Conclusion

The evidence indicates the diruthenium fumaronitrile mixed-valence ion belongs to class II. The evidence includes the calculated value of α^2, the IT bandwidth $\Delta\bar{\nu}_{1/2}$, and the solvent dependence of E_{op}. On the other hand, the spectral and electrochemical properties of the tetraruthenium TCNE mixed-valence species suggest this system is strongly delocalized. Of the three mixed-valence ions (9+, 10+, 11+), the doubly oxidized 10+ species was the most stable.

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Registry No. $[(H_3N)_5RuFum](PF_6)_2$, 85748-65-8; $[(H_3N)_5RuFum](PF_6)_3$, 85748-67-0; $[(H_3N)_5Ru]_2Fum(PF_6)_4$, 85748-69-2; $[(H_3N)_5Ru]_2Fum(PF_6)_5$, 85748-71-6; $[(H_3N)_5Ru]_2Fum(PF_6)_6$, 85748-73-8; $[(H_3N)_5RuTCNE](PF_6)_2$, 85748-75-0; $[(H_3N)_5RuTCNE](PF_6)_3$, 85748-77-2; $[(H_3N)_5Ru]_4TCNE(PF_6)_8$, 85748-79-4; $[(H_3N)_5Ru]_4TCNE(PF_6)_9$, 85748-81-8; $[(H_3N)_5Ru]_4TCNE(PF_6)_{10}$, 85748-83-0; $[(H_3N)_5Ru]_4TCNE(PF_6)_{11}$, 85748-85-2; $[(H_3N)_5Ru]_4TCNE(PF_6)_{12}$, 85748-87-4; $[Ru(NH_3)_5OH_2](PF_6)_2$, 34843-18-0.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Autoxidation of Binuclear Ruthenium(II) Ammines

DAVID M. STANBURY, DENNIS GASWICK, GILBERT M. BROWN, and HENRY TAUBE*

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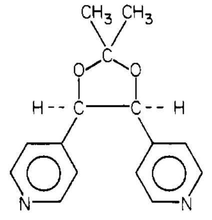
The reduction of oxygen to hydrogen peroxide by a series of binuclear ruthenium(II) ammines has been studied in acidic aqueous solution. The complex $[(Ru(NH_3)_5)_2L]^{4+}$, where L = BPDO = *meso*-4,5-bis(4-pyridyl)-2,2-dimethyl-1,3-dioxolane, was studied in greatest detail. BPDO has a geometry such as to force the two ruthenium centers into close proximity. The kinetics of the autoxidation of the BPDO binuclear complex, as measured by the decay of the charge-transfer band characteristic of ruthenium(II) pyridyl type complexes, showed biphasic behavior. The first phase corresponds to the pseudo-first-order reaction of the fully reduced complex, while the second phase corresponds to the reaction of the mixed-valence species. Inhibition of the second phase by Ru(III) at higher pH is taken as evidence that the mechanism involves outer-sphere electron transfer to form free superoxide. Subsequent protonation of superoxide and reduction to hydrogen peroxide complete the reaction. By comparison of the rates and expected steric and electrostatic effects, it is argued that the mechanism of the first phase likewise has a rate-limiting step involving outer-sphere generation of superoxide.

Introduction

A major kinetic barrier in the reactions of small molecules is that they often proceed through unstable free-radical intermediates. Two-electron transfers have been well documented for certain inner-sphere reactions of mononuclear complexes,[1] and the chemistry of platinum ammines provides some especially interesting examples.[2] There is growing interest in binuclear species as providing a means of bypassing the unstable intermediates that attend a one-electron change, and the validity of this approach has been convincingly demonstrated for the reactions with O_2 of certain cofacial cobalt-containing porphyrins.[3] These reagents undoubtedly react with O_2 by inner-sphere mechanisms. Whether there can be cooperation between two centers when reaction occurs by an outer-sphere mechanism is more problematical, but the possibility that cooperativity of this kind might be documented provided the incentive for the work to be described.

Our continuing interest in binuclear ruthenium ammines[4] suggested them as a logical starting point in the search for multielectron reactions. The choice of oxygen as the redox partner was dictated by a certain familiarity with its chemistry,[5,6] its known participation in two-electron reactions,[1b] and its relevance to the development of an efficient oxygen electrode. Our first goal was to delineate the behavior of a system in which two weakly interacting metal centers are held in a geometry such that oxygen could interact with both centers simultaneously. The bifunctional ligand BPDO[7] served this purpose.



BPDO

When each nitrogen carries a pentaammineruthenium unit, the metal centers are separated by ~7 Å.

When the rates of reaction of the binuclear complexes are compared with the mononuclear ones based on the same ligands, rate accelerations for the reducing agents presented in the binuclear mode compared to mononuclear are observed. Though these rate enhancements are not large, any unambiguous evidence of cooperativity ascribable to concerted attack by the two centers would be significant and would encourage us to try to enhance the effects. We therefore considered it important to analyze the results critically. Our conclusion is that the rate enhancements we observe do not arise from the kind of cooperativity we were searching for. Nevertheless, we

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(7) Abbreviations: BPDO = *meso*-4,5-bis(4-pyridyl)-2,2-dimethyl-1,3-dioxolane, BPA = 1,2-bis(4-pyridyl)ethane, BPED = *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol, TFA = trifluoroacetate, DMF = dimethylformamide, TFMS = trifluoromethanesulfonate. Units: wavelength, nm; ϵ, $M^{-1}\,cm^{-1}$ (subscript on ϵ specifies wavelength).

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feel that the treatment of the kinetic data for these systems, exhibiting as they do biphasic behavior, is a contribution in its own right.

Experimental Section

Materials and Instruments. Water was purified by distillation of deionized water from alkaline permanganate. Sodium chloride, ferrous ammonium sulfate, ferric ammonium sulfate (Baker reagent grade), trifluoroacetic acid (Aldrich), *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol (Aldrich), and 1,10-phenanthroline hydrate (G. F. Smith) were used without further purification. Solutions of HCl were prepared by diluting Titrisol ampules. LiCl (Baker reagent grade) was purified by recrystallization from H_2O. Solutions of LiCl were standardized by titration with 0.100 N $AgNO_3$ to a chromate end point.[8] Solutions of H_2O_2 were prepared by diluting commercially available solutions and were standardized iodometrically; Mo(VI) was used to catalyze the reaction of I^- with H_2O_2.[9] Solutions of HCF_3CO_2 were prepared gravimetrically. Solutions of Br_2 in CH_3CN (MCB Spectrograde) were standardized spectrophotometrically (ϵ_{392} ($\equiv \epsilon$ at 392 nm) = 182 M^{-1} cm^{-1}).[10] 1,2-Bis(4-pyridyl)ethane (Aldrich) was purified by converting it to the dihydrochloride salt and then by precipitating the free base from aqueous solution by neutralization with NaOH.

Electronic spectra were recorded on Beckman Acta VII, Cary 14, and Cary 15 spectrophotometers. Electrochemical measurements were made on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Potentials were measured vs. an SCE and were uncorrected for junction potentials. Measured values were then corrected to the NHE scale by adding 0.244 V to the observed potential. NMR spectra were recorded on a Varian Model T-60 spectrometer. Microanalyses were performed by the Stanford Microanalytical Laboratory, Stanford, CA.

Preparations. BPDO was synthesized by the reaction of *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol with 2,2-dimethoxypropane. The diol (5.4 g, 25 mmol) and *p*-toluenesulfonic acid hydrate (4.9 g, 26 mmol) were dissolved in 200 mL of DMF and warmed to 80 °C. Upon dissolution, 50 mL of 2,2-dimethoxypropane was added. The mixture was allowed to react for 6 h at 80 °C; it slowly turned red, with temporary formation of a precipitate. Then the solution was cooled to room temperature and added to rapidly stirred ether to yield a precipitate. This precipitate was collected by filtration and washed with ether. It was added to a solution of 6 g of $NaHCO_3$ in 60 mL of H_2O to neutralize the *p*-toluenesulfonic acid. The product was then extracted into $CHCl_3$ (3 × 60 mL), leaving behind the unreacted diol. Roto-evaporation of the $CHCl_3$ layer yielded 2.8 g (44% yield) of highly colored crude product. Pure BPDO was then obtained by column chromatography. The crude product was divided into two parts and eluted from a 1.75 in. × 15 in. silica gel column (Grace, 60–200 mesh) with 10% ethanol/benzene. The desired fraction was determined by spotting a silica gel TLC plate with the eluate and exposing it in an I_2 vapor tank. Rotary evaporation of this fraction yielded 1.8 g of crystalline material (28% yield): TLC R_f 0.4, silica gel, 30% ethanol/benzene; mp 122–123 °C; $\epsilon_{256} = (9.3 \pm 0.15) \times 10^3$ M^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.06; H, 6.33; N, 10.88.

$[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_5H_2O](TFMS)_3$, and $[Ru(NH_3)_4C_2O_4]_2S_2O_6$ were prepared as described previously.[6]

cis-$[Ru(NH_3)_4(H_2O)_2](TFMS)_3$ was prepared as described by Krentzien;[11] $[Ru(NH_3)C_2O_4]_2S_2O_6$ was dissolved in a minimum volume of warm (40–60 °C) 8 M HTFMS. After the hot solution was filtered and cooled in the refrigerator, long, light pink needles precipitated. The product *cis*-$[Ru(NH_3)_4(H_2O)_2](TFMS)_3$ was collected by filtration and washed with ether; yield 60%.

$[(Ru(NH_3)_5)_2BPDO](TFMS)_4$ was prepared by adding $[Ru(NH_3)_5H_2O](TFMS)_3$ (133 mg, 2.02×10^{-4} mol) to 6 mL of absolute ethanol. After the Ru solution was degassed with Ar, BPDO (25.8 mg, 1.01×10^{-4} mol) dissolved in 2 mL of ethanol was added. A few pieces of Zn/Hg were added, and the mixture was allowed to react for 6 h in the dark under Ar flow. The product precipitated as yellow-orange microcrystals, which were collected by filtration and washed with peroxide-free ether; yield 50 mg (40%). The compound was stored in a vial flushed with Ar and kept in the refrigerator (~5 °C) with protection from light. It was found to be stable in air for periods of $^1/_2$–$^3/_4$ h but discolored noticeably over longer periods. With the protection noted above, the material decomposed only 10% after 1 week. Anal. Calcd for $Ru_2N_{12}C_{19}H_{46}O_{14}F_{12}S_4 \cdot 2H_2O$: Ru, 16.0; C, 18.1; N, 13.3; H, 3.97. Found: Ru, 16.1; C, 17.94; N, 13.05; H, 3.96.

$[(Ru(NH_3)_5)_2BPA](PF_6)_4$. BPA (18.5 mg, 1.01×10^{-4} mol) and $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ (131 mg, 2.02×10^{-4} mol) were dissolved in 12 mL of 1:1 (v/v) ethanol/water, which had been degassed with a stream of Ar. Several pieces of Zn/Hg amalgam were added, and the reaction was allowed to proceed for 6 h under an atmosphere of Ar with protection from room light. At the end of the reaction period, the product was precipitated by adding the solution via syringe to a concentrated Ar-degassed solution of NH_4PF_6 in ethanol (5–6 mL). The flask was sealed under Ar with a rubber septum cap and cooled to −5 °C. The product was collected by rapid filtration in air and washed with peroxide-free ether.

$[(Ru(NH_3)_5)_2BPA](CF_3SO_3)_6 \cdot nH_2O$. The PF_6^- salt of the Ru(II)–Ru(II) BPA binuclear complex was dissolved in acetone and converted to the Cl^- salt by the addition of several drops of concentrated HCl. The Cl^- salt was collected by filtration and immediately dissolved in 2 mL of 0.1 M HCl. The Ru(II)–Ru(II) complex was oxidized to the Ru(III)–Ru(III) complex with ~1.5 mL of 0.1 N Br_2 in CH_3CN. The complex was precipitated from solution by the addition of 4 mL of 6 M CF_3SO_3H and cooling at −5 °C overnight. The product was collected by filtration, washed with ether, and dried in a vacuum desiccator over Drierite. Anal. Calcd with two waters of crystallization: C, 14.5; H, 3.12; N, 11.3. Found: C, 14.4; H, 2.90; N, 10.7.

$[Ru(NH_3)_5BPDOH](PF_6)_3 \cdot nH_2O$. Ag_2O (115 mg, 5×10^{-4} mol) was dissolved in 1.5 mL of 1.0 M CF_3COOH. To this solution was added 147 mg of $[Ru(NH_3)_5Cl]Cl_2$ (5×10^{-4} mol), and the mixture was warmed to 40–50 °C with stirring until all of the $[Ru(NH_3)_5Cl]^{2+}$ had dissolved and the AgCl had coagulated. The AgCl was removed by filtration, and the solution of $[Ru(NH_3)_5Cl]^{2+}$ was added to a solution of BPDO (256 mg, 1×10^{-3} mol) in 5 mL of 0.10 M CF_3COOH (net concentration of H^+ after reaction with Ag_2O is 1.0 equiv of H^+/1.0 equiv of BPDO). The solution was degassed with Ar, several pieces of Zn/Hg amalgam were added, and the mixture was allowed to react for 2 h under Ar with protection from room light. The pH was adjusted to 5–6 with $NaHCO_3$, and the excess ligand was extracted with $CHCl_3$. The aqueous solution was returned to a covered flask, reacidified with CF_3COOH to protonate the uncoordinated pyridine, and reduced for an additional 15 min over Zn/Hg amalgam. The reduced solution was added via syringe to a degassed solution of NH_4PF_6 (5 mL, ca. half-saturated) and cooled to −5 °C to precipitate the desired product as a yellow-orange powder. The complex was collected by rapid filtration in air and washed with diethyl ether (peroxide free). Yields were generally around 20% (~100 mg of product). Samples were stored in an Ar-flushed tube in the refrigerator (~+5 °C) with protection from light. A sample for analysis was handled in a similar manner. Anal. Calcd for $RuC_{15}H_{32}N_7O_2P_3F_{18} \cdot 5H_2O$: C, 18.6; H, 4.37; N, 10.1. Found: C, 18.4; H, 3.56; N, 10.6. Experimental ratio: $N_{7.0}$:$C_{14.2}$.

$[Ru(NH_3)_5BPAH](PF_6)_3$. The preparation of the salt $[Ru(NH_3)_5BPA](PF_6)_2$ has been reported.[10] The preparation to be described is more convenient since the ruthenium starting material, $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$, is an air-stable salt. BPA (360 mg, 2.0×10^{-3} mol) was dissolved in 6 mL of ethanol. Water (6 mL) was added to the solution, and it was degassed with a stream of Ar. $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ (130 mg, 2.0×10^{-4} mol) was dissolved in the ethanol/water mixture, and several pieces of Zn/Hg amalgam were added. The reaction was allowed to proceed at room temperature for 1 h under an Ar atmosphere with protection from room light. The reaction mixture was added by syringe to ~10 mL of a degassed, nearly saturated solution of NH_4PF_6 in ethanol. The flask was sealed under argon and cooled to −5 °C to allow the complex to precipitate. The salt was collected by rapid filtration in air and washed with peroxide-free ether. This salt was stored in an Ar-flushed tube in the refrigerator (+5 °C).

$[(Ru(NH_3)_5)_2BPDO]^{4+}$ in Solution. Approximately 50 mg of $[Ru(NH_3)_5(H_2O)](TFMS)_3$ was added to 3 mL of Ar-degassed 0.01 M HCl. A stoichiometric amount of BPDO (BPDO:Ru = 1:2) was

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added along with four pieces of Zn/Hg. After 45-min reduction under Ar, 0.5 mL of 0.10 N tris(hydroxymethyl)aminomethane buffer was added. The solution was allowed to react for 7–8 h under Ar. One gram of weak ion-exchange resin (Bio-Rex 70, 200–400 mesh) was washed with 3 M NaCl and then rinsed with H_2O and finally with Ar-degassed H_2O. The column was kept under an Ar atmosphere during the subsequent purification step. The entire 3.5 mL of the reaction mixture was placed upon the column by using a syringe transfer technique. The column was washed with 0.2 M NaCl, thus removing a yellow band, which was the monomeric species, together with residual BPDO. The binuclear complex was eluted with 1.0 M NaCl. The spectrum and CV characterizations were identical with those obtained from solutions of the solid, and the kinetic plots were very similar.

The concentration of Ru(II) in equiv/L was determined by adding an aliquot of the Ru solution to a standard Fe^{3+} solution. The resulting Fe^{2+} concentration was determined by adding 1,10-phenanthroline and buffer and then measuring the absorbance of $[Fe(phen)_3]^{2+}$ at 510 nm ($\epsilon = 1.10 \times 10^4$ M^{-1} cm^{-1}). The values of ϵ for the Ru compounds are based upon this concentration determination, and they are probably good to only 10%; $\epsilon_{426} = 1.8 \times 10^4$, and $\epsilon_{246} = 8.4 \times 10^3$.

***cis*-$[(Ru(NH_3)_4(H_2O))_2BPDO]^{4+}$ in Solution.** Except for the following changes, the same procedure was used as for the pentaammine binuclear complex. The starting ruthenium compound was *cis*-$[Ru(NH_3)_4(H_2O)_2](TFMS)_3$, and this compound was reduced with Zn/Hg for 45 min before the ligand, BPDO, was added. To avoid complexation by Cl^-, HTFA and NaTFA were used in the preparation of the Bio-Rex 70 column and in the elution of the dimer ($\epsilon_{427} = 1.9 \times 10^4$, $\epsilon_{247} = 8.6 \times 10^3$). The NaTFA solutions were prepared from Na_2CO_3 and HTFA. We found no evidence for the formation of the $(BPDO)_2$ species in the CV and spectral or kinetic work.

$[(Ru(NH_3)_5)_2BPED]^{4+}$ in Solution. The same procedure was used as for the pentaammine BPDO binuclear species except that *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol (BPED) was used instead of BPDO; $\epsilon_{427} = 1.8 \times 10^4$, and $\epsilon_{245} = 8.9 \times 10^3$.

$[Ru(NH_3)_5BPDO]^{2+}$ in Solution. The procedure used was that for the binuclear BPDO species, except that the BPDO:Ru ratio was 1.1:1. The ion-exchange column was washed with H_2O to remove any unreacted BPDO. The monomer was eluted with 0.20 M NaCl. A yellow-orange band remained on the column, which was probably the binuclear species; $\epsilon_{435} = 9.9 \times 10^3$, $\epsilon_{249} = 9.2 \times 10^3$, and $\epsilon_{242} = 9.1 \times 10^3$ M^{-1} cm^{-1}. In acid solution the free pyridine ring is probably protonated, and so this species will be written as the protonated form $[Ru(NH_3)_5BPDOH]^{3+}$.

Stoichiometry. Consumption of O_2 was determined with a Yellow Springs Instrument Co. Clark oxygen electrode. A known volume of an Ar-degassed solution of the Ru(II) complex was added to a magnetically stirred, calibrated thermostated vessel designed to hold the O_2 electrode. The vessel was then completely filled with an O_2-saturated solution. The current from the O_2 electrode, proportional to the concentration of dissolved O_2, was monitored as a function of time on a strip chart recorder. The response time of the electrode (0–100% in 90 s) and the rate of the reactions were such that the concentration of O_2 at zero time could be measured directly or measured by extrapolation. The concentration of O_2 remaining was measured after 6–10 half-lives. The apparatus was found to be free of O_2 leaks by measuring the concentration of O_2 in an air-saturated solution as a function of time with the entire apparatus in a glovebag flushed with a stream of Ar. The initial concentration of Ru(II) was determined by oxidizing an aliquot of the Ru(II) solution with Fe(III) and determining the Fe(II) produced as $[Fe(phen)_3]^{2+}$.

The H_2O_2 produced was analyzed by using the $[Fe(phen)_3]^{2+}$ method.[6] Fe(II) acting on H_2O_2 apparently induces attack on the binuclear complex, and variable results for the peroxide concentration were obtained unless the binuclear species was removed by ion exchange before adding Fe^{2+}. A blank trial done by passing H_2O_2 through the cation resin showed no loss of H_2O_2 nor gain of oxidizing power due to the resin.

The samples were prepared by saturating 15.0 mL of the 0.1 M acid (HCl or HTFA) with oxygen and then adding 1.00 mL of Ru(II) solution ($\sim 4 \times 10^{-3}$ equiv of Ru/L). Oxygen bubbling was continued until the sample aliquot was withdrawn. If the time interval was less than 5 half-lives, an 8-mL sample was injected into an Ar bubbler, and 5.00 mL of the Ar-degassed sample was removed by syringe and injected upon an Ar-flushed ion-exchange column (Bio-Rad AG50W X12 200–400 mesh). The H_2O_2 was eluted with Ar-degassed H_2O. If the time interval was greater than 5 half-lives, the sampling and column work was done without the Ar degassing of the solutions and column. Three milliliters of 1.00×10^{-3} M Fe(II) was added to the eluted H_2O_2, sodium acetate/acetic acid buffer was added, and then 5 mL of 0.014 M phenanthroline solution was added. The sample was diluted to either 50 or 100 mL depending upon the Fe(II) concentration expected.

Kinetics. The kinetics were measured spectrophotometrically by monitoring the loss of Ru(II) at the $\pi^* \leftarrow \pi d$ transition. In all cases a pseudo-first-order (>10-fold) excess of oxidant was maintained. Thermostated quartz cuvettes and platinum syringe needles were used. Two methods were used to initiate the reactions with O_2. With $[Ru(NH_3)_5BPDOH]^{3+}$ and $[(Ru(NH_3)_5)_2BPA]^{4+}$ a saturated solution of O_2 or an O_2/Ar mixture (51.1% O_2, Liquid Carbonic) was generated in a water-jacketed, thermostated vessel in the desired electrolyte medium by purging the solution with the gas for 30 min. The reaction was initiated by adding a small volume of a concentrated, Ar-degassed solution of the Ru complex to the oxygen solution. The ratio of the volume of Ar-saturated Ru solution to the O_2 solution was in the range 0.1–0.005. The O_2 purge was used to pump the reaction mixture through a Teflon tube to a spectrophotometric cell equipped with a stopcock. The cell was filled with the reaction mixture and sealed with 1 atm of O_2 or the gas mixture above the solution.

For the other Ru(II) complexes, the following method of initiation was used. A 2.6–2.8-mL quantity of $\mu = 0.10$ M solution was saturated for 30 min with O_2 by using Pt needles for the intake and exhaust ports. The cell was placed in the constant-temperature bath during the O_2 saturation, wiped dry, and then placed in the thermostated spectrophotometer cell holder after removing the Pt needle. A 0.20-mL or smaller sample of the Ru solution (Ar degassed) was injected through the serum cap, and the cell was quickly mixed by shaking. All runs agreed within 10% and usually were repeatable to within 5%. Because of dilution by Ar contained in the injected sample, the concentration of oxygen was taken to be 1.1×10^{-3} M rather than that of the saturation value, 1.2×10^{-3} M.

Results

With the exception of $[Ru(NH_3)_5BPAH]^{3+}$,[10] the complexes reported herein are novel; they all fall in the general class of ruthenium ammines with substituted pyridine ligands.[12,13] The electronic spectra and the CV results are reported in Table I.

Several of the complexes in this work were never isolated and were only purified in solution. The question as to whether a binuclear species or mononuclear species was present could be answered by two experimental observations. The first is the movement of the species on a weak cation exchange. An intensely yellow band could be eluted with a 0.2 M salt solution, and this band had a spectrum characteristic of a $[Ru(NH_3)_5L]^{2+}$ species while a second band could be eluted with a 1.0 M salt solution, and this band also had qualitatively the spectral properties of $[Ru(NH_3)_5L]^{2+}$ species. Since a mononuclear complex would carry a 2+ charge and the binuclear complex a 4+ charge, the first yellow band was taken to be the mononuclear species and the second band the binuclear species. A third yellow band remained at the top of the column, and this could be moved only slowly with concentrated salt or 0.1 M H^+. This species was assumed to be the oxidized binuclear complex with a 5+ or 6+ charge.

The second characteristic is the ratio of the 250-nm peak and the 400-nm peak. For the free ligand, BPDO, $\epsilon_{257} = 9.3 \times 10^3$ ($\pi^* \leftarrow \pi$), and while the peak position might change upon coordination to a Ru center, the value of ϵ would not change materially. The peak at 400 nm is L ← Ru, and ϵ for it is usually about 10^4. Therefore, the monomeric species should show an absorption ratio of the two peaks of approximately 1 and the binuclear species a ratio of 2, or at least this latter ratio should be twice that of the mononuclear species.

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Table I. Electronic Spectral and CV Data of Ru(II) Complexes

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	$E_{1/2}$, V[b]	$\Delta E_{p/p}$, mV[c]	$\Delta E_{1/2,cor}$,[f] mV
$[(Ru(NH_3)_5)_2BPDO]^{4+}$	426 (1.84×10^4) 246 (8.36×10^3)	0.355[d]	90	27
$[Ru(NH_3)_5BPDOH]^{3+}$	436 (9.9×10^3) 249 (9.2×10^3) 243 (9.1×10^3)	0.34[e]	60	
cis-$[(Ru(NH_3)_4H_2O)_2BPDO]^{4+}$	425 (1.76×10^4) 247 (8.0×10^3)	0.410[d]	100	34
$[(Ru(NH_3)_5)_2BPA]^{4+}$	409 ($(1.70 \pm 0.15) \times 10^4$) 245 ($9.0 \times 10^3$)	0.30[e]	75	17
$[Ru(NH_3)_5BPAH]^{3+}$	411 ($(8.72 \pm 0.12) \times 10^3$) 244 ($8.8 \times 10^3$)	0.29[e]	60	
$[(Ru(NH_3)_5)_2BPED]^{4+}$	427 (1.80×10^4) 245 (8.85×10^3)	0.383[d]	86	24

[a] Spectra in 0.10 M HCl; room temperature; ϵ defined per mole of *complex*. [b] $E_{1/2}$ vs. NHE at 22 ± 2 °C. [c] Separation of the anodic and cathodic peak potentials. [d] In 0.10 M HTFA. [e] In 0.10 M HCl. [f] See text.

Table II. Stoichiometry[a]

complex	$\Delta(O_2)/\Delta(Ru(II))$[b]	$\Delta(H_2O_2)/\Delta(Ru(II))$[c]
$[Ru(NH_3)_5BPAH]^{3+}$	0.48	
$[Ru(NH_3)_5BPDOH]^{3+}$	0.53	
$[(Ru(NH_3)_5)_2BPA]^{4+}$	0.45	
$[(Ru(NH_3)_5)_2BPDO]^{4+}$	0.33	0.50 ± 0.01
cis-$[(Ru(NH_3)_4H_2O)_2BPDO]^{4+}$		0.52 ± 0.10

[a] Room temperature; ratios expressed as mole of O_2 or mole of H_2O_2 per equivalent. [b] $\mu = 1.0$ M (LiCl); pH 1 or 2. [c] $\mu = 0.1$ M, pH 1; HCl or HTFA.

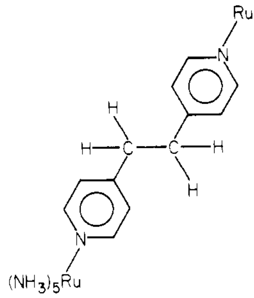
The data in Table I show that these expectations are met for the putative binuclear and mononuclear species that were prepared. In fact, this ratio proved to be the most sensitive measure of purity; kinetic runs using binuclear species of lower peak ratios were not fully consistent with the kinetic runs using binuclear species of higher peak ratios.

Formal potential measurements using cyclic voltammetry of the dimeric complexes can show the extent of interaction of the two Ru centers.[14] The CV results in Table I indicate that the two Ru centers undergo one-electron redox processes at potentials that are nearly the same. The observed separation in peak potentials from cyclic voltammetry, 80 mV, indicates that the comproportionation constant is not much larger than the statistical value of 4.[14]

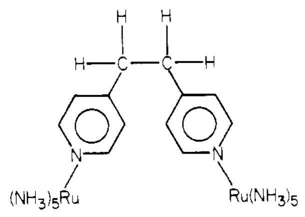
Stereochemistry and Properties of *meso*-4,5-Bis(4-pyridyl)-2,2-dimethyl-1,3-dioxolane (BPDO). NMR confirms the expected meso configuration of BPDO. The spectrum in $CDCl_3$ (vs. Me_4Si) shows singlets at 1.83 and 1.62 ppm assigned to the methyl groups, a singlet at 5.53 ppm assigned to the 4 and 5 dioxolane ring protons, doublets at 7.01 and 6.95 ppm assigned to the β pyridine ring protons, and doublets at 8.40 and 8.33 ppm assigned to the α pyridine ring protons. Molecular models suggest that the methyl groups are nonequivalent in the meso isomer and that the C_4 and C_5 dioxolane ring protons are equivalent. Models also suggest that the *dl* racemic pair have equivalent methyl groups and nonequivalent C_4 and C_5 protons. The magnetic equivalence of the C_4 and C_5 dioxolane ring protons clearly demonstrates a meso configuration about the C_4–C_5 bond.

As anticipated, the dioxolane ring system in BPDO is unstable to decomposition in acidic aqueous solution to acetone and 1,2-bis(4-pyridyl)ethane-1,2-diol. However, the reaction is slow in dilute acid. The half-life at room temperature as measured by NMR in 1 M CF_3COOD/D_2O (0.2 M BPDO) is about 40 h.

Stereochemistry of Ruthenium Complexes. Molecular models show that, because of free rotation about the C–C single bond, the binuclear complexes of BPA and BPED can exist in many configurations. From our particular point of view, the two extreme configurations (for BPA) are I and II.



I



II

In configuration II, the ruthenium ions are very close together (~7 Å is the estimate from molecular models). Because of repulsions, species I undoubtedly is the favored form in solution. The ligand *meso*-BPDO and its binuclear Ru(II) complex were prepared in order to "lock" a bis(pyridyl)ruthenium(II) binuclear complex into configuration II.

The NMR spectrum of the complex $[(Ru(NH_3)_5)_2BPDO]^{4+}$ in 0.1 M CF_3COOD/D_2O shows that, under the conditions of the synthesis and on the time scale of the measurements reported here, the acetonide linkage of BPDO remains intact. NMR shows the C_4 and C_5 dioxolane ring protons to be equivalent and the C_2 methyl groups to be nonequivalent. An attempt to precipitate the Ru(III)–Ru(III) ion $[(Ru(NH_3)_5)_2BPDO]^{6+}$ as a $CF_3SO_3^-$ salt from 4 M CF_3SO_3H did result in hydrolysis of the acetonide linkage.

Stoichiometry. The stoichiometries of representative reactions were investigated by measuring both consumption of O_2 and formation of H_2O_2. The results are listed in Table II.

Ruthenium(II) ammines of this class are known to react as outer-sphere one-electron reductants. The consumption and formation ratios in Table II are therefore consistent with the general stoichiometry

$$2Ru(II) + O_2 + 2H^+ \rightarrow 2Ru(III) + H_2O_2 \qquad (1)$$

The largest deviation was found for consumption of O_2 by $[(Ru(NH_3)_5)_2BPDO]^{4+}$; however, the clean formation of H_2O_2 by that complex suggests the deviation is simply due to experimental error. The above stoichiometry is also consistent with that found in prior studies.[6,15] There appears to be no significant direct reduction of O_2 to H_2O. By analogy, the above stoichiometry was taken as applying to all the complexes investigated here.

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(14) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(15) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639.

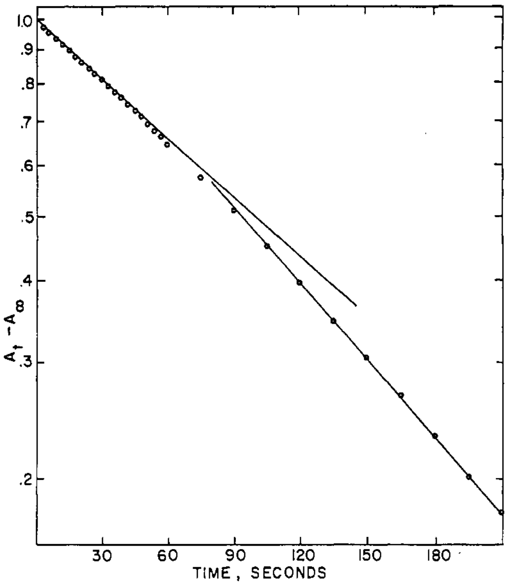

Figure 1. Semilog plot of the autoxidation of $[(Ru(NH_3)_5)_2BPDO]^{4+}$ illustrating biphasic kinetics. $[Ru(II)]_0 = 1 \times 10^{-4}$ M, $[Ru(III)]_0 = 0.0$ M, and $[H^+] = 0.1$ M.

The rate of reaction of H_2O_2 with $[(Ru(NH_3)_5)_2BPDO]^{4+}$ was investigated. As observed in earlier work,[15] the rate of reaction was found to be zero order in $[Ru^{II}]$ and first order in $[H_2O_2]$, suggesting catalysis by some impurity. The rate is so slow as not to interfere with the analysis for H_2O_2.

Kinetics. Two distinct classes of kinetic behavior occurred in these autoxidation studies. The binuclear complexes showed biphasic pseudo-first-order decays, while the mononuclear complexes showed simple pseudo-first-order decays, which were fully analogous with those reported earlier.[6] We treat the $[(Ru(NH_3)_5)_2BPDO]^{4+}$ reaction as a paradigm for reactions of the binuclear complexes.

(a) $[(Ru(NH_3)_5)_2BPDO]^{4+}$. A typical plot of log $(A_t - A_\infty)$ as a function of time for the reaction of O_2 with $[(Ru(NH_3)_5)_2BPDO]^{4+}$ is shown in Figure 1. This non-first-order behavior was reproducible. For reasons discussed below, these plots were most simply analyzed as two reactions: an initial slope, k', and a final slope, k''. Since the two Ru centers are very weakly interacting, the absorbance measures the total Ru(II) concentration, and so, values of k' and k'' are defined as in eq 2, where k is k' at the beginning and k'' at the end of a given run. Table III lists rate constants so obtained.

$$-d[Ru(II)]/dt = k[O_2][Ru(II)] \tag{2}$$

When oxidizing equivalents were added, either as Ce(IV) or as $[(Ru(NH_3)_5)_2BPDO]^{6+}$, the k' portion of the decay vanished, leaving the k'' portion unperturbed. Since comproportionation of $[(Ru(NH_3)_5)_2BPDO]^{4+}$ with $[(Ru(NH_3)_5)_2BPDO]^{6+}$ to give the mixed-valence $[(Ru(NH_3)_5)_2BPDO]^{5+}$ is rapid on this time scale, the effect of oxidized equivalents implies that the k' path is the reaction of the fully reduced binuclear complex, whereas the k'' path is that of the mixed-valence binuclear complex.

The values of k' and k'' are independent of pH between 1 and 2, but at higher values of pH, the semilog plots showed upward curvature at the ends of the runs; the effect became more pronounced for greater amounts of Ru(III) initially present. This curvature is reminiscent of behavior previously found for mononuclear ruthenium(II) ammines. Accordingly, the curvature should be understood as a combined Ru(III)/H^+ inhibition. Conceivably, such inhibition could occur for both the k' and k'' paths, but since the k'' path is dominant under conditions of large [Ru(III)], the inhibition is manifest only for the k'' path.

Table III. Kinetic Data

$10^5 \times [Ru(III)]_0$, equiv L^{-1}	$[H^+]$, M	no. of determins	k', L equiv^{-1} s^{-1}	k'', L equiv^{-1} s^{-1}
		$[(Ru(NH_3)_5)_2BPDO]^{4+\,a}$		
0	0.10	10	5.8 ± 0.3	8.0 ± 0.8
2-50	0.10	5		7.7 ± 0.6
0	0.010	3	5.1 ± 0.3	5.8
2-50	0.010	3		5.8 ± 0.7
0	0.001	2	4.86	*b*
5	0.001	1	0.43	*b*
0	0.10	1		22.1[j]
0	0.10	1		22.5[k]
0	0.10	1	12.9	17.5[j,l]
0	0.10	1	13.8	18.3[k,m]
0	0.10	1	13.0	18.3[k,n]
0	0.10	1	15.6	*k,o*
		$[(Ru(NH_3)_4(H_2O))_2BPDO]^{4+\,a}$		
0	0.10	5	5.90 ± 0.30	10.9 ± 0.2[d]
9	0.10	3		10.8 ± 0.2[d,e]
0	0.01	2	5.82 ± 0.10	7.01 ± 0.10[d]
9	0.01	2		7.92 ± 0.2[b,d,e]
0	0.10	2	6.16 ± 0.11	7.98 ± 0.20
9	0.10	2		8.26 ± 0.20
0	0.01	2	5.42 ± 0.40	
9	0.01	2		6.31 ± 0.20[b]
		$[(Ru(NH_3)_5)_2BPED]^{4+\,a,g}$		
0	0.10	2	1.56 ± 0.06	*p*
3.2-3.6	0.10	2	1.96	*p*
0	0.010	1	1.63	*p*
4.2	0.010	1	1.64	*p*
0	0.001	1	1.54[b]	*p*
0	0.10	4	3.30 ± 0.05[c-e]	*p*
		$[(Ru(NH_3)_5)_2BPA]^{4+\,a,g}$		
0	0.10	1	2.87	*p*
0	0.01	1	2.5[f]	*p*
		$[Ru(NH_3)_5BPDOH]^{3+\,a}$		
0	0.10	2	1.72 ± 0.01	
3.7	0.10	2	1.89 ± 0.16[e]	
0	0.010	1	1.70[b]	
5.5	0.010	1	1.66[b,h]	
		$[Ru(NH_3)_5BPAH]^{3+}$		
0	1.0	1	2.60[i]	
0	0.1	3	8.16 ± 0.16[i]	

[a] $[O_2] = 1.1 \times 10^{-3}$ M; $\mu = 0.10$ M (HCl); 25.0 °C; $[Ru(II)]_0 = (5\text{-}10) \times 10^{-5}$ eq/L. [b] semilog plot showed upward curvature. [c] $[Fe^{2+}] = (6.1\text{-}21) \times 10^{-3}$ M. [d] $\mu = 0.10$ M (HTFA). [e] $[Ru(II)]_0 = 3.0 \times 10^{-5}$ equiv/L. [f] $\mu = 0.01$ M; k' determined by monitoring the loss of O_2 with an oxygen electrode; $[Ru(II)]_0 = 7.74 \times 10^{-4}$ equiv/L; $[O_2]_0 = 7.6 \times 10^{-4}$ M. [g] No appreciable curvature in the semilog plots. [h] $[Ru(II)]_0 = 1.8 \times 10^{-5}$ equiv/L. [i] $\mu = 1.0$ M. [j] $[Fe^{2+}] = 0.0114$ M. [k] $[Fe^{2+}] = 0.0071$ M. [l] $[I^-] = 0.005\,02$ M. [m] $[I^-] = 0.0043$ M. [n] $[I^-] = 0.0010$ M. [o] $[Br^-] = 0.0049$ M. [p] k' and k'' are indistinguishable.

Substitution of TFA for Cl^- produced no observable effect on either k' or k''.

Addition of Fe(II) accelerated k' and k'' by factors of 2.8 and 3.7, but the effect was not very reproducible. For simple catalysis of the reduction of H_2O_2 by Ru(II), only a doubling of rate is expected, as is observed for the mononuclear complexes studied earlier.[6] Addition of Br^- to the Fe(II) solution gave acceleration factors of 2.7 and 1.95, and addition of I^- gave acceleration factors of 2.3 and 2.2; with I^- the accelerations were within experimental error of the expected doubling. The irreproducibility and high rates for the unmoderated reactions are suggestive of an autoxidation chain mechanism involving OH· and the ligand BPDO.

(b) $[(Ru(NH_3)_4H_2O)_2BPDO]^{4+}$. The kinetic behavior of this complex in trifluoroacetate media showed behavior quite similar to that of $[(Ru(NH_3)_5)_2BPDO]^{4+}$ (the Fe(II) effect was not investigated). Thus, biphasic kinetics and a pH-de-

Table IV. Rate Constants

complex	k_1, M^{-1} s^{-1}	k, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
$[(Ru(NH_3)_5)_2BPDO]^{4+}$	5.8		4.0
cis-$[(Ru(NH_3)_4H_2O)_2BPDO]^{4+}$	5.9		5.4
$[(Ru(NH_3)_5)_2BPED]^{4+}$	1.56		0.78
$[(Ru(NH_3)_5)_2BPA]^{4+}$	2.87		1.43
$[Ru(NH_3)_5BPDOH]^{3+}$		0.86	
$[Ru(NH_3)_5BPAH]^{3+}$		1.58	

pendent inhibition of the second reaction phase by Ru(III) were observed. On the other hand, in the presence of 0.10 M HCl a 30% reduction in the value of k'' was observed, while there was no significant effect on k'. The usual Ru(III)/H^+ effect also occurred in 0.10 M HCl.

(c) $[(Ru(NH_3)_5)_2BPED]^{4+}$. In this case, the curvature in the semilog plots was not as strong, and only k' could be obtained from these plots. When Ce(IV) was added to produce the mixed-valence complex, the semilog plots were linear at pH 1 and showed upward curvature at pH 2; the rate constants at pH 1 were taken to be k'', and they were only 25% greater than the k' values. The addition of Fe(II) produced a clean doubling in k'.

(d) $[(Ru(NH_3)_5)_2BPA]^{4+}$. Only a cursory study of the reactivity of this complex was made. There was no significant curvature in the semilog plot, and so it is assumed that k' and k'' are practically identical.

(e) $[Ru(NH_3)_5BPDOH]^{3+}$ and $[Ru(NH_3)_5BPAH]^{3+}$. Both of these mononuclear complexes react with oxygen to give good linear semilog plots for at least 3 half-lives at pH 1, while at pH 2 and 3 upward curvature developed. When Ru(III) is produced by adding Ce(IV), this curvature is enhanced, but the initial specific rates are not affected.

Discussion

In previous reports we have established the general characteristics of the autoxidation of mononuclear ruthenium(II) ammines.[6,15,16] In this report we have found many similar characteristics for autoxidations of the binuclear analogues: these include formation of Ru(III) and H_2O_2 as products, doubling in the rates by small amounts of Fe(II), and pH-independent rates except when considerable amounts of Ru(III) are present. The major difference between the two series of reactions is that, while the mononuclear species react with monophasic kinetics, the binuclear species react with biphasic kinetics. Accordingly, we propose for the binuclear species a mechanism analogous to that established for the mononuclear species, with the added complication that the mixed-valence species is also reactive.

$$\text{(II,II)} + O_2 \rightleftarrows \text{(III,II)} + O_2^- \quad k_1, k_{-1} \tag{3}$$

$$O_2^- + H^+ \rightleftarrows HO_2 \quad 1/K_{a1} \tag{4}$$

$$\text{(II,II)} + \text{(III,III)} \rightleftarrows 2\text{(III,II)} \quad K_{com} \tag{5}$$

$$\text{(III,II)} + O_2 \rightleftarrows \text{(III,III)} + O_2^- \quad k_2, k_{-2} \tag{6}$$

$$\text{(II,II)} + HO_2 \rightarrow \text{(III,II)} + HO_2^- \quad k_3 \text{ (fast)} \tag{7}$$

$$\text{(III,II)} + HO_2 \rightarrow \text{(III,III)} + HO_2^- \quad k_4 \text{ (fast)} \tag{8}$$

$$HO_2^- + H^+ \rightleftarrows H_2O_2 \quad 1/K_{a2} \tag{9}$$

The exact rate law for this mechanism is quite complex, and so we have introduced the simplifications that the k_1 and k_2 steps are rate limiting and the corresponding reverse processes can be neglected because of efficient scavenging of O_2^- by acid. With these simplifications, the rate of change of absorbance as derived in the Appendix is

$$\frac{-\mathrm{d(Abs)}}{\mathrm{d}t} = \frac{2[O_2]}{\alpha}\{k_1[\text{(II,II)}] + k_2[\text{(III,II)}]\} \tag{10}$$

where

$$[\text{(II,II)}] = \frac{\text{Abs} - \epsilon_{\text{II,III}}[\text{(II,III)}]}{\epsilon_{\text{II,II}}} \qquad [\text{(II,III)}] = \frac{B - C}{2A}$$

$$A = \frac{\epsilon_{\text{II,II}}}{K_{com}} + \frac{{\epsilon_{\text{II,III}}}^2}{\epsilon_{\text{II,II}}} - \epsilon_{\text{II,III}}$$

$$B = \frac{2(\text{Abs})\epsilon_{\text{II,III}}}{\epsilon_{\text{II,II}}} - \text{Abs} - \frac{\epsilon_{\text{II,III}}[\text{Ru}]_0}{2}$$

$$C = \left[B^2 - 4A(\text{Abs})\left(\frac{[\text{Ru}]_0}{2} - \frac{\text{Abs}}{\epsilon_{\text{II,II}}}\right)\right]^{1/2}$$

$$[\text{Ru}]_0 = 2[\text{(II,II)}] + 2[\text{(III,II)}] + 2[\text{(III,III)}]$$

$$\alpha = \frac{2}{\epsilon_{\text{II,II}}} - \left(\frac{2\epsilon_{\text{II,III}}}{\epsilon_{\text{II,II}}} - 1\right)\left\{\left(1 - \frac{B}{C}\right)\left(\frac{2\epsilon_{\text{II,III}}}{\epsilon_{\text{II,II}}} - 1\right) \times \left(\frac{1}{2A}\right) - \left(\frac{[\text{Ru}]_0}{2} - \frac{2(\text{Abs})}{\epsilon_{\text{II,II}}}\right)\left(\frac{1}{C}\right)\right\}$$

At the beginning of the reaction, when there is no Ru(III), we find

$$k_{obsd} = \frac{2[O_2]k_1(\epsilon_{\text{II,II}} - \epsilon_{\text{III,II}})}{\epsilon_{\text{II,II}}} \tag{11}$$

while at the end of the reaction the ratio [(II,III)]/[(II,II)] gets large, and so

$$k_{obsd} = 2[O_2]k_2 \tag{12}$$

Thus, pseudo-first-order behavior is expected at the beginning and end of each reaction. Since the ruthenium centers in our systems are only weakly electronically coupled, $\epsilon_{\text{II,II}} \sim 2\epsilon_{\text{II,III}}$ for the charge-transfer bands in Table I. Under these conditions $\alpha = 2/\epsilon_{\text{II,II}}$ and eq 11 simplifies to

$$k_{obsd} = k_1[O_2] \tag{13}$$

The sharpness of the transition between the two limiting slopes of the semilog plots is a complex function of the various parameters. Values of k_1 and k_2 can now be obtained from the values of k' and k'' in Table III, and these are summarized in Table IV.

For the mononuclear complexes, as in previous treatments, $k_{obsd} = 2[O_2]k_1$, and these are also given in Table IV.

Biphasic kinetics as described above are a simple consequence of the comproportionation in the system and the reactivity of both the fully reduced and mixed-valence binuclear species. However, there are alternative mechanisms to the proposed one-electron generation of superoxide that will still show biphasic kinetics. The combined Ru(III)/H^+ effect seen for the k_2 paths is good evidence that they do, in fact, involve one-electron generation of superoxide. One important criterion of the proposed mechanism is that k_{-1} and k_{-2} not exceed the limits of diffusion control. Since the reduction potential for the O_2/O_2^- couple is well established at −0.15 V,[16] values of k_{-1} and k_{-2} can be calculated from measured values of k_1, k_2, and $E_{1/2}$. For the worst case, the *cis*-$[(Ru(NH_3)_4H_2O)_2BPDO]^{5+}$ complex, k_{-2} is found to be 3.1×10^{10} M^{-1} s^{-1}. This is right at the diffusion limit for reactions of this charge type. Therefore, all the reactions considered here meet the criterion of being subject to diffusion control.

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(16) Stanbury, D. M.; Mulac, W. A.; Sullivan, J. C.; Taube, H. *Inorg. Chem.* **1980**, *19*, 3735.

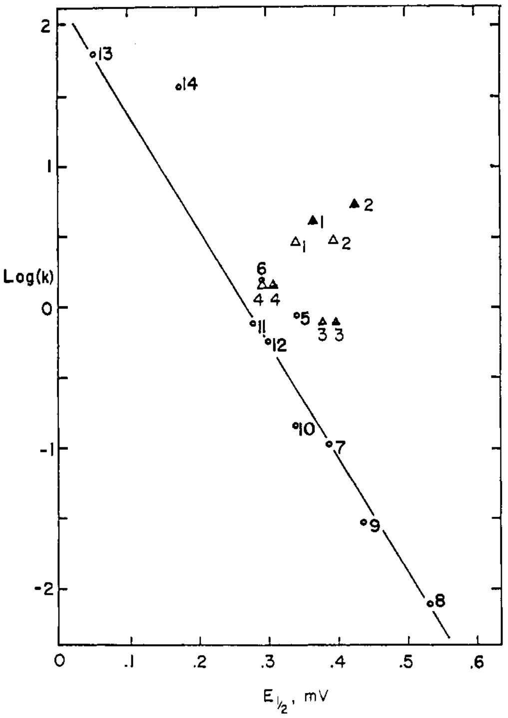

Figure 2. log k vs. $E_{1/2}$ for autoxidations of ruthenium ammines. Circles represent mononuclear complexes, open triangles represent fully reduced binuclears, and solid triangles represent mixed-valence binuclears, and the points are defined as follows: 1, $(Ru(NH_3)_5)_2$-BPDO; 2, *cis*-$(Ru(NH_3)_4H_2O)_2$BPDO; 3, $(Ru(NH_3)_5)_2$BPED; 4, $(Ru(NH_3)_5)_2$BPA; 5, $Ru(NH_3)_5$BPDOH; 6, $Ru(NH_3)_5$BPAH; 7, $Ru(NH_3)_5$isn; 8, $Ru(NH_3)_4$phen; 9, *trans*-$Ru(NH_3)_4$(isn)H_2O; 10, *cis*-$Ru(NH_3)_4(H_2O)$isn; 11, *trans*-$Ru(NH_3)_4$(isn)Cl; 12, $Ru(NH_3)_5$(4-vinylpyridine); 13, $Ru(NH_3)_6$; 14, $Ru(en)_3$.

The central issue of this research is to determine whether the k_1 paths are fundamentally different from the k_2 paths because of the simultaneous presence of two Ru(II) centers. Outer-sphere electron transfer to form superoxide is always an available pathway, and so an alternative mechanism could only appear as an acceleration relative to the rate expected for the outer-sphere pathway. A meaningful comparison may be made if the k_1 values are corrected to $k_1/2$ to account for the statistical effect of having two Ru(II) centers in the encounter complex.

A linear free energy relationship (LFER) has previously been demonstrated for autoxidations of mononuclear ruthenium(II) ammines.[6] This LFER has been reproduced in Figure 2, and our new values of $k_1/2$ and k_2 for autoxidations of binuclear species, as well as our new values of k_1 for mononuclear species, have been added to the figure.

The choice of $E_{1/2}$ for this LFER requires some care. From the measured $\Delta E_{p/p}$ and the tables in Richardson and Taube's paper[14] on the electrochemistry of binuclear species, we can obtain $\Delta E_{1/2}$, the difference between $E_{1/2}$ for the mixed-valence and fully oxidized binuclear species. However, 36 mV of this difference is due to purely statistical effects, and so the appropriate $\Delta E_{1/2,\mathrm{cor}}$ is $\Delta E_{1/2} - 0.036$ V. Table I lists values of $\Delta E_{1/2,\mathrm{cor}}$ so obtained. The new mononuclear data deviate slightly; the $k_1/2$ values deviate significantly and may indicate the presence of an alternate mechanism. Surprisingly, though, the k_2 values deviate more than the $k_1/2$ values even though we are confident that they represent simple outer-sphere electron transfer.

The deviations from the LFER can be reconciled with the proposed outer-sphere mechanism by considering electrostatic and steric effects. Our previous treatment of ruthenium(II) ammine autoxidations used the cross-relationship of Marcus' theory in the form

$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2} \qquad \log f = \frac{\log^2 K_{eq}}{4 \log\left(\dfrac{k_{11}k_{22}}{Z^2}\right)} \tag{14}$$

This is suitable for reactions between redox couples of the same charge type because the work terms to a large extent cancel each other. For autoxidations of most of the monomeric ruthenium(II) ammines, the redox couples are 2+/3+ and 0/−, and eq 14 is not strictly applicable. The neglect of work terms has the effect of introducing a fairly constant error into the analysis for a series of reactions of like charge type. Since the self-exchange rate for the O_2/O_2^- couple was treated as an adjustable parameter, eq 14 accounted for the features of the LFER. A more detailed treatment is required to include the 5+/4+ and 6+/5+ couples of the binuclear species in the same LFER, and so eq 15 is more appropriate.[17,18] On using

$$\Delta G_{12}^* = \tfrac{1}{2}(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12}^\circ - w_{11} - w_{22} + w_{12} + w_{21}) + \frac{(\Delta G_{12}^\circ + w_{21} - w_{12})^2}{8(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22})} \tag{15}$$

$$k = Z \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad w_{iJ} = \frac{4.225 \times 10^{-8} Z_i Z_J}{a(1 + 3.285 \times 10^7 \mu^{1/2} a)}$$

a = distance of closest approach

eq 15 and calculating ΔG_{11}^* iteratively, we find for k_{11} values of 170, 2.8, and 4.3 $M^{-1}\ s^{-1}$ for reactions of $[Ru(NH_3)_6]^{2+}$, $[Ru(NH_3)_5isn]^{2+}$, and $[Ru(NH_3)_4phen]^{2+}$, respectively; these are 1–2 orders of magnitude lower than those reported previously,[16] and if the O_2/O_2^- self-exchange rate is in fact being defined, they are a better estimate of it.

In Figure 2 points 5 ($[Ru(NH_3)_5BPDOH]^{3+}$) and 6 ($[Ru(NH_3)_5BPAH]^{3+}$) deviate from the LFER by 0.5 and 0.4 log unit, respectively. Equation 15 yields deviations of 0.16 log unit if a = 5.9 Å; i.e., the deviations are of the correct sign but of insufficient magnitude.

An additional factor is the enhancement of k_{22} by the increased bulk of the ligand. This appears in Marcus' theory in the solvent reorganization term[20]

$$\Delta G_0^* = 22.7(\Delta Z)^2/r^* \tag{16}$$

where r^* is the radius of the complex, and

$$\Delta G_{22}^* = \Delta G_i^* + \Delta G_0^* + w_{22} \tag{17}$$

where ΔG_i^* is the inner-sphere reorganization energy. Since $BPAH^+$ is a more extended ligand than $BPDOH^+$, eq 16 should be more suitable for the $BPDOH^+$ complex, and so the greater enhancement in rate for the $BPDOH^+$ complex may be rationalized. Equation 16 predicts an increase in log k_{12} of 0.4 unit for an increase in radius from 4.0 to 5.0 Å and is large enough to accommodate these points on the LFER.

In reference to the binuclear complexes, several interrelated features may be discussed. The two BPDO complexes show

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(18) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

(19) Our prior calculations[6] of k_{11} using the quadratic solution to eq 14 were slightly in error. The correct form of the quadratic solution is given by: Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715. Also, the calculations of ΔG_i^* and ΔG_0^* were slightly in error. The correct equation for a diatomic is

$$\Delta G_i^* = \Delta r^2 f_1 f_2 / 2(f_1 + f_2)$$

so that ΔG_i^* = 3.7 kcal/mol for the O_2/O_2^- couple and ΔG_0^* = 7.2 kcal/mol. This does not alter our conclusion that ΔG_0^* is more significant than ΔG_i^*, and it gives greater strength to the argument that ΔG_0^* is surprisingly small for such small reactants.

(20) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

biphasic kinetics, while for the BPA and BPED complexes the two phases are indistinguishable; the BPDO complexes are compact but the BPA and BPED complexes are extended; the BPDO complexes have greater $\Delta E_{1/2,\mathrm{cor}}$ than the BPA and BPED complexes; and the BPDO complexes show greater deviations from the LFER than do the BPA and BPED complexes. The ligand systems are all saturated, which means that these effects must be electrostatic in origin, and this explains the dependence of $\Delta E_{1/2,\mathrm{cor}}$ on ligand conformation. The greater electrostatic effect for the BPDO complexes means that w_{22} should be more sensitive to charge type; thus $k_2 > k_1$ and biphasic kinetics are observed. The more compact complexes should have a *greater* effective radius which decreases ΔG_0^*, and so the BPDO binuclear species deviate more strongly from the LFER.

The above considerations provide qualitative support for the proposed mechanism involving one-electron generation of superoxide for both the fully reduced and mixed-valence binuclear complexes. The results demonstrate that simple proximity of two Ru(II) centers is not sufficient to induce the multielectron reduction of dioxygen. The analysis presented provides a general basis for interpreting the redox reactions of binuclear complexes in the search for effects ascribable to cooperativity.

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Appendix

Rate law 10 was derived as follows: Ru(III,III) does not absorb appreciably in the region being monitored, so

$$\mathrm{Abs} = \epsilon_{\mathrm{II,II}}[(\mathrm{II,II})] + \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})] \tag{A1}$$

Thus

$$[(\mathrm{II,II})] = \frac{\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})]}{\epsilon_{\mathrm{II,II}}} \tag{A2}$$

By the definition of K_{com}

$$[(\mathrm{III,III})] = \frac{[(\mathrm{III,II})]^2}{K_{\mathrm{com}}[(\mathrm{II,II})]} \tag{A3}$$

so

$$\frac{[\mathrm{Ru}]_0}{2} = \frac{\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})]}{\epsilon_{\mathrm{II,II}}} + [(\mathrm{III,II})] + \frac{[(\mathrm{III,II})]^2\epsilon_{\mathrm{II,II}}}{K_{\mathrm{com}}(\mathrm{Abs} - \epsilon_{\mathrm{III,II}}[(\mathrm{III,II})])} \tag{A4}$$

or

$$0 = \mathrm{Abs}\left(\frac{[\mathrm{Ru}]_0}{2} - \frac{\mathrm{Abs}}{\epsilon_{\mathrm{II,II}}}\right) + [(\mathrm{III,II})]B - [(\mathrm{III,II})]^2A \tag{A5}$$

Using the correct root of the quadratic equation leads to

$$[(\mathrm{III,II})] = \frac{(B - C)}{A} \tag{A6}$$

where A, B, and C have been defined in the text.

From the proposed mechanism

$$\frac{-\mathrm{d}[\mathrm{Ru(II)}]}{\mathrm{d}t} = 2[\mathrm{O_2}](k_1[(\mathrm{II,II})] + k_2[(\mathrm{III,II})]) \tag{A7}$$

and since

$$[\mathrm{Ru(II)}] = 2[(\mathrm{II,II})] + [(\mathrm{III,II})] \tag{A8}$$

then

$$\frac{-\mathrm{d}[\mathrm{Ru(II)}]}{\mathrm{d}t} = \frac{-2\mathrm{d}[(\mathrm{II,II})]}{\mathrm{d}t} - \frac{\mathrm{d}[(\mathrm{III,II})]}{\mathrm{d}t} \tag{A9}$$

Equations A2 and A6 give [(II,II)] and [(III,II)] in terms of the absorbance, and so the two derivatives on the right-hand side of eq A9 can be solved. This leads to

$$2[\mathrm{O_2}](k_1[(\mathrm{II,II})] + k_2[(\mathrm{III,II})]) = \frac{-\mathrm{d(Abs)}}{\mathrm{d}t}\alpha \tag{A10}$$

where α is defined after eq 10. Rearrangement of eq A10 gives eq 10.

Registry No. $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPDO}](\mathrm{TFMS})_4$, 85894-02-6; $[\mathrm{Ru(NH_3)_5BPDO}]^{2+}$, 85894-06-0; $[\mathrm{Ru(NH_3)_5BPDOH}](\mathrm{PF_6})_3$, 85894-08-2; *cis*-$[(\mathrm{Ru(NH_3)_4(H_2O)})_2\mathrm{BPDO}]^{4+}$, 85894-10-6; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPA}](\mathrm{PF_6})_4$, 85894-04-8; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPA}](\mathrm{CF_3SO_3})_6$, 85894-05-9; $[\mathrm{Ru(NH_3)_5BPAH}](\mathrm{PF_6})_3$, 85894-09-3; $[(\mathrm{Ru(NH_3)_5})_2\mathrm{BPED}]^{4+}$, 85894-11-7; $[\mathrm{Ru(NH_3)_5(H_2O)}](\mathrm{TFMS})_3$, 53195-18-9; BPDO, 85894-00-4; $\mathrm{O_2}$, 7782-44-7; $\mathrm{H_2O_2}$, 7722-84-1; *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol, 4972-49-0; 2,2-dimethoxypropane, 77-76-9.

Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Photochemical Studies of Bis(dibenzoylmethanato)dioxomolybdenum

MARK W. PETERSON, REUEL B. VAN ATTA, and ROBERT M. RICHMAN*

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We have observed the photochemistry of bis(dibenzoylmethanato)dioxomolybdenum(VI), $\mathrm{MoO_2(DBM)_2}$, at 380 nm in 1,2-dichloroethane at 23 °C. The primary photoprocess is loss of ligand to form $\mathrm{MoO_2(DBM)}$ and DBM. The quantum yield for loss of $\mathrm{MoO_2(DBM)_2}$ exhibits apparent Stern–Volmer behavior without addition of any quencher: this is attributed to a back-reaction that regenerates $\mathrm{MoO_2(DBM)_2}$. Quantum yield extrapolated to zero time is 0.097. Ideas concerning the identity of the ESR-active molybdenum-containing photoproduct are discussed.

Introduction

Molybdenum(VI) complexes have been shown to be strong oxidants in both biological and chemical systems.[1,2] In particular, complexes of the general form $\mathrm{MoO_2L_2}$ (L = bidentate ligand) have been shown to oxidize $\mathrm{PPh_3}$ to $\mathrm{OPPh_3}$ with production of $\mathrm{MoOL_2}$. Excited states are known to be even stronger oxidants and reductants than ground states.[3] We have recently examined the photochemistry and subsequent thermal chemistry of $\mathrm{MoO_2(Et_2NCS_2)_2}$, which results in

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[1] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

[2] Peterson, M. W.; Richman, R. M. *Inorg. Chem.* **1982**, *21*, 2609.

[3] Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6384.

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