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Water Exchange Rates in the Diruthenium μ-Oxo Ion *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$

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Abstract: Addition of 2 equiv of Ce^{4+} to the dimeric ruthenium μ-oxo ion *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$ (formal oxidation state III−III, subsequently denoted {3,3}) or addition of 1 equiv of Ce^{4+} to the corresponding {3,4} ion gave near-quantitative conversion to the {4,4} ion, confirming our recent assignment of this oxidation state as an accumulating intermediate during water oxidation by the *cis,cis*-$[(bpy)_2Ru(O)]_2O^{4+}$ ({5,5}) ion. The rates of water exchange at the cis-aqua positions in the {3,3} and {3,4} ions were investigated by incubating $H_2{}^{18}O$-enriched samples in normal water for predetermined times, then oxidizing them to the {5,5} state and measuring by resonance Raman (RR) spectroscopy changes in the magnitudes of the O-isotope sensitive bands at 780 and 818 cm^{-1}. These bands have been assigned to $Ru{=}{}^{18}O$ and $Ru{=}{}^{16}O$ stretching modes, respectively, for ruthenyl bonds formed by deprotonation of the aqua ligands upon oxidation to the {5,5} state. An intermediate accumulated during the course of the isotope exchange reaction that gave a {5,5} ion possessing both ~782 and ~812 cm^{-1} bands; this spectrum was assigned to the mixed-isotope species, $(bpy)_2Ru({}^{16}O){}^{16}ORu({}^{18}O)(bpy)_2{}^{4+}$. Kinetic analysis of solutions at various levels of oxidation indicated that only the {3,3} ion underwent substitution; the exchange rate constant obtained in 0.5 M trifluoromethanesulfonic acid, 23 °C, was 7×10^{-3} s^{-1}, which is (10^3-10^5)-fold larger than rate constants measured for anation of monomeric $(bpy)_2Ru(III)X(H_2O)^{3+}$ ions bearing simple σ-donor ligands (X).

Introduction

The μ-oxo bond appears to be essential to catalysis of many complex chemical and biological oxidations by group 8 dinuclear ions, as well as to O_2 transport by the dinuclear nonheme iron protein, hemerythrin.[1] Extensively studied examples of reaction catalysts include ions of the general type *cis,cis*-$[L_2Ru(OH_2)]_2O^{n+}$ (L = 2,2′-bipyridine (bpy) or a related diimine), which in their higher oxidation states are capable of oxidizing a variety of inorganic and organic species,[2] and the enzymes methane monooxygenase[3] and ribonucleotide reductase,[3,4] which contain dinuclear Fe centers that activate O_2 for insertion into methane and for formation of reactive tyrosyl radicals, respectively. Although these compounds and reaction centers are now structurally relatively well-characterized, their reaction mechanisms remain obscure. We report herein measurement of a remarkable labilization of the cis-coordinated aqua ligand by the μ-oxo group in *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$ that may have relevance to its capacity to function as a catalyst for oxidation of water to O_2 and other reactions involving oxidation of coordinated ligands.[5−7]

Experimental Section

Materials. The μ-oxo-bridged dimeric ruthenium coordination complex *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$ was prepared from its monomeric *cis*-$(bpy)_2Ru^{II}Cl_2$ precursor following well-established synthetic procedures.[5] Specifically, 1.0 g of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ was dissolved in 12.5 mL of water and heated for 1 h at 100 °C in a water bath, following which 0.65 g of $AgNO_3$ was added and the mixture was heated another 2.5 h in the water bath. The AgCl that formed was filtered off with use of fine porosity filter paper and the filtrate was diluted with 30 mL of water. Then 10 mL of saturated $NaClO_4$ was added and precipitation was induced by overnight storage in a refrigerator. As previously described,[8] the crude product contained as a minor impurity a green species that was readily apparent upon one-electron titration with Ce^{4+} ion. This impurity could be removed by repetitive recrystallization of the perchlorate salt, although typically 4−5 cycles were required. Although we have not characterized this compound in detail, it does not catalyze water oxidation by Ce^{4+} and its optical and RR spectroscopic features and redox properties suggest that it is the cis−trans−cis trimeric bipyridyl analogue of ruthenium red, $[(bpy)_2(H_2O)Ru^{III}ORu^{IV}(bpy)_2ORu^{III}(OH_2)(bpy)_2]^{6+}$, described by Meyer and associates.[9]

Earlier studies had established that the bridging μ-oxo atom in *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$ (hereafter, {3,3}[10]) and its higher oxidation states were inert to substitution,[7,8] even when undergoing catalytic turnover. In contrast, ligand substitution at the cis-aqua positions in the {3,3} ion is relatively facile at room temperature,[7,8,12] although no

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[10] This notation is intended to indicate only the overall oxidation level of the dimer. Magnetic[11,12] and structural data[5,13] have established that the electrons involved in forming the μ-oxo bridge are extensively delocalized over the Ru−O−Ru unit. Thus, for example, the notation {3,4} signifies that the Ru−O−Ru bond contains 13 π-symmetry electrons (with 4 originating in O^{2-}), one fewer than in the {3,3} ion, but is not meant to imply the existence of discrete valence-localized ruthenium d^4 and d^5 ions.

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prior measurement of these rates has been reported. Solutions of the {3,3} ion containing isotopically substituted cis-aqua $H_2{}^{18}O$ were prepared by dissolving the highly purified perchlorate salt in 95% [^{18}O]-H_2O for several hours. As will be shown, this time is sufficient to permit complete exchange between the aqua ligands and bulk water. The {3,3} ion in solution therefore has the isotopic distribution $[(bpy)_2Ru(^{18}OH_2)]_2{}^{16}O^{4+}$. To obtain the corresponding ion with ^{18}O in the bridging position, it was necessary to carry out the synthesis of the μ-oxo dimer in $H_2{}^{18}O$. Because we had available only small amounts of the isotopically enriched water, the amount of ^{18}O-bridged dimer that we could prepare was insufficient to allow extensive purification. Nonetheless, the limited number of studies made with this complex ion, i.e., $[(bpy)_2Ru(^{18}OH_2)]_2{}^{18}O^{4+}$, indicated that the impurity did not affect the ligand substitution dynamics.

Trifluoromethanesulfonic (triflic) acid (CF_3SO_3H) was redistilled under vacuum and stored at 4 °C as 1 M aqueous solutions. Other chemicals were reagent grade and used as received from commercial suppliers; water was purified by using a Milli-Q ion exchange/reverse osmosis system.

Analytical Methods. Water exchange was initiated by diluting $H_2{}^{18}O$ solutions of the isotopically substituted {3,3} ions into normal H_2O and was subsequently quenched at various times by oxidizing the complex ion with Ce^{4+} to the {5,5} state.[8,14] All solutions were also 0.5 M in triflic acid. Following oxidation, the extent of substitution was immediately determined by measuring by resonance Raman spectroscopy the relative intensities of the ruthenyl Ru═O stretching modes, which appear at 818 and 780 cm^{-1}, respectively, in the spectra of the ^{16}O- and ^{18}O-substituted {5,5} ions.[7] In practice, the reaction vessel was a syringe that was mounted in a Harvard PHD 2000 syringe pump; during the course of the water exchange reaction, portions of this solution were slowly mixed with triflic acid solutions that contained a 20-fold excess of the Ce^{4+}ion. The effluent from the mixer was passed through a section of flexible Teflon tubing to a glass capillary where the RR spectra were periodically recorded on the flowing solution. The reaction times for water exchange corresponding to each RR spectrum were equated with the incubation time of the complex ion in the reactant syringe prior to acquiring that spectrum. The Raman spectrometer used in these experiments and the methods for acquiring and analyzing the spectra have been described in detail elsewhere.[15] The concentrations of {3,3} ions in solution were determined from the visible absorption maxima of their optical spectra assuming $\epsilon_{636} = 2.2 \times 10^4$ M^{-1} cm^{-1}.[8] Solutions of the complex ion in its higher oxidation states were prepared by electrochemical flow electrolysis by using a Hokuto Denko Model HX-201 cell coupled to an EG&G/PAR Model 273 potentiostat/galvanostat as previously described.[8] Optical spectra were recorded with use of either Perkin-Elmer Lambda 9 or Hewlett-Packard 8452A diode array spectrophotometers.

Results and Discussion

Oxidation by Ce^{4+}. Prior studies from our laboratory with RR and optical spectral analyses have shown that in dilute triflic acid the {3,3} ion can be oxidized to the {5,5} ion in a sequence that involves the {3,4} and {4,4} ions as accumulating intermediates.[8] The {5,5} ion is distinct from the others in exhibiting a pronounced band at 818 cm^{-1} in its RR spectrum that shifts ~40 cm^{-1} to lower energies upon substitution of $H_2{}^{18}O$ at the cis-aqua positions in the {3,3} precursor.[7] On the basis of precedents established with diiron μ-oxo ions, this band might be assigned variously to the Ru−O−Ru asymmetric stretching mode,[16] the O−O stretching mode of a μ-1,2 bridging peroxo group,[17] or the Ru−O stretching mode of a terminal ruthenyl bond formed by deprotonation of the cis-aqua ligands accompanying two-electron oxidation of the ruthenium centers.[18] In the present case, the Ru−O−Ru asymmetric stretch can be excluded because the bridging μ-oxo atom does not exchange with solvent.[7,8] Furthermore, the absence of an RR band of intermediate energy in the spectra of $^{18}O-^{16}O$ mixed-isotope complexes excludes the possibility that the 818 cm^{-1} band is due to a coordinated peroxide.[7] Consequently, we have assigned this band to a Ru═O stretching mode.

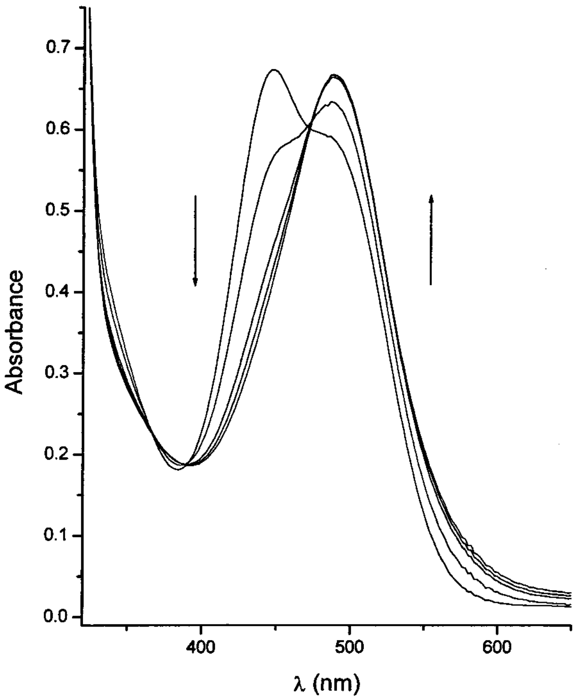

Figure 1. Optical spectral changes accompanying oxidative titration of the {3,4} ion by Ce^{4+}. The solid lines showing progressive loss of absorption at 448 nm with a corresponding increase at 488 nm are spectra taken after addition of 0, 0.5, 1.0, 1.2, and 1.5 equiv of $Ce(NH_4)_2(NO_3)_6$ to a solution of 4.5×10^{-5} M {3,4} ion in 0.5 M triflic acid.

Our assignment of the oxidation sequence {3,3} → {3,4} → {4,4} → {5,5}, with the {4,5} ion being unstable with respect to disproportionation, differs from that of Meyer and associates,[19] who have concluded on the basis of global kinetic analyses of optical spectra obtained from multimixing experiments in similar media that the {5,5} ion does not accumulate and that the detectable oxidation states follow the sequence {3,3} → {3,4} → {4,5}. Additional support for our assignment is given in Figure 1, where results of Ce^{4+} titration of electrochemically prepared {3,4} ion are displayed. Addition of a stoichiometric equivalence of Ce^{4+} causes nearly complete conversion of the asymmetric absorption band of the {3,4} ion, whose maximum appears at 450 nm,[5] to a symmetric band at 490 nm (Figure 1), which we have assigned to the {4,4} ion.[8] Further addition of oxidant to a Ce^{4+}/dimer ratio of 1.5 caused small losses of intensity in the 450 nm region with retention of three isosbestic points at 368, 390, and 472 nm. At higher Ce^{4+}/

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dimer ratios, the peak decreased in intensity and underwent a small shift toward higher energies with a loss of isosbestic properties, indicative of oxidation to a higher level.[8] Similar behavior was observed when the {3,3} ion was titrated with Ce^{4+}, although here slightly in excess of 2 equiv of oxidant were required to achieve complete oxidation to the {4,4} level. Estimating from Figure 1 that 85−90% conversion to the {4,4} ion has occurred when 1 equiv of Ce^{4+} is added, one obtains from the Nernst equation a value of $\Delta E° \cong 0.10$ V for the following reaction: $Ce^{4+} + \{3,4\} \rightarrow Ce^{3+} + \{4,4\}$. Using our previously determined reduction potential for these medium conditions of $E°(\{4,4\}/\{3,4\}) = 1.52$ V (NHE),[8] one calculates $E°(Ce^{4+/3+}) = 1.62$ V (NHE). This potential is very similar to values reported for strongly acidic media.[20] Thus, the properties of the intermediate appear to be in quantitative accord with predictions based upon our assignments. The reduction potential for the {5,5} ion under these conditions is $E°(\{5,5\}/\{4,4\}) =$ 1.59 V (NHE).[8] Addition of a 20-fold excess of Ce^{4+} to a solution of {3,3} is therefore sufficient to oxidize >99% of the ion to {5,5}, i.e., $K = ([\{5,5\}][Ce^{3+}]^2)/([\{4,4\}][Ce^{4+}]^2) \cong 10$. Cyclic voltammetric measurements have indicated that both terminal oxygen atoms are retained in the {5,5} ion, i.e., that its structure is $[(bpy)_2Ru(O)]_2O^{4+}$.[8] Evidence supporting this structure, namely, that the terminal ruthenyl oxygens act as weakly coupled oscillators, is obtained from analysis of the RR spectra of various isotopically substituted isomers, as discussed below.

Dynamics of Water Exchange. To initiate substitution of $H_2{}^{16}O$ for $H_2{}^{18}O$ at the cis-aqua positions, concentrated solutions of the {3,3} ion (or mixtures of the {3,3} and {3,4} ions) that had been prepared in 95% $H_2{}^{18}O$ containing 0.5 M triflic acid were diluted into water of normal isotopic composition that also contained 0.5 M triflic acid. Following various incubation times, portions were oxidized by flow-mixing with a 20-fold excess of Ce^{4+} in 0.5 M triflic acid and the RR spectra in the region of the ruthenyl stretching vibrational modes (700−900 cm^{-1}) were recorded. Progressive loss of the $Ru{=}{}^{18}O$ band at 780 cm^{-1} with increasing time was accompanied by appearance of the $Ru{=}{}^{16}O$ band at 818 cm^{-1}. A typical result, obtained for a solution containing 11% {3,3} and 89% {3,4}, is reproduced in Figure 2. Careful examination of the data reveals that, as the reaction proceeds, the band maximum at 780 cm^{-1} shifts ~2 cm^{-1} to higher energies and the developing band assigned to $Ru{=}{}^{16}O$ undergoes a comparable shift from ~815 cm^{-1} to 818 cm^{-1}. These shifts are clearly seen in the difference spectra obtained from RR spectra taken at various times during the reaction (Figure 3, inset). They can be interpreted in terms of a model that involves sequential substitution at the two ruthenium centers, i.e.,

$$[(bpy)_2Ru({}^{18}OH_2)]_2{}^{16}O^{4+} + H_2{}^{16}O \rightarrow [(bpy)_2Ru({}^{16}OH_2){}^{16}O(H_2{}^{18}O)Ru(bpy)_2]^{4+} + H_2{}^{18}O \quad (1)$$

$$[(bpy)_2Ru({}^{16}OH_2){}^{16}O(H_2{}^{18}O)Ru(bpy)_2]^{4+} + H_2{}^{16}O \rightarrow [(bpy)_2Ru({}^{16}OH_2)]_2{}^{16}O^{4+} + H_2{}^{18}O \quad (2)$$

Upon oxidation to the {5,5} ions, the energy of the Ru═O stretching mode on a particular metal center will depend on the isotopic substitution at the other center if the normal coordinate vibration describing that ruthenyl stretch is coupled to movement of the other terminal O atom within the (O═Ru)−O−Ru(═O) core. In the present case, the small shift to higher energies in the $Ru{=}{}^{18}O$ band as the reaction proceeds can be attributed to replacement of the ^{18}O atom on the other ruthenium atom by ^{16}O through water exchange, forming the $({}^{18}O{=}Ru){-}{}^{16}O{-}Ru({=}{}^{16}O)$ mixed isotope intermediate. Similarly, the increase in energy observed for the $Ru{=}{}^{16}O$ band can be attributed to replacement of ^{18}O in the intermediate by ^{16}O in the final product. Assuming that the Ru═O scattering intensities of all of the isotopically substituted {5,5} ions are identical,[21] the RR spectrum of the mixed isotope intermediate can be constructed from the measured difference spectra. This spectrum, which is consistent with published RR spectra for directly prepared solutions of the mixed-isotope complex,[7] is given in Figure 3, along with the spectra of the symmetrically substituted {5,5} ions. The absence of appreciable absorption at 800 cm^{-1} in the intermediate spectrum confirms that the RR band is not attributable to a peroxo O−O stretching mode.

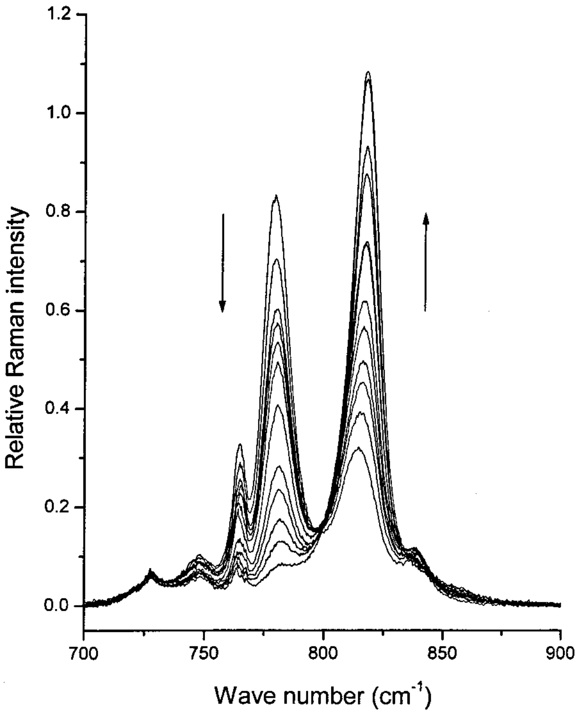

Figure 2. Measurement of exchange of cis-coordinated H_2O by resonance Raman spectroscopy. RR spectra of the {5,5} ion obtained by oxidation of an $H_2{}^{18}O$-substituted mixture of {3,3} and {3,4} at various times following dilution into $H_2{}^{16}O$. Conditions: 0.8 mM Ce^{4+} in 0.5 M triflic acid was added to a 0.5 M triflic acid solution containing 4.5 μM {3,3} and 35.5 μM {3,4} ions. RR spectra of the {5,5} ion recorded at 3, 5, 7, 9, 12, 15, 21, 27, 35, 45, 60, and 90 min after dilution show progressive loss of intensity at 780 cm^{-1} with a corresponding increase at 818 cm^{-1}. Spectra are averages of 10 × 6 s accumulations recorded on flowing solutions at 40 mW power using the 488 nm line from an Ar^+ laser. Scattering intensities have been normalized to the intense 1040 cm^{-1} band of CF_3SO_3H; a band from triflic acid appearing at 765 cm^{-1} has been computer-subtracted from the displayed spectra.

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[20] *Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994; pp 8−22.

[21] The intensity of the $Ru{=}{}^{18}O$ band in the initial spectrum displayed in Figure 2 is ~77% of the $Ru{=}{}^{16}O$ band intensity in the final product. At the time corresponding to acquisition of the first spectrum, ~20% of the $H_2{}^{18}O$ symmetrically substituted {3,3} ion had converted to the mixed isotope intermediate (Figure 4). In 95% $H_2{}^{18}O$, the initial composition of the reactant solution was ~90% of the symmetrically substituted ^{18}O complex and ~10% of the mixed-isotope intermediate. If the scattering intensities are independent of isotopic composition, the intensity in the first spectrum at 780 cm^{-1} is predicted to be ~81% of the final intensity at 818 cm^{-1} Thus, within experimental uncertainty, the scattering intensities of the Ru═O bands are identical for ions of different ^{18}O-isotopic composition.

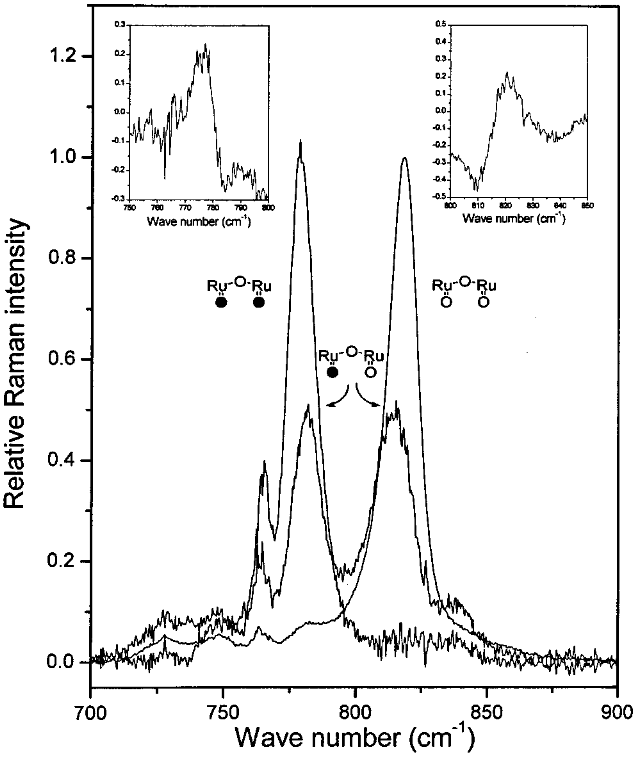

Figure 3. Resonance Raman spectra of the ruthenyl symmetric stretching modes for various O-isotopes of the {5,5} ion. The spectrum of $[(bpy)_2Ru(^{16}O)]_2{}^{16}O^{4+}$ is the final spectrum recorded at 90 min in Figure 2. The spectrum of the mixed isotope intermediate $[(bpy)_2Ru(^{16}O)^{16}ORu(^{18}O)(bpy)_2]^{4+}$was estimated by subtracting the spectrum obtained at 45 min from this spectrum and normalizing the scattering intensity of each ruthenyl site to 0.5; at 45 min, $[(bpy)_2Ru(^{18}O)]_2{}^{16}O^{4+}$ contributes <2% to the RR spectrum. The spectrum of the $[(bpy)_2Ru(^{18}O)]_2{}^{16}O^{4+}$ isotope was obtained by subtracting the contribution of the intermediate from the spectrum recorded at 3 min; by this time, 22% of the starting material had converted to the mixed isotope intermediate, and the final product was present at <2% (see, e.g., Figure 4). The influence of isotopic substitution at the adjacent Ru center upon the $Ru{=}^{18}O$ and $Ru{=}^{16}O$ stretching frequencies is displayed in the insets as $\{[(bpy)_2Ru(^{18}O)]_2{}^{16}O^{4+}$-$[(bpy)_2Ru(^{16}O)^{16}ORu(^{18}O)(bpy)_2]^{4+}\}$ (left) and $\{[(bpy)_2Ru(^{16}O)]_2{}^{16}O^{4+}$-$[(bpy)_2Ru(^{16}O)^{16}ORu(^{18}O)(bpy)_2]^{4+}\}$ (right) difference spectra. The filled circles in the drawings labeling the spectra indicate the positions of ^{18}O atoms.

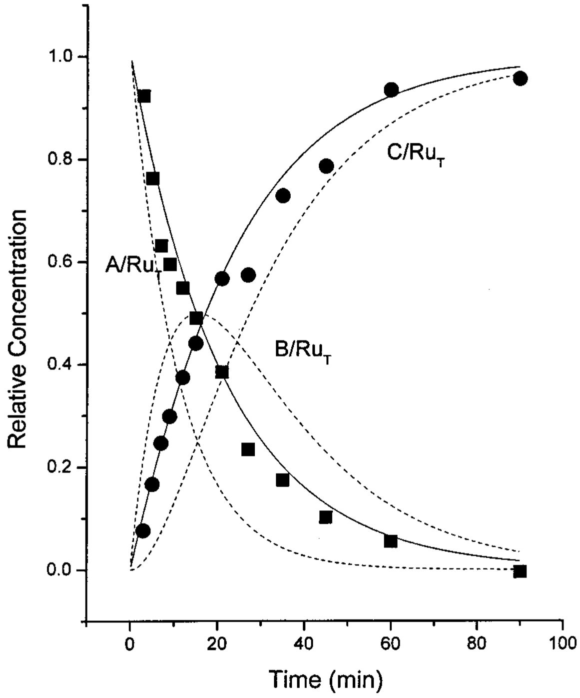

Figure 4. Kinetic analysis of the resonance Raman spectral changes. The experimental points are data from Figure 2. The dashed lines give the relative concentrations of $[(bpy)_2Ru(^{18}O)]_2{}^{16}O^{4+}$ (A/Ru_T), $[(bpy)_2Ru(^{16}O)^{16}ORu(^{18}O)(bpy)_2]^{4+}$ (B/Ru_T), and $[(bpy)_2Ru(^{16}O)]_2{}^{16}O^{4+}$ (C/Ru_T), calculated from $A/Ru_T = \exp(-k_1t)$, $B/Ru_T = 2\{\exp(-k_1t/2) - \exp(-k_1t)\}$, and $C/Ru_T = 1 - (A + B)/Ru_T$ using $k_1 = 9.0 \times 10^{-2}$ min^{-1}; Ru_T is the total amount of dimer present in solution. The solid lines are the predicted relative intensities for the bands at 780 and 818 cm^{-1} calculated from the following relationships: $I_{780} = (A + 0.49B)/Ru_T$ and $I_{818} = (0.43B + C)/Ru_T$.

As required by reactions 1 and 2, the temporal changes in intensities of the bands at 780 and 818 cm^{-1} followed the familiar two-step sequential first-order reaction: A → B → C (Figure 4). In this case, the corresponding rate law is subject to the constraint that $k_1 = 2k_2$, where the coefficient 2 reflects the fact that statistically only one-half of the exchange reactions on the mixed-isotope intermediate lead to net formation of C. For the data analysis, it was also necessary to consider the contribution of the intermediate B to the intensities of the bands at 780 and 818 cm^{-1}. This was done by approximating the bands in Figure 3 as Gaussian curves and comparing their relative intensities at these frequencies. By this analysis, the intensity at 780 cm^{-1} at any time was proportional to the sum [A] + 0.49[B] and at 818 cm^{-1} to [C] + 0.43[B]. The result of the data fit to the reaction shown in Figure 2 is given in Figure 4, where k_1 is the only adjustable parameter. The dashed lines give the temporal changes for the individual species and the solid lines are the calculated resultant changes in relative intensities at 780 and 818 cm^{-1}. The agreement between the experimental data and behavior predicted by the rate law is excellent. Equally good data fits were obtained for reactions in which the {3,3}/{3,4} ratio was varied over the range 0−1.0. No exchange was observed within 3 h when the complex was completely oxidized to the {3,4} state, and the apparent rate constant for exchange (k_1) increased linearly with the fraction of the complex in the {3,3} oxidation state (Figure 5). These data indicate that only the {3,3} ion undergoes water exchange on these time scales, i.e., because electron transfer between {3,3} and {3,4} is rapid relative to water exchange, the apparent rate constant is proportional to the fraction present as {3,3}. Comparable values for k_1 were estimated for the {3,3} ion containing ^{18}O as the bridging ligand (Figure 5), although in this case the green impurity present in the preparations (Experimental Section) contributed a RR band in the 800 cm^{-1} region that hampered full kinetic analysis of the reaction.

The first-order rate constant obtained for water exchange on the {3,3} ion at 23 °C is $k = 7 \times 10^{-3}$ s^{-1}. This is the same order of magnitude as the rate of O_2 evolution from the {5,5} ion, which is ~10^{-2} s^{-1} under these experimental conditions.[8,22] ^{18}O-Isotope labeling studies have established that water oxidation involves replacement of coordinated H_2O on the ruthenium dimer;[6,7,19] consequently, catalytic turnover sets a lower limit on the rate of water substitution on the {5,5} ion, which is comparable to that on the {3,3} ion. An upper limit of $k \leq 10^{-5}$ s^{-1} for water exchange on the {3,4} ion can be set from the observation of no detectable isotopic substitution after 3 h. No direct information is available from these studies on the rate of water exchange in the {4,4} ion.

Comparison to Other Ligand-Substitution Reactions. The measured rate constant for water exchange is exceptionally large

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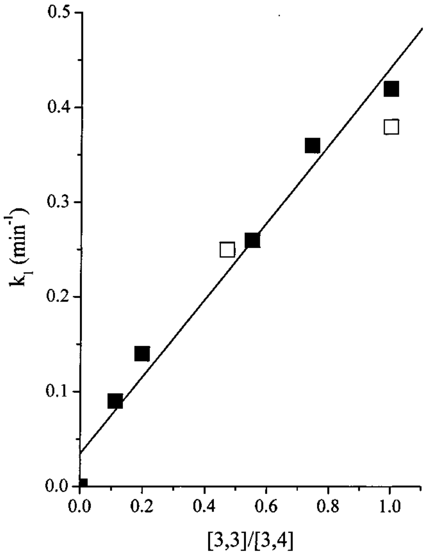

Figure 5. Dependence of the apparent first-order rate constant for water exchange (k_1) upon the relative amount of {3,3} ion in solution. Conditions: 37−40 μM total dimer in 0.5 M triflic acid at ambient temperature (22−23 °C). The open squares are data for water substitution on the complex ion containing a bridging ^{18}O atom.

for substitution at a Ru(III) center, but is comparable to rates commonly observed for ligand substitution on Ru(II). For example, the rate constant for water exchange on $Ru(OH_2)_6^{2+}$ is $\sim 2 \times 10^{-2}$ s^{-1} and for $Ru(OH_2)_6^{3+}$ the constant is $\sim 4 \times 10^{-6}$ s^{-1}.[23] Replacement of aqua or ammine ligands by bipyridine or related π-acceptor ligands generally results in a substantive decrease in the rates of substitution of water or other simple ligands on Ru(II), typically by 10^2-fold.[24,25] This effect has been attributed to inductive withdrawal of electronic charge on the metal center.[26] Since these substitution reactions appear to be dissociative in character, the attendant increase in strength of the coordinate bond of the leaving group increases the activation barrier for substitution. Water exchange on Ru(III) may be more associative in nature; for example, an associative interchange (I_a) mechanism has been assigned to water exchange on $Ru(OH_2)_6^{3+}$, based upon the pressure and temperature dependencies of that reaction, whereas the same study suggests an interchange mechanism (I) for $Ru(OH_2)_6^{2+}$.[23] Although increasing the charge on the central metal ion may promote substitution by associative pathways, it is highly unlikely that substitution of bipyridine for coordinated water could account for the 2000-fold greater rate of water exchange in the {3,3} ion than in $Ru(OH_2)_6^{3+}$.

In Ru(II) tetraammine and bis-bipyridine complexes with the general formulas $Ru(NH_3)_4X(OH_2)^{2+}$ and $Ru(bpy)_2X(OH_2)^{2+}$, anation rates are strongly modulated by the fifth nonexchangeable ligand (X).[24,26,27] Simple π-acceptor ligands reduce the anation rates and σ-donors accelerate the rates, consistent with the general inductive effects mentioned above. Ligands capable of strong synergistic $\sigma-\pi$ interactions exhibit a more complex behavior, namely, they markedly labilize ligands in the trans position while apparently reducing lability at the cis-coordination sites. The magnitude of these effects can be large; reported rate constants span a range of $>10^6$-fold for $RuN_4X(OH_2)^{2+}$ and $\sim 10^4$-fold for $Ru(bpy)_2X(OH_2)^{2+}$. It is therefore propitious to consider the possible effects of substitution of the $[(bpy)_2Ru(OH_2)O]^+$ moiety for H_2O in the Ru(III) coordination sphere. Several lines of evidence indicate the existence of strong electronic coupling within the Ru−O−Ru unit in the {3,3} ion, including weak paramagnetism at room temperature and the absence of a low-temperature EPR signal, implying spin coupling of the single unpaired electrons on the individual metal centers,[12,14] and a short Ru−O bond length evident in the crystal structure, indicating multiple bonding to the bridging oxo ligand.[5] Molecular orbital schemes describing the Ru−O−Ru unit are based upon the assumption that the Ru d_π and O p_π orbitals are strongly overlapping, forming essentially three-center bonds.[2,11−14,28] For the {3,3} ion, a single net three-center π-bond arises in the ground electronic state from the summation of four electrons in bonding, eight electrons in nominally nonbonding, and two electrons in antibonding molecular orbitals constructed from the six d_π orbitals on the two Ru atoms and the two p_π orbitals of the oxo bridging atom. Thus, in addition to strong σ-donation from the bridging O^{2-}, one anticipates significant π-back-bonding from the Ru centers.

The net effect of replacement of H_2O by $-ORu(OH_2)(bpy)_2^+$ in the fifth ligand position is apparently to increase the electronic charge on the Ru(III) center. The one-electron reduction potential for the $[(bpy)_2Ru(OH_2)]_2O^{4+}$ ion is ~0.1 V vs SCE, based upon the first irreversible reduction wave observed in its cyclic voltammogram.[5] In contrast, the $E_{1/2}$ value for the corresponding reduction wave for *cis*-$(bpy)_2Ru(OH_2)_2^{3+}$, measured in 1 M triflic acid, is ≥0.63 V vs SCE.[29] The lower limit arises because this ion is strongly acidic and may be partially deprotonated even in this environment. Its pK_a has not been reported, but that for the similar *cis*-$(bpy)_2Ru(py)(OH_2)^{3+}$ is 0.85.[28] In contrast, for the {3,3} ion the first pK_a for deprotonation of coordinated water is 5.9.[5] Since the one-electron reduction potential measures the relative ease of placing additional charge on the Ru(III) centers, the large differences in measured potentials (≥0.5 V) indicate that the electronic charge on the Ru atoms in the dimer is considerably greater than that in the monomer. Similarly, the large difference in acidities of coordinated water in the two ions is also a manifestation of the differences in electronic charge on the metal atoms.[30] By analogy with the behavior observed for simple $(bpy)_2RuX(OH_2)^{2+}$ ions,[24,25] one might therefore expect the coordinated water to be strongly labilized in the dimer.

A second factor that could contribute to the lability of coordinated water in the {3,3} ion is hydrogen bonding of the incoming water molecule to the bridging μ-oxo atom. Evidence for this type of interaction in the {3,3} ion can be found in the small shifts in υ_s(Ru−O−Ru) to lower energies in D_2O relative

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[26] A further effect, reported by Meyer and co-workers (Sullivan, B. P.; Conrad, D.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3640−3645), is a marked ligand *labilization* accompanying one-electron reduction of the bpy ligands. Relative substitution rates for various complexes inferred from linear sweep potentiometry paralleled the electron-donating capacity of the nonexchanging ligands. This dynamical behavior provides additional evidence that the dominant factor controlling ligand substitution rates is the magnitude of electronic charge on the Ru(II) center.

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[29] Durham, B.; Wilson, S. R.; Hodgson, D. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600−607.

[30] Similar comparisons of relative redox potentials and protonic equilibrium constants have been used to argue that the $ORu(py)(bpy)^{2+}$ group is much more strongly electron-donating as a ligand than is pyridine (py) (Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027−2034).

to H_2O measured by RR spectroscopy[7] and in apparent protonation of the bridging oxygen in strongly acidic media, which is inferred from the pH dependence of its one-electron oxidation potential.[9] Hydrogen bonding would increase the nucleophilicity of the attacking water and promote reaction by associative pathways.

A third potential factor arises from the electronic asymmetry associated with multiple bonding to the bridging O atom. $Ru(edta)(OH_2)^-$ is representative of another class of Ru(III) ions that exhibit anomalously rapid substitution at the aqua position.[31−33] In this case, labilization of bound H_2O is uniquely associated with the existence of a pendant edta carboxyl group. This group is thought to distort the coordination environment via hydrogen bonding to the aqua ligand in a manner that generates a steric "hole" in the primary coordination sphere, facilitating approach of the incoming ligand. Consistent with this interpretation, the kinetic activation parameters measured for $Ru(edta)(OH_2)^-$ anation indicate that the reaction mechanism is associative in character.[32] The crystal structure of the {3,3} ion also reveals a large distortion in the primary coordination sphere away from pseudo-O_h symmetry in which the Ru−O bond to the coordinated water is unusually long, i.e., approximately the same length as found in $Ru(OH_2)_6^{2+}$ and significantly longer than that in $Ru(OH_2)_6^{3+}$.[5] This structural asymmetry, which implies that water is relatively weakly bound, might be caused by a ground-state trans effect arising from synergistic $\sigma-\pi$ bonding in the bridge or, alternatively, could be a manifestation of crystal packing forces. Attempts to directly measure vibrational frequencies of coordinated H_2O in the solubilized μ-oxo ions have been unsuccessful.[13] However, the bending angles in the μ-oxo bridge for the {3,3} and {3,4} ions in solution calculated from ^{18}O-induced isotopic shifts in the Ru−O−Ru symmetric stretching vibration (υ_s)[7] are essentially the same as those determined in the crystals by X-ray diffraction, which suggests that steric constraints within the crystal are not the source of the molecular asymmetry.

In any event, these factors associated with the bridging O atom—inductive increase in electron density on the Ru atoms, nucleophilic activation of the entering water molecule by H-bonding, and possibly the structural asymmetry generated by multiple bonding—appear capable in principle of accounting for the unusual lability of coordinated H_2O in the {3,3} ion. Meyer and co-workers have emphasized the importance of deprotonation of the aqua ligand in achieving the high formal oxidation states on ruthenium that are necessary for water oxidation.[5,18] The strong σ-donor character of the μ-oxo bridge that is evident from the physical properties of the dinuclear ion may be equally important in this context. Whether or not the bridging oxo atom also functions as a template to increase the nucleophilic character of solvent H_2O involved in O−O bond formation, as we have previously proposed,[7] remains to be established.

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