In view of the constancy of the ground-state geometry and the $\delta \rightarrow \delta^*$ electronic transition energy among the various ruthenium carboxylates, it seems highly unlikely that $\delta \rightarrow \delta^*$ excited-state distortions are changing among them. Thus, a vibrational coupling, with a predominant distortion remaining along the metal–metal coordinate, is likely responsible for the formate results.

The bridged $M_2(O_2CR)_4$ structure necessarily imposes a coupling among the totally symmetric $\nu(M_2)$, $\nu(MO)$, and $\delta(OM_2)$ modes. We think that the key to understanding the formate results is that the bridging ligand is exceptionally light among those of the compounds examined. Accordingly, the low amplitude changes in MO bond distance to be associated with a "pure" M_2 distortion are closer to those associated with $\nu(MO)$ than is true for the heavier carboxylates (larger effective masses, hence larger amplitudes for $\nu(MO)$) for a given frequency. Thus, vibrational coupling is expected, so long as the frequency difference between the modes is not large, and this remains true for the formate compounds.

We have thus far avoided assignment of ν_1 in the $\delta \rightarrow \delta^*$ transitions of the formates. The most likely assignment, following the above analysis, is to $\delta(OM_2)$, uniquely strongly active for the formate bridging ligand. However, the frequency of ν_1 varies strongly among compounds I, II, and III, suggesting the possibility that the mode might be $\nu(RuX)$. Additionally, we do not possess single-crystal data for the formates, so it remains possible that ν_1 might be a non totally symmetric mode,[2] and the assignment is therefore doubtful.

We emphasize that vibronic intensity profiles for nominally pure metal–metal excitations such as $\delta \rightarrow \delta^*$ may, without any change in electronic structure of ground and excited states, be strongly perturbed by vibrational coupling effects. We think that the effects seen here are somewhat peculiar to the $M_2(O_2CR)_4$ structure, with its tight coupling of internal motions, and the interpretation of the vibronic structure of electronic transitions of unbridged binuclear compounds is probably simpler. In a bridged case, a great deal of caution is, however, desirable in the interpretation of vibronic structure.

We wish to comment on a probable additional example of such effects. Martin and co-workers[12] have reported that $Mo_2(O_2CH)_4$ in its various polymorphic crystalline forms exhibits, in addition to progressions in $\nu(Mo_2)$ ($\sim$350 cm^{-1}), two strong vibronic origins $\sim$380–390 and $\sim$770–780 cm^{-1} above the $^1(\delta \rightarrow \delta^*)$ electronic origin. It was noted that these frequencies were considerably higher than for "analogous" features[13] of the $^1(\delta \rightarrow \delta^*)$ transition of $Mo_2(O_2CCH_3)_4$. It is likely that the 380–390-cm^{-1} origin is the excited-state $\nu(MoO)$, whose frequency reasonably is much larger[14] than for the acetate (assigned[13] at 275 cm^{-1}), and that the 770–780-cm^{-1} origin is simply $2\nu(MoO)$. Both of these assignments are consistent with what we have observed for $\delta \rightarrow \delta^*$ of the ruthenium formate complexes but were not considered by Martin et al.,[12] presumably because they appeared to be inconsistent with the interpretation of the $^1(\delta \rightarrow \delta^*)$ system of the acetate.

Acknowledgment. This research was supported by National Science Foundation Grant CHE84-19828.

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Spin Trapping of Superoxyl and Hydroxyl Radical Complexes of Ruthenium(II) and -(IV) Polyaminopolycarboxylates

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$Na[Ru^{II}(hedta)(H_2O)]\cdot 4H_2O$ has been oxidized in solution by $Na_2S_2O_8$ to form a Ru^{IV} complex, isolated as $Ru_2O(hedta)_2\cdot(15.4 \pm 0.4)H_2O$. Cyclic voltammetry and Na^+ analysis supports a bridging Ru–O–Ru structure; analogous results were obtained for $Ru^{II}(edta)^{2-}$. Ru^{III} complexes formed in the H_2O_2 or O_2 oxidation of $Ru^{II}(edta)^{2-}$, $Ru^{II}(hedta)(H_2O)^-$, and $Ru^{II}{}_2(ttha)(H_2O)_2{}^{2-}$ also undergo water replacement by H_2O_2. The bound $(L)Ru^{III}(O_2{}^{2-})$ species (L = edta^{4-}, hedta^{3-}, ttha^{6-}) exhibit substantial $(L)Ru^{II}(O_2{}^-)$ character, forming spin adducts with DMPO. The $LRu^{II}(O_2{}^-)$DMPO adducts exhibit a seven-line ESR pattern of intensities nearly 1:2:2:2:2:2:1 with couplings $A_N \simeq 8.0$ G, $A_{H_\beta} \simeq A_{H_\gamma} \simeq 5.0 \pm 0.5$ G for L = ttha^{6-}, edta^{4-} and $A_N = 10.0$ G, $A_{H_\beta} \simeq A_{H_\gamma} \simeq 5.0$ G for hedta^{3-}. The couplings are independent of D_2O in the solvent. No DMPO radical adducts are observed with $Ru^{II}L$, $Ru^{III}L$, or $Ru^{IV}L$ complexes alone. Oxidation of $Ru^{II}L$ or $Ru^{III}L$ complexes with $(CH_3)_3COOH$ generates a different radical species, trappable by DMPO. The spin adduct has the character of Ru^{III}–O atom or $Ru^{IV}(OH^\bullet)$, giving rise to a triplet of triplets pattern. The spectral intensity decreases with increasing percentage of D_2O in the solvent. This shows an exchangeable proton is present that couples in the spin adduct. Couplings are $A_N = 7.5$ G, A_H (2 equivalent H couplings) = 4.2 G (L = edta^{4-}), 4.0 G (hedta^{3-}). The spin adduct is therefore assigned as the $LRu^{IV}(OH)$DMPO species. The Ru^{III}–O atom species epoxidize olefin bonds while the $Ru^{II}(O_2{}^-)$ species add to olefins, giving nonradical products. Thus, the O atom channel mimics aspects of monooxygenase systems and the superoxo channel mimics aspects of dioxygenase systems.

Introduction

The reduction of O_2 and H_2O_2 by transition-metal reductants is a long-standing chemical problem. It impinges on the autoxidations of a diverse array of inorganic and organic substrates, as well as metabolic reactions in biological cells. Coordinated oxygen radicals are the proposed intermediates in oxygen activation by dioxygenases and monooxygenases.[1,2] The hydroxylations and epoxidations carried out by these enzymes are attributed to $Fe^{III}(O_2{}^-)$ (superoxo) and $Fe^{II}(O_2{}^-)$ (superoxo) $\leftrightarrow$ $Fe^{III}(O_2{}^{2-})$ (peroxo) species. The superoxo complexes are capable of radical addition to double bonds[1] while the peroxo species can participate in O atom transfer reactions. The reactive entity in the peroxo case may be more properly assigned to the ferryl Fe^{III}–O atom species if cleavage of the O–O bond, liberating H_2O, precedes atom

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transfer.[1,28,43] The last two processes even include insertion into C–H σ bonds and may be important in both aliphatic and aromatic hydroxylation reactions. These reactions are carried out by liver microsomial monooxygenases and by organisms that utilize methane monooxygenase to metabolize hydrocarbons.[3,4] Synthetic metalloporphyrin complexes of iron,[44] manganese,[45] chromium,[46] and ruthenium[47] have been examined for cytochrome P-450 like monooxygenase activity; particularly, the Mn(IV) and -(V) porphyrins have been utilized for olefin epoxidations and unactivated C–H hydroxylations.[45,46] The transfer of O atoms via the ferryl Fe^{III}–O atom intermediates is also important in the action of bleomycin during O_2-activated DNA strand scissions.[48,49] O atom transfer to small-molecule substrates such as *cis*-stilbene has been carried out by using Fe^{II}–bleomycin and O_2, Fe^{III}–bleomycin and H_2O_2, or Fe^{III}–bleomycin plus iodosylbenzene by the method of Hecht.[50]

Complexes of O_2^- bound to transition metals as stable species and as intermediates are being reported with increasing frequency for Cu^I, Fe^{II}, Mn^{II}, Co^{II},[5,39] and Ti^{III}.[6] Oxygenated hemes have been shown to possess the properties of $Fe^{III}(O_2^-)$ species.[5] However, identifying coordinated oxygen free radicals by spectroscopic techniques has often proven difficult. Short-lived, but strongly bound, adducts of $HO_2^\bullet$ ($k_f \approx 10^3$ M^{-1}) are known by flow ESR methods for a variety of high-oxidation-state labile metal centers including Ti^{IV}, U^{IV}, Zr^{IV}, Cu^{II}, Mo^{VI}, and Co^{III}.[7,8]

Free O_2^- and its protonated form $HO_2^\bullet$ ($pK_a = 4.22$)[9] are trappable by the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin trap ($k_{HO_2} = 6.6 \times 10^3$ M^{-1} s^{-1}, $k_{O_2^-} = 10$ M^{-1} s^{-1}),[9] and these adducts have much longer lifetimes. The $HO_2DMPO^\bullet$ radical exhibits six ESR resonance lines in water ($A_N = 17.1$ G, $A_H = 3.7$ G), which are readily distinguished from the hydroxyl radical adduct's characteristic four-line pattern ($(HO(DMPO))^\bullet$; $A_N = A_H = 15.0$ G).[10,13] DMPO spin trapping has been used to establish the inner-sphere reduction of O_2 by several binuclear transition-metal reductants ($V_2O(ttha)^{2-}$ and $Fe_2(ttha)(H_2O)_2^{2-}$)[11,12] and to probe 1e vs 2e pathways used by Ti^{III}, Fe^{II}, and Ru^{II} complexes in reaction with H_2O_2 and O_2.[13,14]

Rather surprisingly, only one transition-metal–superoxide complex has proven previously to be amenable to spin trapping. Drago et al. were able to generate the DMPO adduct of Co^{III}(SMDPT)(O_2^-) in dry toluene at room temperature (SMDPT = bis(3-(salicylcideneamino)propyl)methylamine).[15] The Co(SMDPT)(O_2^-)–DMPO adduct exhibits a six-line spectrum ($A_N = 12.8$ G, $A_{H_\beta} = 7.68$ G)[15] compared to the spectrum of the free $HO_2^\bullet$ adduct in benzene ($A_N = 12.9$ G, $A_H = 6.9$ G).[9,13] In this paper we present data in which a Ru^{II}-coordinated O_2^- or $HO_2^\bullet$ radical is trapped by DMPO in aqueous solution and show that the more reactive $HO^\bullet$ radical can also be coordinated to Ru^{IV} and spin-trapped by DMPO. Very little mention of coordinated hydroxyl radicals exists in the literature. Simple electron shifts between metal hydroxo–metal oxo species can account for the hydroxylation capability of high-oxidation-state oxometal complexes. This is equivalent to the following resonance situations in which the $M^{n+}O$ or $M^{n+1}(OH)$ species serve as the hydroxylators:

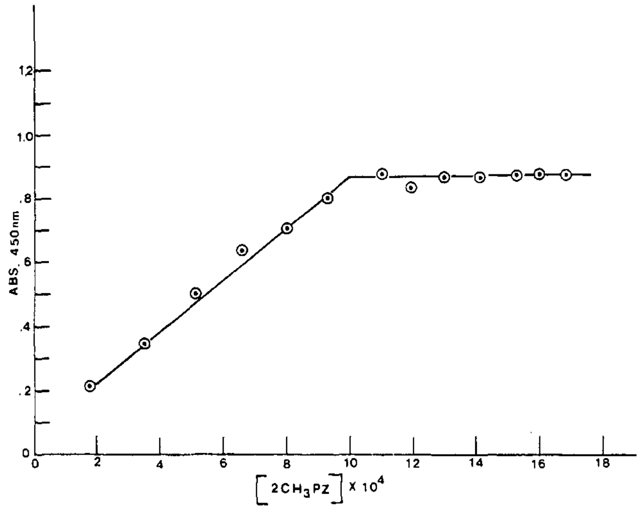

Figure 1. Titration of $Na[Ru(hedta)(H_2O)]\cdot 4H_2O$ by 2-CH_3pz. $[Ru^{II}(hedta)(H_2O)^-] = 1.00 \times 10^{-3}$ M; [2-CH_3pz] = 0–18 $\times 10^{-4}$ M; T = 22 °C; b = 0.100 cm (cell).

$$M^{n+2}\text{—}(OH^-) \longleftrightarrow M^{n+1}(\ddot{\underset{\cdot}{O}}H)$$

$$M^{n+2}{=}\underset{\cdot\cdot}{\dot{O}}\!: \longleftrightarrow M^{n+1}\text{—}\underset{\cdot\cdot}{\ddot{O}}\!: \longleftrightarrow M^{n+}\text{—}\underset{\cdot\cdot}{\ddot{O}}$$

Groves has suggested that the related resonance

$$(P^+)Fe^{IV}{=}\underset{\cdot\cdot}{\dot{O}} \longleftrightarrow (P^+)Fe^{III}\text{—}\underset{\cdot\cdot}{\ddot{O}}\cdot$$

(P^+ = porphyrin π cation radical) accounts for the hydroxylation capacity of P-450 model compounds and probably the P-450 enzyme itself.[17] We believe our present report is the first one of spin trapping of coordinated $HO^\bullet$ by DMPO and of the coordinated O_2^- complex in aqueous solution.

Experimental Section

Reagents. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO), 2-methylpyrazine (2-CH_3pz), 1,1-bis(hydroxymethyl)-3-cyclohexene, $RuCl_3\cdot 3H_2O$, and *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (H_3hedta) were obtained from Aldrich. Triethylenetetraminehexaacetic acid (H_6ttha) was obtained from Sigma.

Spin-Trapping Methods. ESR spectra were obtained in the X-band region (frequency ~9.395 GHz) with 100-KHz modulation on a Varian E-4 ESR spectrometer. Handling procedures have been reported previously.[11-13] Solutions were prepared in glass bubblers attached to an Ar line. Oxygen removal was achieved by passage of Ar, scrubbed through Cr(II) solution towers, through the samples. Standard gastight syringe techniques were used.

Syntheses of Ru^{II} Compounds. $Na_2Ru(edta)$, $Na_2Ru_2(ttha)$, and $NaRu(hedta)(H_2O)$ ($edta^{4-}$ = ethylenediaminetetraacetate; $ttha^{6-}$ = triethylenetetraminehexaacetate; $hedta^{3-}$ = *N*-(2-hydroxyethyl)ethylenediaminetriacetate) preparations were carried out by using Shimizu's procedures[18] as modified by Myser.[19] In this method $RuCl_3\cdot 3H_2O$ is reduced by refluxing in hot ethanol and HCl (3 M). The

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solution is evaporated, and the residue is combined with the appropriate chelating ligand. Ru(III) and Ru(II) derivatives have also been prepared by the methods of Matsabura and Creutz,[20] Diamantis and Dubrawski,[21] and Taqui Khan et al.[22] The $Na_2Ru(edta)$, $Na_2Ru_2(ttha)$, and $NaRu(hedta)(H_2O)$ salts were shown to have additional waters of crystallization as shown below for $Na[Ru(hedta)(H_2O)]\cdot 4H_2O$.

IR and NMR Spectra. IR spectra were obtained as KBr pellets, pressed at 9-ton pressure, on an IBM IR/32 FTIR instrument. ^1H NMR spectra for characterization work were obtained on a Bruker AF300 NMR instrument at 300.13 MHz.

Electrochemical Procedures. Cyclic voltammograms were performed at 22 °C in a 30.0-mL closed glass cell under N_2 at a standard three-electrode assembly. The working electrode was glassy carbon, and the reference electrode was a saturated calomel electrode. The sweep rate of 50 mV/s was carried out from 1.10 to 0.70 V vs SCE as discussed in the main text. The electrolyte was 0.10 M NaCl to prevent problems of ClO_4^- interaction with Ru^{II} complexes.

Results and Discussion

Ru^{IV} Complexes. The Ru^{II} solutions of $Ru(edta)^{2-}$, $Ru(hedta)^-$, and $Ru_2(ttha)(H_2O)_2^{2-}$[24] were prepared by dissolving weighed solids. The dissolved Ru^{II} salts were also pretreated with the Zn/Hg reduction step to assure the absence of Ru^{III} in the initial solutions. All of the isolated Ru^{II} and Ru^{III} salts showed completely coordinated carboxylate donors having a ν_{COOM} stretch at ca. 1643 cm^{-1}. The correct formula of the Na^+ salt of the $Ru(hedta)(H_2O)^-$ complex was shown to be $Na[Ru(hedta)(H_2O)]\cdot 4H_2O$ by means of a spectrophotometric titration at 450 nm using 2-methylpyrazine ($2\text{-}CH_3pz$) as the titrant (Figure 1). The $Ru(hedta)(H_2O)^-$ and related $Ru(edtaH)(H_2O)^-$ complexes are known to undergo monosubstitution of π-acceptor ligands such as pyridine, CO, CH_3CN, N_2, pyrazine, and isonicotinamide.[20,21] The $2\text{-}CH_3pz$ titration was followed at the MLCT band of the $Ru(hedta)(2\text{-}CH_3pz)^-$ product as shown in eq 1. The effective molecular weight was determined to be 488.8,

$$Ru^{II}(hedta)(H_2O)^- + 2\text{-}CH_3pz \rightleftharpoons Ru^{II}(hedta)(2\text{-}CH_3pz)^- + H_2O \quad (1)$$

consistent with a total of five water molecules in the formula $Na[Ru(hedta)(H_2O)]\cdot 4H_2O$.

A Ru^{IV} complex of the $hedta^{3-}$ chelate was prepared by oxidation of $Ru^{II}(hedta)(H_2O)^-$ with 1 equiv of $Na_2S_2O_8$.[41] The resulting solution of the Ru^{IV} complex was treated with $BaCl_2$ to remove the SO_4^{2-} as $BaSO_4$ by filtration. The colorless Ru^{IV} complex was precipitated from solution by addition of ethanol, collected as $[Ru_2O(hedta)_2]\cdot xH_2O$. The bridged structure is supported by evidence given below. The oxidation state of the isolated product was shown to be IV by means of the electron-transfer cross-reaction between $Ru^{II}(hedta)(H_2O)^-$ and the isolated Ru^{IV} complex. Samples were prepared by weight so that between 25 and 50% excess of Ru^{II} would be present if the cross-reactant partner were Ru^{IV}. Under these conditions, if the isolated salt were Ru^V or Ru^{VI}, no Ru^{II} would remain after the cross-reaction. The presence of excess Ru^{II} after reaction of $Ru(hedta)(H_2O)^-$ with the isolated salt rules out Ru^V or Ru^{VI} as was shown by the development of the color of $Ru^{II}(hedta)(2\text{-}CH_3pz)^-$ at 450 nm ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}) using excess $2\text{-}CH_3pz$. The electron-transfer cross-reaction is shown in eq 2 as required for Ru^{IV}. The

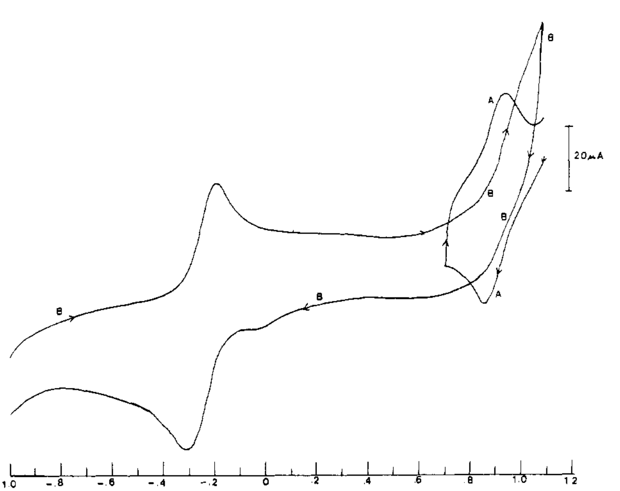

Figure 2. Cyclic voltammograms of the isolated Ru^{IV}–hedta species: (A) scanned at high potential only; (B) scanned after holding at −1.0 V.

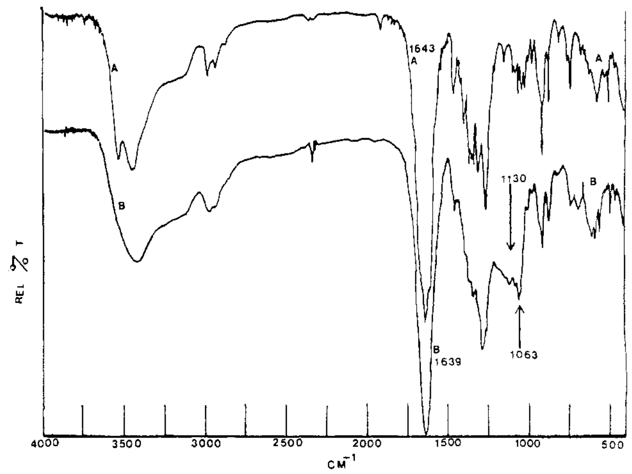

Figure 3. Infrared spectra of (A) $Ru^{III}(hedta)(H_2O)$ and (B) $[Ru_2O(hedta)_2]\cdot(15.4 \pm 0.4)H_2O\cdot 0.9NaCl$ in KBr.

$$Ru^{IV}{}_2O(hedta)_2 + 2Ru^{II}(hedta)(H_2O)^- \xrightarrow{2H^+} 4Ru^{III}(hedta)(H_2O) \quad (2)$$

$Ru^{III}(hedta)(H_2O)$ product has been prepared previously by O_2 oxidation of $Ru(hedta)(H_2O)^-$ and by a 1-equiv oxidation of $Ru(hedta)(H_2O)^-$ by Ce(IV). $Ru(hedta)(H_2O)$ does not react with $2\text{-}CH_3pz$ to product any absorbance at 450 nm. Therefore, only the excess $Ru(hedta)(H_2O)^-$ reacts with $2\text{-}CH_3pz$ and contributes to the absorbance. Three possible formulations for the Ru^{IV} complex need to be considered. One is the mononuclear hydroxy complex $[Ru(OH)(hedta)]\cdot xH_2O$, another is the mononuclear oxo complex $Na[RuO(hedta)]\cdot xH_2O$, and the last is the binuclear oxo-bridged complex $[Ru_2O(hedta)_2]\cdot xH_2O$. The mononuclear oxo formulation requires the presence of one Na^+ per Ru^{IV}. This situation was ruled out by means of a potentiometric Na^+ analysis using a sodium ion selective electrode. Calibration with Na^+ standard solutions in the range of 0.50×10^{-4}–1.00×10^{-3} M showed the instrument response was Nernstian. The Ru^{IV} complexes of $hedta^{3-}$ and the related $edtaH^{3-}$ complex showed only 0.450:1 Na^+:Ru^{IV} in the $hedta^{3-}$ complex and even less, 0.192:1 Na^+:Ru^{IV} in the $edtaH^{3-}$ complex. Coprecipitation of NaCl (or $Na_2S_2O_8$) during the isolation procedure from C_2H_5OH solutions accounts for the presence of nonstoichiometric Na^+. The choice between the hydroxy monomer and the oxo-bridged Ru^{IV} complex is more difficult. The electrochemical behavior of the isolated complexes of Ru^{IV}–hedta and

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[23] Oxidation of DMPO is rejected on the basis of the observed ESR pattern; DMPOX has a three-line pattern with $A_N = 13.0$ G.[15]

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[26] Coordination of $HO_2^\bullet$ should raise the acidity and lower the pK_a below 4.11. Thus, at neutral pH the species should be formulated as the superoxo complex. However, spin trapping might influence the acidity of the coordinated $HO_2^\bullet$ or kinetically favor trapping of the hydroperoxyl form as is the case for free $HO_2^\bullet$–O_2^-.

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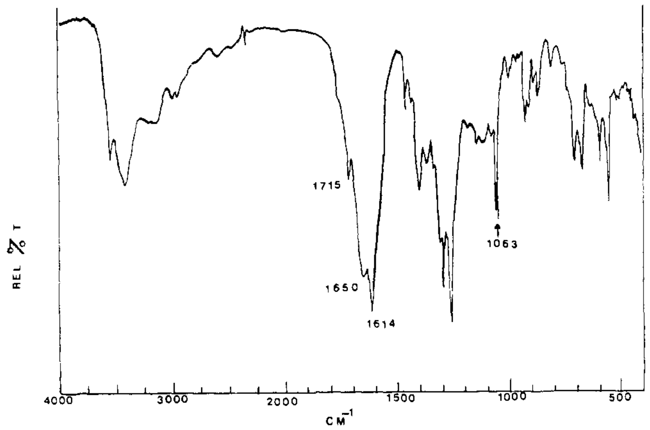


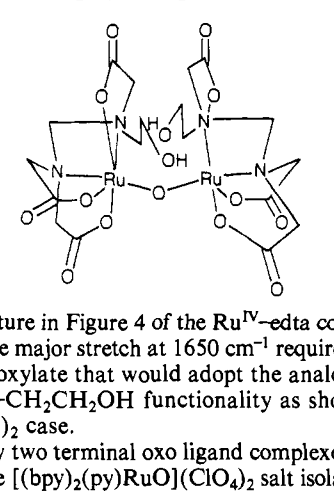
Figure 4. Infrared spectrum of $Ru_2O(edtaH)_2$ in KBr.

Ru^{IV}–edtaH indicates the bridged binuclear complex as discussed below. On the basis of the required stoichiometry of reaction 2 the effective molecular weight is consistent with the formula $[Ru_2O(hedta)_2]\cdot(15.4 \pm 0.4)H_2O\cdot0.9NaCl$.

The Ru^{IV}–hedta solid was dissolved in 0.10 M NaCl and examined by cyclic voltammetry. The presence of the $Ru^{III/IV}$ reversible wave was detected at 1.15 V vs NHE as shown in Figure 2A if the scanning of potential (glassy-carbon working electrode) commenced at 1.34 V and ended at 0.94 V vs NHE. When scanning was carried out from −0.76 to +1.34 V, the Ru^{IV} complex was already reduced to Ru^{II} at the glassy-carbon surface. Only the $Ru^{II/III}$ wave at −0.01 V was observed (Figure 2B), and the $Ru^{III/IV}$ wave was missing. Therefore, reduction to $Ru^{II}(hedta)^-$ at the electrode surface ruptures the Ru^{IV}–O–Ru^{IV} bridge; reoxidation at 50 mV/s sweep rate is too rapid for the parent binuclear species to re-form, and the wave is absent on the −0.76 to +1.34 V scan.

The IR spectra of $Ru^{III}(hedta)(H_2O)$ and $[Ru_2O(hedta)_2]\cdot(15.4 \pm 0.4)H_2O\cdot0.9NaCl$ are shown in parts A and B, respectively, of Figure 3. The ν_{COOM} stretch is almost unchanged in the Ru^{IV} product. A distinct increase in the intensity of the IR absorption occurs in the region between 1130 and 1063 cm^{-1}. All other bands are virtually unchanged. The analogous Ru^{IV} complex, derived from $Ru^{II}(edta)^{2-}$, was prepared by the same procedures with $S_2O_8^{2-}$ oxidation. The isolated salt also has an even sharper new stretch at 1063 cm^{-1} (Figure 4). The bands at 1063 cm^{-1} were shown to be due to coprecipitation of $Na_2S_2O_8$ and represent an impurity band.

No additional band appears at 870 cm^{-1}, which has been attributed to a coordinated peroxo ligand in the $Ru(edta)(O_2)Ru(edta)^{2-}$ complex.[22] The absence of pendant carboxylate moieties and the bridging implied from cyclic voltammetry suggest the structure shown for $Ru_2O(hedta)_2$:



The shoulder feature in Figure 4 of the Ru^{IV}–edta complex at 1715 cm^{-1} riding on the major stretch at 1650 cm^{-1} requires one pendant protonated carboxylate that would adopt the analogous position of the pendant $-CH_2CH_2OH$ functionality as shown above for the $Ru_2O(hedta)_2$ case.

There are only two terminal oxo ligand complexes reported for Ru^{IV}.[29-32,42] The $[(bpy)_2(py)RuO](ClO_4)_2$ salt isolated by Moyer and Meyer[29] has its Ru=O stretch at 792 cm^{-1}, which shifts to 752 cm^{-1} with ^{18}O labeling. A tetramesitylporphyrin complex, $Ru^{IV}O(TMP)$, has recently been prepared by Groves and Ahn.[42] The Ru=O stretch occurs at 823 cm^{-1} for the Ru^{IV} porphryin. The region near 800 cm^{-1} (±40 cm^{-1}) is weak in both the Ru^{IV}(hedta) and Ru^{IV}(edta) derivatives. This provides added evidence for the absence of a terminal Ru^{IV}=O coordination, in concert with the Na^+ analysis.

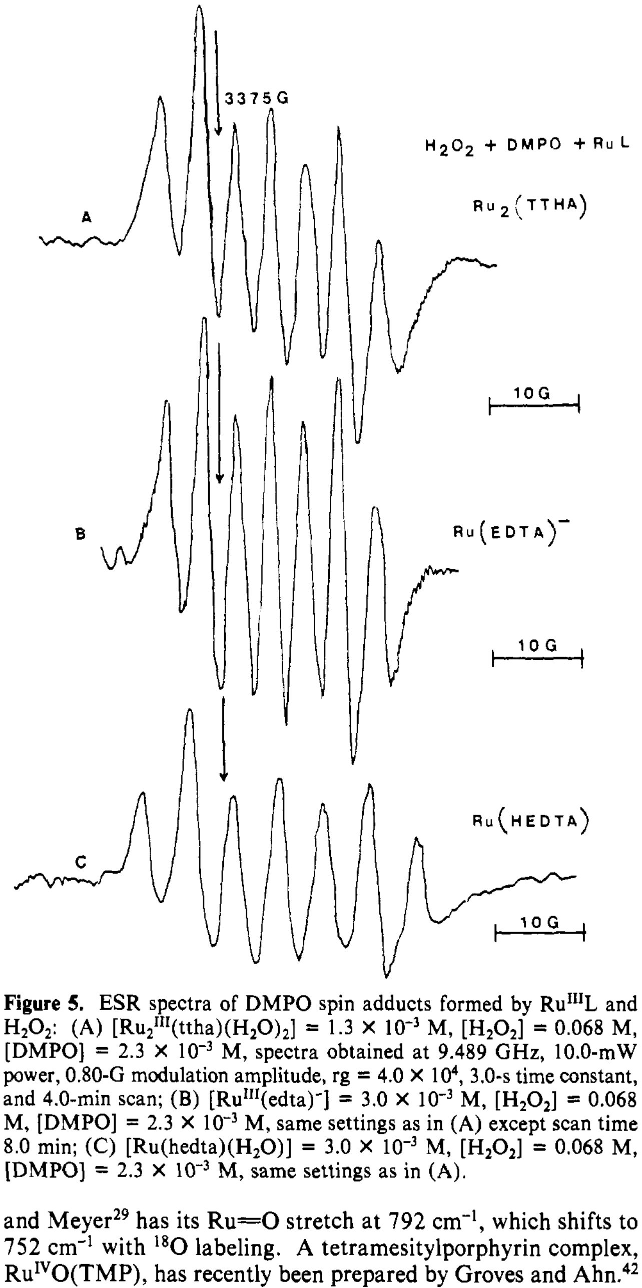


Figure 5. ESR spectra of DMPO spin adducts formed by $Ru^{III}L$ and H_2O_2: (A) $[Ru_2^{III}(ttha)(H_2O)_2] = 1.3 \times 10^{-3}$ M, $[H_2O_2] = 0.068$ M, $[DMPO] = 2.3 \times 10^{-3}$ M, spectra obtained at 9.489 GHz, 10.0-mW power, 0.80-G modulation amplitude, rg = 4.0×10^4, 3.0-s time constant, and 4.0-min scan; (B) $[Ru^{III}(edta)^-] = 3.0 \times 10^{-3}$ M, $[H_2O_2] = 0.068$ M, $[DMPO] = 2.3 \times 10^{-3}$ M, same settings as in (A) except scan time 8.0 min; (C) $[Ru(hedta)(H_2O)] = 3.0 \times 10^{-3}$ M, $[H_2O_2] = 0.068$ M, $[DMPO] = 2.3 \times 10^{-3}$ M, same settings as in (A).

Spin Trapping of Superoxyl Complexes. When (1–3) × 10^{-3} M $Ru^{II}L$, $Ru^{III}L$, and $Ru^{IV}L$ complexes (L = $edta^{4-}$; $hedta^{3-}$) or $Ru^{II}_2(ttha)(H_2O)^{2-}$ and $Ru^{III}_2(ttha)(H_2O)_2$ complexes were combined under Ar with DMPO (0.010 M), no detectable ESR signals were obtained.

When (1–3) × 10^{-3} M $Ru^{II}(edta)^{2-}$, $Ru^{II}(hedta)(H_2O)^-$, and $Ru^{II}_2(ttha)(H_2O)_2^{2-}$ were oxidized to Ru^{III} derivatives by H_2O_2 (0.068 M) in the presence of DMPO, the one-electron-reduction product ($HO^\bullet$) was trapped as the $HO(DMPO)^\bullet$ adduct ($A_N = A_H = 15.0$ G) in the first 10 s. However, if the initial Ru^{II} to Ru^{III} oxidation process was allowed to become complete before

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DMPO was added at 45 s, a new species was trapped by DMPO for each complex as shown by ESR (Figure 5).

The slower addition of H_2O_2 by substitution on the Ru^{III} oxidation products is indicated. The solution species are yellow-brown in the presence of excess H_2O_2; the Ru^{IV} complexes are nearly colorless and are reduced by H_2O_2 to Ru^{III} (vide infra). The Fe^{III}(edta)$^-$–H_2O_2 system is well-known to form a stable [Fe^{III}(edta)(O_2)]$^{3-}$ purple species by coordination of the peroxo anion,[34,35] and the same species is generated from the reaction of O_2^- with Fe^{II}(edta)$^{2-}$ in Me_2SO–H_2O mixtures.[36] The yellow-brown species in solutions of the Ru^{III} polyaminopolycarboxylates carry out a slow Fenton's-reagent-like decomposition of H_2O_2.[37] O_2 evolution occurs from the Ru^{III}L–H_2O_2 samples as for the Fe^{III}(edta)$^-$–H_2O_2 system with time. The intensity of the yellow-brown solution color is also dependent on the [H_2O_2]:[Ru^{III}] ratio, supporting a substitution equilibrium for the Ru^{III} complexes involving addition of H_2O_2 or HO_2^-. The amount of radical species trapped by DMPO decreased above pH ≈ 5, which suggests competitive binding of OH^- on the Ru^{III} center. The presence of OH^- on Ru^{III}, in place of H_2O at lower pH, should show the substitution of H_2O_2. The addition of H_2O_2 to Fe^{III}(edta)OH^{2-} is general-acid-catalyzed and appears to require H_2O_2 substitution via a dissociated aqua complex.[36b] Thus, the Fe^{III}(edta)OH^{2-} species is also much less reactive.

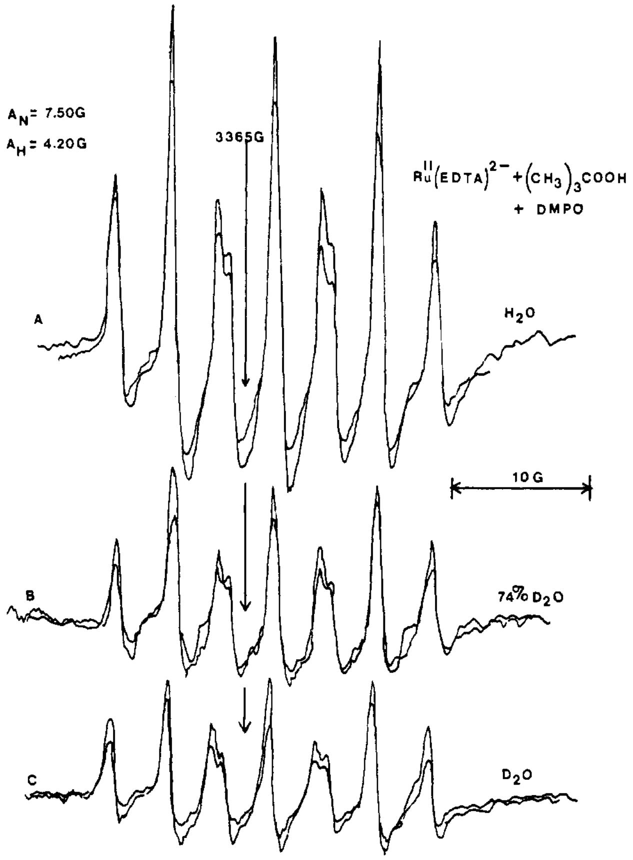
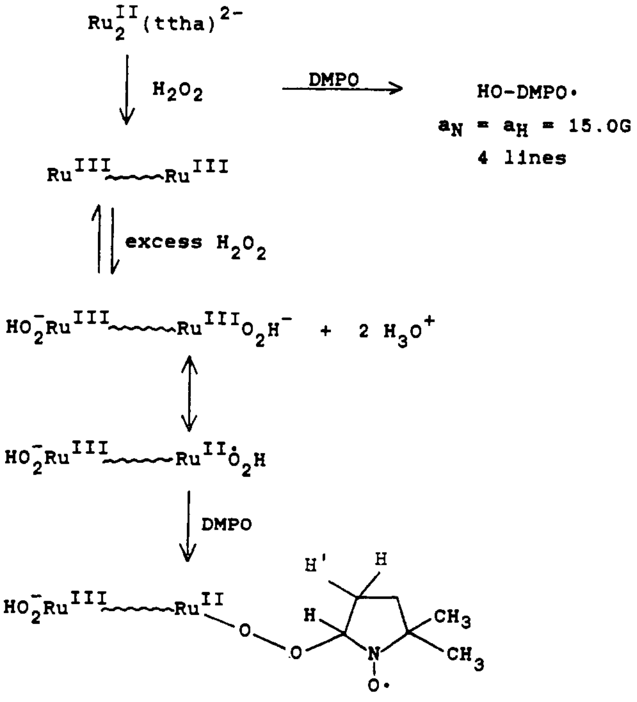


Figure 6. ESR spectra of Ru^{III}(edta)$^-$–(CH$_3$)$_3$COOH oxidation product adduct of DMPO·[Ru^{III}(edta)$^-$] = 2.54 × 10^{-3} M; [DMPO] = 1.0 × 10^{-2} M; [(CH$_3$)$_3$COOH] = 0.26 M; spectra were obtained at 9.483 GHz, 10.0-mW power, 0.80-G modulation amplitude, rg = 3.2 × 10^4, 3.0-s time constant, and 4.0-min scan.

Scheme I



The seven-line ESR pattern, which is produced by any of the Ru^{III}L–H_2O_2–DMPO solutions after 45 s, consists of outside lines of intensity ca. 1.0 and five inside lines of intensity ca. 2.0.[23] Absolute coincidence of the overlapping sets of lines does not occur, and some distortion is evident in the 1.0:2.0 ratios. The sequence

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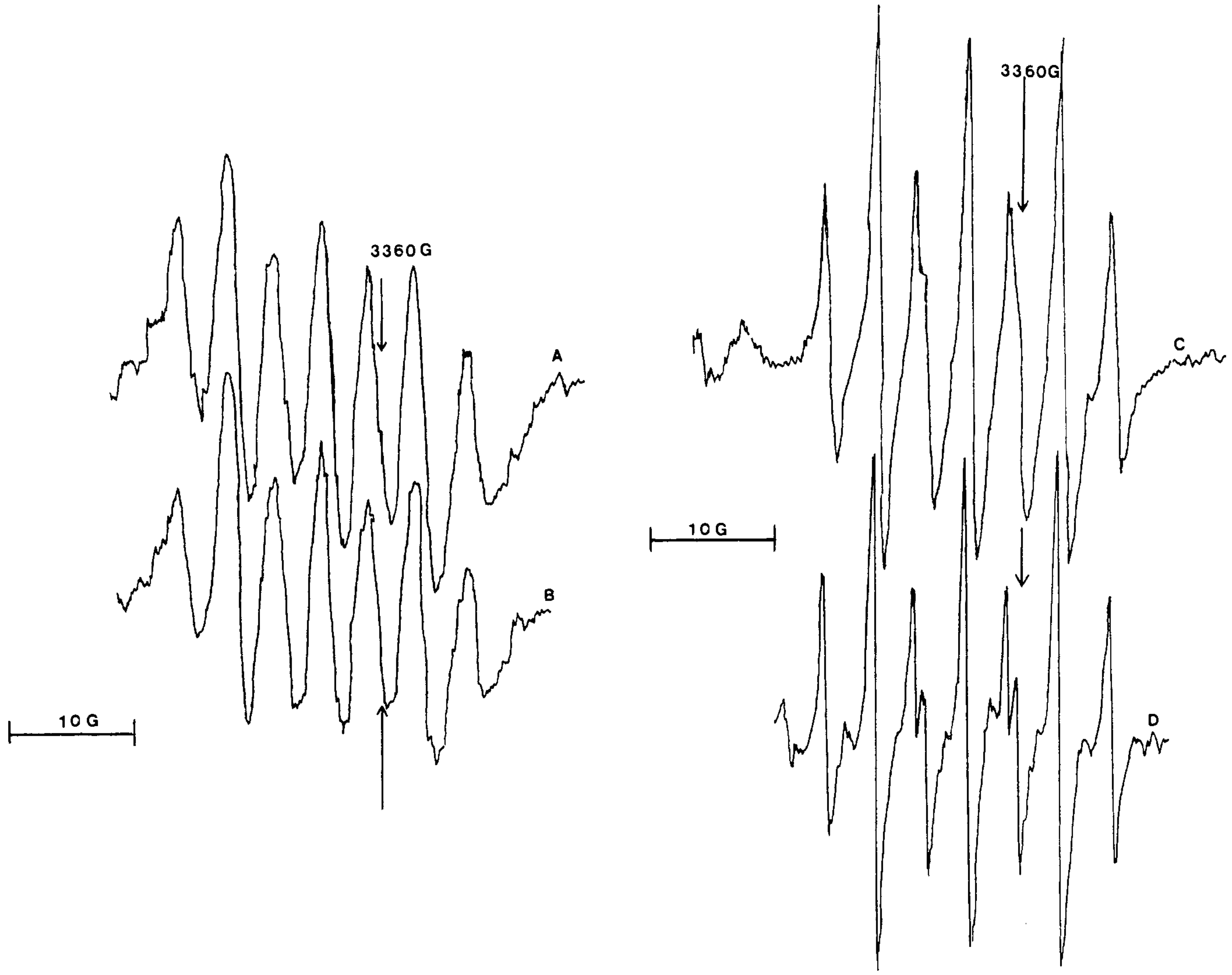


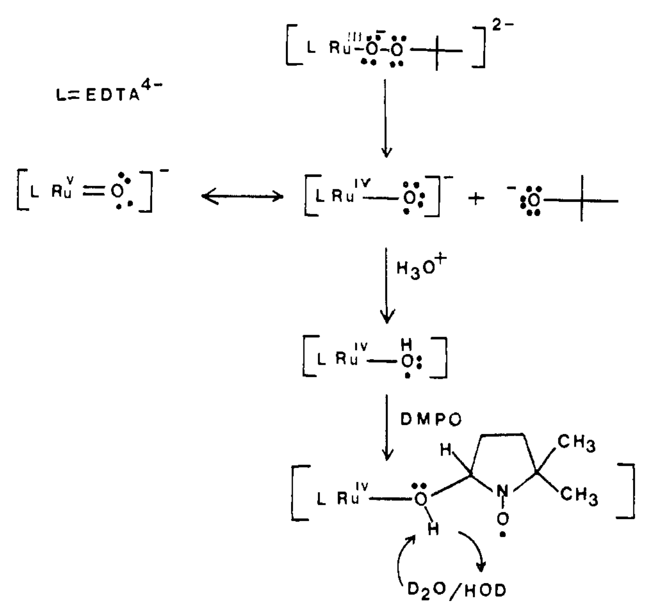
Figure 7. Modulation amplitude study of Ru(hedta)-produced radicals for H_2O_2 and $(CH_3)_3COOH$ oxidation ($[Ru^{III}(hedta)] = 3.16 \times 10^{-3}$ M, $[DMPO] = 3.0 \times 10^{-2}$ M): (A and B) $[H_2O_2] = 0.088$ M; (C and D) $[(CH_3)_3COOH] = 9.08 \times 10^{-2}$ M. Spectra A and C were at 0.80-G modulation amplitude; spectra B and D were at 0.50-G modulation amplitude. All other settings were as follows: 10.0-mW power, 9.482 GHz, 3.0-s time constant, 8.0-min scan time, rg = 4.0×10^4 for A–C and 3.2×10^4 for D.

of chemical events is given in Scheme I for the binuclear $ttha^{6-}$ complex $Ru^{II}_2(ttha)(H_2O)_2^{2-}$. The availability of two labile solvent positions, one per Ru(II) or Ru(III) center, and characterization of CO and other π-acceptor adducts of the Ru^{II} complex were reported elsewhere;[24] the analogous single substitutionally labile site of $Ru(edta)^-$ and $Ru(hedta)(H_2O)$ is known from the literature.[20-22] The apparent spacing in the seven-line pattern is slightly different for each of the parent $Ru^{III}(edta)^-$, $Ru^{III}(hedta)$, and $Ru^{III}_2(ttha)$ complexes, giving assurance that the detected radical species is not an impurity from either one of the isolated Ru(III) salts or from the DMPO trapping agent. The pattern of seven lines is explained by the overlapping set of lines produced by an additional H atom coupling from the ring H_γ hydrogen; only one of the γ-hydrogen is in the proper orientation with the nitrogen p orbital to exhibit coupling.[25] No coupling is observed to the bridging $HO_2^\bullet$ (or O_2^-) unit.[26] This observation was confirmed by spectra of the same radical prepared in D_2O. No change in intensity (within 4% reproducibility between runs) was observed for the radical in D_2O. The extent of coupling to the H_γ position is very sensitive to the bond angles in the $RDMPO^\bullet$ adduct.[8,15] Small changes in steric or solvation influences on this coupling may account for the differences between the radicals trapped from $Ru(edta)^-$, Ru(hedta), and $Ru_2(ttha)$ moieties. For example, when $CH_3O^\bullet$ is trapped by DMPO in benzene, A_{H_γ} is only 1.85 G.[8] For L = $ttha^{6-}$ and $edta^{4-}$, the principal couplings $A_N \simeq 8.0$ G and $A_{H_\beta} \simeq A_{H_\gamma} = 5.0 \pm 0.5$ G are slightly smaller than those observed in $Co(SMDPT)(O_2)DMPO$, where coupling to the H_γ hydrogen is not observed.[15] For L = $hedta^{3-}$, values of $A_N \simeq 10.0$ G and $A_{H_\beta} = A_{H_\gamma} = 5.5$ G fit the spectra reasonably well in a suitable hand-fit spectrum. The patterns can also be fit reasonably well with $A_N = 10.0$ G, $A_{H_\beta} = 7.0$ G, and $A_{H_\gamma} = 4.0$ G. No coupling to the Ru(II) center ($I = {}^5/_2$, 17.0%) was observed as in the Co(III) case. Values have only integer significance for A_N, A_{H_β}, and A_{H_γ} because variation in the choice of any one variable can be compensated by adjustments of 1.5 G in the magnitudes of the others without strongly influencing the results.

Trapping of Coordinated Hydroxyl Complexes. When 0.30 M *tert*-butyl peroxide (*t*-BuOOH) was used in place of H_2O_2 as the oxidizing agent for $Ru^{II}(edta)^{2-}$, a distinctly different species (Figures 6 and 7) was produced. The same spectrum was obtained by t-BuOOH oxidation of the $Ru^{III}(edta)^-$ ion, produced by O_2 oxidation of $Ru^{II}(edta)^{2-}$. Excess O_2 was removed by an Ar purge, and final addition of *t*-BuOOH was made to generate the new species. These experiments show that the key step, generating the new species, commences with *t*-BuOOH oxidation of Ru^{III}, which can be produced by an earlier Ru^{II} to Ru^{III} oxidation by *t*-BuOOH or another reagent such as O_2. The yield of DMPO-trapped radical (Figure 6) of the $Ru^{III}L$–*t*-BuOOH oxidation also decreases with increasing pH. Almost no radical signal could be obtained above pH = 7.23. The need for a substitutionally labile form of the $Ru^{III}L$ complexes in order to allow for substitution of *t*-BuOOH is implicated by these results.

A strong ESR signal pattern of nine lines as a triplet of triplets is observed (Figure 6). The pattern suggests contact of the un-

Scheme II



paired spin with one nitrogen atom and two nearly equivalent hydrogens (A_N = 7.50 G, A_H = 4.20 G). It is well-known that *t*-BuOOH has the strength to oxidize Ru^{II} porphyrins to Ru^{IV} porphyrins and that its oxidizing power is greater than that of H_2O_2.[27,28] No ESR signals were produced in the presence of DMPO by the Ru^{IV} complex prepared via $S_2O_8^{2-}$ oxidation or by Ru^{IV} with the further addition of *t*-BuOOH to the Ru^{IV} solution. However, addition of H_2O_2 to the Ru^{IV} complex solution returned the color from nearly colorless to yellow-green with immediate formation of the identical seven-line ESR pattern of Figure 5. This shows that the higher oxidation state species prepared by either $S_2O_8^{2-}$ or the $S_2O_8^{2-}$–*t*-BuOOH sequence are reduced by H_2O_2 to species of lower oxidation state (e.g. Ru^{III}), which are responsible for the trappable coordinated superoxyl radicals as shown in Figure 5 (Scheme I).

The DMPO-trappable species that is formed by the oxidation of $Ru^{II}(edta)^{2-}$ by *t*-BuOOH must be at an oxidation-state level of Ru^{III}–O atom (or Ru^V) as shown in Scheme II, since no such radical species occurs with $Ru^{II}L$, $Ru^{III}L$, or $Ru^{IV}L$ plus DMPO alone. Furthermore, the peroxy anion *t*-BuOO⁻ is well-known to transfer an O atom in oxidations with *t*-BuOOH.[28] Supporting evidence for the Ru^{III}–O atom character of this species has been obtained by the catalytic epoxidation of *cis*-stilbene by the Ru(hedta)–*t*-BuOOH reagent. This result will be reported elsewhere.[16] An important additional factor is that *cis*-stilbene was not epoxidated by the Ru(hedta)–H_2O_2 system. This shows additionally that the two radical species are not the same. The resultant resonance between

$$Ru^{V}{=}\ddot{O}\!:\ \longleftrightarrow\ Ru^{IV}{-}\ddot{O}\!:\ \longleftrightarrow\ Ru^{III}{-}\ddot{O}$$

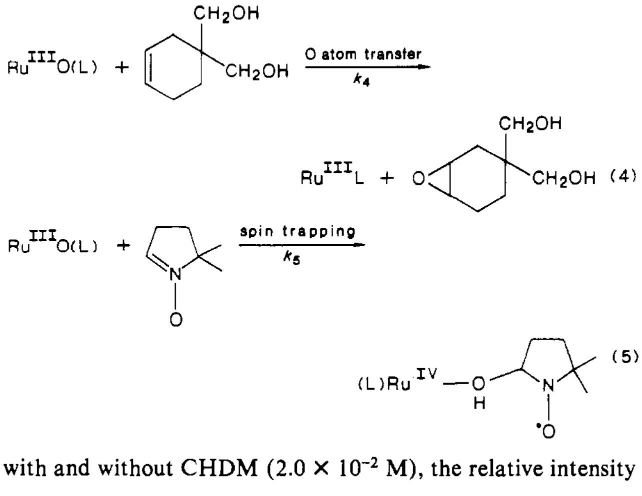
appears to be necessary for trapping the coordinated hydroxyl radical by DMPO. The signal is reduced in intensity as a function of the percentage of D_2O when the H:D percentage of the solvent is changed by carrying out the *t*-BuOOH oxidation in D_2O–H_2O mixtures. The amplitude is 43% in 74% D_2O (Figure 6B) of that in water (Figure 6A). This contrasts with the absence of a solvent H–D exchange broadening for the coordinated superoxyl; this suggests that the trapped radical is the $(L)Ru^{II}(O_2^-)(DMPO)$ adduct in the Ru^{III}–H_2O_2 systems. In the case of *t*-BuOOH oxidation of $Ru^{II}(edta)^{2-}$ in D_2O we were unable to achieve 100% D_2O solvent because of the proton component of *t*-BuOOH and the waters of hydration from the original Na[Ru(edta)]·$2H_2O$ salts. Exchange of the bridging OH group of Ru(edta)OH(DMPO) is anticipated to be rapid due to the high acidity of the proton as promoted by the Ru^{IV} center. The loss of signal amplitude in the D_2O solvent would occur via two components: (1) chemical exchange broadening of the signal and (2) reduction in amplitude and further splitting of the triplet of triplets pattern (one N, $I = 1$; two equivalent H, $I = {}^1/_2$) into an overlapped set of 18 lines (one N, $I = 1$; one H, $I = {}^1/_2$; one D, $I = 1$). This complicated pattern of broadened intensity would be overlapped with the triplet of triplets pattern from the residual unexchanged system. This accounts for a discernible residual pattern in Figure 6C even at the highest percentage of D_2O. The same triplet of triplets pattern with virtually identical coupling constants (A_N = 7.5 G, A_H = 4.0 G) (confirmed by Figure 7D) was obtained from the spin adduct of Ru(hedta)(H_2O) and *t*-BuOOH with DMPO.

A skeptical reviewer has questioned whether the radical species produced by H_2O_2 oxidation of $Ru^{II}L$ complexes (via addition to $Ru^{III}L$, vide infra) and the *t*-BuOOH oxidation of $Ru^{II}L$ with second substitution on the $Ru^{III}L$ products are not indeed the same species. His claim was that broadening from different RuL samples could account for the absence of a similar ESR spectrum. That this view is incorrect is seen by the evidence in Figure 7. Ru^{II}(hedta) was oxidized by H_2O_2 and spin-trapped by DMPO (Figure 7A). The same Ru^{II}(hedta) solution was oxidized with *t*-BuOOH and spin-trapped with DMPO (Figure 7C). Both spectra Figure 7A,C) were obtained under identical ESR settings and pH (5.54). When the modulation amplitude was reduced from 0.80 to 0.50 G, the radical obtained from *t*-BuOOH exhibited the fully resolved, sharp derivative of an overlapped triplet of triplets pattern shown in Figure 7D. The radical obtained from H_2O_2 oxidation exhibited no change in the resolution or line widths with decreasing modulation amplitude from 0.50 to 1.25 G (Figure 7B). Furthermore, the chemical reactivities of the coordinated radicals produced by H_2O_2 and *t*-BuOOH oxidation are not the same as described below. Also, suitable A_N values are not the same for the Ru(hedta) derivatives of these radicals: 10.0 G for the $Ru^{II}O_2^-$ case and 7.5 G for $Ru^{III}O$.

Chemical Behavior of $(L)Ru^{II}O_2^-$ and $(L)Ru^{III}O$ Species. $Ru^{II}L$ or $Ru^{III}L$ complexes catalyze O atom transfer from *t*-BuOOH to *cis*-stilbene (eq 3);[16] the appearance of the *cis*-stilbene oxide is unambiguously identified by ^1H NMR.[16,50] In order to have

(3)

a more homogeneous phase for spin-trapping studies, the water-soluble olefin 1,1-bis(hydroxymethyl)-3-cyclohexene (CHDM) was utilized in the present studies at 2.0 × 10^{-2} M. When $Ru^{II}L$ (L = hedta³⁻, edtaH³⁻) was oxidized with *t*-BuOOH in the presence of CHDM, no species giving a triplet of triplets pattern or any other new radical was spin-trapped by DMPO at 3.0 × 10^{-2} M. Therefore, reaction 4 proceeds much more rapidly than reaction 5. In contrast when $Ru^{II}L$ was oxidized by H_2O_2 with and without CHDM (2.0 × 10^{-2} M), the relative intensity



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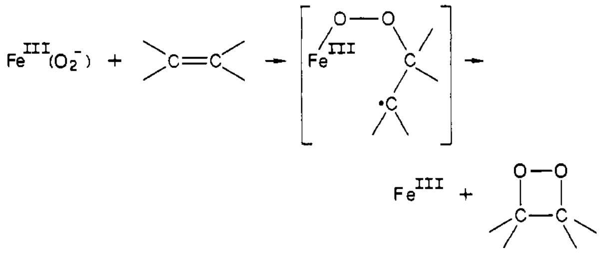
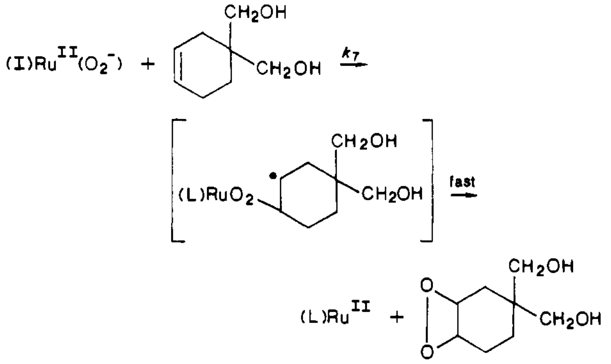
(50) (a) Heimbrook, D. C.; Carr, S. A.; Mentzer, M. A.; Long, E. C.; Hecht, S. M. *Inorg. Chem.* **1987**, *26*, 3835. (b) Heimbrook, D. C.; Mulholland, R. L.; Hecht, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 7839. (c) Murugesan, N.; Hecht, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 493.

of the seven-line radical spectrum of $LRu^{II}(O_2^-)$DMPO changed from 1.0 to $^1/_7$ in the presence of CHDM and 3.0×10^{-2} M DMPO. In addition, no other C-centered radical was detectable in the ESR spectrum.

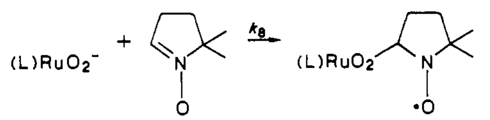
It is known that iron–superoxo complexes can carry out dioxygenase activity by addition across double bonds, yielding a dioxetane product[1,51] (eq 6). Therefore, in the presence of both CHDM and DMPO a kinetic competition between addition to the two double-bond systems is consistent with a reduced yield of the seven-line radical when the $LRu^{II}(O_2^-)$ species is produced (eq 7 and 8). Under the conditions of our experiment $k_7/k_8 \approx$ 6. Therefore, while O atom transfer from $Ru^{III}O(L)$ shows $k_4 \gg k_5$ (for trapping by DMPO), the additions of $(L)Ru^{II}(O_2^-)$ species to the double bonds of CHDM and DMPO are within 1 order of magnitude of each other. This provides added chemical evidence that the spin-trapped radicals formed via H_2O_2 and *t*-BuOOH are chemically very different. The one prepared via *t*-BuOOH oxidation exhibits O atom transfer or monooxygenase activity toward olefin substrates. The other formed via H_2O_2 addition to $Ru^{III}L$ complexes produces nonradical products, presumably with dioxetane formation, as in the dioxygenase systems.



(6)



(7)



(8)

Study of the $Fe^{III}(edta)^-$ System. Parallel experiments were carried out with the $Fe^{III}(edta)^-$–H_2O_2 system using DMPO as a potential trap of an $Fe^{II}(O_2^-)$ species similar to the $Ru^{II}(O_2^-)$ complex trapped as described above. No signal of any DMPO radical adduct was found. It seems probable that the $Fe(edta)(O_2)^{3-}$ complex is more like an $Fe^{III}(O_2^{2-})$ moiety with much less $Fe^{II}(O_2^{\bullet -})$ character or, if an adduct is formed, that the paramagnetic broadening of the high-spin $Fe^{II/III}$ center completely broadens the spectrum of the spin adduct.

The $Fe^{III}(edta)^-$–*t*-BuOOH–DMPO system also failed to show any discernible DMPO radical adduct. Therefore, no Fe^{III}–O atom species was trapped by a path parallel to Scheme II.

Conclusion

The DMPO spin trapping of a coordinated hydroxyl ligand has been accomplished via O atom transfer from *t*-BuOOH to $Ru^{III}(edta)^-$. The less oxidizing H_2O_2 ion binds to Ru^{III} polyaminopolycarboxylates. The product exhibits significant $Ru^{II}O_2^-$ character. The substitution-inert character of the d^6 Ru^{II} complex, together with its diamagnetism, has allowed observation of the $(L)Ru(O_2^-)$ (L = $edta^{4-}$, $hedta^{3-}$, $ttha^{6-}$) complexes by the DMPO spin-trapping procedure. This moiety is a low-spin analogue of the $Fe^{II}(O_2^-)$ intermediate proposed in monooxygenase chemistry. A metal ion superoxo complex has been trapped in aqueous solution for the first time. It has been shown to react with olefin bonds in competition to DMPO spin trapping.

A coordinated hydroxyl group that readily exchanges with deuterium ion in D_2O solvent was trapped by DMPO from the

$$Ru^{V}{=}\ddot{O}\!: \longleftrightarrow Ru^{III}{-}\ddot{\underset{..}{O}}\!: \xrightarrow{H^+} Ru^{IV}{-}\ddot{\underset{..}{O}}H$$

resonance. This was accomplished by O atom transfer to $Ru^{III}(edta)^-$. This species successfully epoxidizes *cis*-stilbene similarly to the ferryl form of active bleomycin.[50] Epoxidation of normal olefin bonds by $Ru^{III}O(edta)^-$ occurs much more rapidly than for spin-trapping by DMPO. It is interesting to note that Coon and White have chosen to describe the activated oxygen species of cytochrome P-450 enzymes as being "as an oxygen atom coordinated to the ferric iron since this species would be most expected to exhibit the reaction characteristics observed with P-450.[38] Groves and Watanabe observed the decay of Fe^{III}(porphyrin)(peroxybenzoate) species by heterolytic O–O cleavage; the resulting species has the same oxidation-state level as Fe^{III}–O atom or the Fe(V)–oxo species, but the spectrum is consistent with one oxidation equivalent stored as the porphyrin π cation radical in an $(P^+)Fe^{IV}{=}O$ species.[40] Therefore, the coordinated radical species that have been observed in this report are themselves candidates for hydroxylation reactions and as models for a number of enzymatic systems that activate oxygen for incorporation into organic substrates during metabolism.

Acknowledgment. We gratefully acknowledge the National Science Foundation under Grant CHE-8417751 for support of this work.

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(51) (a) Other authors prefer rearrangements of stabilized hydroperoxides in the oxidation of catechols: see ref 2. (b) Wood, J. M. In *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Metal Ions in Biology 2; Wiley: New York, 1980; Chapter 4.