Table III. Unfortunately this pattern for the magnitudes of the radial parameters in these trigonal complexes is not readily explicable but should have predictive utility in the future. It would appear, as has been suggested previously, that the ultimate origin of the trigonal splitting must be sought in the molecular orbital theory.[38-40]

Table III. Correlation of Sign of Trigonal Field Splitting Parameter, K, with the Polar Angle, σ, for Ruthenium(III)

	K^k	σ
LuGaG[a]	+387	49° 48′
YGaG[b]	+371	50° 36′
LuAlG[a]	+280	51° 36′
YAlG[b]	+273	52° 24′
$Ru(acac)_3$[c]	+233	53° 36′[h]
Al_2O_3[d]	−250	55° 24′
$Ru(en)_3{}^{3+}$[e]	−418	57° 19′
$Ru(ox)_3{}^{3-}$[f]	−440	57° 30′[i]
$Ru(phen)_3{}^{3+}$[g]	−605	57° 45′[j]
$Ru(bipy)_3{}^{3+}$[g]	−670	?

[a] Reference 15. [b] Reference 14. [c] Reference 10 and B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966). [d] Reference 11. [e] This work and ref 20. [f] R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2467 (1964). [g] Reference 17. [h] Polar angle estimate from the crystal structure of the rhodium analog, $Rh(acac)_3$: E. B. Parker, *Diss. Abstr.*, **24**, 3654 (1966); J. C. Morrow, University of North Carolina, personal communication. [i] Polar angle estimate from the crystal structure of the rhodium analog, $Rh(ox)_3{}^{3-}$: B. Dalzell and K. Ericks, *J. Amer. Chem. Soc.*, **93**, 4298 (1971). [j] Polar angle estimate from the crystal structure of the iron analog, $Fe(phen)_3{}^{2+}$: D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr., Sect. A*, **21**, 154 (1966). [k] Where only values of $3K/\zeta$ were cited, a value for ζ of 1050 cm^{-1} was used to compute K.

In this regard Schaffer[41] has treated trigonal complexes using his angular overlap model, which is founded on the molecular orbital approach, and has predicted from it a negative K value for the $Co(en)_3{}^{3+}$ complex based only on the known angular distortions of the coordinated nitrogens from octahedral positions. Similarly, O'Reilly and Offenbacher,[42] performing a more in-depth molecular orbital calculation, were able to account successfully for the positive K values observed for the Ru^{3+} ion in the axially elongated RuO_6 units in garnets.

Registry No. $[Ru(NH_2CH_2CH_2NH_2)_3]Br_3 \cdot xH_2O$ ($x \cong 2$), 37668-71-6; $[Ru(en)_3]Cl_3 \cdot xH_2O$ ($x \cong 4$), 37668-72-7.

Acknowledgment. This work was supported in part by a research grant from the National Science Foundation.

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Reduction of Oxygen by Hexaammineruthenium(II) and by Tris(ethylenediamine)ruthenium(II)

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The reaction of $Ru(NH_3)_6{}^{2+}$ with oxygen takes place quantitatively according to the stoichiometry: $2Ru(NH_3)_6{}^{2+} + 2H^+ + O_2 = 2Ru(NH_3)_6{}^{3+} + H_2O_2$. The rate law over a wide range of Ru(II), O_2, and H^+ concentrations (1.00 M H^+ to pH 6.05) has the form $-d[O_2]/dt = k[Ru(II)][O_2]$. At 25° and $\mu = 1.00$ maintained with LiOAc, $k = 1.26 \times 10^2$ M^{-1} sec^{-1}. With $Ru(en)_3{}^{2+}$ as the reducing agent, the first stage involving oxidation to $Ru(en)_3{}^{3+}$ takes place rapidly enough so that this stage can be studied with initially no complication caused by oxidation of the ligand. If published values of $E°$ for the Ru(III)–Ru(II) and O_2–$O_2{}^-$ couples are correct, we conclude that the reaction does not involve $O_2{}^-$ as an intermediate. The oxidation of $Ru(NH_3)_6{}^{2+}$ by H_2O_2 is a very slow reaction, and under the optimum conditions we were able to realize, we were dealing not with the intrinsic reaction but with a path involving catalysis by iron salts. The specific rate for the oxidation of $Ru(NH_3)_6{}^{2+}$ by O_2 is at least 10^4 times greater than for the oxidation by H_2O_2.

A particular point of interest in the reactions with oxygen to be described is that the metal ion reducing agents retain their primary coordination spheres intact. To our knowledge, no other system of this type has been subjected to a detailed kinetic analysis. A second point of interest is that the reduction of O_2 to H_2O_2 is much more facile than that of H_2O_2 to H_2O. In this respect, the system is by no means unique, H_2O_2 having been identified as an intermediate stage in the reduction of O_2 by Eu(II)[1] and Pu(III).[2] However, with Eu(II) and Pu(III) as reducing agents there is no ready means of establishing whether, when oxygen acts upon them, the oxidant makes use of a normal coordination position on the metal. For our system, it can be concluded with certainty that O_2 does not occupy a normal coordination position in oxidizing $Ru(NH_3)_6{}^{2+}$, and this places an important limitation on the mechanisms which are possible for the reaction. Another point of interest has been emphasized by recent work[3-5] on the reaction of molecular oxygen with tris(ethylenediamine), hexakis(methylamine), and other substituted amine complexes of ruthenium(II) which describe evidence for oxidation of the ligands. We have established the first step in the reaction of molecular oxygen with tris(ethylenediamine)ruthenium(II) as being oxidation to tris(ethylenediamine)ruthenium(III). By continued action of oxygen or of other oxidizing agents tris(ethylenediamine)-

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(2) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 60, 1417 (1956).

(3) W. R. McWhinnie, J. D. Miller, and J. B. Watts, *Chem. Commun.*, 629 (1971).

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(5) H. Elsbernd and J. K. Beattie, *J. Chem. Soc. A*, 2598 (1970).

ruthenium(III) is converted to the diimine-bis(ethylenediamine) complex, $Ru(en)_2(C_2H_2N_2H_2)^{2+}$.[4]

Experimental Section

We have made repeated attempts over a period of several years to study the rate of the reaction between $Ru(NH_3)_6{}^{2+}$ and O_2 by spectrophotometric means. Until the work described here was done, our efforts were plagued by irreproducible absorbance changes which could not be accounted for in terms of reactants or of reasonably expected products. In addition, attempted kinetic studies were frustrated by irreproducible rate data. These effects have been eliminated thanks to rigorous purification of the ruthenium complex as its hexaammineruthenium(III) trichloride salt and to using rapid and efficient techniques for reduction and subsequent reaction of the ruthenium(II) complex.

Materials. Distilled water was prepared by redistillation of laboratory distilled water from alkaline permanganate.

Lithium acetate and lithium chloride, Baker Reagent grade, were recrystallized twice from distilled water. Acetic acid and hydrochloric acid, Baker Reagent grade, were diluted and used without further purification.

Europium(III) solutions were prepared by dissolving weighed amounts of Eu_2O_3 (99.99% purity purchased from Grace Chemical) in acid solution.

Hexaammineruthenium(III) trichloride was purchased from Matthey Bishop and purified[6] as follows. Twelve grams of $[Ru(NH_3)_6]Cl_3$ was dissolved in 150 ml of water and filtered. Acetone (250 ml) was then added to the filtrate to reprecipitate the ruthenium complex. The complex was redissolved in 80 ml of water and reprecipitated with 300 ml of acetone. The complex was redissolved in 80 ml of water and reprecipitated by adding 200 ml of concentrated HCl. The solution was cooled and the complex collected by filtration. The solid was then recrystallized three times from warm (<40°) 1 *M* HCl by dissolving the solid in a minimum of warm 1 *M* HCl and cooling the solution slowly over a period of several hours. The crystals were collected by filtration, washed with cold 1 *M* HCl followed by acetone and then ether, and dried under vacuum.

Hexaammineruthenium(II) solutions were prepared by weighing an amount of hexaammineruthenium(III) trichloride and dissolving it in a known volume of LiOAc-HOAc buffer under argon. This solution was then reduced with a deficient amount of a stock Eu(II) solution prepared by reducing a Eu(III) solution under argon with Zn-Hg for 30 min. This method is preferable to Zn-Hg reduction of the $Ru(NH_3)_6{}^{3+}$ directly since it shortens by 30 min the time that $Ru(NH_3)_6{}^{2+}$ is kept before use. All solutions were prepared, stored, and transferred under argon using glass syringes and platinum needles. Hexaammineruthenium(II) solutions prepared in this manner were used immediately.

Tris(ethylenediamine)ruthenium(III) tribromide was prepared, purified, and analyzed as described by Meyers.[7]

Tris(ethylenediamine)ruthenium(II) solutions were prepared in a manner analogous to that used for the hexaammineruthenium(II) solutions already described.

Oxygen (Liquid Carbonic) of 99.5% purity was used without further purification. However, in saturating reaction solutions with oxygen, prebubblers of the same composition as the desired solution were used to prevent depletion of acetic acid or hydrochloric acid in the reaction solutions.

Analysis. The initial concentrations of hexaammineruthenium(II) and tris(ethylenediamine)ruthenium(II) were determined by sampling the reaction vessel prior to reaction and injecting the sample into an excess of iron(III) solution buffered at pH 5.4 which had been purged with argon. An excess of *o*-phenanthroline was then added and the iron(II) produced by the Fe(III)-Ru(II) reaction[7] was determined spectrophotometrically as the tris(*o*-phenanthroline) complex (λ_{max} 508 nm, ϵ 1.1×10^4 M^{-1} cm^{-1}). The hexaammineruthenium(III) in the reaction was taken to be the difference between Ru(II) found by analysis and the amount of Ru(III) salt weighed out.

The analysis for oxygen in solution was carried out as follows. A sample of an oxygen-saturated solution, taken by syringe, was slowly injected under the surface of an argon-purged Cr(II) solution with reducing agent in excess (the concentration of Cr(II) in an identical solution with no oxygen added was determined by adding excess iron(III) solution and analyzing the iron(II) produced as described in the $Ru(NH_3)_6{}^{2+}$ analysis). The Cr(II) that remained after reaction was then determined by adding iron(III) and determining the iron(II) produced as above. Blanks were done on water saturated solutions at 25°. Comparing our values of oxygen content to handbook values, we found the method to be accurate to only 3%. Oxygen-saturated buffer solutions analyzed in like manner were then diluted with argon-purged solutions to give the desired oxygen concentrations.

Methods. All uv and visible spectral and kinetic measurements were made on either a Cary Model 14 or 15 recording spectrophotometer. In the kinetic experiments, to magnify the small absorbance changes accompanying the reactions, the reactions were run in 5- and 10-cm cells and a 0.0-0.1 absorbance unit slide-wire was used. Typical absorbance changes in a 10-cm path length were between 0.06 and 0.15 absorbance unit. Two types of experiments were carried out; in one type, the ruthenium(II) complex concentration was in at least a 10-fold stoichiometric excess of the oxygen concentration and in the second type the oxygen concentration was in 10-fold stoichiometric excess of the ruthenium(II) complex. Experiments with ruthenium(II) in excess were performed by preparing a ruthenium(II) solution in a spectrophotometric cell, analyzing the solution for Ru(II), and after temperature equilibration injecting a small volume of oxygen-saturated buffer to initiate the reaction. Experiments with oxygen in excess were done by diluting a saturated standardized oxygen solution in a spectrophotometric cell with an argon-purged solution. Time was then allowed for temperature equilibration and the reaction was initiated by injecting a small volume of Ru(II). All experiments were done under pseudo-first-order conditions and all first-order plots were linear to greater than 90% completion of reaction.

For the reaction of $Ru(NH_3)_6{}^{2+}$ with O_2, the stoichiometry was determined by two methods. In both methods the Ru(II) complex was injected into an oxygen-saturated solution containing a tenfold excess of oxygen. The H_2O_2 formed was then determined in one method by addition of excess Ce(IV). The excess Ce(IV) was then determined by reduction with excess iron(II) followed by analysis of the iron(II) remaining as its *o*-phenanthroline complexes as described earlier. The H_2O_2 present is obtained by difference from the amount of Ce(IV) initially added and that consumed by the iron(II). In the second method excess iron(II) was injected into the reaction product solution containing the H_2O_2. The iron(II) is oxidized by the H_2O_2 to iron(III).[8] The iron(II) remaining was again obtained by the *o*-phenanthroline analysis. The stoichiometry studies were carried out at pH 5.44 for $Ru(NH_3)_6{}^{2+}$ and pH 2.0 for $Ru(en)_3{}^{2+}$, $\mu = 1.00$ (LiOAc-HOAc) and $\mu = 1.00$ (HCl-LiCl), respectively. In the case of the $Ru(en)_3{}^{2+}$ reaction only the Ce(IV) oxidation method was used to determine H_2O_2 produced. Since $Ru(en)_3{}^{3+}$ could be further oxidized by Ce(IV), the $Ru(en)_3{}^{3+}$ was removed by rapid ion exchange prior to adding Ce(IV). All solutions were acidified to pH 1 before Ce(IV) or Fe(II) was added and were then brought to pH 5.4 before *o*-phenanthroline addition.

Results

Stoichiometry. The stoichiometry of the reaction of hexaammineruthenium(II) with oxygen is given by eq 1.

$$2Ru(NH_3)_6{}^{2+} + O_2 + 2H^+ \rightarrow 2Ru(NH_3)_6{}^{3+} + H_2O_2 \qquad (1)$$

The evidence for this stoichiometry is multiple. First we note that $Ru(NH_3)_6{}^{2+}$, when oxidized by O_2, has a uv-visible spectrum that is identical (within 5% and making proper allowance for H_2O_2 and other ingredients) with that of $Ru(NH_3)_6{}^{3+}$. Second, the presence of H_2O_2 in the reaction products is detected by removing the oxidized ruthenium complex by passing the solution through a cation-exchange column and then treating the product solution with $K_2Cr_2O_7$-H_2SO_4. The development of the deep blue color of "perchromic" acid represents a positive test for H_2O_2. Third, we have analyses for H_2O_2 produced in reaction 1 by both oxidizing it with Ce(IV) or reducing it with Fe(II). Results of Ce(IV) oxidation and Fe(II) reduction of a reaction solution immediately after O_2 oxidation are given in Table I. It should be pointed out that during the time of these titrations $Ru(NH_3)_6{}^{3+}$ does not react with either Fe(II) or Ce(IV). Hence the quantitative production of

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(6) J. N. Armor, Ph.D. Thesis, Stanford University, 1970.

(7) T. J. Meyers, Ph.D. Thesis, Stanford University, 1966.

(8) W. G. Barb, J. M. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, 47, 462 (1951).

Table I. Stoichiometry Data for Molecular Oxygen Oxidation of $Ru(NH_3)_6^{2+}$

Amt, mmol			
$Ru(NH_3)_6^{2+}$ oxidized	Ce(IV) consumed by H_2O_2 produced	Fe(II) consumed by H_2O_2 produced	% of expected amt
2.89	2.80		97
2.62	2.72		104
2.62	2.62		100
2.60	2.70		103
2.78		2.66	96
2.93		2.52	86
2.54		2.39	94
2.54		2.21	87

H_2O_2 has been established both in an oxidative and a reductive test.

Fourth, to ensure that the coordination sphere of $Ru(NH_3)_6^{2+}$ remains intact throughout the oxidation and to show that $Ru(NH_3)_6^{3+}$ was the only ruthenium product of this reaction, it was necessary to prove that no $Ru(NH_3)_5OH_2^{3+}$ or more highly aquated forms of ruthenium(III) were produced in significant amounts. It is well known[9] that isonicotinamide (INA) reacts with $Ru(NH_3)_5OH_2^{2+}$ and $Ru(NH_3)_4(OH_2)_2^{2+}$ to give the intensely colored $Ru(NH_3)_5(INA)^{2+}$ and $Ru(NH_3)_4(INA)_2^{2+}$ complexes. These complexes have extinction coefficients of approximately (1-2) × 10^4 M^{-1} cm^{-1} at 480 nm. $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ are transparent in this spectral region. To search for aquated species, a solution of $Ru(NH_3)_6^{2+}$ was oxidized with oxygen and subsequently rereduced with Eu(II). After this reduction isonicotinamide was added to convert any $Ru(NH_3)_5OH_2^{2+}$ that had been produced to the readily detectable $Ru(NH_3)_5(INA)^{2+}$ complex. Within an experimental error of 1%, no aquoruthenium(II) complexes were detected in this way.

The stoichiometry of the reaction of tris(ethylenediamine)ruthenium(II) and oxygen is given by

$$2Ru(en)_3^{2+} + O_2 + 2H^+ \rightarrow 2Ru(en)_3^{3+} + H_2O_2 \tag{2}$$

The stoichiometry of this reaction was established in a similar manner to that already described for the oxidation of $Ru(NH_3)_6^{2+}$. The reaction of O_2 with $Ru(en)_3^{2+}$ suffers from the additional complication that the $Ru(en)_3^{3+}$ produced can undergo subsequent oxidation of the ligand accompanied by metal reduction.[4] This subsequent oxidation by additional oxygen is slow compared to the step shown in eq 2 under all conditions studied here, as is any subsequent reaction with H_2O_2.

Oxygen oxidation by O_2 of a buffered solution of $Ru(en)_3^{2+}$ produced by Eu(II) reduction yields the spectrum of the original $Ru(en)_3^{3+}$ solution. In addition, the H_2O_2 produced by this oxidation, can be titrated with Ce(IV) after the $Ru(en)_3^{3+}$ is removed by ion exchange. The results of Ce(IV) titrations are given in Table II.

Table II. Stoichiometry Data for Molecular Oxygen Oxidation of $Ru(en)_3^{2+}$

Amt, mmol		
$Ru(en)_3^{2+}$ oxidized	Ce(IV) consumed by H_2O_2 produced	% of expected amt
2.79	2.68	96
2.64	2.51	95
2.64	2.51	95

H_2O_2 + $Ru(NH_3)_6^{2+}$. In the reaction of oxygen with $Ru(NH_3)_6^{2+}$, eq 1, the formation of H_2O_2 leads to the possibility of subsequent reaction of unreacted $Ru(NH_3)_6^{2+}$ with H_2O_2 as in eq 3. Since this represents a kinetic complication to the study of the first step and because we are interested in the relative rates of oxygen reduction to hydrogen peroxide reduction by metal ion complexes, attempts were made to measure the kinetics of reaction 3 independently. Experiments with $Ru(NH_3)_6^{2+}$ in 20-fold excess over H_2O_2 established a first-order dependence of the reaction rate on H_2O_2. However, the observed rate constants were irreproducible. In addition, experiments with either H_2O_2 or $Ru(NH_3)_6^{2+}$ in excess were found to be cleanly zero order in $[Ru(NH_3)_6^{2+}]$. These observations suggest that a catalytic impurity was controlling the reaction. A drastic reduction in the rate was observed on replacing stainless steel syringe needles with platinum needles. The rates, while slower, were still irreproducible. Copper(II) and iron(III) were tested for catalytic activity in the reaction and only Fe(III) was found to be effective. The mode of catalysis is suggested by eq 4a and 4b. The rates of both

$$2Ru(NH_3)_6^{2+} + H_2O_2 + 2H^+ \rightarrow 2Ru(NH_3)_6^{3+} + 2H_2O \tag{3}$$

$$2H^+ + 2Fe^{II} + H_2O_2 \xrightarrow{R.D.} 2Fe^{III} + 2H_2O \tag{4a}$$

$$2Fe^{III} + 2Ru^{II} \xrightarrow{fast} 2Fe^{II} + 2Ru^{III} \tag{4b}$$

reactions are known.[7,8] Under all conditions used in our study, step 4a would be rate determining. This would explain the first-order dependence on (H_2O_2), the zero-order dependence on [Ru(II)], the irreproducible rates, and the catalytic effects of small (1 × 10^{-7}-1 × 10^{-5} M) amounts of either iron(II) or iron(III).

Efforts to diminish the amount of iron present by purifying the solvent and reactants decreased the rates slightly but did not eliminate the irreproducibility. Attempts to analyze the iron present as its iron(II) *o*-phenanthroline complex indicated that the residual iron concentration in these experiments was less than 4 × 10^{-7} M. Even at these levels the rate was independent of $[Ru(NH_3)_6^{2+}]$ and hence the reaction is likely being carried completely by the iron-catalyzed path.

Addition of 8 × 10^{-6} M iron(III) to the reaction mixture enhanced the rate greatly and also rendered the reaction reproducible. This is as would be expected since the iron concentration is now being controlled.

EDTA was added to the reaction mixture in an attempt to complex the residual iron. Experiments with EDTA added had slightly accelerated rates. This is not surprising in view of other comparisons of rates of reduction by $Fe(OH_2)_6^{2+}$ and Fe(EDTA).[2-10]

While we have not been able to establish the intrinsic reaction rate between $Ru(NH_3)_6^{2+}$ and H_2O_2, our results do show that if iron impurities are kept below 4 × 10^{-7} M, the H_2O_2-$Ru(NH_3)_6^{2+}$ reaction will not interfere with kinetic studies of the O_2 oxidation of $Ru(NH_3)_6^{2+}$. Furthermore, by using the slowest observed reaction rates (presumably those with the least amount of iron impurity) an upper limit can be obtained for the H_2O_2-$Ru(NH_3)_6^{2+}$ reaction. Under reaction conditions of $[Ru(NH_3)_6^{2+}]_0 = 3.8 \times 10^{-3}$ M, $[H_2O_2] = 2 \times 10^{-4}$ M, pH 5.44, and $\mu = 1.00$ in LiOAc-HOAc at 25° the lowest pseudo-first-order observed rate constant was 4.5 × 10^{-4} sec^{-1}. Even if all of the reaction is being carried by the intrinsic H_2O_2-$Ru(NH_3)_6^{2+}$ reaction

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(9) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 6170 (1970).

(10) W. L. Reynolds and R. Lumry, *J. Chem. Phys.*, **23**, 2560 (1955).

under these conditions one would derive an upper limit for the second-order rate constant of $0.12\,M^{-1}\,\mathrm{sec}^{-1}$ for the H_2O_2-$Ru(NH_3)_6^{2+}$ reaction. Furthermore, several facts (zero-order dependence on [Ru(II)], estimates of trace amounts of iron present in these reactions, and extrapolation of rate data from experiments with added iron(III)) indicate that much, if not all, of the observed rate for the experiment in question is a result of the iron-catalyzed path and not the intrinsic H_2O_2-$Ru(NH_3)_6^{2+}$ reaction. Hence, we feel that no more than one-tenth of the observed reaction could have resulted from the intrinsic H_2O_2-$Ru(NH_3)_6^{2+}$ reaction and that a more reasonable upper limit for this rate constant is $0.012\,M^{-1}\,\mathrm{sec}^{-1}$.

Rate Laws and Kinetic Data. $Ru(NH_3)_6^{2+} + O_2$. The oxidation of $Ru(NH_3)_6^{2+}$ by molecular oxygen, eq 1, was found to obey the rate law

$$-\tfrac{1}{2}\mathrm{d}[Ru(NH_3)_6^{2+}]/\mathrm{d}t = -\mathrm{d}[O_2]/\mathrm{d}t = k[Ru(NH_3)_6^{2+}] \times [O_2] \qquad (5)$$

The data used to establish this rate law and to determine k are given in Table III. The second-order rate constant, k, was found to be independent of hydrogen ion concentration from pH 6.05 to 1.00 *M* HCl. All kinetic measurements were made by following the decrease in absorbance at 250 nm where $Ru(NH_3)_6^{2+}$ (ϵ_{250} 540 $M^{-1}\,\mathrm{cm}^{-1}$) is oxidized to $Ru(NH_3)_6^{3+}$ (ϵ_{250} 300 $M^{-1}\,\mathrm{cm}^{-1}$). Experiments with each $Ru(NH_3)_6^{2+}$ and O_2 in large excess were done. In experiments with oxygen in excess the observed rate constant, k_{obsd}, is given by eq 6, where A_t and A_∞ refer to absorbance

$$k_{\mathrm{obsd}} = -\mathrm{d}\ln(A_t - A_\infty)/\mathrm{d}t \cong 2k[O_2]_{\mathrm{av}} \qquad (6)$$

at time t and infinity, respectively. The subscript "av" refers to the average of initial and final reactant concentration in an experiment. For experiments with $Ru(NH_3)_6^{2+}$ in excess the observed rate constant is given by eq 7. In these

$$k_{\mathrm{obsd}} = -\mathrm{d}\ln(A_t - A_\infty)/\mathrm{d}t \cong k[Ru(NH_3)_6^{2+}]_{\mathrm{av}} \qquad (7)$$

experiments, the large absorbance background accompanying the excess $Ru(NH_3)_6^{2+}$ increases the signal to noise ratio slightly and is reflected in a somewhat greater uncertainty in observed rate constants. All pseudo-first-order rate plots from which k_{obsd} was obtained were linear to greater than 90% reaction completion.

From the data at 6.8, 16.3, and 25.5° $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are calculated as 11.5 ± 0.3 kcal/mol and −10.4 ± 1.0 eu, respectively. At 6.8° only the data at pH 5.44 are used in the activation energy computations since most of the data were obtained at that pH and since changing [H⁺] causes unavoidable changes in reaction medium.

$Ru(en)_3^{2+} + O_2$. The oxidation of tris(ethylenediamine)ruthenium(II), eq 2, was found to obey the same rate law as that found for $Ru(NH_3)_6^{2+}$, eq 5, including the observation that the rate is independent of hydrogen ion concentration. The data for this reaction were obtained by monitoring the decrease in absorbance at λ 304 nm where $Ru(en)_3^{2+}$ (ϵ_{304} 1000 $M^{-1}\,\mathrm{cm}^{-1}$) is oxidized to $Ru(en)_3^{3+}$ (ϵ_{304} 345 $M^{-1}\,\mathrm{cm}^{-1}$).[7] The results of the rate experiments are given in Table IV. Again all pseudo-first-order rate plots were linear to greater than 90% reaction completion. From the data at 8.5 and 25.3° $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 12.1 ± 0.4 kcal/mol and −9.5 ± 1.4 eu, respectively, were computed. All experiments were recorded with $\mu = 1.00$ maintained with LiCl-HCl.

Table III. Kinetic Data for O_2 Oxidation of $Ru(NH_3)_6^{2+}$ [a]

pH	$10^4[Ru(NH_3)_6^{2+}]_0$, *M*	$10^4[O_2]_0$, *M*		k, M^{-1} sec^{-1}
		6.8°		
5.44	2.87 ± 0.06	0.15		32.1 ± 0.9 (5)[b]
5.44	3.92	0.15		31.3
5.44	5.98 ± 0.17	0.30		31.5 ± 2.5 (2)
5.44	9.67 ± 0.02	0.40		34.2 ± 0.4 (2)
5.44	0.40	2.05 ± 0.05		33.9 ± 1.9 (2)
5.44	0.80	4.28 ± 0.05		29.6 ± 0.3 (2)
5.44	0.40	2.04		31.5[c]
5.44	0.40	2.00		30.8[d]
			Av	32.0 ± 1.7 (16)
6.05	3.07 ± 0.16	0.15		26.0 ± 0.3 (2)
6.05	0.30	2.06		32.4
4.44	2.81 ± 0.11	0.15		33.0 ± 1.7 (2)
4.44	5.05	0.30		34.3
4.44	0.30	2.05		33.2
1.00	3.03 ± 0.02	0.15		28.6 ± 2.0 (2)
0.0	0.30	1.64		24.8
		16.3°		
5.44	3.00	0.15		66.2 ± 1.2 (2)
5.44	0.40	2.03		61.5 ± 2.9 (2)
			Av	63.8 ± 2.7 (4)
		25.5°		
5.44	2.87 ± .09	0.15		126 ± 3 (3)

[a] All data at $\mu = 1.00$ maintained with HOAc–LiOAc (pH 5.44, 6.05, 4.44) and HCl–LiCl (pH 1.00, 0.00). [b] The numbers given in parentheses indicate that this row represents the average of the given number of similar experiments. [c] $Ru(NH_3)_6^{3+}$ was added in this experiment such that $[Ru(NH_3)_6^{3+}]_0 = 2.8 \times 10^{-4}\,M$. [d] $Ru(NH_3)_6^{3+}$ was added in this experiment such that $[Ru(NH_3)_6^{3+}] = 4.13 \times 10^{-4}\,M$.

Table IV. Kinetic Data for the O_2 Oxidation of $Ru(en)_3^{2+}$ [a]

[H⁺], *M*	$10^4[Ru(en)_3^{2+}]_0$, *M*	$10^4[O_2]_0$, *M*		k_2, M^{-1} sec^{-1}
	8.5°			
0.010	2.75	0.15		20.8
0.010	3.07	0.15		22.6
0.010	3.60	0.15		19.8
0.010	8.20	0.40		19.9
0.010	0.40	1.78		19.2
0.010	0.40	1.78		17.5
0.010	0.20	2.18		21.6
0.010	0.20	2.18		22.2
0.010	0.40	2.04		19.8
0.100	3.01	0.15		20.3
			Av	20.4 ± 1.1
	25.3°			
0.010	3.47	0.15		71.3
0.010	3.21	0.15		75.4
0.010	1.85	0.07		69.0
0.010	1.87	0.07		73.4
			Av	72.3 ± 2.4

[a] All data at $\mu = 1.00$ maintained with HCl–LiCl.

Discussion

Oxidation of various transition metals ions [$Fe(OH_2)_6^{2+}$,[4] $Cr(OH_2)_6^{2+}$,[11] $V(OH_2)_6^{2+}$,[12] $Co(CN)_5^{3-}$,[13] $Cr(NH_3)_5OH_2^{2+}$ [14]] by molecular oxygen occur with involvement of O_2 in the primary coordination sphere as a possibility. Only one previously studied reaction, the oxidation of Cr(II) in CN⁻ medium,[13] which yields $Cr(CN)_6^{3-}$ as a product, seems certain not to have such an inner-sphere involvement. The oxidations of $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$ in this study are examples of reactions that must occur without involvement of O_2 in normal coordination positions, and they clearly

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establish that reduction of molecular oxygen with transition metal ions can occur while the primary coordination sphere remains intact. They also show that such reduction can occur without the aid of an electron "conducting" ligand such as cyanide.

While the production of H_2O_2 as the immediate product for these reactions is not surprising, the very large difference in reactivities toward $Ru(NH_3)_6{}^{2+}$ of O_2 ($126\,M^{-1}\ sec^{-1}$) and H_2O_2 ($\leqslant 0.012\,M^{-1}\ sec^{-1}$), a factor of $\geqslant 10^4$, is remarkable. While specific rate studies on the H_2O_2-$Ru(en)_3{}^{2+}$ reaction were not carried out, indications from the O_2-$Ru(en)_3{}^{2+}$ kinetic and stoichiometric studies are that $Ru(en)_3{}^{2+}$ too reacts slowly with H_2O_2 as compared to its reaction rate with O_2. It is possible that for these complexes part of this vast disparity in rates will only be observed when substitution in a normal coordination position is excluded. For this reason studies of reaction of H_2O_2 and O_2 with $Ru(NH_3)_5OH_2{}^{2+}$ or $Ru(OH_2)_6{}^{2+}$ would be of interest.

With regard to mechanism, the rate law implies a rate-determining step involving one molecule of Ru(II) and one molecule of O_2, and not involving additional protons. It does not, however, distinguish between a one-electron step to give Ru(III) and superoxide ion, mechanism A, or a two-electron step to give a Ru^{IV}-$O_2{}^{2-}$ intermediate, mechanism B

$$Ru(NH_3)_6{}^{2+} + O_2 \rightleftharpoons Ru(NH_3)_6{}^{3+} + O_2{}^-$$

$$O_2{}^- + Ru(NH_3)_6{}^{2+} \xrightarrow[2H^+]{fast} Ru(NH_3)_6{}^{3+} + H_2O_2 \qquad (A)$$

$$Ru(NH_3)_6{}^{2+} + O_2 \rightleftharpoons (Ru^{IV}(NH_3)_6O_2{}^{2-})^{2+}$$

$$Ru(NH_3)_6O_2{}^{2+} + Ru(NH_3)_6{}^{2+} \xrightarrow[2H^+]{fast} 2Ru(NH_3)_6{}^{3+} + H_2O_2 \qquad (B)$$

(energetically it is unlikely that free $O_2{}^{2-}$ could be generated). Using an $E°$ value of 0.10 V for the $Ru(NH_3)_6{}^{2+}$-$Ru(NH_3)_6{}^{3+}$ potential and a calculated[15] value of -0.38 V for the O_2-$O_2{}^-$ potential, an equilibrium constant for the first step of mechanism A of 10^{-8} is calculated. This value combined with the measured rate constant of $126\,M^{-1}\ sec^{-1}$ at 25.5° would yield a reverse rate for that step of *ca.* $10^{10}\,M^{-1}\ sec^{-1}$ or a value very close to the diffusion-controlled limit. Considering the large driving force and the nature of the reactants for the second step of mechanism A, it is likely that this step is also diffusion controlled. Hence, in experiments with oxygen in excess of $Ru(NH_3)_6{}^{2+}$ and with added $Ru(NH_3)_6{}^{3+}$ in initial tenfold excess of $Ru(NH_3)_6{}^{2+}$ concentration, deviation from first-order kinetics should be observed as the reverse of step 1 in mechanism A becomes important. The deviation should be most dramatic near the end of reaction where the $Ru(NH_3)_6{}^{2+}$ concentration approaches zero and the ratio of the concentration of $Ru(NH_3)_6{}^{3+}$ to $Ru(NH_3)_6{}^{2+}$ becomes very large. In fact, this deviation was not observed and experiments under these conditions were linear to greater than 95% completion of reaction.

It should be noted that the acid dissociation constant of HO_2 has been reported as 2×10^{-5}.[16] The experiments with $Ru(NH_3)_6{}^{3+}$ added initially were done at pH 5.44, and the argument advanced is therefore not vitiated by possible association of $O_2{}^-$ with H^+.

It is possible of course that the $E°$ value for the O_2-$O_2{}^-$ couple which has been estimated is in error and consequently that the reverse of step 1 in mechanism A is not diffusion controlled. If this is the case, then there is no experimental conflict with mechanism A.

Mechanism B suggests that the intermediate formed is a complex of Ru(IV) with $O_2{}^{2-}$, in which Ru(IV) is assumed to have a coordination number of 7. Similar species can reasonably be inferred to figure in the release of NH_3 from $Ru(NH_3)_6{}^{2+}$ under the influence of H^+ [17] and in the reaction of $Ru(NH_3)_6{}^{2+}$ with HONO.[6]

In a recent communication[4] it has been reported that the oxidations with O_2 of $Ru(en)_3{}^{2+}$ and $Ru(en)_3{}^{3+}$ yield $Ru(en)_2(C_2H_2N_2H_2)^{2+}$. The results of oxidation of $Ru(en)_3{}^{2+}$ in our study show that O_2 oxidation, under the conditions employed here, results first in $Ru(en)_3{}^{3+}$. This indicates that ligand oxidation must occur subsequent to metal oxidation by O_2 of $Ru(en)_3{}^{2+}$. Whether or not this is a general feature that applies to other ruthenium complexes with oxidizable ligands and/or other oxidizing agents is not yet known.

Registry No. $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $Ru(en)_3{}^{2+}$, 21393-86-2; O_2, 7782-44-7; H_2O_2, 7722-84-1; iron, 7439-89-6.

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