extracted with *n*-hexane for at least five times. Deoxybenzoin was added to the combined extracts and rotary evaporated to dryness at room temperature. The residue was quantitatively transferred to an NMR tube by using CD_2Cl_2 or $CDCl_3$ as the solvent, and the

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spectrum was run on the Jeol Model FX90Q spectrometer.

Quantitative analysis of chloride oxidation to give chlorine was monitored by the UV-vis spectrophotometric method by using DPD (Lovibond, Palintest) as the color-developing reagent, where DPD = *N,N*-diethyl-*p*-phenylenediamine. $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})(\text{ClO}_4)_2]$ (2 mg) was dissolved in 1 M HCl (2 mL) and stirred for 0.5 h in a water bath at room temperature. At the end of the reaction, 0.2 mL of the reaction mixture was withdrawn, double-distilled water was added to increase the mixture's volume to 20 mL, and a DPD no. 4 tablet (100 mg) was added with thorough mixing. The absorbance at 515 nm was measured immediately. Control experiments in the absence of the ruthenium(V) complex and in the presence of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ were performed to correct for any Cl_2 gas existing in the 1 M HCl. No chlorine was detected when $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ was used as the oxidant. Calibration was obtained by using potassium permanganate as oxidant in the DPD reaction.

X-ray Structure Determination. Crystal Data. $[\text{Ru}^{\text{III}}(\text{C}_{21}\text{H}_{23}\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ crystallized from 0.1 M HClO_4 as golden-brown flat prisms, $M = 666.43$; monoclinic, space group $P2_1/c$ (no. 13), $a = 11.644$ (1) Å, $b = 11.937$ (3) Å, $c = 18.856$ (6) Å, $\beta = 105.39$ (2)°, $V = 2527$ (1) Å³, D_x (floatation in $\text{CCl}_4/\text{BrCH}_2\text{CH}_2\text{Br}$) = 1.753 g cm⁻³, $Z = 4$, $D_c = 1.752$ g cm⁻³, $F(000) = 1348$, $\mu(\text{Mo K}\alpha) = 8.82$ cm⁻¹; crystal dimensions 0.18 × 0.16 × 0.08 nm.

Intensities ($h, k, \pm l$; 4463 unique data) were measured at 22 °C on a Nicolet R3m diffractometer by using the ω - 2θ variable-scan (2.02–8.37 deg min⁻¹) technique in the bisecting mode up to $2\theta_{\text{max}} = 50^\circ$. Azimuthal scans of selected strong reflections over a range of 2θ values were used to define a pseudoellipsoid for the application of absorption corrections ($\mu_r = 0.058$, transmission factors 0.825–0.926).^{13–16}

Atomic coordinates for the Ru atom were deduced from a sharpened Patterson function, and the other non-hydrogen atoms were located from subsequent difference Fourier maps. Two independent perchlorate groups occupy sites of crystallographic symmetry 2. The remaining perchlorate group in the asymmetric unit is disordered, with two distinct orientations of unequal population centered at the Cl(1) atom. A common site occupancy factor, g , was associated with the set of atoms O-(3)–O(6) (representing the preferred orientation) and varied as a parameter and that for the O(3')–O(6') (less favored orientation) was accordingly held at 1.0 – g . To facilitate refinement of the disordered O atoms, the Cl(1)–O bond distances were subjected to a constraint of 1.400 ± 0.005 Å by the method of additional observational equations.¹⁴ Blocked-cascade least-squares refinement proceeded with isotropic thermal parameters for all ordered non-hydrogen atoms and isotropic ones for the disordered O atoms.

The aromatic, methylene, and methine H atoms were generated geometrically (C–H fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms; they were included in structure factor calculations with assigned isotropic thermal parameters. The H atoms of the aqua ligand failed to appear in the final difference map.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL programs.¹⁵ Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.¹⁶ Convergence for 3519 observed data ($|F_o| > 3\sigma(F_o)$) and 356 variables was reached at $R = 0.056$, $w_R = 0.060$, and $s = 1.531$ with weighting scheme $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$. The final difference Fourier map showed residual extrema in the range +0.84 to –0.58 eÅ⁻³, with the three highest peaks lying in the neighborhood of the disordered O atoms. The free variable g refined to the value 0.707 (2).

Results and Discussion

The tetradentate tepa ligand was previously reported by Karlin and co-workers.¹¹ In this work, this ligand was found to react with $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ to give *cis*- $[\text{Ru}^{\text{III}}(\text{tepa})\text{Cl}_2]^+$ in a manner similar to the reported synthesis of *trans*-dichlororuthenium(III) macrocyclic amine complexes.^{17a,b} The IR spectra of the *cis*- $[\text{Ru}^{\text{III}}(\text{tepa})\text{Cl}_2]\text{Y}$ ($\text{Y} = \text{Cl}, \text{ClO}_4$) complexes show the absence of $\nu(\text{OH})$ stretch in the 3600–3000-cm⁻¹ region, indicating that oxidation of the ligand to N_4OH does not occur in the metal insertion reaction. The structure of *cis*- $[\text{Ru}^{\text{III}}(\text{tepa})\text{Cl}_2]\text{ClO}_4$ is

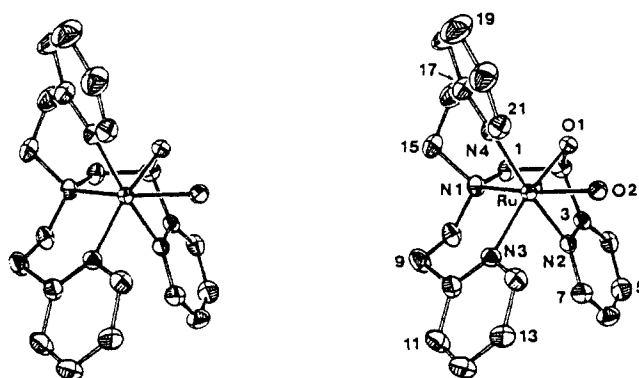
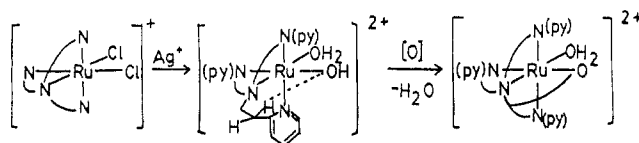


Figure 2. An ORTEP diagram of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})\text{OH}_2]^{2+}$ with atom labeling.

Scheme I



also inferred from its osmium analogue, *cis*- $[\text{Os}^{\text{III}}(\text{tepa})\text{Cl}_2]\text{ClO}_4$, which has the same IR spectrum as the $\text{Ru}(\text{III})$ species and has been characterized by X-ray crystallography.^{17c}

Removal of chloro groups of *cis*- $[\text{Ru}^{\text{III}}(\text{tepa})\text{Cl}_2]^+$ by $\text{Ag}(\text{I})$ with subsequent oxidation by H_2O_2 and addition of NaClO_4 yielded $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$,¹⁸ which has been confirmed by X-ray crystallography. The formation of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ as the product with the aliphatic C–H bond adjacent to one of the pyridine rings being oxidized to C–OH does not meet our expectations. It was found that absence of H_2O_2 had no effect on the result, suggesting H_2O_2 was not involved in the crucial step for the oxidation of the tepa ligand. Presumably, the presence of the $\text{Ru}(\text{III})$ metal center was responsible for the C–H bond activation. The C–H bond adjacent to the pyridine ring, being an activated benzylic C–H bond, is easily oxidized via a proposed mechanism (Scheme I). The oxidant ($[\text{O}]$) could be $\text{Ag}(\text{I})$ or the $\text{Ru}(\text{III})$ metal center. We believe that intramolecular oxidation by $\text{Ru}(\text{III})$ is the feasible pathway since it has been found that $\text{Ru}(\text{III})\text{--H}_2\text{O}$ complexes of 2,2'-bipyridine such as *trans*- $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ are able to oxidize benzyl alcohol to benzaldehyde.¹⁹ In fact, copper-mediated hydroxylation of a similar pyridine type of ligand has also been reported by Karlin and co-workers.²⁰

The measured μ_{eff} of 1.79 μ_B for $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ at room temperature is close to the spin-only value for one unpaired electron $[\text{Ru}(\text{III}), (t_{2g})^5]$. The $\text{Ru}(\text{III})$ complex exists as a 1:2 electrolyte in fluid solution and has an average pK_a value of 4.7 which is comparable to the corresponding value of 4.1 for $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$.²¹ Compared to the pK_a value of 10.2 for $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{py})(\text{H}_2\text{O})]^{2+}$ ($\text{py} = \text{pyridine}$)²² which is also a di-

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(18) In the synthesis of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$, a dark blue-green solid was sometimes isolated as a side-product if the chloro removal step was performed at too high a temperature. Its relative ease of conversion back to $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ upon warming with 0.1 M HClO_4 suggested its identity as a polymeric ruthenium species, most probably a μ -oxo species. Elemental analysis suggested its structure to be $\{[(\text{H}_2\text{O})(\text{tepa})\text{Ru}^{\text{III}}]_2\text{O}\}(\text{ClO}_4)_2 \cdot \text{HClO}_4$ [UV-vis, λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) in CH_3CN : 604 (7540), 315 (9160), 250 (15780), 196 (53125). Anal. Calcd: C, 35.58; H, 3.94; N, 7.90; Cl, 12.53. Found: C, 36.34; H, 4.08; N, 7.50; Cl, 12.20.] No further attempts have been made to identify this species further. Removal of this side-product could be achieved by the careful control of temperature in the chloro removal step or, if formed, by washing it off with acetonitrile.

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Table I. Atomic Coordinates ($\times 10^5$ for Ru; $\times 10^4$ for Other Atoms) and Thermal Parameters^a ($\text{\AA}^2 \times 10^4$ for Ru; $\times 10^3$ for Other Atoms)

| atom | x | y | z | U_{eq} or U |
|---|-----------|-----------|-----------|-----------------|
| (i) Complex cation | | | | |
| Ru | 16096 (4) | 20733 (4) | 37026 (2) | 278 (1)* |
| O(1) | 1556 (3) | 1830 (3) | 2666 (2) | 26 (1)* |
| N(1) | 3207 (4) | 1193 (4) | 3864 (3) | 39 (1)* |
| N(2) | 2560 (4) | 3474 (4) | 3520 (2) | 34 (1)* |
| N(3) | 1816 (4) | 2601 (4) | 4791 (2) | 34 (1)* |
| N(4) | 580 (4) | 663 (4) | 3796 (3) | 37 (1)* |
| C(1) | 3602 (5) | 1314 (5) | 3163 (3) | 44 (1)* |
| C(2) | 2742 (5) | 2092 (5) | 2645 (3) | 41 (1)* |
| C(3) | 2981 (5) | 3317 (5) | 2934 (3) | 36 (1)* |
| C(4) | 3568 (5) | 4131 (5) | 2654 (3) | 47 (1)* |
| C(5) | 3748 (6) | 5144 (5) | 3013 (4) | 54 (1)* |
| C(6) | 3359 (5) | 5312 (5) | 3623 (4) | 53 (1)* |
| C(7) | 2744 (5) | 4472 (5) | 3863 (3) | 41 (1)* |
| C(8) | 4148 (5) | 1665 (6) | 4496 (3) | 49 (1)* |
| C(9) | 3832 (5) | 1704 (6) | 5216 (3) | 54 (1)* |
| C(10) | 2876 (5) | 2555 (5) | 5303 (3) | 42 (1)* |
| C(11) | 3097 (6) | 3200 (6) | 5940 (4) | 57 (1)* |
| C(12) | 2202 (7) | 3859 (6) | 6065 (4) | 61 (1)* |
| C(13) | 1103 (6) | 3859 (5) | 5570 (3) | 53 (1)* |
| C(14) | 937 (6) | 3235 (5) | 4935 (3) | 44 (1)* |
| C(15) | 3073 (6) | -48 (5) | 3391 (4) | 52 (1)* |
| C(16) | 2069 (6) | -576 (6) | 3438 (4) | 64 (1)* |
| C(17) | 829 (6) | -365 (5) | 3601 (3) | 51 (1)* |
| C(18) | -1 (7) | -1232 (6) | 3527 (4) | 73 (1)* |
| C(19) | -1067 (7) | -1034 (6) | 3667 (4) | 74 (1)* |
| C(20) | -1296 (6) | 7 (5) | 3912 (4) | 58 (1)* |
| C(21) | -459 (5) | 818 (5) | 3969 (3) | 44 (1)* |
| O(2) | -26 (3) | 2941 (3) | 3346 (2) | 33 (1)* |
| (ii) Disordered ClO_4^- Group | | | | |
| Cl(1) | 2894 (2) | 2907 (2) | 428 (1) | 75 (1)* |
| O(3) | 1780 (4) | 3335 (7) | 353 (6) | 258 (2)* |
| O(4) | 3030 (9) | 2470 (8) | -238 (3) | 187 (2)* |
| O(5) | 3168 (9) | 2045 (7) | 956 (4) | 219 (2)* |
| O(6) | 3769 (6) | 3751 (6) | 655 (6) | 195 (2)* |
| O(3') | 2860 (7) | 1743 (3) | 357 (4) | 92 (2) |
| O(4') | 2163 (5) | 3244 (8) | 875 (3) | 60 (2) |
| O(5') | 4062 (4) | 3263 (7) | 745 (6) | 442 (3) |
| O(6') | 2469 (10) | 3404 (6) | -268 (3) | 266 (3) |
| (iii) Ordered ClO_4^- Groups Each Lying on a 2-Fold Axis | | | | |
| Cl(2) | 5000 | 1389 (2) | 7500 | 48 (1)* |
| O(7) | 4311 (6) | 2062 (6) | 7832 (4) | 122 (1)* |
| O(8) | 4263 (5) | 703 (4) | 6953 (3) | 81 (1)* |
| Cl(3) | 0 | 4169 (2) | 7500 | 56 (1)* |
| O(9) | 10 (7) | 4857 (5) | 6896 (3) | 115 (1)* |
| O(10) | 1022 (5) | 3474 (5) | 7657 (4) | 101 (1)* |

^a Asterisk indicates equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalized U matrix. The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

positive cation, the much lower pK_a value for $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ is expected given the fact that $p_r(\text{OH})$ and $d_r(\text{Ru})$ π -bonding is not significant in the electron-rich Ru(II) center.

X-ray Structure of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$. Tables I and II summarize the atomic coordinates and bond lengths and angles of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$, respectively.

A stereoview of the complex cation is shown in Figure 2. The coordination geometry about the Ru(III) atom is distorted octahedral, and formation of the Ru-O(1) bond forces the six-membered Ru-N(1)-C(1)-C(2)-C(3)-N(2) chelate ring into the boat conformation. Besides serving as an aqua ligand, the water molecule O(2) also forms donor hydrogen bonds with O(9) of an ordered perchlorate group and O(1) of a neighboring complex cation, thereby giving rise to a dimeric unit arranged about a crystallographic C_2 axis.

The trans ligand bond angles around the ruthenium center range from $169.8 (2)^\circ$ to $175.4 (2)^\circ$, indicating distortions from rectilinear geometry. The O(1)-Ru-O(2) angle of $88.1 (1)^\circ$ is

Table II. Bond Lengths (\AA), Bond Angles ($^\circ$), and Selected Torsion Angles ($^\circ$)

| (i) $[\text{Ru}^{\text{III}}(\text{C}_{21}\text{H}_{23}\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ Cation | | | |
|--|------------|---|------------|
| Ru-O(1) | 1.961 (4) | Ru-N(1) | 2.087 (5) |
| Ru-N(2) | 2.083 (5) | Ru-N(3) | 2.099 (5) |
| Ru-N(4) | 2.101 (5) | Ru-O(2) | 2.115 (3) |
| O(1)-C(2) | 1.426 (7) | N(1)-C(1) | 1.517 (8) |
| N(1)-C(8) | 1.498 (7) | N(1)-C(15) | 1.515 (8) |
| N(2)-C(3) | 1.337 (8) | N(2)-C(7) | 1.346 (7) |
| N(3)-C(10) | 1.351 (7) | N(3)-C(14) | 1.357 (8) |
| N(4)-C(17) | 1.334 (8) | N(4)-C(21) | 1.348 (8) |
| C(1)-C(2) | 1.517 (8) | C(2)-C(3) | 1.560 (8) |
| C(3)-C(4) | 1.370 (9) | C(4)-C(5) | 1.375 (9) |
| C(5)-C(6) | 1.357 (10) | C(6)-C(7) | 1.375 (9) |
| C(8)-C(9) | 1.497 (9) | C(9)-C(10) | 1.548 (9) |
| C(10)-C(11) | 1.391 (9) | C(11)-C(12) | 1.375 (11) |
| C(12)-C(13) | 1.369 (9) | C(13)-C(14) | 1.380 (9) |
| C(15)-C(16) | 1.485 (9) | C(16)-C(17) | 1.576 (11) |
| C(17)-C(18) | 1.397 (10) | C(18)-C(19) | 1.356 (13) |
| C(19)-C(20) | 1.377 (10) | C(20)-C(21) | 1.358 (9) |
| O(1)-Ru-N(1) | 82.1 (2) | O(1)-Ru-N(2) | 80.3 (2) |
| N(1)-Ru-N(2) | 86.3 (2) | O(1)-Ru-N(3) | 169.9 (2) |
| N(1)-Ru-N(3) | 98.1 (2) | N(2)-Ru-N(3) | 89.6 (2) |
| O(1)-Ru-N(4) | 95.6 (2) | N(1)-Ru-N(4) | 95.2 (2) |
| N(2)-Ru-N(4) | 175.4 (2) | N(3)-Ru-N(4) | 94.5 (2) |
| O(1)-Ru-O(2) | 88.1 (1) | N(1)-Ru-O(2) | 170.2 (2) |
| N(2)-Ru-O(2) | 91.6 (2) | N(3)-Ru-O(2) | 91.4 (2) |
| N(4)-Ru-O(2) | 86.2 (2) | Ru-O(1)-C(2) | 102.7 (3) |
| Ru-N(1)-C(1) | 106.8 (3) | Ru-N(1)-C(8) | 111.2 (4) |
| C(1)-N(1)-C(8) | 109.3 (5) | Ru-N(1)-C(15) | 113.0 (4) |
| C(1)-N(1)-C(15) | 107.3 (5) | C(8)-N(1)-C(15) | 109.0 (4) |
| Ru-N(2)-C(3) | 110.6 (4) | Ru-N(2)-C(7) | 131.0 (4) |
| C(3)-N(2)-C(7) | 118.3 (5) | Ru-N(3)-C(10) | 122.2 (4) |
| Ru-N(3)-C(14) | 117.8 (3) | C(10)-N(3)-C(14) | 118.3 (5) |
| Ru-N(4)-C(17) | 123.0 (5) | Ru-N(4)-C(21) | 118.6 (4) |
| C(17)-N(4)-C(21) | 117.9 (5) | N(1)-C(1)-C(2) | 108.6 (5) |
| O(1)-C(2)-C(1) | 109.1 (5) | O(1)-C(2)-C(3) | 106.3 (5) |
| C(1)-C(2)-C(3) | 108.8 (4) | N(2)-C(3)-C(2) | 110.4 (5) |
| N(2)-C(3)-C(4) | 123.3 (5) | C(2)-C(3)-C(4) | 126.3 (6) |
| C(3)-C(4)-C(5) | 117.4 (6) | C(4)-C(5)-C(6) | 120.3 (6) |
| C(5)-C(6)-C(7) | 119.4 (6) | N(2)-C(7)-C(6) | 121.2 (6) |
| N(1)-C(8)-C(9) | 115.4 (5) | C(8)-C(9)-C(10) | 118.2 (5) |
| N(3)-C(10)-C(9) | 119.8 (5) | N(3)-C(10)-C(11) | 121.3 (6) |
| C(9)-C(10)-C(11) | 118.8 (5) | C(10)-C(11)-C(12) | 119.3 (6) |
| C(11)-C(12)-C(13) | 119.8 (6) | C(12)-C(13)-C(14) | 118.8 (7) |
| N(3)-C(14)-C(13) | 119.8 (6) | C(12)-C(13)-C(14) | 118.8 (7) |
| N(3)-C(14)-C(13) | 122.4 (5) | N(1)-C(15)-C(16) | 113.5 (5) |
| C(15)-C(16)-C(17) | 112.7 (6) | N(4)-C(17)-C(16) | 118.6 (6) |
| N(4)-C(17)-C(18) | 120.9 (7) | C(16)-C(17)-C(18) | 120.5 (6) |
| C(17)-C(18)-C(19) | 119.7 (7) | C(18)-C(19)-C(20) | 119.4 (7) |
| C(19)-C(20)-C(21) | 118.2 (7) | N(4)-C(21)-C(20) | 123.6 (6) |
| Ru-N(1)-C(1)-C(2) | 4.2 (5) | N(1)-C(1)-C(2)-C(3) | 73.8 (6) |
| C(1)-C(2)-C(3)-N(2) | -74.6 (6) | C(2)-C(3)-N(2)-Ru | -6.5 (5) |
| C(3)-N(2)-Ru-N(1) | 62.2 (3) | N(2)-Ru-N(1)-C(1) | -58.5 (3) |
| Ru-N(1)-C(8)-C(9) | 56.7 (6) | N(1)-C(8)-C(9)-C(10) | -70.5 (7) |
| C(8)-C(9)-C(10)-N(3) | 50.7 (8) | C(9)-C(10)-N(3)-Ru | -24.9 (8) |
| C(10)-N(3)-Ru-N(1) | 14.9 (5) | N(3)-Ru-N(1)-C(8) | -28.4 (4) |
| Ru-N(1)-C(15)-C(16) | 49.4 (7) | N(1)-C(15)-C(16)-C(17) | -80.4 (7) |
| C(15)-C(16)-C(17)-N(4) | 44.3 (8) | C(16)-C(17)-N(4)-Ru | 11.9 (7) |
| C(17)-N(4)-Ru-N(1) | -30.2 (4) | N(4)-Ru-N(1)-C(15) | -0.7 (4) |
| (ii) Hydrogen Bonding | | | |
| O(2)···O(1) ^a | 2.60 (1) | O(2)···O(9) ^b | 2.67 (1) |
| O(1) ^a ···O(2)···O(9) ^b | 114.3 (8) | Ru-O(2)···O(1) ^a | 111.5 (6) |
| Ru-O(2)···O(9) ^b | 119.4 (8) | O(2)···O(1) ^a -C(2) ^a | 110.3 (7) |
| O(2)···O(9) ^b -C(3) ^b | 135.0 (1) | | |

^a Symmetry transformations: $-x, y, 1/2 - z$. ^b Symmetry transformations: $-x, 1 - y, 1 - z$.

comparable to the value of $89.4 (2)^\circ$ for the $[(\text{H}_2\text{O})-(\text{bpy})_2\text{Ru}^{\text{III}}]_2\text{O}^{4+}$ reported by Gilbert and co-workers.²³ The *cis*-O(1)-Ru-N ($80.3 (2)^\circ$ - $95.6 (2)^\circ$) and N-Ru-O(2) angles ($86.2 (2)^\circ$ - $91.6 (2)^\circ$) are quite comparable to the analogous angles in $[(\text{H}_2\text{O})(\text{bpy})_2\text{Ru}^{\text{III}}]_2\text{O}^{4+}$ ²³ and *trans*- $[\text{Ru}^{\text{III}}(\text{bpy})_2-(\text{OH})(\text{H}_2\text{O})]^{2+}$.²⁴

An important structural feature of the molecule is the marked difference in the Ru-O bond distances. The measured Ru-O(2) distance of $2.115 (3) \text{ \AA}$ is a normal Ru-OH₂ bond. It is similar to the value of $2.136 (4) \text{ \AA}$ in $[(\text{H}_2\text{O})(\text{bpy})_2\text{Ru}^{\text{III}}]_2\text{O}^{4+}$ ²³ but significantly longer than distances observed in the structures of

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(22) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

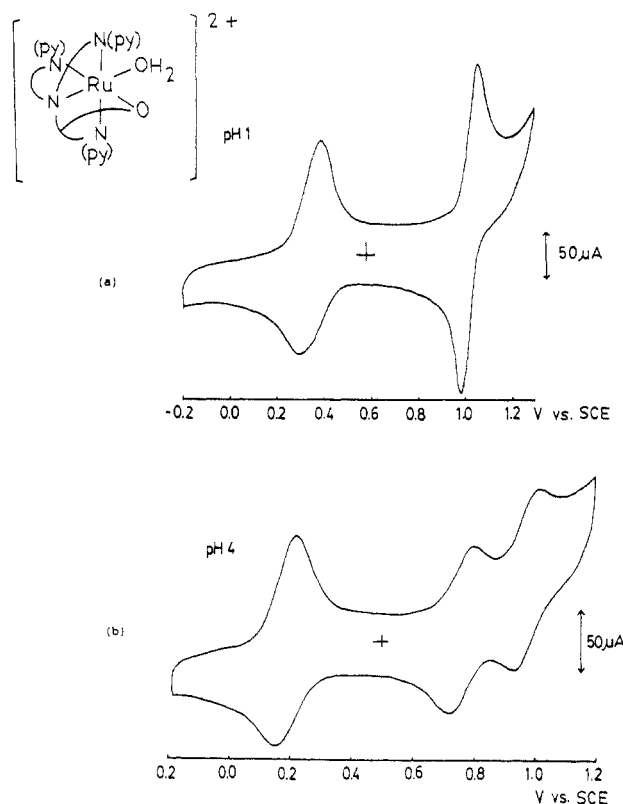


Figure 3. Cyclic voltammogram of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})](\text{ClO}_4)_2$ in (a) 0.1 M HClO_4 + 0.1 M NaClO_4 (pH 1) and (b) acetate buffer (pH 4): working electrode, EPG; scan rate, 100 mV s^{-1} .

$[\text{Ru}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ [2.016 (4)–2.037 (5) Å]²⁵ and *trans*- $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ (2.007 (3) Å).²⁴ The Ru–O(1) distance of 1.961 (4) Å for the alkoxy group is considerably shorter than the Ru–O(2) distance. This is understandable since the alkoxy group is a better σ donor than H_2O , and there is considerable overlap between the $p_\pi(\text{O})$ and $d_\pi(\text{Ru})$ orbitals. To the best of our knowledge, there are few structures on alkoxyruthenium, and the reported examples all show short metal–alkoxide distance, for example, Ru–O(alkoxide) distances in $[\text{Ru}^{\text{IV}}(\text{TPP})(p\text{-OC}_6\text{H}_4\text{CH}_3)]_2\text{O}^{26}$ and $[\text{Ru}^{\text{III}}(\text{TPP})(\text{OEt})(\text{EtOH})]^{26}$ (H_2TPP = *meso*-tetraphenylporphyrin) are 1.944 (11) and 2.019 (3) Å, respectively.

The measured Ru–N(tertiary) and Ru–N(py) distances of 2.087 (5) and 2.083 (5)–2.101 (5) Å are similar and are comparable to those values found in other Ru(III) systems. For example, the Ru–N distances in $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ ²⁷ and $[(\text{H}_2\text{O})(\text{bpy})_2\text{Ru}^{\text{III}}]_2\text{O}^{4+}$ ²³ are 2.104 (4) and 2.029 (5)–2.089 (4) Å, respectively.

The Ru–O(1)–C(2) angle of 102.8 (3)° is much smaller than the values of 128.4 (8)°–132.2 (10)° for the alkoxy Ru–O–C angle in $[\text{Ru}(\text{TPP})(p\text{-C}_6\text{H}_4\text{CH}_3)]_2\text{O}^{26}$ and 124.5 (2)° in $[\text{Ru}^{\text{III}}(\text{TPP})(\text{OEt})(\text{EtOH})]^{26}$ reflecting the distortion required for the coordination. The O(1)–C(2)–C(1) bond angle of 109.1 (5)° is similar to the analogous angle in $[\text{Ru}^{\text{III}}(\text{TPP})(\text{OEt})(\text{EtOH})]$ (111.6 (3)°).²⁶ The bond distances and angles in the pyridine rings are typical of those found in other pyridine systems where values of about 118° and 122°, respectively, are usually observed.²⁸

Electrochemistry. The cyclic voltammogram of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ shows two couples, I and II, at 0.35 and 1.02

Table III. pH Dependence on Cyclic Voltammetric Data of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in Aqueous Medium^a

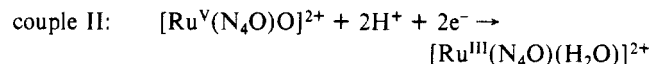
| (i) pH 1.0–3.0 | | | |
|------------------|------------------------------|------------------------------|----------------------------|
| pH | $E_{1/2}[\text{Ru(III/II)}]$ | $E_{1/2}[\text{Ru(V/III)}]$ | |
| 1.1 | 0.35 | 1.02 | |
| 2.0 | 0.28 | 0.97 | |
| 3.0 | 0.24 | <i>b</i> | |
| (ii) pH 4.0–10.0 | | | |
| pH | $E_{1/2}[\text{Ru(III/II)}]$ | $E_{1/2}[\text{Ru(IV/III)}]$ | $E_{1/2}[\text{Ru(V/IV)}]$ |
| 4.0 | 0.19 | 0.76 | 0.98 |
| 5.0 | 0.13 | 0.67 | 0.96 |
| 6.0 | 0.04 | 0.57 | 0.96 |
| 7.0 | −0.06 | 0.50 | 0.97 |
| 10.0 | −0.26 | 0.33 | 0.97 |

^a All potentials are reported in V vs SCE. Working electrode, EPG; scan rate, 100 mV s^{-1} ; ionic strength, 0.20 M. ^b A broad couple at 0.89 V vs SCE is observed, assignable to the Ru(IV/III) couple.

V vs SCE with an edge-plane pyrolytic graphite electrode in aqueous medium at pH = 1 (Figure 3a). Couple I has been assigned as the Ru(III/II) couple (controlled potential coulometry, $n = 0.987$; $\Delta E_p \approx 60 \text{ mV}$; $i_{pa}/i_{pc} \approx 1$). Couple II is a two-electron Ru(V/III) couple which begins to split as the pH is increased into two quasi-reversible one-electron couples, III and IV, appearing at 0.76 and 0.98 V vs SCE, respectively, at pH = 4.0 (Figure 3b). Couple III has been assigned to a Ru(IV/III) couple and couple IV to a Ru(V/IV) couple. Rotating disc voltammetric experiments also verified the two-electron nature of couple II with limiting currents of couples III and IV being the same as that of couple I (rotating speed, 400 rpm; scan speed, 5 mV s^{-1} ; EPG; pH = 4, acetate buffer) (Supplementary Material, Figure S1).

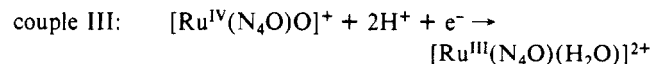
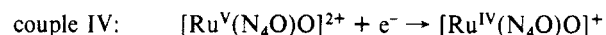
As the pH of the medium is raised, the formal potentials of couples I, II, and III will shift cathodically, while that of couple IV remains relatively independent of pH. A Pourbaix diagram of the half-wave potentials versus pH of the medium over the pH range 1–10 is shown in Figure 4, and a summary of the results is tabulated in Table III.

At pH < 3.5, the Ru(V/III) couple appears at the expense of the Ru(V/IV) and Ru(IV/III) couples. Its E° increases linearly with decreasing pH with a slope of –57 mV/pH unit. This is in accordance with a two-proton two-electron process represented by



Similar proton-coupled electron-transfer reactions have also been observed in other oxo/aquo complexes of osmium,²⁹ ruthenium,^{22,29c,30} and rhenium.³¹

At 5.5 > pH > 3.5, the wave for the Ru(V/III) couple splits into two waves, a pH-independent one-electron wave for the Ru(V/IV) couple (slope = 0 mV/pH unit) and a two-proton one-electron wave with a slope of –117 mV per pH unit, consistent with the $2\text{H}^+/1\text{e}^-$ nature of the couple. These are represented by



The direct reduction of Ru(V) to Ru(III) in acidic medium (pH < 3.5) implies that Ru(IV) is thermodynamically unstable

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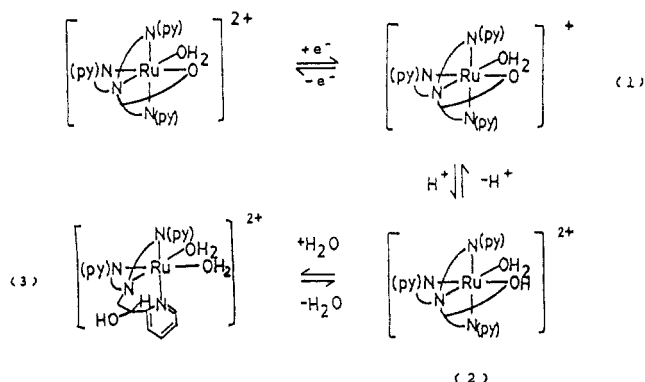
(28) Cheng, P. T.; Loescher, B. R.; Nyburg, S. C. *Inorg. Chem.* **1971**, *10*, 1275.

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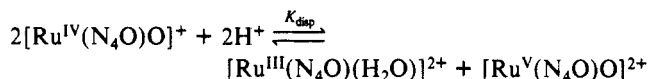
(30) (a) Che, C. M.; Wong, K. Y.; Poon, C. K. *Inorg. Chem.* **1985**, *24*, 1797. (b) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

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Scheme II

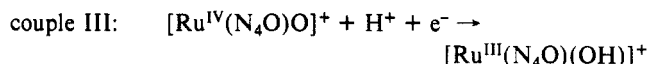


with respect to disproportionation into Ru(III) and Ru(V) under these conditions:

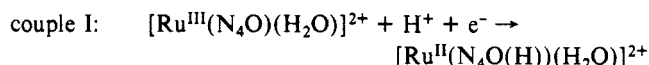


where K_{disp} is calculated to be $110 \text{ mol}^{-2} \text{ dm}^6$ ($\Delta G_{\text{disp}} = -11.6 \text{ kJ mol}^{-1}$, $\Delta E_{1/2\text{disp}} = 0.12 \text{ V}$ at 25°C at $\text{pH} = 1$).³² The positive K_{disp} value suggests that at $\text{pH} < 3.5$ E° for Ru(IV/III) must occur at more positive potential than for Ru(V/IV) so that thermodynamically, no Ru(IV) can build up in solution to a significant degree.

At $10 > \text{pH} > 5.5$, the Ru(IV/III) couple remains quasi-reversible with a slope of -61 mV/pH unit. The change of slope suggests a one-proton one-electron process in this pH range:

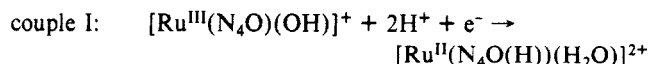


Similarly, the Ru(III/II) couple shows changes of slope in the Pourbaix diagram. At $\text{pH} < 5.5$, the Ru(III/II) couple has been shown to be a one-proton one-electron wave as demonstrated by the slope of -58 mV/pH unit in the Pourbaix diagram where



The one-electron reduced form of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ in 0.1 M HClO_4 has been characterized by UV-vis spectrophotometry.³³ At $1 < \text{pH} < 4$, both the $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ and $[\text{Ru}^{\text{II}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^+$ ions should exist in the nonprotonated form. Hence the redox potential accompanying the electrode reaction, $\text{Ru(III)} + \text{e}^- \rightarrow \text{Ru(II)}$, is expected to be pH independent. The fact that the E° for the Ru(III/II) couple decreases by 60 mV per pH unit suggests that one site in the N_4O^- ligand is protonated during reduction. We believe that this is due to the presence of the alkoxide group which easily dissociates off from the electron-rich Ru(II) center and undergoes protonation to N_4OH as shown in Scheme II. The observed reversibility of the Ru(III)/Ru(II) couple indicates that the reverse steps in eq 2 and 3 are very fast in the time scale of electrochemical measurements.

At $5.5 < \text{pH} < 7$, the slope becomes -114 mV/pH , consistent with a two-proton one-electron process which is represented by



As the pH is increased further, the couples Ru(III/II) and Ru(IV/III) become more and more irreversible, probably resulting from the difficulties encountered in the protonation step.

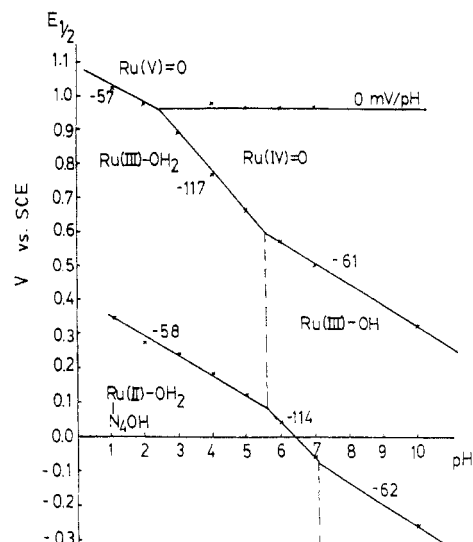


Figure 4. Pourbaix diagram of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ at different pH values: working electrode, EPG; scan rate, 100 mV s^{-1} .

Oxoruthenium(V) Complex. Magnetic susceptibility measurement showed that this Ru(V) complex is paramagnetic. The measured μ_{eff} of $2.2 \mu_{\text{B}}$ is higher than that found in *trans*- $[\text{Ru}^{\text{V}}(\text{TMC})\text{O}_2]^+$ (μ_{eff} , $1.93 \mu_{\text{B}}$).³⁴ With reference to previous spectroscopic studies on metal-oxo system, the energies of the d orbitals fall in the order, $d_{xy} < d_{xz}, d_{yz} \ll d_{x^2-y^2} < d_{z^2}$.³⁴ A $(d_{xy})^2(d_{\pi^*})^1$ ($d_{\pi^*} = d_{xz}, d_{yz}$) ground-state electronic configuration is expected for $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$. The measured higher μ_{eff} than the spin-only value for one unpaired electron suggests orbital contribution to the magnetic moment.

In the spectrophotometric redox titration of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ in 0.1 M HClO_4 using $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{bpy})]^{2+}$ as the redox titrant, the visible absorption peak of $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{bpy})]^{2+}$ at 522 nm is found to decrease in intensity with the occurrence of isosbestic points at 440 , 372 , and 345 nm (Supplementary Material, Figure S2). A stoichiometry of $1:3$ has been obtained suggesting the three-electron reduction of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$. This is in accordance with the Ru(V) formulation since at $\text{pH} = 1$, the E° of the Ru(III/II) couple for $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ is lower than that for $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{bpy})]^{2+}$ ($E^\circ = 0.26 \text{ V vs SCE}$).³⁵

The IR spectrum of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$ shows an intense Ru=O stretch at 872 cm^{-1} (Supplementary Material, Figure S3), which is absent in the $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ complex. The much higher ν (Ru=O) than those values of $790\text{--}810 \text{ cm}^{-1}$ found in monooxoruthenium(IV) complexes such as *trans*- $[\text{Ru}^{\text{IV}}(\text{TMC})\text{O}(\text{X})]^{n+}$ ($\text{X} = \text{Cl}, \text{NCO}, \text{N}_3, \text{CH}_3\text{CN}$)³⁴ and $[\text{Ru}^{\text{IV}}(\text{trpy})(\text{bpy})\text{O}]^{2+}$ ³⁶ suggests a stronger Ru=O bond in Ru(V) than Ru(IV). Except for the differences noted, the IR spectra of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ in the range $4000\text{--}600 \text{ cm}^{-1}$ appear quite similar, which support the conclusion that the $\text{Ru}(\text{N}_4\text{O})$ unit remains intact in the oxidation process. The close resemblance of the electronic absorption spectra of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ (Figure 5) suggests that the spectra are dominated by the $\pi \rightarrow \pi^*$ transition of the ligand, and d-d transitions, if present, are usually very weak and will be masked by the intense intraligand transitions.

Oxidation Reactions of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$. The $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$ complex is fairly stable in solid state for several days when kept at low temperature (ca. 0°C). In fluid solutions, it is easily reduced back to the $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ complex, and the reaction rate appears to be much faster at high concentration of the ruthenium complex. Unlike *trans*- $[\text{Ru}^{\text{V}}(\text{TMC})\text{O}_2]^+$,^{4b} this Ru(V) complex does not disproportionate in acidic solutions. It

(32) $K_{\text{disp}} = [\text{Ru}^{\text{III}}\text{--H}_2\text{O}][\text{Ru}^{\text{V}}\text{=O}]/[\text{Ru}^{\text{IV}}\text{=O}]^2[\text{H}^+]^2$ is the disproportionation equilibrium constant for the reaction, which can be estimated by using the $E_{1/2}$ values for the couples II, III, and IV at $\text{pH} = 1$, i.e., $E_{1/2\text{disp}} = E_{1/2}(\text{IV/III}) - E_{1/2}(\text{V/IV})$ where $E_{1/2}(\text{IV/III}) = 2E_{1/2}(\text{V/III}) - E_{1/2}(\text{V/IV})$ and $\Delta G_{\text{disp}} = -nF\Delta E_{1/2\text{disp}}$ and $K_{\text{disp}} = \exp(-\Delta G_{\text{disp}}/RT)$.

(33) UV-vis spectrum of $[\text{Ru}^{\text{II}}(\text{N}_4\text{O}(\text{H}))(\text{H}_2\text{O})]^{2+}$ [λ/nm ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$)] in 0.1 M HClO_4 : 395 ($12\,640$), 248 ($15\,030$), 200 ($20\,000$).

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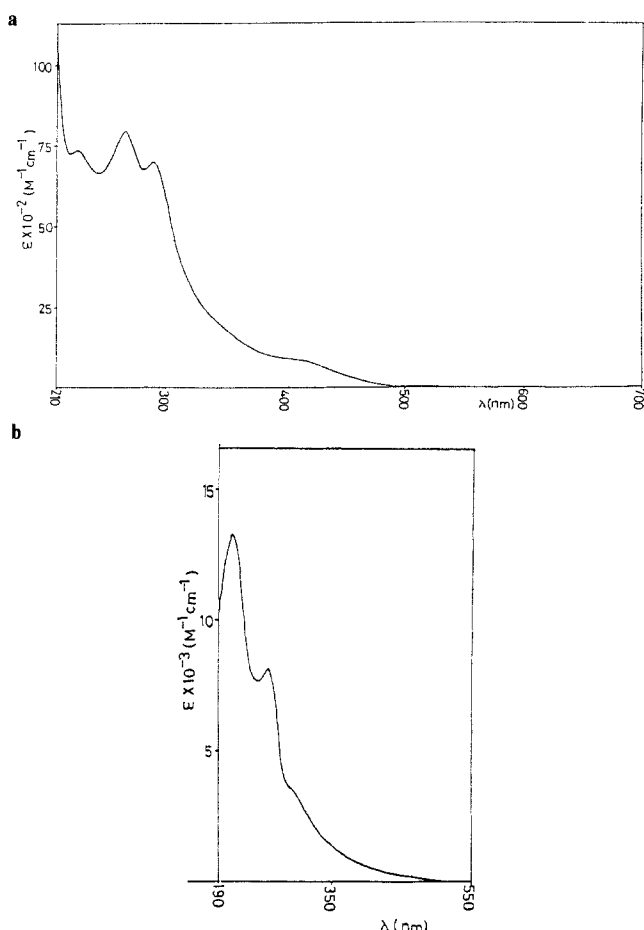


Figure 5. (a) UV-vis spectrum of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})\text{OH}_2](\text{ClO}_4)_2$ in deionized water and (b) UV-vis spectrum of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$ in deionized water.

is found to oxidize NaCl or HCl to Cl_2 under mild conditions (yield, 26% at 25 °C). The oxidation reaction occurs readily with immediate spectral change from $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$. Moreover, the $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex is found to be a powerful stoichiometric oxidant for organic substrates, the results of which are summarized in Table IV. All reactions occur at room temperature under degassed conditions and are completed within 10–20 min. These stoichiometric oxidation reactions have been found to be accompanied by the concomitant reduction of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$. For alcohols, it oxidizes benzyl alcohol, 4-methylbenzyl alcohol, and heptan-1-ol to the respective benzaldehyde, *p*-tolualdehyde, and heptanal in quantitative yields.³⁷ With arenes such as styrene and *cis*- and *trans*-stilbenes, oxidative cleavage of the C=C double bond to give benzaldehyde appears to be the dominant reaction pathway. The $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ is also capable of oxidizing tetrahydrofuran to γ -butyrolactone in almost quantitative yield. More important is the finding that $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ is capable of oxidizing saturated hydrocarbons such as cyclohexane and adamantane, with the reaction completed within 20 min. The detection of cyclohexanone indicates that this $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex is effective in the oxidation of unactivated C–H bonds.³⁸ Oxidation of adamantane gave 1-adamantanol exclusively with only trace amounts of 2-adamantanol and 2-adamantanone detected, indicating the higher selectivity of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ toward oxidation of the tertiary C–H bond. On the other hand, oxidation of norbornylene with $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ affords no *exo*-2,3-ep-

Table IV. Oxidation of Organic and Inorganic Substrates by $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$ in Acetonitrile at 25 °C

| substrate | product | yield, ^a % |
|------------------------|----------------------------|-----------------------|
| benzyl alcohol | benzaldehyde | 100 |
| 4-methylbenzyl alcohol | <i>p</i> -tolualdehyde | 90 |
| styrene | benzaldehyde | 39 |
| | styrene oxide | 3 |
| heptan-1-ol | heptan-1-al | 90 |
| cyclohexane | cyclohexanone | 60 |
| <i>trans</i> -stilbene | benzaldehyde | 58 |
| <i>cis</i> -stilbene | benzaldehyde | 55 |
| tetrahydrofuran | γ -butyrolactone | 70 |
| adamantane | 1-adamantanol ^b | 40 |
| hydrochloric acid | chlorine | 26 |
| sodium chloride | chlorine | 26 |

^a Based on metal complex used. ^b Trace amounts of 2-adamantanol and 2-adamantanone were also detected.

oxynorbornane. However, immediate spectral change from $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ is observed upon addition of norbornylene to an acetonitrile solution of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$. Most probably the norbornylene is oxidized to some unknown products, possibly via the oxidative cleavage of the C=C double bond.

In a previous study, we reported that $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ catalyzes the oxidation of olefins by PhIO.⁹ In this work, we find that the catalytic oxidation probably involves $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ as one of the possible reactive intermediates. Addition of PhIO to an acetonitrile solution of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ readily generated $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$, which can be rapidly and quantitatively reduced back to the starting Ru(III) complex upon addition of styrene, alcohols, and norbornylene. A direct comparison between the reactivities of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ –PhIO with arenes and olefins reveals that the two systems react differently. In the “ $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ –PhIO” system,⁹ epoxides were found as one of the major organic products, which are different from the results found for the stoichiometric oxidation by $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ (Table IV). It is likely that in the “ $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})]^{2+}$ –PhIO” system, more than one reactive intermediate may be present.³⁹ Nevertheless, results clearly demonstrate that the $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex is an active oxidant in the oxidation of both organic and inorganic substrates.

Concluding Remarks

Two new ruthenium complexes, $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})(\text{H}_2\text{O})](\text{ClO}_4)_2$ and $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$, were synthesized. The successful isolation of the highly oxidizing $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex lies in the fact that the N_4O^- ligand, with its anionic chelating nature and resistance toward oxidation, renders the stabilization of high oxidation state and hence formation of stable strongly oxidizing metal complexes possible. In fact, the approach of employing oxidation resistant anionic ligands to produce metal complexes in high oxidation states capable of exhibiting unique forms of oxidation reactivity has been a major direction in the design of potential oxidants. The $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ complex has provided us an opportunity to investigate the oxidation chemistry of the Ru(V)=O system. Simple molecular orbital theory would predict that the metal-oxo bond in oxoruthenium(V) with only one electron in the antibonding d_{π}^* orbitals should be stronger than that in oxoruthenium(IV) $[\text{Ru}(\text{IV}), (d_{xy})^2(d_{xz})^1(d_{yz})^1]$. The fact that the $\nu(\text{Ru}=\text{O})$ stretching frequency of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ is substantially higher than that for other monooxoruthenium(IV) complexes^{3a,36} indicates a stronger metal-oxo bond in Ru(V). The strong metal-oxo bond together with the high redox potential of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ would render the oxo group to be very electrophilic, leading to a high affinity of Ru(V)=O in hydrogen atom/hydride abstraction.

(37) No benzoic acids were detected by both UV-vis and ¹H NMR spectroscopy. This is understandable since alcohols were present in large excess in the oxidation reactions.

(38) Preliminary results showed that the oxidation of substituted benzyl alcohols, tetrahydrofuran, cyclohexane, and styrene by $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ in CH₃CN revealed a second-order kinetics with rate = $k[\text{Ru}(\text{V})][\text{substrate}]$. Mechanistic details will be reported subsequently.

(39) Hill and co-workers reported that the reaction between Mn(TPP)-(OAc) (H₂TPP = tetraphenylporphyrin) and PhIO yielded a manganese complex with coordinated PhIO, $[\text{PhI}(\text{OAc})\text{O}]_2\text{Mn}^{\text{IV}}(\text{TPP})$, which is active toward alkane oxidation and olefin epoxidation (Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 2920). It is likely that similar Ru–PhIO intermediates may be present in the catalytic oxidation reactions.

The high E° for the Ru(V/III) couple renders $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ capable of oxidizing Cl^- to Cl_2 in aqueous solution. Similar results were obtained by Meyer and co-workers based on the $[(\text{bpy})_2(\text{O})\text{Ru}^{\text{V}}]_2\text{O}^{4+}$ dimeric species.⁴⁰ This suggests that oxidation of Cl^- to Cl_2 depends only on the redox potential of the oxidant concerned, irrespective of its dimeric or monomeric nature.

The observation that $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ is capable of oxidizing the unactivated C–H bond in cyclohexane leads us to believe that high-valent ruthenium-oxo complexes, if suitably designed, have potential application in selective oxidation of alkanes. We believe that the ability of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ in cyclohexane oxidation probably lies in its high redox potential since other complexes such as *trans*- $[\text{Ru}^{\text{VI}}(\text{TMC})\text{O}_2]^{2+}$ ^{3b} and $[\text{Ru}^{\text{IV}}(\text{trpy})(\text{bpy})\text{O}]^{2+}$ ⁴¹ having lower reduction potentials are found to be relatively unreactive in cyclohexane oxidation.

In a previous study, it has been found that *trans*-dioxo-ruthenium(V) of amines rapidly disproportionates in solution^{4b} and that Ru(IV)=O complexes such as *trans*- $[\text{Ru}^{\text{IV}}(\text{TMC})\text{O}(\text{CH}_3\text{CN})]^{2+}$ ^{3d} and $[\text{Ru}^{\text{IV}}(\text{trpy})(\text{bpy})\text{O}]^{2+}$ ⁴¹ remain stable in acidic

solutions. In this work, the $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}]^{2+}$ ion remains stable in acidic solution, whereas the $[\text{Ru}^{\text{IV}}(\text{N}_4\text{O})\text{O}]^+$ ion disproportionates. It thus appears that the stability of Ru=O complexes toward disproportionation may not have any correlation with the oxidation state and hence electronic configuration of the central ruthenium ion. The nonlabile coordinated ligands, which will affect the redox potentials of the Ru=O complexes and the pK_a values of the "Ru=O" moiety may contribute significantly to the stability of Ru=O complex in a given oxidation state.

Acknowledgment. Financial support from the University of Hong Kong and the Croucher Foundation (C.M.C. and V.W.W.Y.) are gratefully acknowledged. We thank Clare Ho for repeating some of the stoichiometric oxidations in acetonitrile. V.W.W.Y. acknowledges the receipt of scholarships from Li Po Chun and Croucher Foundation.

Supplementary Material Available: Tables of hydrogen atomic coordinates and thermal parameters and anisotropic thermal parameters, rotating disk voltammogram of $[\text{Ru}^{\text{III}}(\text{N}_4\text{O})\text{OH}_2](\text{ClO}_4)_2$ in pH 4 acetate buffer, (Figure S1), spectrophotometric redox titration of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$, (Figure S2), and IR spectrum of $[\text{Ru}^{\text{V}}(\text{N}_4\text{O})\text{O}](\text{ClO}_4)_2$ (Figure S3) (5 pages); table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Solid-Phase Peptide Synthesis of the α and β Domains of Human Liver Metallothionein 2 and the Metallothionein of *Neurospora crassa*

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Abstract: The Cys-rich peptides corresponding to the α and β domains of human liver metallothionein 2 (MT-2) and the MT from *Neurospora crassa* (NcMT) have been prepared for the first time by solid-phase peptide synthesis and purified by HPLC. These synthetic peptides bind Cd(II), Ag(I), and Cu(I) in identical stoichiometries with the proteolytically derived domains from rat and rabbit liver MT and the natural NcMT. Absorption and CD features observed upon Cd(II) and Cu(I) binding to the synthetic peptides are qualitatively similar to those reported for the natural domains and NcMT. ¹¹³Cd NMR of the synthetic Cd₄ α domain indicates that three of the metal ions are in environments identical with those in the whole protein and in the proteolytically derived α domain; the chemical shift of the fourth Cd(II), which is located near the junction with the β domain, indicates this metal ion is in a somewhat different environment than in the native protein. Thus, we have shown that it is possible to use solid-phase peptide synthesis to prepare MT. This demonstrates the successful use of solid-phase methods for peptides with high Cys content and now provides a methodology for the facile sequence modification of MT.

Metallothioneins (MT)¹ are a class of small (~61 amino acids), ubiquitous, cysteine-rich (~30%) proteins that typically bind 7 (Cd(II), Zn(II)) or ~12 (Cu(I), Ag(I)) metal ions through metal–thiol ligation. They have been shown to bind essential (Cu(I), Zn(II)) as well as toxic (Cd(II), Hg(II)) metal ions in vivo, and although their biological role is not clear, it is likely they are involved in metal ion metabolism. The 25-residue MT from *Neurospora crassa* (NcMT) shows² Cys homology with the N-terminal (β) domain of MT from higher organisms and appears to play a role in Cu metabolism in the fungus.

Initial ¹¹³Cd NMR studies³ of Cd₇MT indicated that this metal ion was bound in isolated three- and four-metal clusters with Cys

ligation. Subsequently, enzymatic cleavage methods were developed to isolate⁴ the 31–61-residue α domain that binds the four-Cd(II) cluster and later separate⁵ the 1–31-residue β domain that binds the three-Cd(II) cluster. Proteolytic preparation of the two domains is possible on the basis of differential metal ion binding by the two peptide segments; Cd(II) binds more strongly as a four-ion cluster in the α domain and stabilizes it toward

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