(μ-Hydroxo)(triethylenetetraminehexaacetato)diruthenate(II,III) and Related -(II,II), -(III,III) and -(III,IV) Complexes

Songsheng Zhang and Rex E. Shepherd*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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A series of binuclear $[Ru_2(ttha)]^{n-}$ complexes, $ttha^{6-}$ = triethylenetetraminehexaacetate, have been prepared. These include $[Ru^{II}_2(ttha)(H_2O)_2]^{2-}$ = (II,II), $[Ru^{III}_2(ttha)(H_2O)_2]$ = (III,III), $[Ru^{II}Ru^{III}(OH)(ttha)]^{2-}$ = (II,III), and $[Ru^{III}ORu^{IV}(ttha)]^-$ = (III,IV). The stable forms of (II,II) and (III,III) are the extended chain species having separate Ru centers in chemical binding sites virtually equivalent to the monomeric $[Ru^{II/III}(hedta)]^{-/0}$ complexes. CO complexes of (II,II) and the open-chain isomer (II,III)$_o$, which exists below pH 4, readily form (ν_{CO} = 1943 and 1941 cm^{-1}, respectively) showing the presence of labile $Ru^{II}-OH_2$ sites. Above pH 5 (II,III) exists as the hydroxy-bridged $Ru^{II}(OH^-)Ru^{III}$ mixed-valence species having a band at 527 nm (ϵ/Ru = 1.47 × 10^3 M^{-1} cm^{-1}) which is most likely of $\sigma^*(d_{x^2-y^2}, d_{z^2}) \leftarrow d\pi^*$ origin. The Ru^{II} site is inaccessible to CO in the bridged complex, (II,III)$_b$. $[Ru^{II}Ru^{III}(OH)(ttha)]^{2-}$ is a unique example of a $M^{II}XM^{III}$ bridged complex of the iron group which exists in solution without secondary, rigid bridging ligands such as carboxylate and phosphate ions, in addition to the X bridge (oxo or hydroxo), enforcing the stability of the $M^{II}M^{III}$ species; all known prior examples dissociate into monomeric complexes. However, the proximity of the binuclear centers which is afforded by the $ttha^{6-}$ ligand with a central ethylene bridge between two metal ion sites facilitates formation of $Ru^{III}ORu^{III}$, $Ru^{III}ORu^{IV}$, and $Ru^{II}(OH)Ru^{III}$ entities without additional inflexible metal-bridging ligand attachments, typical of μ-oxo–bis-(μ-carboxylate) bridging. Electrochemical methods have been used to measure a comproportionation constant, K'_c, for the reddish-purple (II,III) complex equal to 18, indicative of a delocalization energy of less than 1.7 kcal/mol and a type II mixed-valence species. Oxidation of (II,III) by Ce^{IV}, O_2, or H_2O_2 yields a metastable golden yellow-brown (III,III)$_b$ species. (III,III)$_b$ has an oxo-bridged structure which aquates into the extended chain structure (III,III)$_o$ that appears straw yellow (k = 2.50 × 10^{-3} s^{-1}). Prolonged air oxidation of (III,III)$_o$ generates the oxo-bridged (III,IV) complex with virtually identical spectral properties of the known $[Ru^{III}ORu^{IV}(edta)_2]^{3-}$ complex. A band at 620 nm (ϵ/Ru = 1.18 × 10^3 M^{-1} cm^{-1}) imparts the characteristic green color to the type III mixed-valence (III,IV) complex. The (III,IV) complex exhibits an enhanced IR band at 877 cm^{-1} similar to a band at 870 cm^{-1} for the $[Ru^{III}ORu^{IV}(edta)_2]^{3-}$ analogue. Oxidation of (III,IV) to (IV,IV) occurs at 1.20 V vs NHE while the (III,IV) to (III,III)$_b$ reduction appears at 1.14 V. An oxidation wave for the (III,III)$_o$ → (III,IV)$_b$ process was identified at 0.83 V.

Introduction

Metal hydroxy- and oxo-bridged mixed-valence complexes play the central chemical role for some biomolecules in photosystem II and mammalian purple acid phosphatases and in some gem minerals such as sapphire. Mixed-valence oxo- and hydroxy-bridged complexes are also of considerable interest for understanding intervalence electron transfer chemistry as a complement to the many studies wherein organic N-heterocycles serve as electron conduits between the metal sites.[1–6]

Numerous binuclear complexes containing Ru^{II} and Ru^{III} sites connected by bridging N-heterocyclic ligands L such as pyrazine, 4,4'-bipyridine and pyrimidine have been prepared with the generalized formulas $(L')_5RuLRu(L')_5$, L' = NH$_3$ or 2,2'-bipyridine (bpy). The spectroscopic, electrochemical, and theoretical aspects of these pentaammine and bipyridine complexes have been extensively reviewed.[1–6] Fewer studies have

been made with polyaminopolycarboxylate (pac) complexes of ruthenium wherein the (L')$_5$ donor set is composed of combinations of amine and carboxylate donors.[7–13]

Our current paper presents observations concerning ruthenium-bridged binuclear complexes of $ttha^{6-}$ ($ttha^{6-}$ = triethylenetetraminehexaacetate ion). $[Ru_2(ttha)X]^{n-}$ where X = OH$^-$ or O^{2-} and the Ru centers adopt oxidation states from II to IV. The ligand $ttha^{6-}$ is capable of coordinating metals in either extended configuration as shown in structure **1A** with two

1A   **1B**
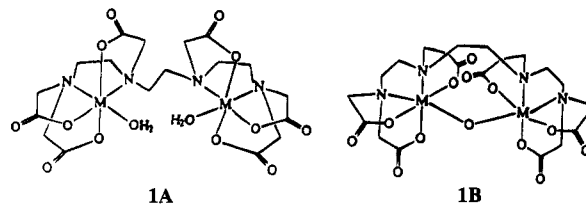
separate N$_2$O$_3$-pac ligating sites or with metal centers placed

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side-by-side and bridged by a suitable intervening ligand (**1B**). The [Ru$^{II}_2$(ttha)(H$_2$O)$_2$]$^{2-}$ complex and its bis adducts with π-acceptor ligands, Ru$^{II}_2$(ttha)L$_2$$^{2-}$ (L = CO, 2-methylpyrazine, olefins, and 4,4'-bipyridine), exist in an extended geometry,[14] also known for Fe^{II};[15] Co^{II}, Ni^{II}, Cu^{II};[16] Zn^{II};[17] Cr^{III};[18] Ti^{III};[19] and VO^{2+}.[20,21] The V^{III} and Fe^{III} binuclear ttha^{6-} complexes are μ-oxo bridged.[15,22,23] The [Ru$^{II}_2$(ttha)]$^{2-}$ unit can be bridged by pyrimidine, which has the proper angles to accommodate the side-by-side ruthenium sites.[24] Pyrimidine affords only weak metal-metal coupling in the (II, pym, III) complex of ttha^{6-}.[24]

Smaller ligand bridges (N$_2$, C$_2$N$_2$, CN$^-$) are known to improve metal–metal coupling in the [(NH$_3$)$_5$Ru^{II}LRu^{III}(NH$_3$)$_5$]$^{5+}$ and [(NH$_3$)$_5$Ru^{III}LRu^{II}(CN)$_5$] series.[1-6,25-27] Therefore, it was of interest to us to obtain complexes of [Ru$_2$(ttha)]$^{n-}$ with short two-atom or single atom bridging ligands to study the extent of coupling through bent bridges. We have accomplished this objective in the preparation of the hydroxy-bridged [Ru^{II}-Ru^{III}(ttha)(OH)]$^{2-}$ complex. In related cases, Baar and Anson[10] have conducted thorough electrochemical studies on the [Ru^{III}-Ru^{IV}(edta)$_2$] complex, shown by Hurst with resonance Raman experiments to be the μ-oxo-bridged [(edta)Ru^{III}ORu^{IV}(edta)]$^{3-}$ complex, (III,O^{2-},IV).[9] It is of importance for comparison with the present study that Baar and Anson[10] found the following: (i) (III,O^{2-},IV) is reduced to (III,O^{2-},III), but this species rapidly aquates into two [Ru^{III}(edta)(H$_2$O)]$^-$ monomers; (ii) no evidence for a (II,O^{2-},III) or (II,OH$^-$,III) bridged complex was obtained. Additionally, a recent study by Wieghardt et. al. pointed out that no stable monohydroxy-bridged Ru^{III}–OH–Ru^{III} complexes are known.[13]

Other related oxo-bridged binuclear ruthenium complexes have received careful study. The [(bpy)$_2$(H$_2$O)Ru^{III}ORu^{III}(H$_2$O)(bpy)$_2$]$^{4+}$ complex of Meyer et al.[28-30] and the 2,2'-bipyridyl-5,5'-dicarboxylic acid analogue of Gratzel and Hurst[31,32] have proven successful as catalysts for the oxidation of water.

Meyer's complex must be oxidized from its (III,III) level to (V,V) in order to catalyze the oxidation of water, but it retains the μ-oxo bridge in the process. Gratzel and Hurst have proposed a similar scheme via [L$_2$Ru^V(O)]$_2$O formation, followed by reductive elimination of O$_2$,[31] but have also claimed activity via L$_2$Ru^{III}–O–Ru^{IV}L$_2$ oxidants for H$_2$O.[32]

Oxo-bridged [(NH$_3$)$_5$RuORu(NH$_3$)$_5$]$^{n+}$ complexes have been characterized for n = 4, (III,III), and n = 5, (III,IV),[33] but no (II,III) complex has been isolated or characterized.[33] A binuclear Ru^{III} complex, [Ru$^{III}_2$(Me$_3$tcn)$_2$(RCO$_2$)(OH)]$^{3+}$, Me$_3$-tcn = 1,4,7-trimethyl-1,4,7-triazacyclonane, has been prepared by Wieghardt et al.[34] This complex may be oxidized from its (III,O^{2-},III) form to the (III,O^{2-},IV) species. Again only irreversible reductions were observed from the (III,O^{2-},III) complex to the (II,O^{2-},III) state; no characterization of any stable (II,III) forms were given.[34] For the related [[(Me$_3$-tcn)(acac)Ru^{III}]$_2$(O$_2$H$_3$)]$^{3-}$ complex, Wieghardt's group detected only dissociation into monomeric Ru^{II} and Ru^{III} complexes upon reduction in acetonitrile.[13]

The absence of stable oxo- or hydroxy-bridged mixed-valence ruthenium complexes is of some biochemical relevance. Binuclear complexes of the iron group having M^{II}M^{III} formal assignments are of interest as models for the purple acid phosphatases and uteroferrin proteins, which are binuclear Fe^{II}-Fe^{III} metalloproteins in their active forms.[35,36] The acid phosphatases catalyze the hydrolysis of phosphate esters.[35-39]

The ligation of the active enzymes is thought to involve tyrosine, aqua, histidine, and the hydroxy bridge for the Fe^{III} site and aspartate or glutamate, histidine, and the hydroxy bridge at Fe^{II}.[35] Therefore, mixed-oxidation state iron group amine and pac complexes could be of considerable interest in understanding the action of such enzymes. Several synthetic models for the oxidized, inactive forms containing μ-oxo-bridged Fe^{III} have been described. These include [(Me$_3$tcn)-Fe^{III}(μ-O)(μ-X)$_2$Fe^{III}(Me$_3$tcn)] complexes (X = phosphate, phenylphosphate, arsenate, or chromate),[40] which are isostructural with the Ru^{III} binuclear complex,[34] and tris(2-pyridylmethyl)amine (TPA) binuclear complexes having one oxo and one X bridge (X = benzoate, acetate, diphenylphosphate), [(TPA)Fe^{III}(μ-O)(μ-X)Fe^{III}(TPA)].[35,41] None of these models has yielded stable Fe^{II},Fe^{III} complexes. By contrast the [Ru^{II}-Ru^{III}(ttha)(OH)]$^{2-}$ complex of the present report is stable in

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aqueous solution under Ar and is chemically generated under mild conditions.

Experimental Section

Ru Complexes. $Na[Ru(hedta)(H_2O)] \cdot 4H_2O$ was prepared previously.[12b] The synthetic procedure was a modification of the synthesis of $Na[Ru(edta)(H_2O)]$ by Shimizu's procedure.[42] $Na_2[Ru_2(ttha)(H_2O)_2] \cdot H_2O$ was prepared by the same method using 2 mol of $RuCl_3$ per ligand. The product was standardized previously by titration with 2-methylpyrazine.[12b] Weighed amounts of $Na_2[Ru_2(ttha)(H_2O)_2] \cdot H_2O$ were dissolved in pipetted volumes of H_2O in bubblers purged by a flowing Ar stream over Zn/Hg. This pretreatment was carried out to assure the removal of traces of Ru^{III} which may form from oxidation of the Ru^{II} salts during storage or transfers. Ru^{II} salts were stored in a vacuum oven to minimize oxidation during storage. The $Ru_2(ttha)(H_2O)_2{}^{2-}$ solutions are very air sensitive. All manipulations were performed using gastight syringe techniques under Ar. The charges on $[Ru_2(ttha)L]^{n-}$ complexes were evaluated by their ion exchange mobility on AG-4X anion exchange resin in the Cl^- form. The column was prewashed with Ar-saturated H_2O in a glovebag prior to loading with the $[Ru_2(ttha)L]^{n-}$ complex. Elution was made with increasing amounts of deoxygenated NaCl solutions. Movement of $[Ru^{II,III}{}_2(ttha)(OH)]^{2-}$ with 1.0 M NaCl indicated an anion of 2- charge.

Oxidation of $[Ru^{II}{}_2(ttha)(H_2O)_2]^{2-}$ to $[Ru^{III}{}_2(ttha)(H_2O)_2]$ was carried out using 2 equiv of Ce^{IV}, 1 equiv of H_2O_2, or O_2. When O_2 was used, bubbling was continued until the reddish-purple color of the $Ru^{II}Ru^{III}$ intermediate had faded and the pale yellow color of the $Ru^{III}Ru^{III}$ complex was obtained. The $[Ru^{III}Ru^{IV}(ttha)]$ analogue of $[(edta)-RuORu(edta)]^{3-}$ was prepared by aerobic oxidation of $[Ru^{III}{}_2(ttha)-(H_2O)_2]$ by stirring a solution of the complex exposed to air for 3 days. The $[Ru^{III}Ru^{IV}(ttha)]$ complex has the green color of and solution spectral parameters similar to those of $[(edta)RuORu(edta)]^{3-}$.[9,10] Anion exchange showed complete conversion to a single product which moved with 0.2 or 0.5 M NaCl as a 1- ion, indicative of $[Ru^{III}Ru^{IV}O(ttha)]^-$, (III,IV).

The mixed oxidation state $Ru^{II}Ru^{III}$ complex was formed in one of several ways as needed. Method 1: $[Ru^{II}{}_2(ttha)(H_2O)_2]^{2-}$ was combined with 1 equiv of Ce^{IV} under Ar. The resultant solution was slowly increased in pH to near 7. The formation of $[Ru_2(ttha)(OH)]^{2-}$ was observed by the development of the reddish-purple solution color. This species was characterized by UV−visible and electrochemical methods described below. Method 2: $[Ru^{II}{}_2(ttha)(H_2O)_2]^{2-}$ was treated with $^1/_2$ equiv of H_2O_2, forming the same species as by the Ce^{IV} route when the pH was adjusted to neutral under Ar. Method 3: The method which proved to be the easiest was the cross-reaction between $[Ru^{II}{}_2-(ttha)(H_2O)_2]^{2-}$, (II,II), pretreated over Zn/Hg in solution, with an Ar-purged sample of $[Ru^{III}(ttha)(H_2O)_2]$, (III,III). (III,III) had been prepared separately by the air oxidation of (II,II). Mixing equal molar solutions of (II,II) and (III,III) then provided the equilibrium mixture of isovalent and mixed-oxidation state complexes. This method was used to prepare samples for electrochemical and spectral study and as a source of the solid containing $Na_2[Ru^{II}Ru^{III}(ttha)(OH)]$ for analysis by infrared, as it was the method most free of contaminants by other reagents. Method 4: Initial observations of the formation of (II,III) were made using O_2 oxidation of $[Ru^{II}(ttha)(H_2O)_2]^{2-}$ by admitting O_2 slowly through a syringe needle fitted to a stopcock which was connected to a balloon filled with O_2. After an aliquot of O_2 gas was admitted, the sample was stirred to allow for oxidation. The color of (II,III) was maximized. This arrangement allowed the slow admission of O_2 and the oxidation of (II,II) to (II,III). However the control of the extent of oxidation, forming (III,III) by over oxidation, was not good; this method was superceded by methods 1 to 3.

Infrared Samples. Solids for infrared examination of (III,III), (II,III), and (III,IV) were obtained as follows. (III,III) was obtained from air oxidation of (II,II) until the reddish-purple complex, (II,III), had oxidized. This procedure required only an hour. Oxidation was quenched well before any detectable amount of the green (III,IV) is generated, the latter process requiring 62 h. The (III,III) complex was obtained by concentration of the solution on a rotary evaporator. The

Na^+ salt precipitation was induced in the concentrated solution by the addition of ethanol. The product was filtered and dried under vacuum to remove excess ethanol. The same procedure was used to induce precipitation of the sodium salt of (III,IV), $Na[Ru_2(ttha)O]$. The sodium salt of the (II,III) complex was similarly obtained by rotary evaporation of a sample maintained under an Ar gas bleed for the duration of the reduction in pressure; precipitation was achieved by addition of Ar-purged ethanol. The salts obtained by this method are most likely contaminated with (II,II) and (III,III), given that the solution from which they are obtained contains about 9.5% of each isovalent species at equilibrium with (II,III). This is shown by the evaluation of K_c electrochemically in this report. No pure solid of (II,III) may be isolated unless there were a special precipitating cation of 2+ charge which selectively precipitates (II,III) faster than the redox isomerism can redistribute the species. The likely probability of precipitating (II,III) in the absence of coprecipitation of (II,II) is not high since both ions are large 2- anions. The resultant mixture of (II,III) with its isovalent forms in ca. 9-fold lesser abundance is qualitatively useful for comparison with the (III,IV) solid. (III,IV) is assigned as oxo-bridged due to its spectral similarity with other known (III,IV) complexes of ruthenium polycarboxylates[10] and the ion exchange behavior. Complexes of CO adducts of (II,II), $[Ru_2(ttha)(CO)_2]^{2-}$, and (II,III), $[Ru^{II}(CO)(ttha)Ru(H_2O)]^-$, were prepared by bubbling CO through either (II,II) or (II,III) at pH ∼ 3 for 1−3 h. Precipitation of the sodium salts were induced by addition of ethanol.

Instrumentation. UV−visible spectra were recorded on a Varian-Cary 118C spectrophotometer in Ar-purged 1.0, 2.0, and 0.20 cm quartz cells. pH-adjustments were made on the ruthenium solutions under Ar by means of microsyringe addition of standard NaOH or HCl. The pH was recorded with a Fisher Accumet digital pH meter, standardized against commercial buffers, prior to mounting the mini-combination glass electrode through one port of the glass Ru−reagent bubbler via a rubber septum. Aliquots for spectral analysis were removed by syringe from a second rubber septum port.

Electrochemical measurements, cyclic voltammetry (CV) and differential pulse polarography (DPP), were made with an IBM EC 225 voltametric analyzer using a glassy-carbon working electrode, saturated sodium chloride calomel electrode as the reference, and a platinum-wire auxiliary electrode. Measurements were made at 22 °C in 0.10 M NaCl as the electrolyte to prevent problems which arise from ruthenium oxidations by ClO_4^-. Standardization procedures vs $Ru(NH_3)_6$-Cl_3 have been described previously.[43,44] A 50 mV/s sweep was used for CV; a 40 mV/s sweep rate and a 50 mV stepping voltage were used for DPP.

EPR work for an attempted spin trapping experiment using DMPO as the radical trap was carried out using a Varian E-4 EPR as described previously.[12b,45] Spectra were obtained at room temperature in flat quartz cells. Seven-line spectra such as those for $[Ru(hedta)O_2]^-$ were absent.[45] Therefore, no free radicals indicative of long-lived superoxo complexes were observed. This method served to establish that the reddish-purple species formed upon admission of O_2 to (II,II) was not a superoxo complex.[45]

Infrared spectra were obtained on ground samples pressed at 9 tons into KBr disks. Infrared spectra were recorded with either an IBM IR/30S FTIR using 64 or 100 averaged scans or with a Cignus-Mattson 100 FTIR using 32 or 64 averaged scans.

Results and Discussion

Spectra of (II,II), (II,III), and (III,III). The N_2O_3 donor sets of the separate metal binding sites on $ttha^{6-}$ are similar to the N_2O_3 donors of the $hedta^{3-}$ ligand (N-hydroxyethylethyl-enediaminetriacetate). The UV−visible spectral maxima and extinction coefficients for Ru^{II} and Ru^{III} complexes of $hedta^{3-}$ and the binuclear ruthenium $ttha^{6-}$ complexes are given in Table 1 for comparison. The $[Ru^{II}{}_2(ttha)(H_2O)_2]^{2-}$ species exists in

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Table 1. UV−Visible Spectral Parameters for Ru(pac) or Related Me₃tcn Complexes[a]

complex	λ_{max} (nm)	ϵ (M⁻¹ cm⁻¹)	ref[b]
[Ru^{II}(hedta)H₂O)]⁻	420	2.00×10^2	
	280	2.92×10^3	
[Ru^{II}(edta)(H₂O)]²⁻	427	2.60×10^2	51
	282	2.90×10^3	51
[Ru^{III}(hedta)(H₂O)]	388	5.13×10^3	
[Ru^{III}(edta)(H₂O)]⁻	350	6.80×10^2	51
	280	2.80×10^3	51
[Ru$^{II}_2$(ttha)(H₂O₂]²⁻, (II,II)ₒ	425	4.25×10^2	
	285	5.75×10^3	
[Ru$^{III}_2$(ttha)(H₂O)₂], (III,III)ₒ	385	6.55×10^3	
[Ru^{II}Ru^{III}(OH)(ttha)], (II,III)ᵦ	527	2.94×10^3	
	385	2.49×10^3	
[Ru^{III}ORu^{IV}(ttha)]³, (III,IV)ᵦ	620	2.35×10^2	10
	388	1.02×10^4	10
[Ru^{III}ORu^{IV}(edta)₂]³⁻	632	4.11×10^2	
	394	2.00×10^4	
[Ru^{II}(OH)Ru^{III}(ttha)]²⁻	527	2.93×10^3	
	385	2.99×10^3	
[Ru^{III}ORu^{III}(Me₃tcn)₂(acac)₂]²⁺	596	1.24×10^4	13
	350	4.6×10^3	13
[Ru^{III}ORu^{IV}(Me₃tcn)₂(acac)₂]³⁺	537;580sh	5.7×10^3	13
	386	8.9×10^3	13

[a] Solution pH conditions were above pH 3 to prevent acid-induced aquations of carboxylato donors and below 4 for Ru^{III} monomeric species. (II,III)ᵦ is unstable below pH 5 (see text). [b] This work unless stated.

Figure 1. UV−visible spectra of (II,II), (II,III), and (III,III) complexes of the [Ru₂(ttha)]ⁿ⁻ series: curve 1 (− · −) [(II,II)] = 3.25 × 10⁻³ M, 1.0 cm cell; curve 2 (−), [(II,III)] = 5.76 × 10⁻³ M, 0.10 cm cell; curve 3 (- - -) [(III,III)] = 2.06 × 10⁻³ M, 0.10 cm cell. T = 22 °C.

solution with isolated ruthenium sites. The similarity of [Ru^{II}(hedta)(H₂O)]⁻, ϵ = 200 M⁻¹ cm⁻¹ at 420 nm, to the Ru^{II}−H₂O chromophore in (II,II) = [Ru$^{II}_2$(ttha)(H₂O)₂]²⁻, ϵ/Ru = 212 M⁻¹ cm⁻¹ at 425 nm, and that of [Ru^{III}(hedta)(H₂O)], λ_{max} 388 nm, ϵ = 5.13 × 10³ M⁻¹ cm⁻¹, compared to Ru^{III}(H₂O) in (III,-III) = [Ru$^{III}_2$(ttha) (H₂O)₂], ϵ/Ru = 3.28 × 10³ M⁻¹ cm⁻¹ at 385 nm is observed. The stable form of (III,III) is the extended chain form with isolated Ru^{III} sites. It will be shown later that an oxo-bridged (III,III) complex is obtained as an unstable intermediate from the oxidation of (II,III). The process which breaks the oxo-bridge yields the equilibrium (III,III) species whose spectral data are given in Table 1. Consistent with the facile oxo-bridge rupture of [Ru^{III}ORu^{III}(ttha)]²⁻, (III,III)ᵦ (the subscript b refers to the bridged form as discussed later), Baar and Anson observed the rapid aquation of [(edta)Ru^{III}ORu^{III}(edta)]⁴⁻ into [Ru^{III}(edta)(H₂O)]⁻ monomers at the mercury drop electrode.[10] The situation here is analogous, except that Ru^{III} sites in (III,III)ₒ and (III,III)ᵦ are held in close proximity by the intervening central (CH₂)₂ bridge along the the ttha⁶⁻ backbone. This contrasts with the [Fe$^{III}_2$O(ttha)]²⁻ complex which is stable in the μ-oxo form.[23]

Martell has offered the explanation that the μ-oxo dimers of [Fe^{III}(hedta)(OH₂)], and related species which form the Fe$^{III}_2$O⁴⁺ core unit, gain stability from superexchange of the d⁵ high-spin Fe^{III} centers across the oxo bridge.[46] Since Ru^{III} is low-spin d⁵ there would be substantially less stabilization offered from superexchange of the remaining unpaired electron. Martell et al.[46] state that this energetic factor is in competition with the energy gained by protonation of the bridge oxygen. When Fe^{III} is present, it is a stronger Lewis acid than Ru^{III} due to smaller size of of Fe^{III}. Thus, the higher acidity of an Fe^{III}−O(H)−Fe^{III} unit favors formation of the μ-oxo bridge when superexchange is allowed. But for Ru^{III} the lesser superexchange and lower acidity of a Ru^{III}−O−Ru^{III} chromophore will disfavor the oxo-bridged species. Additionally, Wieghardt states that none of the hydroxy bridged units have been observed.[13]
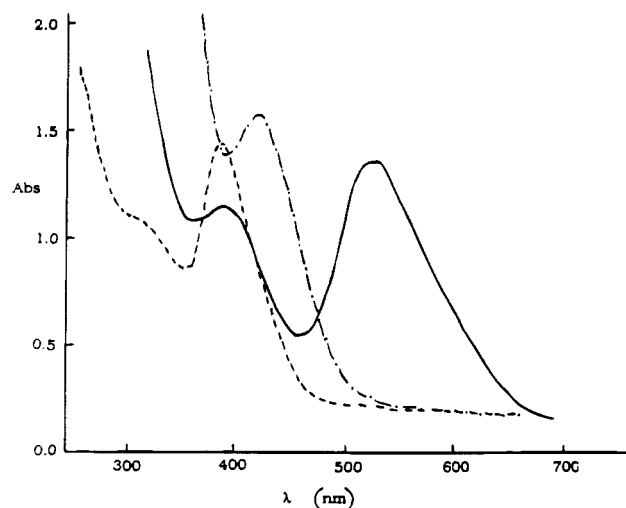
Further addition of H₂O across the oxo-bridged intermediate yields two Ru^{III}−OH bonds; this reaction should be more favorable for Ru^{III}. The net result will be rupture of the Ru^{III}−O−Ru^{III} bond by its reaction with H₂O.

It is interesting to note that the stable Ru^{III}−O−Ru^{III} complexes in solution are all cations[13,33,34] wherein protonation of the bridge oxo unit is disfavored by charge repulsion. With Ru−pacs, the more negative carboxylate donor environment reduces the Lewis acidity of the Ru^{III} centers. This favors Ru^{III}−O−Ru^{III} dissociation as observed both by Baar and Anson[10] for [(edta)Ru^{III}ORu^{III}(edta)]⁴⁻ and in this work with the (III,-III)ᵦ transitory complex [Ru$^{III}_2$O(ttha)]²⁻. It is of interest that the [Ru$^{III}_2$O(edta)₂]⁴⁻ complex dissociates more rapidly (on the electrochemical sweeping time scale) whereas the less basic [Ru$^{III}_2$O(ttha)]²⁻ (as predicted by lower negative charge) persists for 15 min. When the oxidation state of one of the ruthenium centers is raised to IV in (III,IV), the stable solution species is the μ-oxo-bridged complex (shown below). Thus the loss in Lewis acidity in increasing the radius from Fe^{III} to Ru^{III} can be regained by an increase in oxidation state to Ru^{IV}.
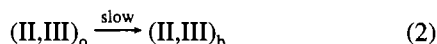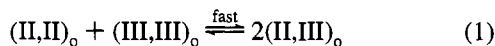
Spectra for (II,II), (II,III) and (III,III) are shown in Figure 1. A prominent band appears at 527 nm (ϵ/Ru = 1.47 × 10³) for (II,III) which is not present for isolated Ru^{II} or Ru^{III} chromophores. (II,III) was first observed by Myser[47] in our laboratories. On the basis of the assignments of Meyer[33] and Wieghardt[13] on related complexes, it is most likely that the 527 nm band originates as a σ* ← π* transition involving the filled nonbonding d$_{xy}$ metal-based MO's and the e*$_g$(d$_{x^2-y^2}$, d$_{z^2}$) metal-based MO's. The filling order for a 15 electron system, one d⁶, one d⁵, and four oxygen π electrons, would be $(\pi^b_1)^2$ $(\pi^b_2)^2$ $(\pi^n_{d_{xy}})^2$ $(\pi^n_{d_{xy}})^2$ $(\pi^n_1)^2$ $(\pi^n_2)^2$ $(\pi^*_1)^2$ $(\pi^*_2)^1$ (e*$_g$(d$_{x^2-y^2}$, d$_{z^2}$))⁰ (cf. refs 13 and 31). The excitation of a π^*_1 or π^*_2 electron to the e*$_g$ levels would possess some oxygen-to-ruthenium charge transfer character which is consistent with the 527 nm extinction coefficient of 2.93 × 10³ M⁻¹ cm⁻¹.

Preparation of (II,III). Several methods for preparation of solutions containing (II,III) are described in the Experimental Section. The most efficient process was found to be the cross-reaction between [Ru$^{II}_2$(ttha)(H₂O)₂]²⁻ and [Ru$^{III}_2$(ttha)(H₂O)₂] in equimolar amounts. Although electron transfer exchange reactions between Ru^{II} and Ru^{III} in ammine and pac ligand

(46) McLendon, G.; Moetkaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 2306.
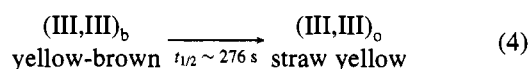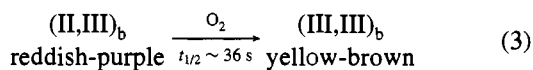
(47) Myser, T. K. Ph.D. Thesis, University of Pittsburgh, 1986.

environments are rapid, when (II,II) and (III,III) are mixed in equimolar amounts, the reddish-purple intensity of the solution increased slowly for over 30 min at pH 7. This suggests the following sequence where the subscripts "o" and "b" refer to the open-chain and bridged complexes of the indicated oxidation states, eqs 1 and 2. The (II,III)$_b$ complex is the species having

$$(II,II)_o + (III,III)_o \xrightleftharpoons{\text{fast}} 2(II,III)_o \quad (1)$$

$$(II,III)_o \xrightarrow{\text{slow}} (II,III)_b \quad (2)$$

the spectral chromophore with an absorption near 527 nm which gives the solution its reddish-purple color. When O_2 was admitted, an initial growth in the absorbance near 527 nm is observed. Stirring with air produced a reduction in the amount of the reddish-purple species with an increase of a yellow-brown one. Mixtures of the reddish-purple and yellow-brown forms appear wine red to the eye. This species faded with time to give a spectrum identical to the open-chain form of (III,III). The oxidation of the reddish-purple solution to a completely golden yellow-brown solution occurred within 6 min.

The golden-yellow brown species then fades to straw yellow (III,III)$_o$ in 45 min. These steps (eqs 3 and 4) are consistent

$$\begin{array}{c}(II,III)_b \\ \text{reddish-purple} \end{array} \xrightarrow[t_{1/2} \sim 36\,s]{O_2} \begin{array}{c}(III,III)_b \\ \text{yellow-brown}\end{array} \quad (3)$$

$$\begin{array}{c}(III,III)_b \\ \text{yellow-brown} \end{array} \xrightarrow[t_{1/2} \sim 276\,s]{} \begin{array}{c}(III,III)_o \\ \text{straw yellow}\end{array} \quad (4)$$

with the rupture of the oxo-bridge in (III,III)$_b$ occurring with a rate constant of ca. 2.5×10^{-3} s^{-1}. This is at least 35 times slower than the rupture of $[Ru^{III}_2O(edta)_2]^{4-}$.[10] In a separate experiment the solid which was precipitated as the (II,III) complex for infrared study was observed later to have undergone air oxidation in the solid state, losing the reddish-purple color. When this solid sample was dissolved in water the solution also appeared golden-brown. Repetitive scanning of the UV—visible region showed the decay of the absorbances near 535 and 600 nm and the growth of a 385 nm band. This process was first-order with $t_{1/2}$, of about 276 s. Since the final product is the open-chain form, (III,III)$_o$, the observed slower change measures the ring-opening process (eq 4) alone.

Electrochemical Studies on (II,III). In prior studies[24] we have used the electrochemical method[48–50] to evaluate K'_c, the comproportionation constant as expressed for formation of the mixed-valence species (eq 5). When coupling between the metal

$$(II,II) + (III,III) \xrightleftharpoons{K_c} 2(II,III) \quad (5)$$
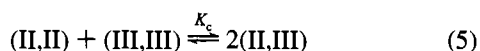
centers is sufficiently large, the DPP waves show distinctly separate waves. This was the case in our former study of the [Ru(hedta)]$_2$(pz)$^-$ system where K'_c (the constant corrected by a factor of 4 as a statistical correction) was found to be 190,[24] in close magnitude to 240 for [Ru(edta)]$_2$(pz)$^{3-}$.[2,8] With [Ru(hedta)]$_2$(pz)$^{n-}$, the waves for the

$$(II,II)_o \xrightarrow{-ne^-} (II,III)_o$$
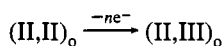
are separated by 0.17 V, and the separate oxidation steps are clearly detectable. When pyrimidine bridges the Ru^{II} and Ru^{III} centers in the mixed-oxidation state species [Ru^{II}Ru^{III}(ttha)(pym)]$^-$

(48) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.
(49) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.
(50) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1980**, *20*, 1278.
(51) Matsubara, T.; Creutz, C. *Inorg. Chem.* **1979**, *18*, 1956.
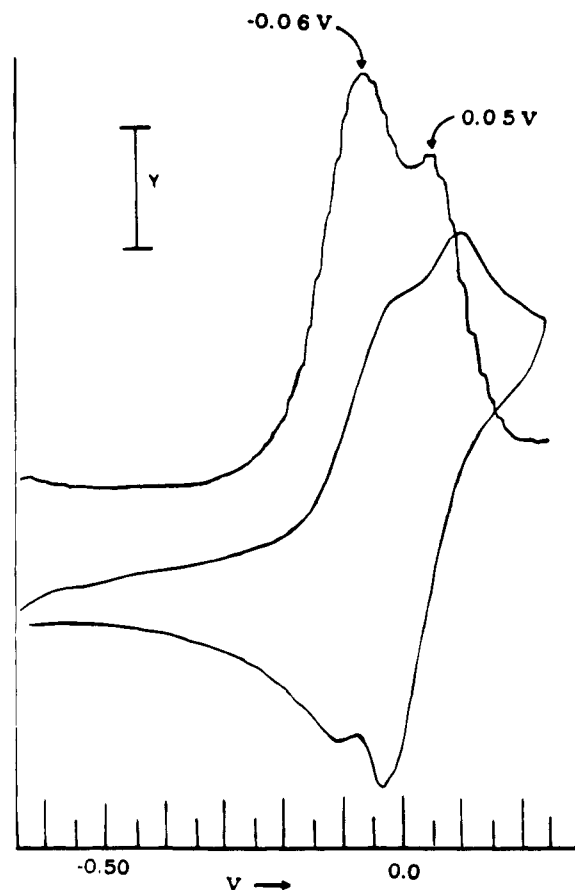
**Figure 2.** Cyclic voltammogram and differential pulse polarogram of [Ru^{II}Ru^{III}(OH)(ttha)]$^{2-}$ in the 2+/3+ window vs NHE. [[Ru$_2$(ttha)]$^{n-}$]$_{tot}$ = 4.02×10^{-3} M; μ = 0.10 M NaCl, T = 22 °C; y axis indicator = 20 μA.

and [Ru(hedta)]^2(pym)$^-$, the separation in E^o_1 and E^o_2 is smaller. The respective values of K'_c were found to be 3.9 and 5.7.[24] The success of this method in the prior studies establishes the reliability of the Sutton—Richardson—Taube approach in the measurement of K'_c in our hands. We applied this procedure to the solution containing the (II,III)$_b$ complex prepared by the cross-reaction method. The waves of E^o_1 and E^o_2 are closely overlapped, with E^o_2 appearing almost as a shoulder at higher potential. The CV and DPP data for the (II,III) complex are presented in Figure 2. Experiments were performed at pH $\sim$ 8 under Ar. The region between -0.74 to $+ 0.64$ V vs NHE was scanned. Only the waves shown in Figure 2 are observed in this electrochemical window which avoids the higher oxidation state (III,IV) complex. Two waves appear, one at -0.06 V vs NHE for the Ru^{II}—Ru^{III}/Ru^{II}—Ru^{II} species, (II,III)$_b$ and (II,II), and another at 0.05 V vs NHE for the Ru^{III}—Ru^{III}/ Ru^{II}—Ru^{III} bridged species, (III,III)$_b$ and (II,III)$_b$. These waves were insensitive to pH above pH 8. The separation of the waves by 0.11 V is indicative of a comproportionation constant of 73 (uncorrected). Correction for the statistical factor of 4 yields K'_c of 18 (corrected).

The small value of K'_c implies that metal—metal coupling via the hydroxy bridge in (II,III)$_b$ is very small and approximately 1.7 kcal/mol or less. This is anticipated because the M—L—M overlaps occur with a node at the bridging hydroxy ligand. This compares in an interesting way with the estimate of ca. 0.03 kcal/mol made recently by Haim for the [(NH$_3$)$_5$Ru^{II}(pz)Ru^{III}(edta)]$^+$ system[8] and 3.1 kcal/mol from a value of K'_c = 190 for [Ru(hedta)]$_2$(pz)$^-$.[24] From these results it is clear that coupling between Ru^{II} and Ru^{III} sites is less for
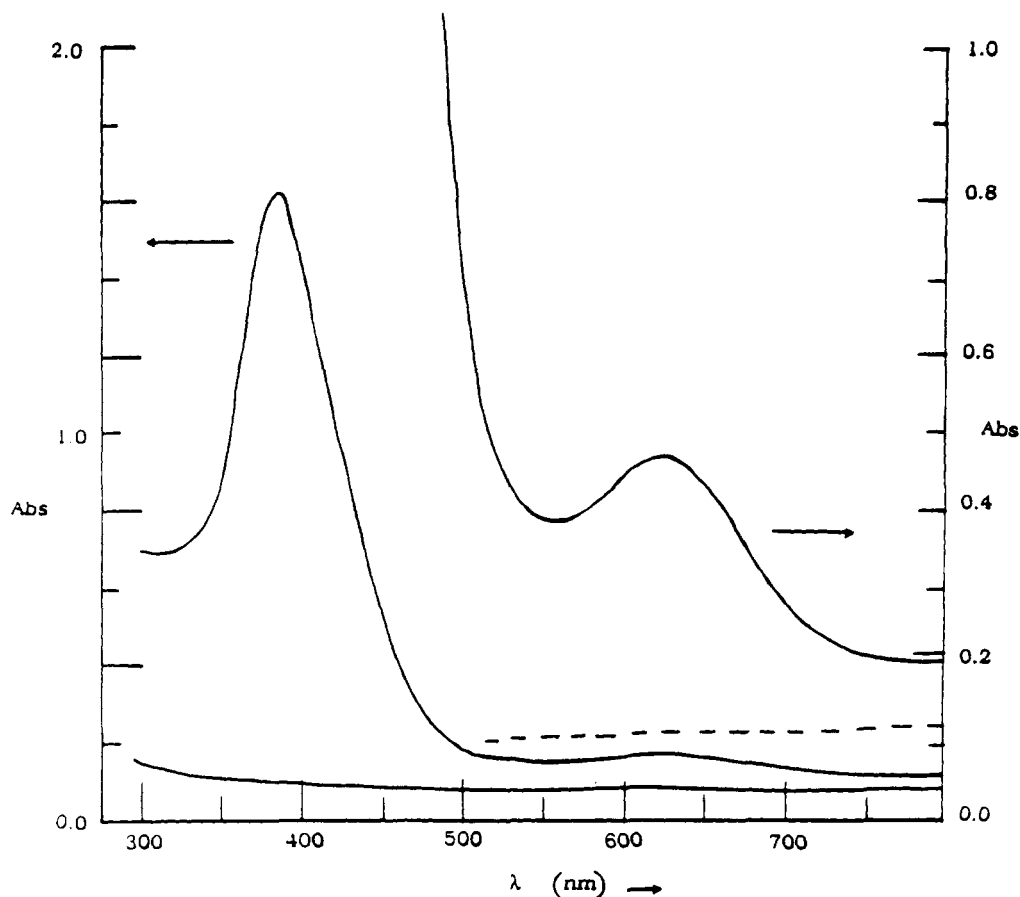
Figure 3. Visible spectrum of [Ru^{III}ORu^{IV}(ttha)]$^-$, (III,IV). [(III,IV)] = 1.50 × 10^{-3} M, μ = 0.10 M NaCl, T = 22 °C. Key: upper curves, 0.10 cm cell, y axis = 0—2.0 absorbance units; expansion, 1.00 cm cell and y axis = 0—1.0 absorbance units; lower solid line is the blank; dashed curve is the blank for the expansion scale.

OH$^-$ than pz in comparing (II,OH$^-$,III) of the ttha^{6-} system with (II, pz,III) of the hedta^{3-} system. Although delocalization is poor for [Ru^{II}Ru^{II}(OH)(ttha)]$^{2-}$, it is still larger than for the [(NH$_3$)$_5$Ru(pz)Ru(edta)]$^+$ complex where unsymmetrical wells, created by asymmetric ligand fields, sharply alter the energetics of electron attraction for the Ru centers.

An additional fruitful comparison is the difference between OH$^-$ and pyrimidine as a bridging ligand within the ttha^{6-} ligand environment. K'_c has been estimated as 5.7^{24} whereas, by the same electrochemical method, K'_c is determined to be 18.3 for OH$^-$ as the bridge ligand. The single atom OH$^-$ bridge places the Ru^{II} and Ru^{III} sites closer in space for through-space coupling. This could surely account for the slightly higher value of K'_c with the OH$^-$-bridged complex compared to pym.

Evidence for [Ru^{III}ORu^{IV}(ttha)]$^-$. The CV and DPP electrochemical waves for (II,II)$_o$ and the species generated by the 3 day aerobic oxidation of (III,III)$_o$ were found to be the same. The solution of the oxidation product of (III,III)$_o$ exhibits the UV—visible spectrum shown in Figure 3. Band maxima intensities at 620 nm (ϵ = 2.35 × 10^2 M^{-1} cm^{-1}) and 388 mn (1.02 × 10^4 M^{-1} cm^{-1}) are within a factor of 2 of the [Ru^{III}ORu^{IV}(edta)$_2$]$^{3-}$ values characterized by Hurst's group.^{9} The parameters for (III,IV) of the ttha^{6-} complex are also similar to those of [(NH$_3$)$_5$RuORu(NH$_3$)$_5$]$^{5+}$: (λ, ϵ) 616 nm, 271; 342 nm, 2.53 × 10^4.^{33} Meyer assigns the transition near 630 mn as a σ^* ← dπ^* transition and the one near 350 mm as a π^* ← n, d$_{xy}$ transition.^{33} The long wavelength band near 630 nm should be slightly sensitive to the ligand field, and indeed, with the (NH$_3$)$_5$ ligand set the transition is at higher energy (616 nm) compared to the strained environment with ttha^{6-} (620 nm) and the less strained (edta^{4-})$_2$ case (632 nm). Meyer's MO order^{31}

is derived for a bent Ru^{III}ORu^{IV} chromophore with the filling $(\pi_1^b)^2$ $(\pi_2^b)^2$ $(\pi_{d_{xy}}^n)^2$ $(\pi_{d_{xy}}^n)^2$ $(\pi_1^n)^2$ $(\pi_2^n)^2$ $(\pi^*_1)^1$ $(\pi^*_2)^0$ wherein p$_x$ and p$_y$ orbitals of the bridging oxo group are mixed with d$_{xy}$, d$_{yz}$, and d$_{xy}$ metal levels. The unused d orbitals provide the essentially pure metal e$^*_g$ levels of σ^* symmetry needed for the transition near 630 nm. The lower extinction coefficients for the [Ru^{III}ORu^{IV}(ttha)]$^-$ species is consistent with a more strained Ru^{III}ORu^{IV} bridge in the ttha^{6-} complex wherein the Ru^{III}ORu^{IV} is forced at closer distance by the (CH$_2$)$_2$ bridging than the unstrained [Ru^{III}ORu^{IV}(edta)$_2$]$^{3-}$ complex. Zhang et al. recently observed that [Fe^{III}$_2$O(ttha)]$^{2-}$ exhibited a lower ϵ/Fe^{III} of 64 M^{-1} cm^{-1} compared to 90 M^{-1} cm^{-1} for the [Fe^{III}$_2$O-(hedta)$_2$]$^{2-}$ binuclear ion; the oxo group bridges the Fe^{III} centers of the ttha^{6-} complex in a side-by-side arrangement.^{15a} However, a tetranuclear species, [Fe^{III}$_4$(O)$_2$(ttha)$_2$]$^{4-}$, in which less strained Fe^{III}-O-Fe^{III} chromophores are present as cross-linking bridges, exhibited an ϵ/Fe^{III} of 107 M^{-1} cm^{-1}. Assuming a similar percentage decrease in overlaps of Ru-centered orbitals and the intervening O^{2-} bridge ligand, one would predict an ϵ for the Ru^{III}ORu^{IV} chromophore of (2.9—2.5) × 10^2 M^{-1}cm^{-1} at ~632 nm. The observed values of 2.35 × 10^2 M^{-1} cm^{-1} (1.18 × 10^2/Ru center) at 620 nm is compatible with this analysis. Zhou et al.^{9} estimate the angle of the Ru^{III}ORu^{IV} chromophore to be 165° in [Ru^{III}ORu^{IV}(edta)$_2$]$^{3-}$; the absorbance data suggests a more accute angle for [Ru^{III}ORu^{IV}(ttha)]$^-$. The charge of 1-on (III,IV) was established by the ion exchange behavior as described in the Experimental Section. Since the more negatively charged [Ru^{III}ORu^{IV}(edta)$_2$]$^{3-}$ ion is deprotonated at the oxo bridge from pH 2 to 11, it is even less likely that the 1-ion, (III,IV), would be protonated on the bridge ligand. This is consistent with the ion exchange results.
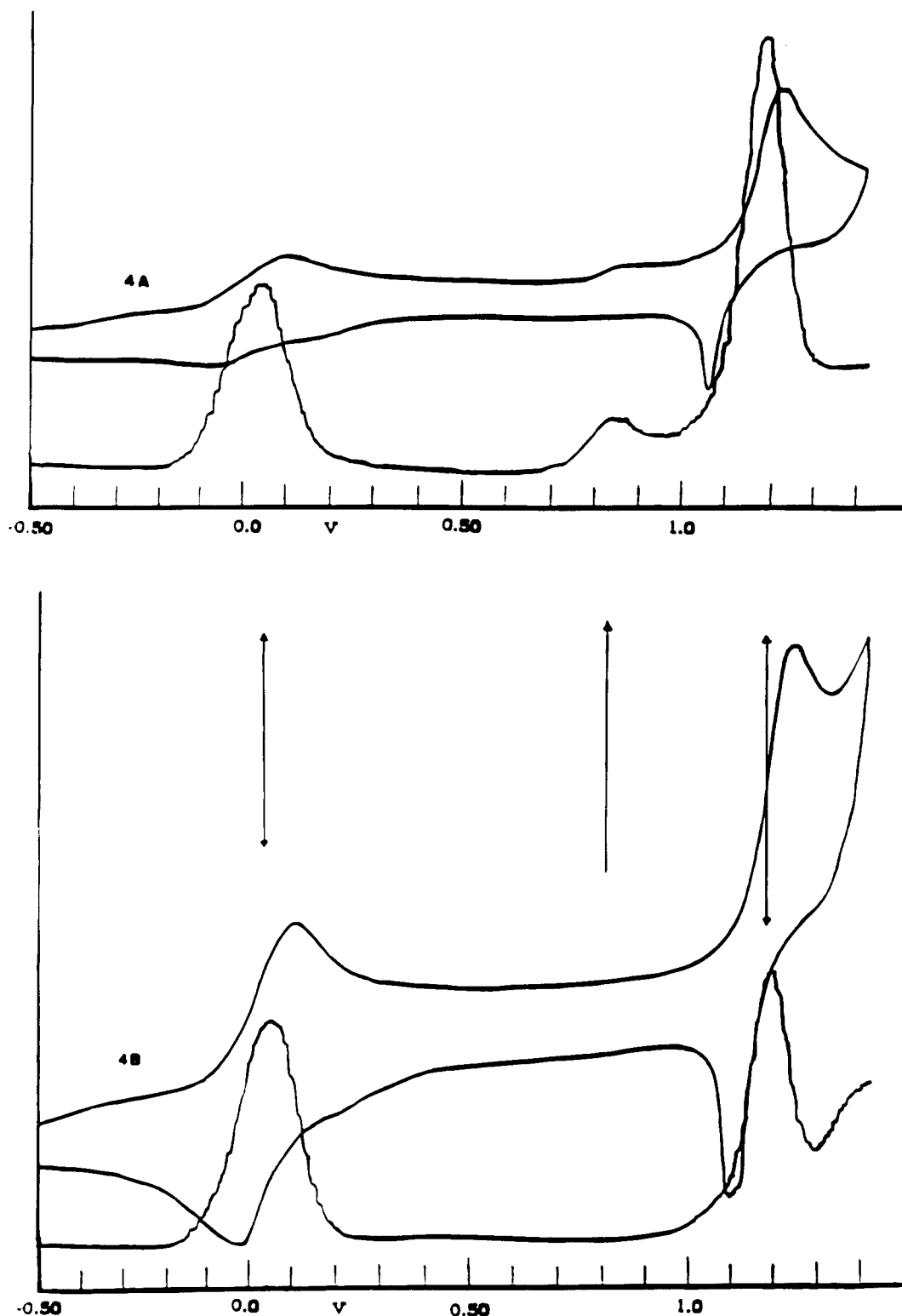
Figure 4. Cyclic voltammogram and differential pulse polarograms of $[Ru_2(ttha)]^{n-}$ complexes: comparison of (II,II) and (III,IV) starting complexes. (A) Sweeps starting with $(II,II)_o$ under Ar, pH = 8.28, μ = 0.10 M NaCl, T = 22 °C. (B) Sweeps starting with $(III,IV)_b$ under Ar. Vertical markers show equivalence of the $E_{1/2}$ wave positions for two waves and the absence of a third wave in B.

The CV and DPP data at pH 8.28 were nearly the same for $(II,II)_o$ as the starting complex or for the $(III,IV)_b$ complex as the starting material in solution. The waves shown in Figure 4 show a $Ru^{II/III}$ broad quasi-reversible wave at 0.05 V vs NHE and a second quasi-reversible wave at 1.20 V vs NHE for the $Ru^{III/IV}$ oxidation wave. Hurst et al. report the $Ru^{II/III}$ wave of the edta ligand system at ca. 0.02 V vs NHE. Baar and Anson[10] assign a wave at 1.16 V vs NHE to the $L_2Ru^{III}Ru^{IV}O \longrightarrow$ $L_2Ru^{IV}_2O$ oxidation; Hurst et al. assign this wave to ca. 1.14 V

vs NHE.[9] The $L_2Ru^{III}Ru^{IV}$ system with L = $edta^{4-}$ is complicated by rapid dissociations into monomeric complexes on the reduction cycle and multiple pathways for binuclear formation on the oxidation cycle. The small additional wave at 0.83 V vs NHE for the sequential oxidation of $(II,II)_o$ is assigned as the $(III,III)_o \longrightarrow (III,IV)_b$ oxidation for the $ttha^{6-}$ system of this report (Figure 4A). This wave is absent in samples which are rapidly scanned from the $(III,IV)_b$ solution (Figure 4B). Thus only small amounts of $(II,II)_o$ and $(III,III)_o$

Table 2. Infrared Data[a] on Selected Ru(pac) Complexes in cm⁻¹

complex	$\nu_{RCO_2^-}$	ν_{CO}	$\nu \sim 870$	$\nu \sim 920$	$I(\nu870/\nu920)$[b]
[Ru^{III}(hedta)(H$_2$O)]	1640		877	914	0.68
Na$_2$[Ru$^{II}_2$(ttha)(H$_2$O)$_2$]	1656		885	912, 932	0.75
Na[Ru^{II}(hedta)(CO)]	1619	1939	876	922	0.80
Na$_2$[Ru$^{II}_2$(ttha)(CO)$_2$]	1624	1943	876	930	0.66
Na$_2$[Ru^{II}Ru^{III}(OH)(ttha)]	1638		875	913, 932	0.68
Na$_2$[Ru^{II}(CO)Ru^{III}(OH$_2$)(ttha)]	1644 (br)	1941	876	914	0.76
Na[Ru^{III}ORu^{IV}(hedta)$_2$]	1637		874	914	0.78
Na[Ru^{III}ORu^{IV}(ttha)]	1641		877	916	0.92
Na$_2$[Zn$_2$(ttha)(H$_2$O)$_2$]	1603		864	995, 974, 927	0.00; 0.64[c]
[Ru(edtaH)(H$_2$O)][9]	1653		876	NR	NR
Na$_3$[Ru^{III}ORu^{IV}(edta)$_2$][9]	1653		870	NR	NR

[a] NR = not reported. [b] Intensity ratio of bands shown in previous columns. [c] Ratio for 864 cm⁻¹ band vs 927 cm⁻¹ band.

are found in the monolayer which is sampled after the reduction wave. Diffusion out of the monolayer with replacement by new (III,IV)$_b$ must be rapid compared to the sweep time. Thus for (III,IV)$_b$ the waves associated with the fully reduced species

$$(II,II)_o \xrightarrow{-ne^-} (II,III)_o$$
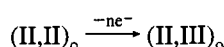
and reoxidation to (III,III)$_o$ are observed near 0.05 V for either sample starting with (II,II)$_o$ or (III,IV)$_b$, the latter reduced rapidly at glassy carbon to (II,II)$_o$ at negative potentials. However, when a significant pool of open-chain (II,III)$_o$ or (II,II)$_o$ can diffuse into the monolayer, the wave associated with step

$$(III,III)_o \xrightarrow{-1e^-} (III,IV)_o \rightarrow (III,IV)_b$$
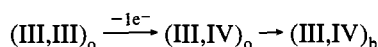
is detected at 0.83 V vs NHE. If the amount of (III,III)$_o$ which is formed at negative potentials is small and bulk (III,IV)$_b$ is available to exchange by diffusion, this wave is absent. Then only the

$$(III,IV)_b \xrightarrow{-1e^-} (IV,IV)_b$$
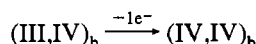
wave is detected at 1.20 V.

A significant result of this work is the reduction in overall complexity for the electrochemical behavior of [Ru$_2$(ttha)]ⁿ⁻ complexes compared to the [Ru$_2$(edta)]ⁿ⁻ system. This is imparted by the proximity effect which stabilizes the Ru^{III}ORu^{IV} chromophore relative to dissociation into monomers, or the formation of binuclear complexes from either 2Ru^{II}L or Ru^{III}L + Ru^{IV}L monomers in the case of L = edta⁴⁻. The ttha⁶⁻ system only provides evidence for the binuclear formation of (III,IV)$_b$ from (III,III)$_o$ (Figure 4A) as a complicating wave. The reduction of (III,IV)$_b$ to (III,III)$_b$ occurs at ca. 1.14 V. The wave at ca. 0.05 V is broadened, suggestive of more than one type of Ru^{III} center being present, but insufficiently resolved for quantitation of the amount of (III,III)$_o$ and (III,III)$_b$ which has been generated electrochemically.

However, the data from an earlier section of this paper has shown that the (III,III)$_b$ species would survive the 40 s sweep time in one direction. Therefore, the cathodic sweep in the CV spectrum is a composite of the reduction of (III,III)$_o$ and (III,III)$_b$, complicated by diffusional effects at the monolayer when reduction starts with (III,IV)$_b$.

Infrared Studies of Ru(pac) Complexes. In order to characterize the nature of the bridging groups, particularly in the (III,IV)$_b$ species, a number of solids including salts of (II,II), (II,III)$_b$, (III,IV)$_b$, the Zn analogue of (II,II), the Ru(hedta) analogue of (III,IV)$_b$, and [Ru(hedta)(H$_2$O)] were prepared. IR spectra were obtained in KBr pellets. These data are presented in Table 2. Complete IR spectra of (II,II), (II,III)$_b$ and (III,IV)$_b$

are given as supplemental Figures S1, S2, and S3. As an additional diagnostic tool, the carbonyl derivatives Na[Ru^{II}-(hedta)(CO)] and Na$_2$[Ru$^{II}_2$(CO)$_2$(ttha)] were prepared by passage of CO through the respective Ru^{II} solutions for several hours, followed by precipitation of the Na⁺ salts with addition of ethanol. The purpose of the formation of the carbonyl complexes is to provide Ru^{II}, air-stable complexes in which the aqua positions are replaced by the π-accepting CO ligand. This removes Ru^{II}OH$_2$ functionalities. It was also determined that when (II,III)$_b$ at pH ~ 7 was adjusted to pH ~ 3, the reddish-purple color of the bridged complex fades, but can be recovered reversibly by raising the pH. Loss of the reddish-purple species (II,III)$_b$ is interpreted as the protonation of the bridge OH⁻ group which induces opening of the bridge and forms the open-chain (II,III)$_o$ species in which each Ru site is converted to an aqua derivative (eq 6). The open-chain species was similarly treated

$$(II,III)_b + H_3O^+ \rightarrow (II,III)_o \tag{6}$$

$$(II,III)_o + CO \rightarrow (II(CO),III)_o \tag{7}$$
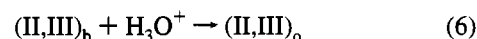
with CO and precipitated as the Na⁺ salt salt with ethanol. The isolated compound clearly shows the presence of the carbonyl (Table 2) where a band at 1941 cm⁻¹ is observed, similar to the values of 1943 cm⁻¹ for the CO derivativatized (II,II)$_o$ and the Na[Ru(hedta)(CO)] monomeric complex of 1939 cm⁻¹. (II,III)$_b$ is not rapidly changed upon treatment with CO. *This shows that the Ru^{II}(OH⁻)Ru^{III} unit is not rapidly labile.*

The nature of the bridging species for the (III,IV)$_b$ complex was sought by means of the infrared spectra. Hurst et al.[10] have presented a detailed discussion which predicts that the asymmetric M−O−M stretch for oxo-bridged species such as (III,IV)$_b$ and the edta analogue should appear between 750 and 950 cm⁻¹. In the [Ru^{III}(edta)(H$_2$O)] complex the Ru^{III}-O-H stretch is at 876 cm⁻¹ and shifts to 870 cm⁻¹ for Ru^{III}−O−Ru^{IV} in the edta binuclear complex.[9] Preparation of the same species in ¹⁸O water give indistinguishable spectra.[9] Thus, Hurst et al. Zhou avoided assignment of this band as the asymmetrical RuORu stretch.[9] However, Hurst et al. report a 2-fold increase in intensity of the 870 cm⁻¹ band of the binuclear [Ru^{III}-ORu^{IV}(edta)$_2$]³⁻ complex compared to monomeric [Ru^{III}(edtaH)-(H$_2$O)]. With these observations in mind, we have paid close attention to the 750−950 cm⁻¹ region; the bands associated with the ~870 cm⁻¹ stretch and another near 920 cm⁻¹ which are reported for the complexes in Table 2. The stretch at 877 cm⁻¹ in (III,IV)$_b$ is about twice as intense as the same stretch for [Ru^{III}(hedta)(H$_2$O)] at 877 cm⁻¹ relative to the 914 cm⁻¹ nearby band. The same feature is also less intense for (II,II)$_o$. Perhaps significantly, the 875 cm⁻¹ band for the hydroxy-bridged (II,III)$_b$ is at an intensity comparable to that for [Ru^{III}(hedta)(H$_2$O)] and (II,II)$_o$. The same features are weak for the Zn^{II} analogue of

$(II,II)_o$. An 876 cm^{-1} band in the carbonyl-substituted $(II,II)_o$ is virtually absent compared to a strong band at 930 cm^{-1}. Thus there is some evidence that the ~870 cm^{-1} band is sensitive to a Ru-O chromophore, but it does not distinguish well between Ru^{III}–O–Ru^{IV}, Ru$^{II/III}$–OH$_2$ or Ru^{II}(OH)Ru^{III} functionalities. If the intensity pattern suggested by Hurst et al.[10] is correct, then the observations for $(III,IV)_b$ as bridged by the oxo functionality is supported by our infrared data. Unfortunately, the Na[Ru^{III}ORu^{IV}(hedta)$_2$] analogue shows an intensity of the 874 cm^{-1} band relative to its 914 cm^{-1} neighbor only slightly higher than for [Ru^{III}(hedta)(H$_2$O)].

Conclusions

[Ru^{II}$_2$(ttha)(H$_2$O)$_2$]$^{2-}$ complex, $(II,II)_o$, exhibits self-exchange with the $(III,III)_o$ analogue, forming a mixed-valence complex (II,III) which can be kept in the open-chain form $(II,III)_o$ and derivatized by the π-acceptor CO on the Ru^{II} site or allowed above pH 5 to form a hydroxy-bridged complex $(II,III)_b$, which has a characteristic band at 527 nm related to the filling of the MO's of two Ru$^{II/III}$ centers bridged by an oxo or hydroxo ligand. The separation of the electrochemical

$$Ru^{II}Ru^{II} \xrightarrow{E^o_1} Ru^{II}Ru^{III} \xrightarrow{E^o_2} Ru^{III}Ru^{III}$$

waves leads one to conclude that the comproportionation constant K'_c is about 18.3 and that delocalization across the OH$^-$ bridge is only about 1.7 kcal/mol. The favorability of forming the mixed-valence species is only slightly greater than has been found for the pyrimidine-bridged complex.[24]

Like the [(edta)Ru^{III}ORu^{III}(edta)]$^{4-}$ ion, which can be generated only electrochemically and which aquates to the monomers rapidly, the [Ru^{III}ORu^{III}(ttha)] complex exists only as an intermediate prepared by chemical or electrochemical oxidation of [Ru^{II}Ru^{III}(OH)(ttha)]$^{2-}$, $(II,III)_b$. The half-life for the decay to its open-chain equation product, $(III,III)_o$, is 4.6 min. This is much longer than for the edta transitory species ($t_{1/2} < 7.5$s). Therefore, the $(III,III)_b$ rupture of the Ru–O–Ru bridge bond occurs ≥ 35 times more slowly. Further oxidation of $(III,III)_o$ either by prolonged exposure to O$_2$, or electrochemically, generates the [Ru^{III}ORu^{IV}(ttha)]$^-$ species, $(III,IV)_b$ which has spectral characteristics very similar to those of [Ru^{III}-ORu^{IV}(edta)$_2$]$^{3-}$ as reported by Hurst et al.[9] Both exhibit as bands near 630 nm (620 and 632 nm, respectively). A lower extinction coefficient by $(III,IV)_b$ is consistent with a greater strain in the Ru^{III}–O–Ru^{IV} bridge. The electrochemical behavior is virtually identical for the $(III,III)_b \rightarrow (III,IV)_b$ conversion with respective $E_{1/2}$ values of 1.20 and 1.14 V for the ttha^{6-} and (edta^{4-})$_2$ derivatives. Both species exhibit an enhancement of the infrared band near 870 cm^{-1}: 877 cm^{-1} for L = ttha^{6-} and 870 cm^{-1} for L$_2$, = (edta^{4-})$_2$) compared to monomeric or nonbridged analogues. The origin of such bands is yet uncertain, being in the proper region for an M–O–M asymmetric stretch, but failing to show the sensitivity to O^{18} isotopic substitution in the edta derivative.

The significant outcome of these studies is the detection of a long-lived hydroxy-bridged mixed-valence species of the LM^{II}(OH$^-$)M^{III}L type for the first time with an iron group, water-soluble complex. Such species are known for Fe^{II}(OH$^-$)Fe^{III} bridged complexes in the purple acid phosphatases, but have been elusive for study in model systems. It is also shown that Ru^{III}–O–Ru^{III} chromophores are unstable to aquation, unlike the Fe^{III} counterpart which gains from superexchange between Fe^{III} centers. The low-spin Ru^{III} complexes gain much less stability from superexchange. Therefore, Ru^{III}–O–Ru^{III} structures which are unsupported by rigid ligand coordination which connects the Ru sites, in contrast to the stable, supported bridged LRu(RCO$_2$)$_2$ORu^{III}L (L = Me$_3$-tcn) complex of Wieghardt et al.,[34] will spontaneously aquate into monomeric species or the open-chain configuration for ligands like ttha^{6-}, which possess two separable binding pockets for metal centers. Although the $(II,III)_b$ complex containing the Ru^{II}(OH$^-$)Ru^{III} chromophore has been clearly identified in this work, there has been no evidence for the [Fe^{II}(OH$^-$)Fe^{III}(ttha)]$^{2-}$ complex in prior studies from our laboratories[23,15a] or in prior reports of ruthenium binuclear complexes.[13] Again the high-spin Fe^{II} and Fe^{III} centers are probably less strongly bonded to OH$^-$ since both oxidation states have two antibonding electrons directed toward the formal bond axes. The low-spin Ru species are unaffected in this manner. This would impart a weaker Fe–O bond compared to Ru–O that should be rapidly broken by aquation, making detection of such a transient unlikely.